

# 8-OXOHEPTAFULVENE

YOSHIO KITAHARA

*Department of Chemistry, Faculty of Science, Tohoku University,  
Sendai 980, Japan*

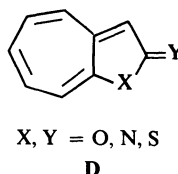
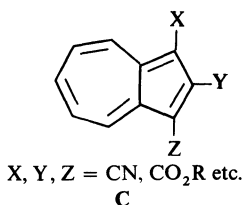
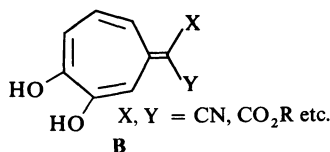
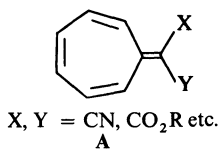
## ABSTRACT

Our chemical and physical studies of heptafulvene and related compounds provided an occasion to get into research on 8-oxoheptafulvene chemistry.

8-Oxoheptafulvene which has both heptafulvene and ketene moieties undergoes several modes of cycloaddition reactions with various olefins and ketones. In many cases, the initial cycloadducts further undergo rearrangement reactions or extrusion of carbon dioxide depending on the reactants. Particularly the reactions with tropones provide one-step synthesis of heptafulvalenes.

## INTRODUCTION

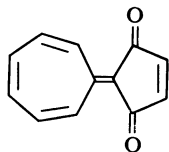
Since 1960, we have investigated the chemistry of heptafulvenes (**A** and **B**)<sup>1-31</sup> involving syntheses, halogenation under irradiation, cycloadditions with various dienophiles and dienes, and some physical properties. Azulenes and heteroazulenes (**C** and **D**) have also been derived from heptafulvenes.



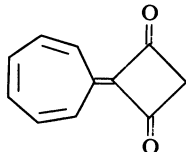
Furthermore, sesquifulvalene and its quinone (**E**) and related compound (**F**), biheptafulvenyl (**G**), fulvenylheptafulvene (**H**) and a new type of cation (**I** and **J**) have been synthesized, and some properties of them were also studied.

The remarkable feature of the cation (**I**:R = **H**) is its high  $pK_{R^+}$  value ( $7.49 \pm 0.05$ ) which is the highest value among the cations ever reported.

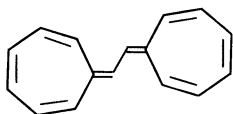
These researches have provided some information on the aromaticity of heptafulvenes.



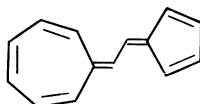
E



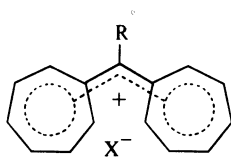
F



G

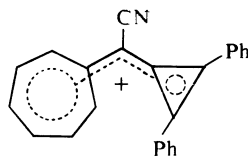


H



$X = \text{BF}_4^-, \text{ClO}_4^-$

I



$\text{BF}_4^-$

J

R = CN	$pK_{R^+}$	3.44
R = CH <sub>3</sub>		5.86
R = H		7.49

$pK_{R^+}$  3.41

Heptafulvenes having electron-attracting groups at the 8-position are stabilized by the contribution of dipolar structures<sup>32</sup> relative to the ground state in contrast to heptafulvene itself<sup>33</sup>.

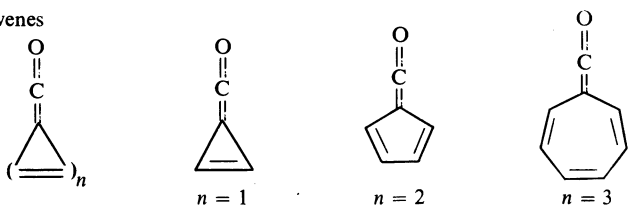
As a part of the heptafulvene chemistry, we have been interested in the syntheses and properties of oxofulvene and its analogues. Only 6-oxofulvene has been synthesized among the three oxofulvenes illustrated opposite, but a little on the chemistry has been reported. 8-Oxoheptafulvene may be represented by the resonance hybrid (I ~ Ic). I wish here to talk about our chemistry on 8-oxoheptafulvene (I) involving its formation and reactions.

### FORMATION OF 8-OXOHEPTAFULVENE<sup>34</sup>

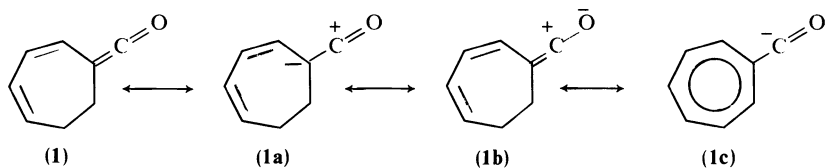
After the addition of triethylamine to a solution of tropyl-7-carboxylic acid chloride (2) in ether at  $-60^\circ$ , methanol-*d* was added to the resultant reddish solution. Work-up of the reaction mixture afforded methyl tropyl-7-

## 8-OXOHEPTAFULVENE

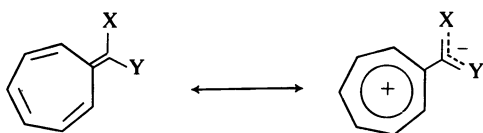
Oxofulvenes



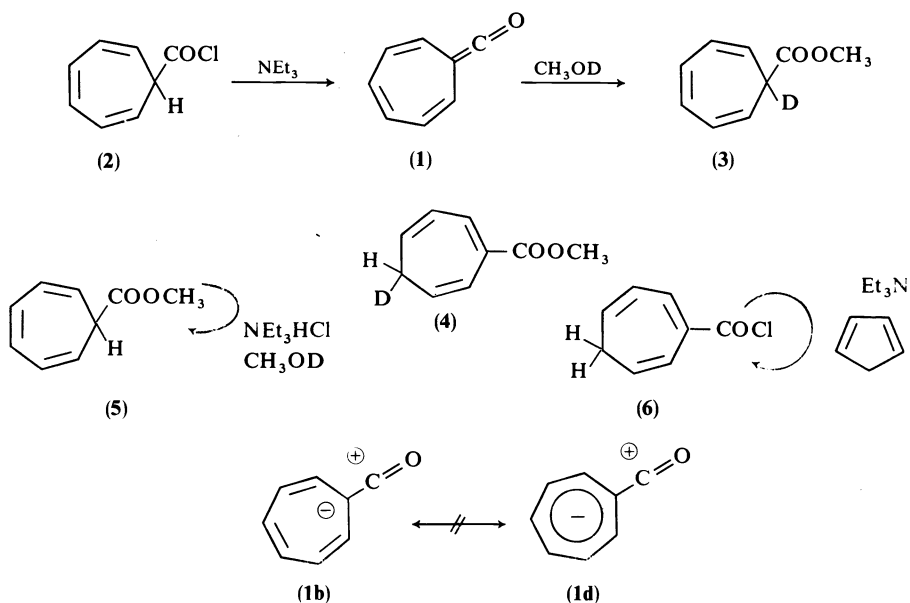
8-Oxoheptafulvene



Heptafulvene



carboxylate-7-*d* (**3**), without formation of (**4**), whose structure was determined by i.r., n.m.r., and mass spectroscopy. Only a small amount of deuterium exchange at the 7 position was observed for methyl tropyl-7-carboxylate (**5**) in the presence of triethylamine, hydrogen chloride, and an excess of



methanol-*d*, even after the mixture was stirred at room temperature for one day.

The reaction of troyl-3-carboxylic acid chloride (6) with triethylamine in the presence of cyclopentadiene did not occur and the starting materials were recovered.

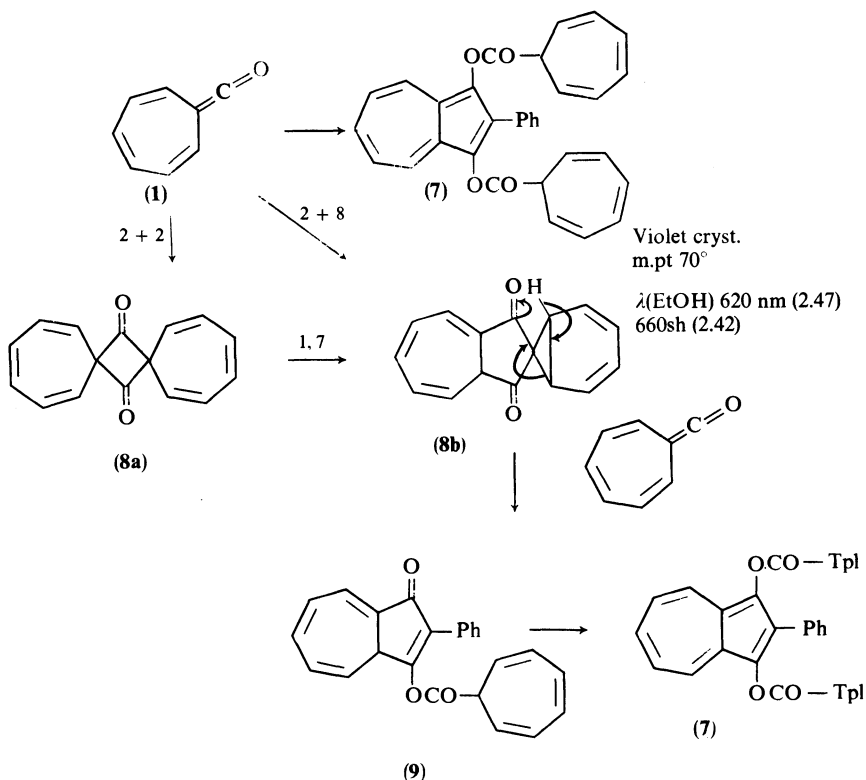
Therefore, it must be concluded that compound (3) was formed by the reaction of 8-oxoheptafulvene (1) and methanol-*d*. This reaction pattern is analogous to that of ketenes<sup>35</sup> rather than heptafulvenes with eight- $\pi$ -electron systems (1b, 1d).

Although a multiplet around 6 p.p.m. in the n.m.r. of a mixture of the acid chloride (2) and triethylamine can be assigned to the ring protons of 8-oxoheptafulvene (1), attempted isolation of (1) has been unsuccessful to date.

## DIMERIZATION

Standing a solution of (1) at room temperature for several hours afforded, in low yield, the azulene derivative (7) as violet crystals<sup>36</sup>. The mechanism of the formation of (7) may be as shown below.

That is, [2 + 2] dimerization of (1) followed by [1, 7] migration or directly [2 + 8] dimerization gives (8b) whose rearrangement and further reaction with (1) afford (7) via (9).

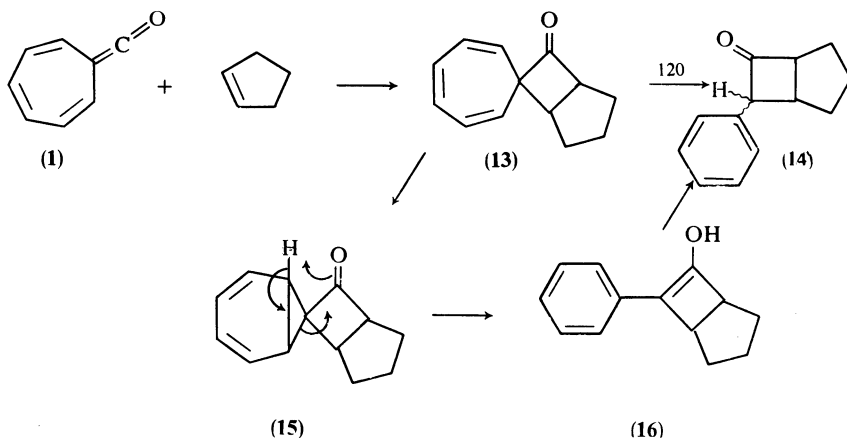
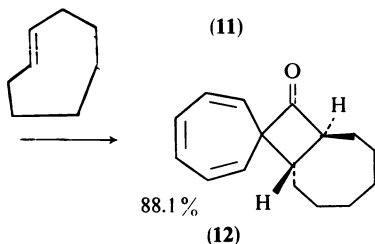
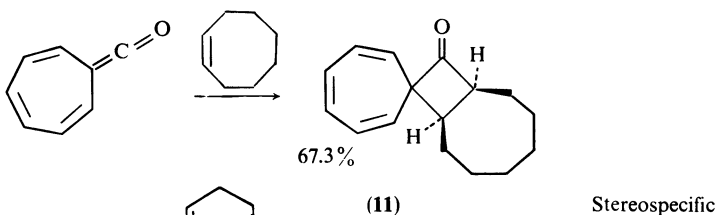
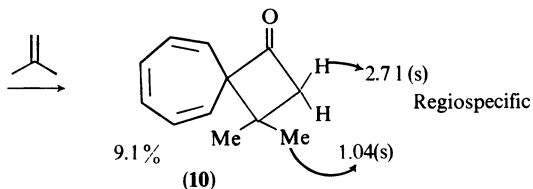


## REACTION WITH OLEFINS

Reaction of (1) with isobutene<sup>36</sup> gave the regiospecific [2 + 2] cycloaddition product (10) in low yield along with a small amount of the azulene derivative (7). In general, reactions of (1) with poorly reactive compounds are always accompanied by the formation of (7). When *cis* and *trans* cyclooctene<sup>36</sup> are used, the stereospecific *cis* and *trans* adducts (11) and (12) were obtained, respectively.

Therefore, the reaction of (1) with olefins must proceed by a concerted mechanism.

Reaction with olefins

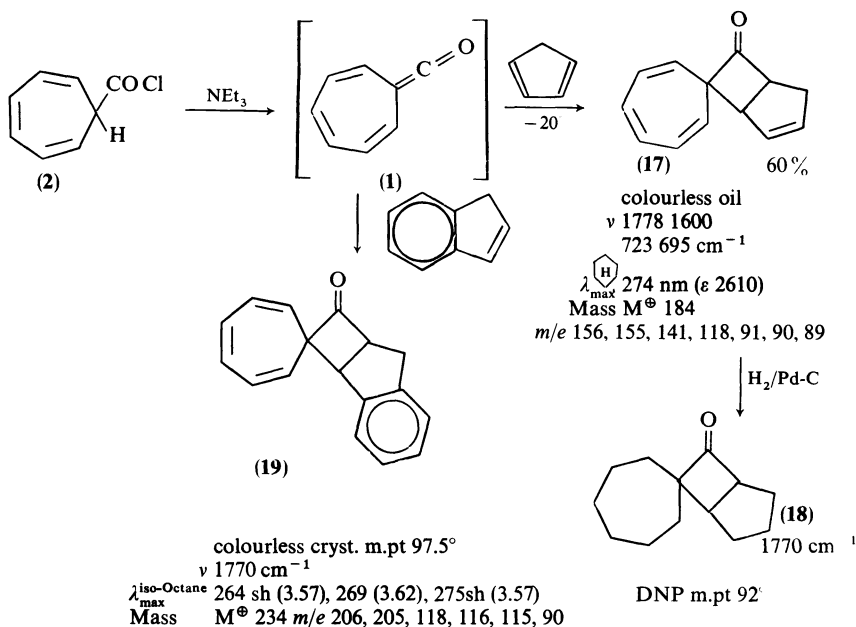


The cyclobutanone derivative (13) was also formed by reaction of (1) with cyclopentene<sup>36</sup>. Heating of (13) furnished a phenylcyclobutanone derivative (14) by rearrangement of the spiro tropilidene moiety to a phenyl group. The mechanism may be accounted for by the process (13) → (15) → (16) → (14).

8-Oxoheptafulvene (1) also reacted with cyclopentadiene to give the [2 + 2] cycloadduct (17) in 60 per cent yield. Compound (17) exhibits infrared bands (neat) at 1778 (four-membered cyclic ketone), 1600, 723, and 695  $\text{cm}^{-1}$  tropilidene moiety). The structure was further established by 100 MHz n.m.r. spectroscopy. The chemical shift assignments and coupling constants were verified by an application of a shift reagent,  $\text{Eu}(\text{DPM})_3$ , as well as by double and triple resonance experiments.

A similar reaction in the presence of indene<sup>34</sup> instead of cyclopentadiene gave a 24 per cent yield of the crystalline adduct (19) which shows an infrared band (KBr) at 1770  $\text{cm}^{-1}$ . The chemical shift assignments and couplings were also confirmed by a double resonance technique.

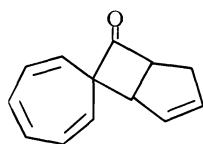
Hydrogenation of (17) over palladium/charcoal led to the uptake of 4 mol of hydrogen and afforded the oily tricyclic saturated ketone (18).



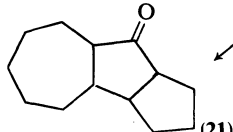
The attempted distillation of the adduct (17), or standing a solution of (17) at room temperature for a week or so, resulted in a rearrangement to give the isomeric cyclopentanone derivative (20)<sup>34</sup> in good yield differing from the case of the adduct (13). Compound (20) absorbed 4 mol of hydrogen on catalytic hydrogenation to give the oily ketone (21). The deuterium exchange reaction of (21) in sodium methoxide-methanol-*d* afforded a dideuterio derivative confirmed by mass spectroscopy. Stereochemistry of (20) was

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established by n.m.r. The small coupling constant (*ca.* 1 Hz) between H-3a and H-3b suggests their relationship to be *trans*.

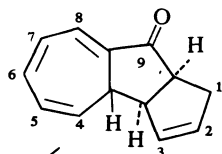


(17)



(21)

1728 cm<sup>-1</sup>  
DNP  
m.pt 177°C

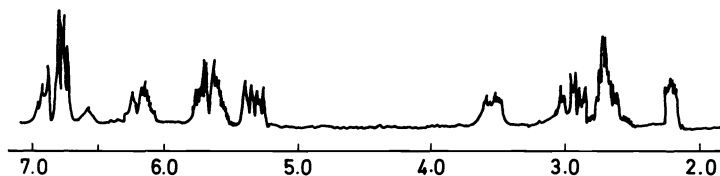


(20)

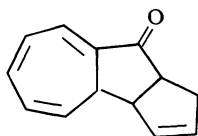
colourless oil  
1700 cm<sup>-1</sup>  
224.5 (12 500)  
303.5 nm (4500)

n.m.r. CDCl<sub>3</sub>  
2.22 (1H, m, H-3b)  
2.71 (2H, m, H-1)  
2.95 (1H, m, H-9a)  
3.56 (1H, d, m, *J* = 8 Hz, H-3a)  
5.33 (1H, d, d, *J* = 9.5, 4.1 Hz, H-4)  
5.60, 5.73 (2H, m, H-2, H-3)  
6.20 (1H, d, m, *J* = 9.5 Hz, H-5)  
6.76 (2H, m, H-6, H-7)  
6.96 (1H, m, H-8)

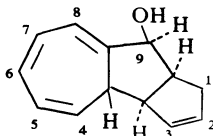
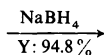
DNP m.pt 193°C



Reduction of (20) with NaBH<sub>4</sub> gave an alcohol, whose n.m.r. is consistent with the structure (22), further supporting the structure (20).



(20)



(22)

m.pt 87–89°C

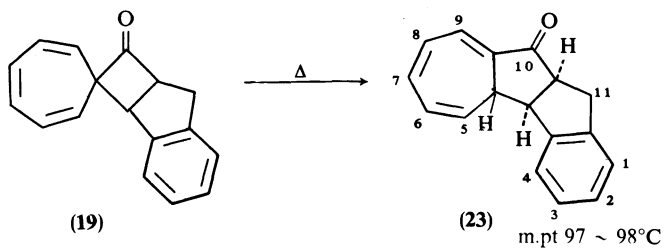
n.m.r. CDCl<sub>3</sub>

δ 1.82 (s, OH), 2.17 (1H, m, H-3b), 2.35 (1H, d, d, m, *J* = 16, 7.1 Hz, exo H-1), 2.60 (1H, d, d, m, *J* = 16, 4.2 Hz, endo H-1), 3.05 (1H, d, d, d, d, *J* = 7.1, 7.1, 7.1, 4.2 Hz H-9a), 3.28 (1H, m, H-3a), 4.65 (1H, br d, *J* = 7.1 Hz, H-9), 5.10 (1H, d, d, *J* = 9.5, 4.6 Hz, H-4), 5.75 (2H, m, H-2, 3), 6.02 (1H, d, m, *J* = 9.5 Hz, H-5), 6.27 (1H, m, H-8), 6.55 (2H, m, H-6, -7)

Furthermore, compound (19) was also isomerized by heating in refluxing benzene to give a ketone, m.pt 98°, whose n.m.r. supported the structure (23).

When a mixture of (19) and an excess of indene-1-*d* was heated, no deuterium was introduced into the product (23). This result indicates that the rearrangement of (19) is intramolecular.

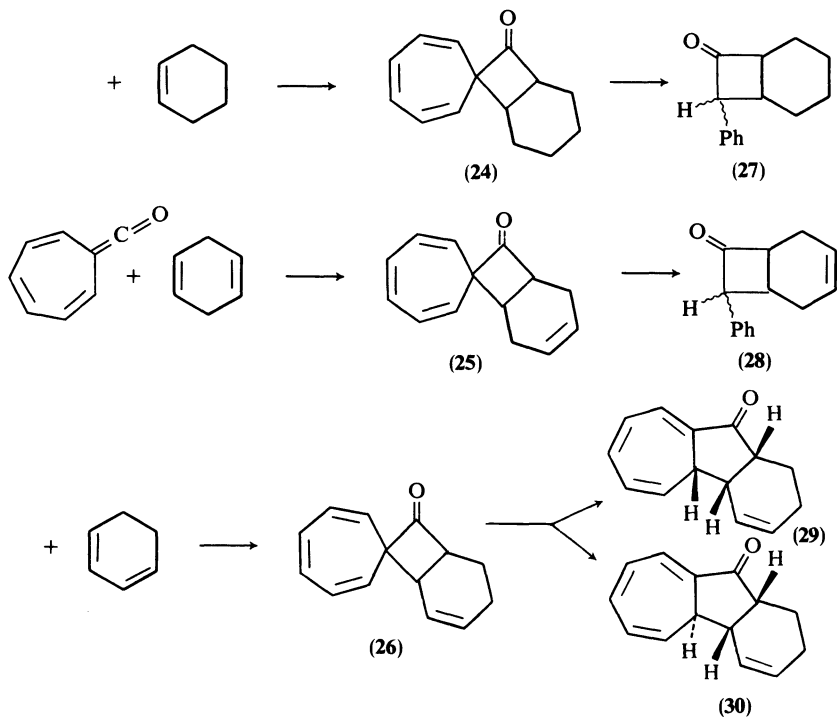
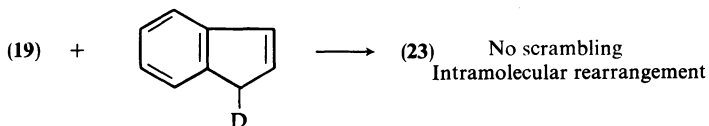
To get information about these rearrangements we carried out similar reactions with cyclohexene, 1,4-cyclohexadiene and 1,3-cyclohexadiene. Only the adduct with 1,3-cyclohexadiene (26) gave the cyclopentanone derivatives, (29) and (30), without stereospecificity, while (24) and (25) gave



i.r. (KBr)  $1695\text{ cm}^{-1}$

$\lambda_{max}$  217 nm ( $\epsilon$  17400), 228 (15900), 277–286 (7320), 310 (sh) (6210)  
n.m.r. (CDCl<sub>3</sub>)

$\delta$  2.56 (1 H, m, H-4c), 3.15–3.5 (3 H, m, H-10a, -11), 4.09 (1 H, d, m,  $J = 5.5$  Hz, H-4b), 5.56 (1 H, d, d,  $J = 9.5, 4.5$  Hz, H-5), 6.32 (1 H, m, H-6), 6.75 (2 H, m, H-7, -8), 6.95 (1 H, m, H-9), 7.15 (4 H, m, H-1 ~ 4)

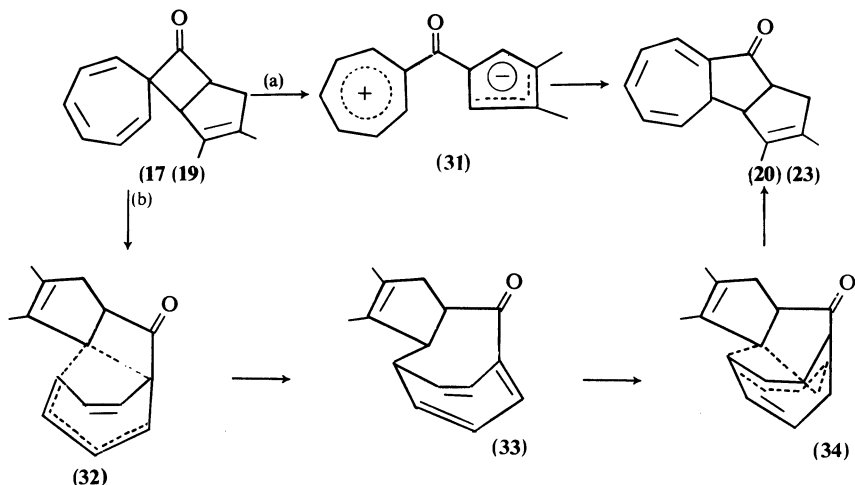




the phenylcyclobutanone derivatives, (27) and (28), respectively. These results indicate that a suitably located double bond is necessary to rearrange to the cyclopentanone derivatives.

The mechanism of the respective formation of (20) and (23) from (17) and (19) is interesting in the light of the well known orbital symmetry selection rules<sup>37</sup>. From the results mentioned above, we tentatively propose two pathways for this rearrangement; one is an ionic (a) through (31) and the other (b) involves two consecutive sigmatropic [1,5] shifts through (33). However, as mentioned previously, the cycloaddition product with cyclopentene does not rearrange to the compound corresponding to (20). Therefore, ionic mechanism (a) may be favourable. The kinetic study must provide further information about the rearrangement.

#### Mechanism

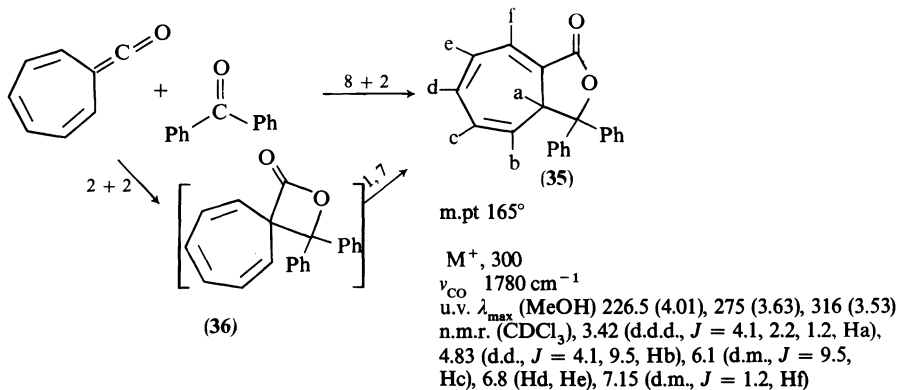


## REACTION WITH KETONES

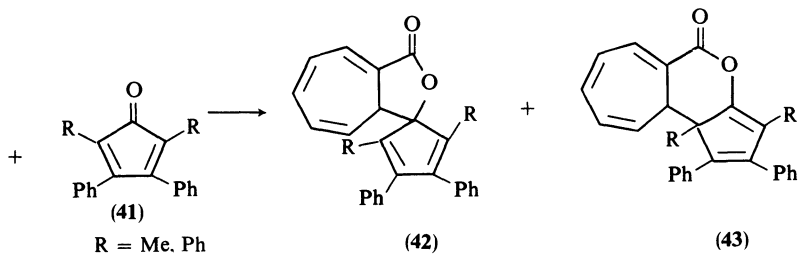
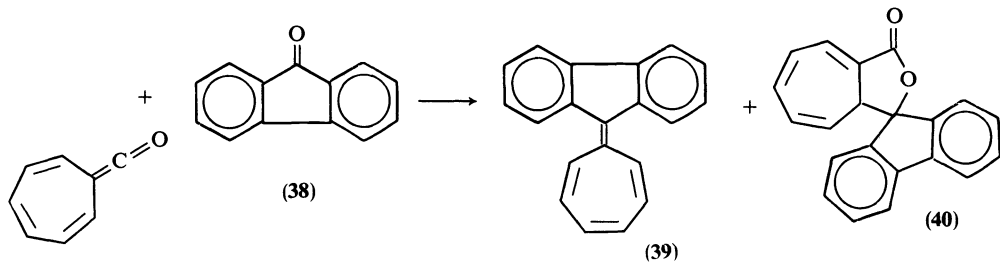
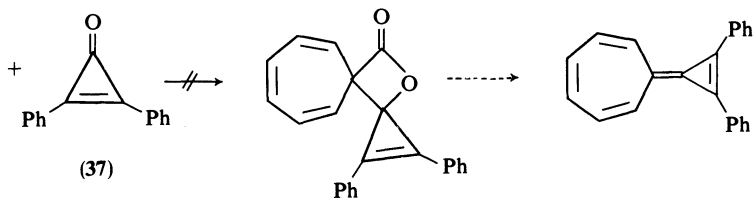
Reaction of 8-oxoheptafulvene with benzophenone in refluxing *n*-hexane afforded a compound, m.pt 164 ~ 165°, in *ca.* 10 per cent yield<sup>38</sup>. The compound shows  $M^+$ , 300; i.r. (KBr)  $\nu_{C=O}$ , 1780  $cm^{-1}$ ; u.v.  $\nu_{max}^{MeOH}$ , 226.5 nm ( $\log \epsilon$  4.01), 275 (3.63) and 316 (3.53), suggesting that it is a 1:1 addition product containing a conjugated  $\gamma$ -lactone formed by [8 + 2] cycloaddition of 8-oxoheptafulvene. Furthermore, the n.m.r. spectroscopic data indicated the structure (35) for the product. The process of the formation of compound (35) may also be explained by [1, 7] rearrangement of the [2 + 2] cycloaddition product (36).

The following illustration shows the reaction of 8-oxoheptafulvene (1) with cyclopropenone and cyclopentadienone derivatives<sup>36</sup>. From the result described later, we expected a new type of compound, a triheptafulvalene derivative by the reaction of (1) with 2,3-diphenylcyclopropenone (37), but (37) was recovered unreacted. However, fluorenone (38) afforded dibenzo-

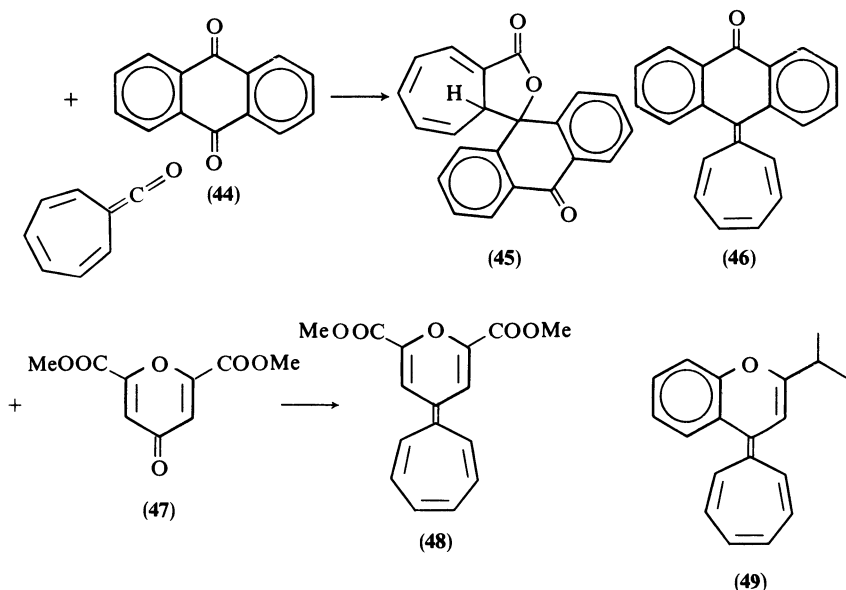
## Reaction with ketones



sesquifulvalene (39) as a result of elimination of carbon dioxide from the initially formed [2 + 2] cycloadduct besides the  $\gamma$ -lactone (40). The action of tetrasubstituted cyclopentadienones (41) produced the  $\gamma$ -lactones (42) and the  $\delta$ -lactones (43), the latter of which may be a [1, 5] rearrangement product of (42).



Reaction of (1) with anthraquinone furnished the  $\gamma$ -lactone (45)<sup>36</sup>. The expected quinarene (46) was not obtained. However, the reactions with  $\gamma$ -pyrone derivatives afforded the heptafulvene derivatives, (48) and (49), which are isoelectronic compounds to heptafulvalene.



### REACTION WITH TROPONES

The reaction of 8-oxoheptafulvene (1) with tropones (50) gave the 1:1 addition product (52), in good yield, together with a small amount of heptafulvalenes (51)<sup>38, 39</sup>. The structures (52) were deduced as shown in the scheme having novel norcaradiene and cycloheptatriene moieties in a molecule from the spectroscopic evidence, although an alternative structure (53) was also considered instead of the structure (52, X = H). In all cases, the substituents are exclusively located at the X-position.

The mechanism of the formation of heptafulvalenes and norcaradiene type compounds can be explained by [2 + 2] and/or [8 + 2] cycloaddition processes, followed by decarboxylations or valence bond isomerizations (54  $\rightarrow$  51 and/or 55  $\rightarrow$  52).

The nuclear Overhauser effects between Hb (or Ha) and any protons of the norcaradiene moiety could not be observed; however, the structure (53) can be excluded by the application of shift reagent for the n.m.r. The differences in p.p.m. on the n.m.r. of the compound (52) in the presence of paramagnetic chelate complex  $\text{Eu}(\text{DPM})_3$  are also shown in Table 1. It is clear from the table that cyclopropane ring protons (Hg and Hh) show the largest shift, which indicates these protons are located at the nearest position to the carbonyl oxygen<sup>38</sup>.

Reaction with tropones

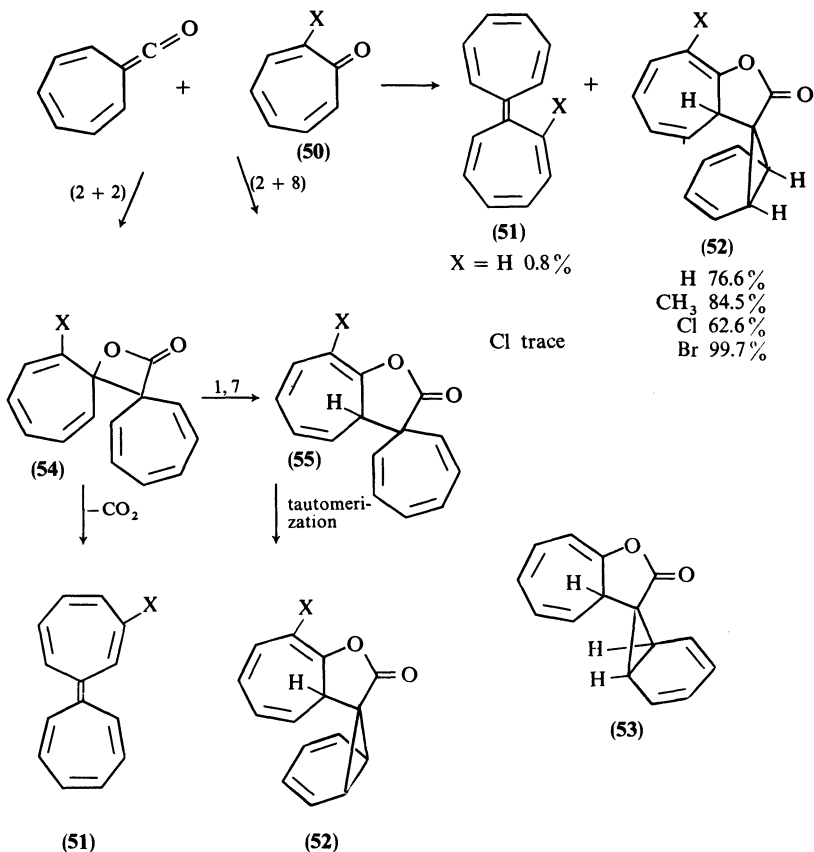


Table 1

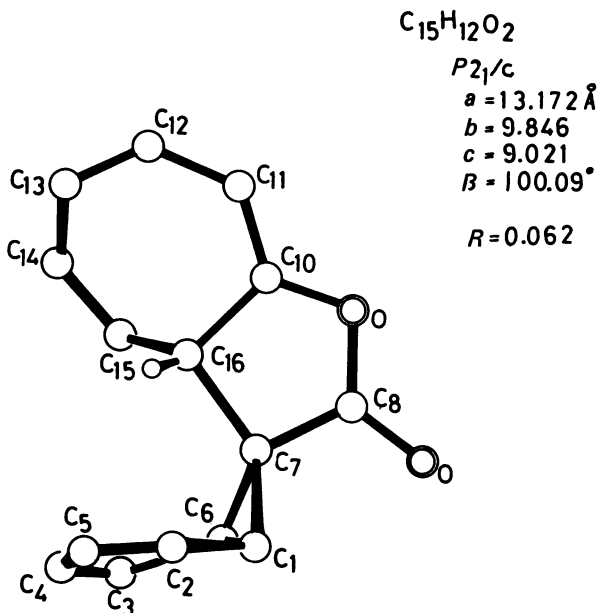
		Δp.p.m.,* Eu(DPM) <sub>3</sub>
<p>(52)</p>	Ha	1.70 d,t 1.27
	Hb	4.68 d,d 1.10
	Hc	5.9 m <1.0
	Hd, He	6.0 ~ 6.5 m <1.0
	Hf	5.75 ~ 5.9 m <1.0
	Hg, Hh	3.09 d, d 2.73
	Hi ~ Hl	6.0 ~ 6.5 m <1.0
	Jab	4.8
	Jac	1.7
	Jaf	1.7
	Jbc	9.8
	Jgh	7.5

\* Values (Δ p.p.m.) in the presence of 0.59 molar equivalents of Eu(DPM)<sub>3</sub>.

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Furthermore, the structure (52) was confirmed by x-ray analysis using a direct method, as shown below.

## X-Ray Analysis



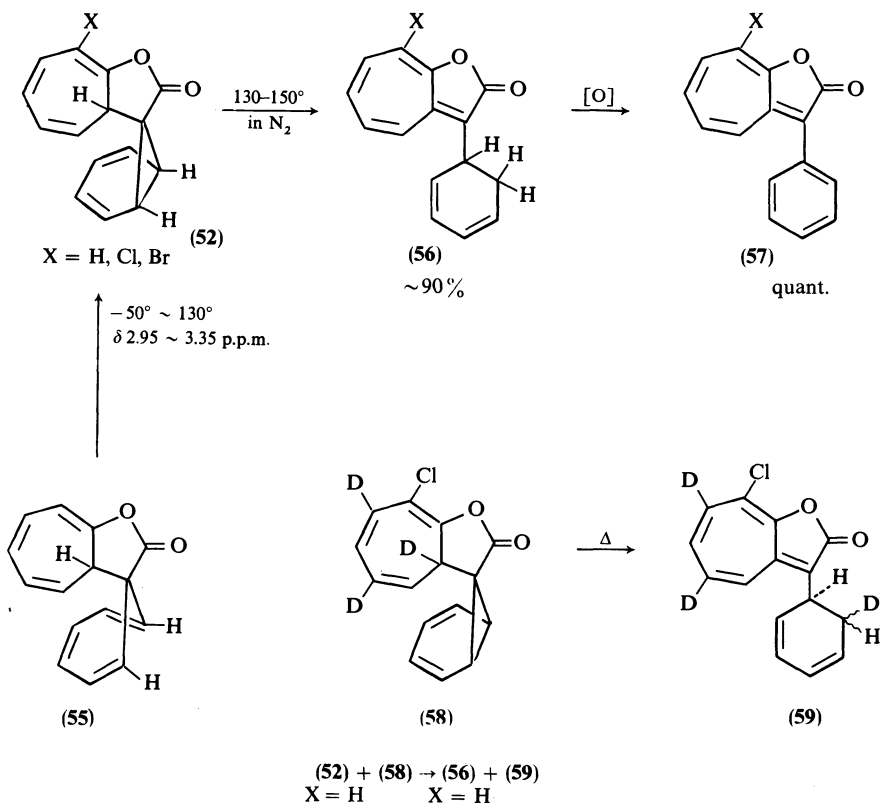
A variable temperature n.m.r. study of the compound (52: X = H) from  $-50^\circ$  to  $130^\circ$  exhibited that the chemical shift of the H-1 and H-6 protons shifted to lower field by 0.4 p.p.m. from  $\delta$  2.95 p.p.m., which indicated a mixture of valence isomers, norcaradiene (52) and cycloheptatriene (55), was present although norcaradiene structure was predominant.

When the compound (52) was heated in various solvents (chloroform-*d*, xylene, or dimethylsulphoxide) above  $130^\circ$  (effectively at  $150 \sim 180^\circ$ ) under nitrogen atmosphere, irreversible isomerization occurred, and the compound (56) was obtained.

Treatment of (56) with *O*-chloranil or heating of (52) at  $180^\circ$  under oxygen atmosphere afforded 3-phenyloxaazulan-2-one (57) in good yield. In a similar manner, the chloro derivative (52: X = Cl) afforded the 8-chloro derivative (56: X = Cl), and 8-chloro-3-phenyl-1-oxaazulan-2-one (57: X = Cl).

The thermolysis of the trideuterated adduct (58) afforded the rearranged product (59). The deuterium atoms were found to locate at 5, 7 and 6' positions by analysis of the n.m.r. spectrum, although the stereochemistry of deuterium at the 6' position could not be clarified. The thermolysis of equimolar amounts of (52: X = H) and (58) in refluxing xylene gave (56: X = H) and (59), and any crossover products of the deuterium atom were not obtained. These facts indicate that the rearrangement is intramolecular and must be a concerted reaction because if the rearrangement is initiated

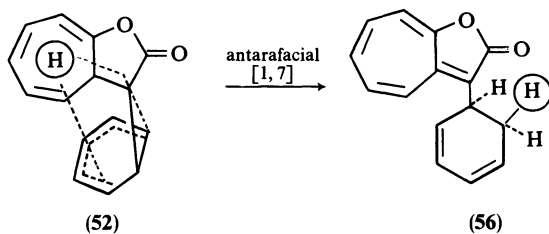
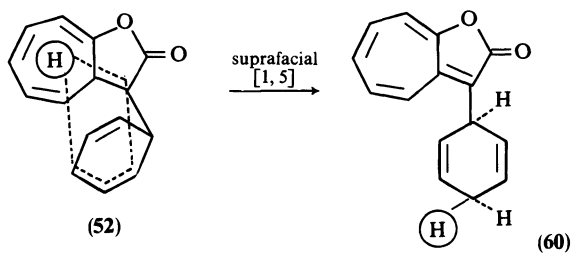
by ionic or radical reaction, the scrambling must be observed in the above cross reaction.



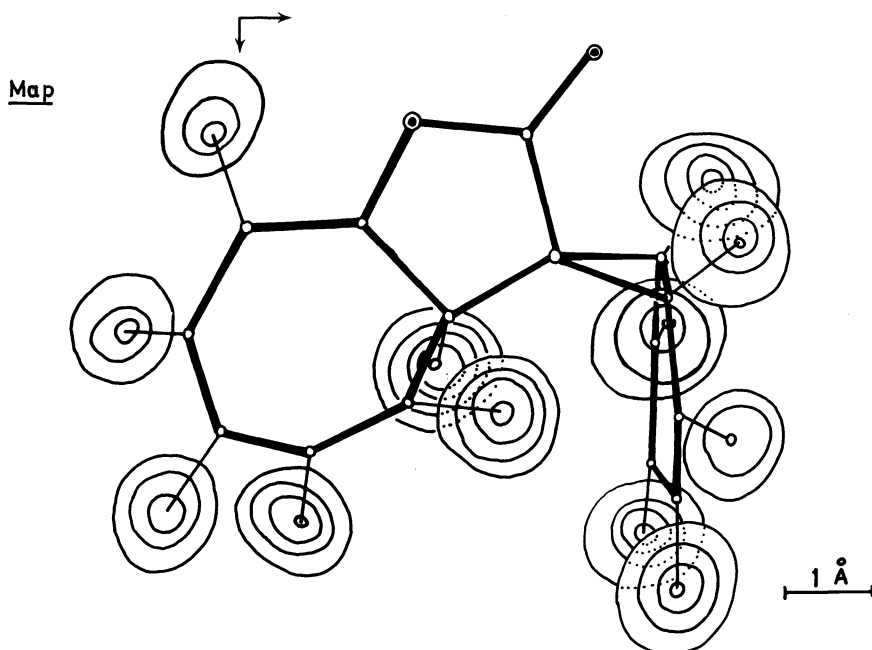
The kinetics of this reaction have been studied by n.m.r. measurement in chloroform-*d*, which indicated that the reaction is of the first order and the data of activation energy ( $E_a$ ) = 21.4 kcal mol<sup>-1</sup>, enthalpy of activation ( $\Delta H^\ddagger$ ) = 20.6 kcal mol<sup>-1</sup>, and entropy of activation ( $\Delta S^\ddagger$ ) = -25.8 e.u. were obtained. These data are comparable with those ( $E_a$  = 14 ~ 21.6 kcal mol<sup>-1</sup> and  $\Delta S^\ddagger$  = -25.2 ~ -13.6 e.u.) obtained for [1, 7] sigmatropic rearrangements in the mobile system<sup>44</sup>. Furthermore, the  $E_a$  value (21.4 kcal mol<sup>-1</sup>) is lower than those (26.4 ~ 32 kcal mol<sup>-1</sup>) for [1, 5] sigmatropic rearrangements in the cycloheptatriene system<sup>45</sup>.

According to the Woodward-Hoffmann rule<sup>37</sup>, suprafacial [1, 5] and antarafacial [1, 7] sigmatropic rearrangements of H-16 are allowed for (52) depending upon which bond of the cyclopropane ring cleaves, to give 3-(cyclohexa-2,5-dienyl)-1-oxazulone (60) and (56), respectively. Our result is the first example of antarafacial [1, 7] sigmatropic rearrangement in a rigid system, although many examples of the rearrangement in mobile systems have been reported<sup>44</sup>.

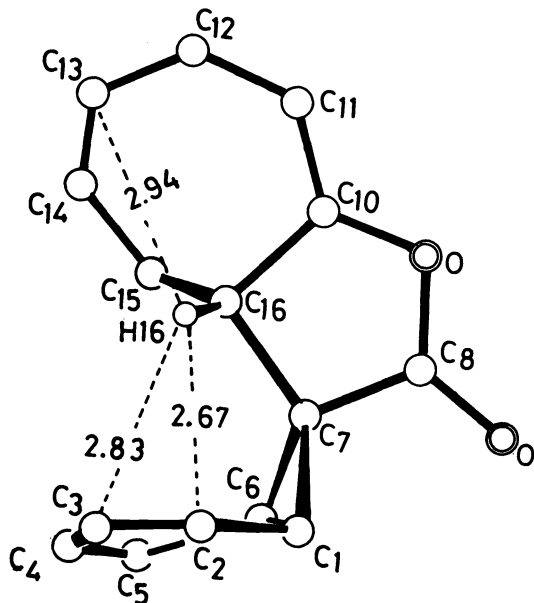
## 8-OXOHEPTAFULVENE



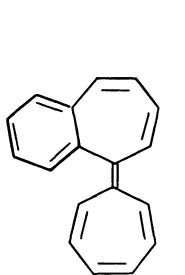
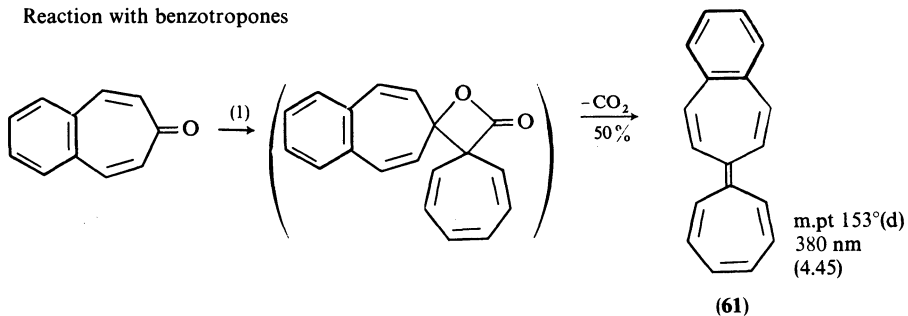
The map which follows was obtained by x-ray crystallography of the compound (52) and the electron density of hydrogen was found by difference synthesis.



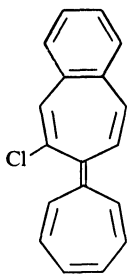
The structure overlaid was transferred from the preceding map for easy understanding. The structure shows that the distance (2.67 Å) between H-16 and C-2 is shorter than the distances (2.83 Å and 2.94 Å) between H-16 and C-3, and H-16 and C-13, respectively. This may be the reason that the facile [1, 7] shift occurs in this system.



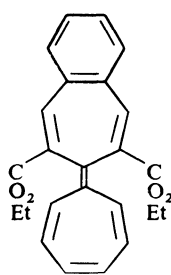
Reaction with benzotropone



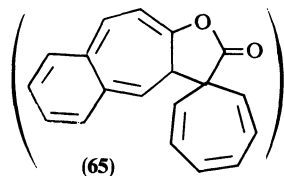
(62) Y 59.4%  
red oil  
344 (4.17)



(63) Y 50.5%  
red oil  
372 (3.96)



(64) Y 24.7%  
m.pt 136 ~ 7°  
361 (4.01)





It can be expected the [8 + 2] process might not occur in the reaction of (1) with benzotropones instead of tropone because the product of the [8 + 2] process must involve an unstable *o*-quinonoid benzene ring (65) as an intermediate.

Reaction of (1) with 4,5-benzotropone afforded fairly stable deep brown crystals (61), m.pt 153° (decomp) (benzene) in 50 per cent yield, which was proved to be 3,4-benzoheptafulvalene (61) by spectroscopic data<sup>46</sup>.

Similarly, the reaction of (1) with 2,3-benzotropone gave 1,2-benzoheptafulvalene (62) as deep brown oil in 59.4 per cent yield. The compound (62) is less stable than (61) and gradually polymerized on standing in a refrigerator under nitrogen atmosphere.

In the same way, compounds (63) and (64) were obtained.

The mechanism of formation of the heptafulvalenes can be explained by decarboxylation of the initially formed [2 + 2] cycloadducts of tropone carbonyls with 8-oxoheptafulvene as in the case of the reaction of benzotropone and diphenylketene to give diphenylbenzoheptafulvene<sup>47</sup>.

Reaction of 2-methoxytropone (66) with 8-oxoheptafulvene (1) afforded four products, (67), (68), (69) and (70). From the facts that the u.v. spectrum of (67) was very similar to those of heptafulvalene and its derivatives<sup>48</sup> and that the reaction of (1) with benzotropones gave benzoheptafulvalene in good yield<sup>46</sup>, as mentioned above, the compound (67) was found to be 2-methoxyheptafulvalene<sup>49</sup>.

The compound (69) was found to be methoxydihydro-1-oxaazulanone containing a norcaradiene moiety from the similarity of spectroscopic data to those of norcaradiene compounds obtained by the reaction of tropones and 8-oxoheptafulvene (1). The u.v. spectrum of (70) was similar to those of 1-oxaazulanones, and the double resonance experiments of the n.m.r. of (70) indicated the presence of a novel cyclohexa-1,4-diene moiety.

Alkaline hydrolysis of the compound (70) followed by decarboxylation of the resultant (71) afforded the tropone derivative (72) condensed with homobarrelene at 2 and 3 positions of tropone<sup>49</sup>.

The structure of the compound (70) was finally determined by the x-ray crystallographic analysis of its bromo-derivative (76) obtained in the following reaction.

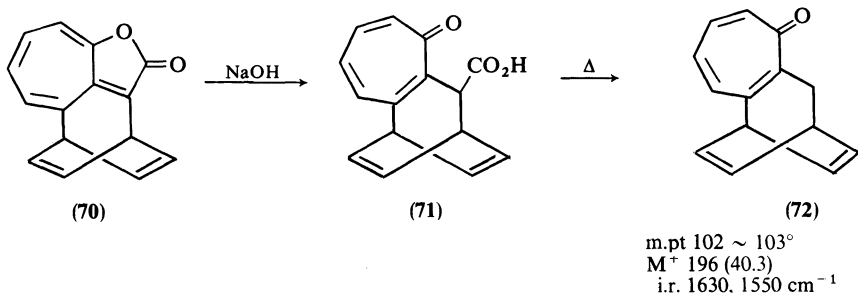
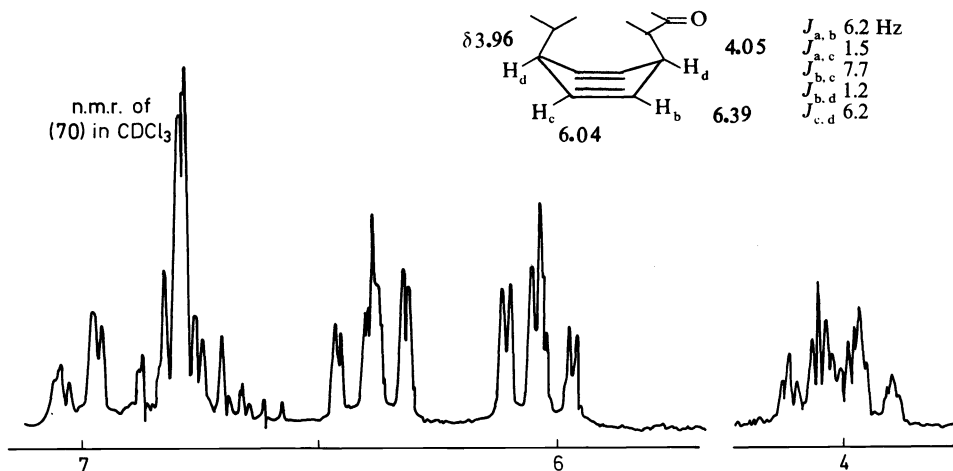
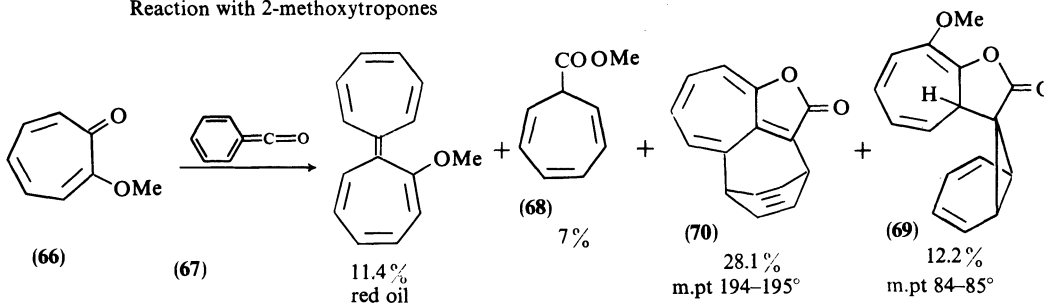
The reaction of 8-oxoheptafulvene (1) with 5-bromo-2-methoxytropone (73) also afforded the similar four products (74), (68), (75) and (76)<sup>49</sup>. The structures of these compounds were determined as shown in the scheme from the similarity of the spectroscopic data to the corresponding compounds (67-70).

A perspective drawing of the molecule of the compound (76) is shown overleaf. The structure was solved by the heavy atom method.

The reactions of 4-isopropyl-, 6-isopropyl-, 3-deuterio-, and 7-deuterio-2-methoxytropones with 8-oxoheptafulvene<sup>36,50</sup> provide some evidence for the mechanism of the formation of (70).

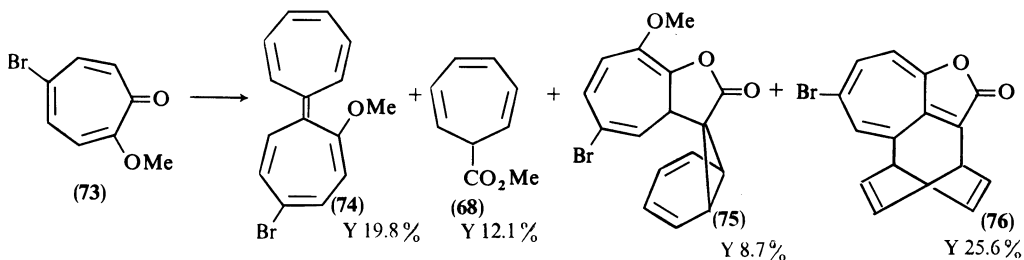
Reaction of 4-isopropyl-2-methoxytropone with 8-oxoheptafulvene resulted in the formation of four products: (68), (78), (79) and (80). In the case of 6-isopropyl-2-methoxytropone, compounds (68), (82), (83) and (84) were obtained. It is noteworthy that oxaazulanone derivative (83) is obtained instead of homobarrelene derivative corresponding to (80).

## Reaction with 2-methoxytropone



From the above result, it is found that the cyclohexa-1,4-diene moiety of (80) is formed between the positions of carbonyl oxygen and C-7 of 4-isopropyl-2-methoxytropone. However, it would be possible that the cyclization occurred at C-7 due to steric influence of the isopropyl group at C-4. Therefore, the similar reaction was studied using monodeuterated 2-methoxytropone<sup>50</sup>.

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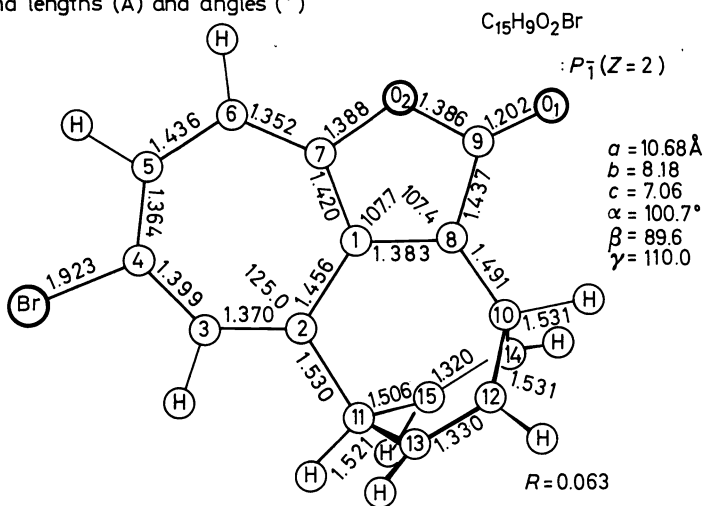


red oil  
 $M^+$  290, 288  
 $\lambda_{\text{CCl}_4}^{\text{max}}$  368 (3.97) nm  
 i.r. 1613, 1570  $\text{cm}^{-1}$

m.pt 130 ~ 131° (d)  
 $M^+$  334, 332  
 i.r. 1790,  
 1650  $\text{cm}^{-1}$

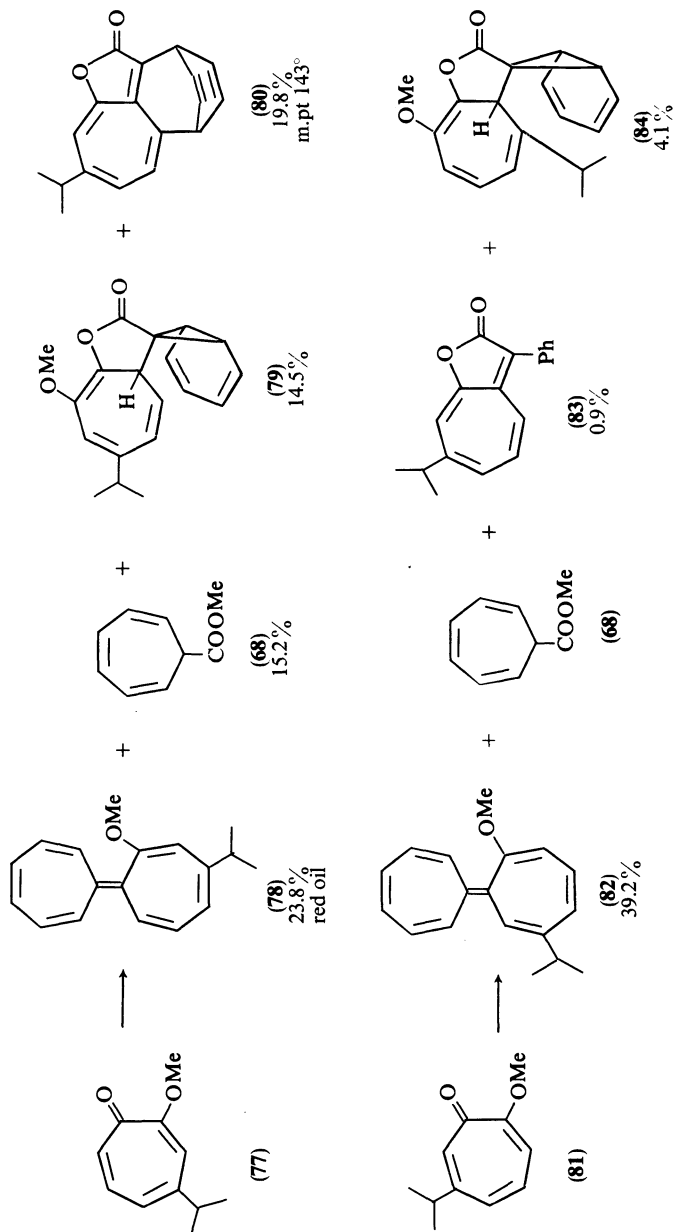
m.pt 234 ~ 235°  
 $M^+$  302, 300  
 $\lambda_{\text{iso-Octane}}^{\text{max}}$   
 225 sh (4.10), 250 (4.31),  
 382 sh (4.04), 396 (4.11),  
 406 (4.04), 415 (4.01),  
 440 (3.52), 480 (3.34),  
 516 (3.17), 560 (3.03)  
 i.r. 1740  $\text{cm}^{-1}$

Bond lengths (Å) and angles (°)

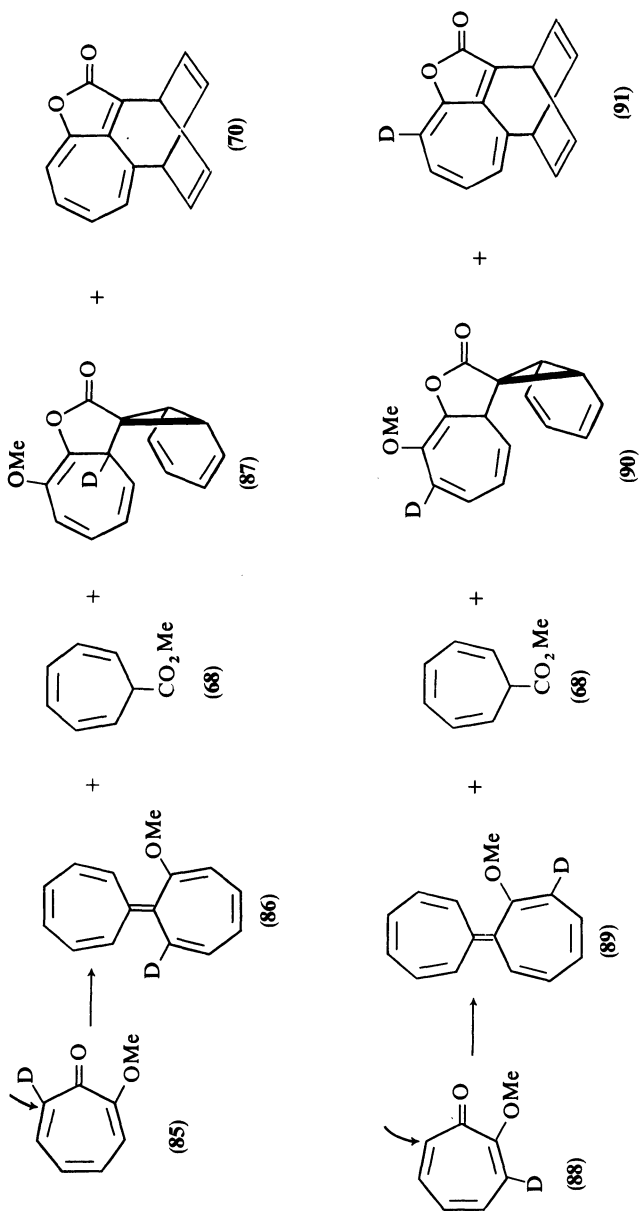


Reaction of 7-deuterio-2-methoxytropone (85) with 8-oxoheptafulvene afforded the corresponding four products, (86), (68), (87) and (70). 3-Deuterio-2-methoxytropone (88) also gave (89), (68), (90) and (91). The position of a deuterium atom in the compound (91) was determined to be at C-8 by the analysis of 300 MHz n.m.r.

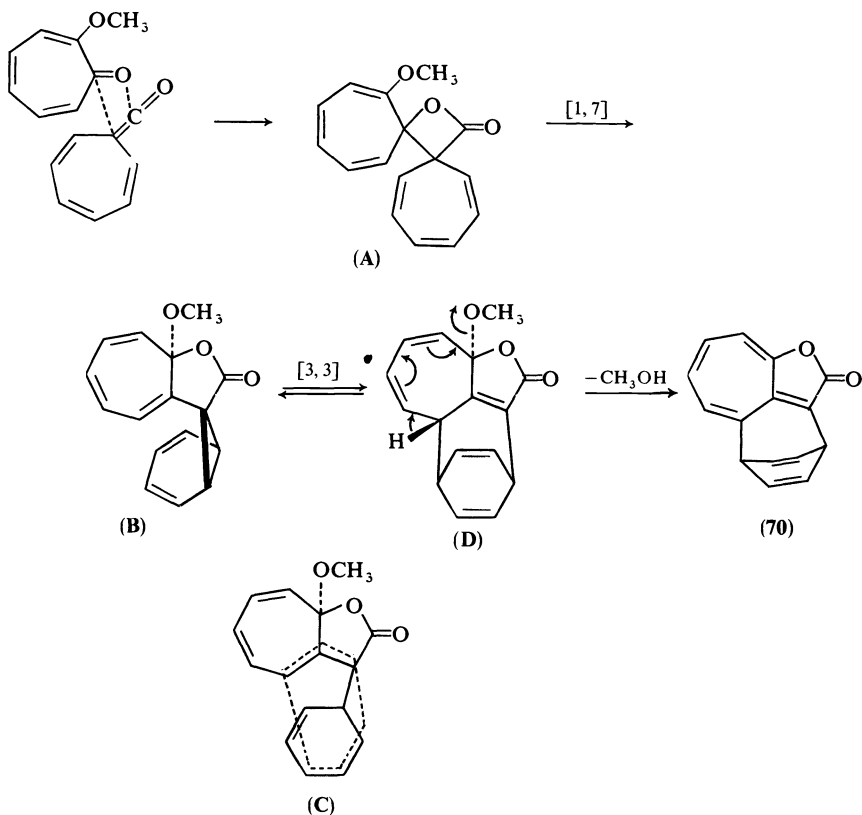
The above results are consistent with the fact that the cyclohexa-1,4-diene moiety formed between the positions of carbonyl oxygen and C-7 of 4-isopropyl-2-methoxytropone.



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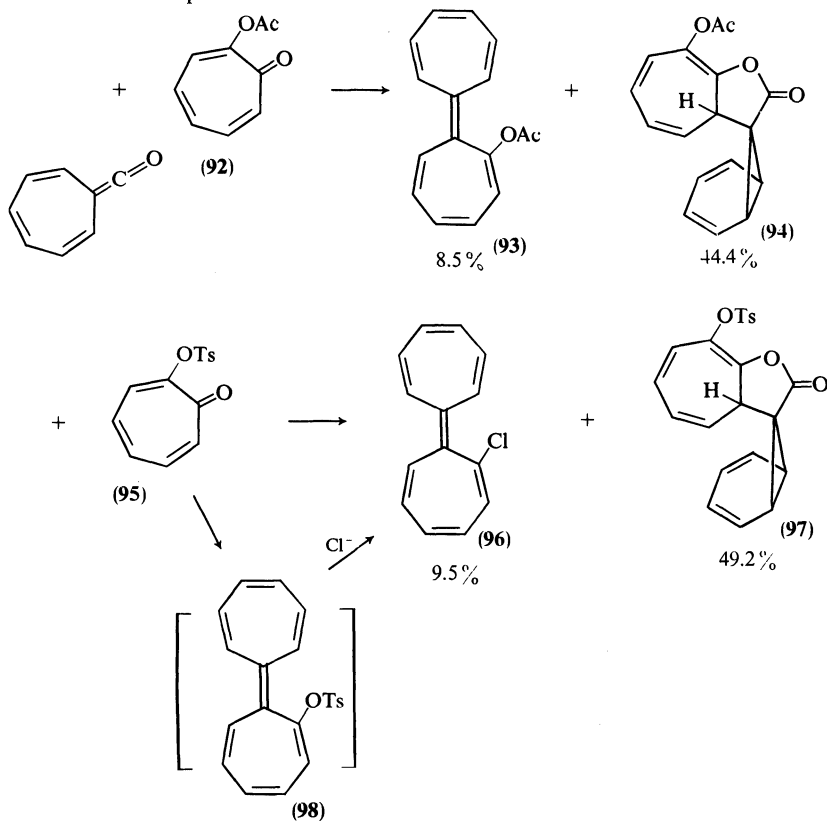
For the mechanism of the formation of (70) and (76) involving novel rearrangement, we propose the following scheme starting from the [2 + 2] cycloadduct (A) followed by [1,7] oxygen migration to norcaradiene intermediate (B), [3, 3] sigmatropic shift to (D), and elimination of methanol to give (70). It is known that Cope rearrangement easily proceeds even at low temperature in a sterically favourable system. The intermediate (B) would be ideally disposed to rearrange via the quasi-boat transition state (C).



The reaction of 2-acetoxytropone (92) with 8-oxoheptafulvene (1) afforded 1-acetoxyheptafulvalene (93) and [2 + 8] cycloadduct (94)<sup>51</sup>. On the other hand, the reaction of (1) and 2-tosyloxytropone (95) gave 1-chloroheptafulvalene (96) (9.5 per cent) and [8 + 2] cycloadduct (97). The formation of (96) can be explained by substitution of the tosyloxy group of the initially formed 2-tosyloxyheptafulvalene (98) with chloride ion formed from tropylcarboxylic acid chloride and triethylamine. An alternative explanation which consists of the initial formation of 2-chlorotropone from 2-tosyloxytropone followed by the reaction with 8-oxoheptafulvene (1) can be ruled out because the reaction of 2-chlorotropone with (1) has been known to give the [8 + 2]

cycloadduct substituted with chlorine atom as major product<sup>46</sup>. The nucleophilic substitution is the first example in the heptafulvalene series although the detailed reaction mechanism is not yet clear.

Reaction with other tropones

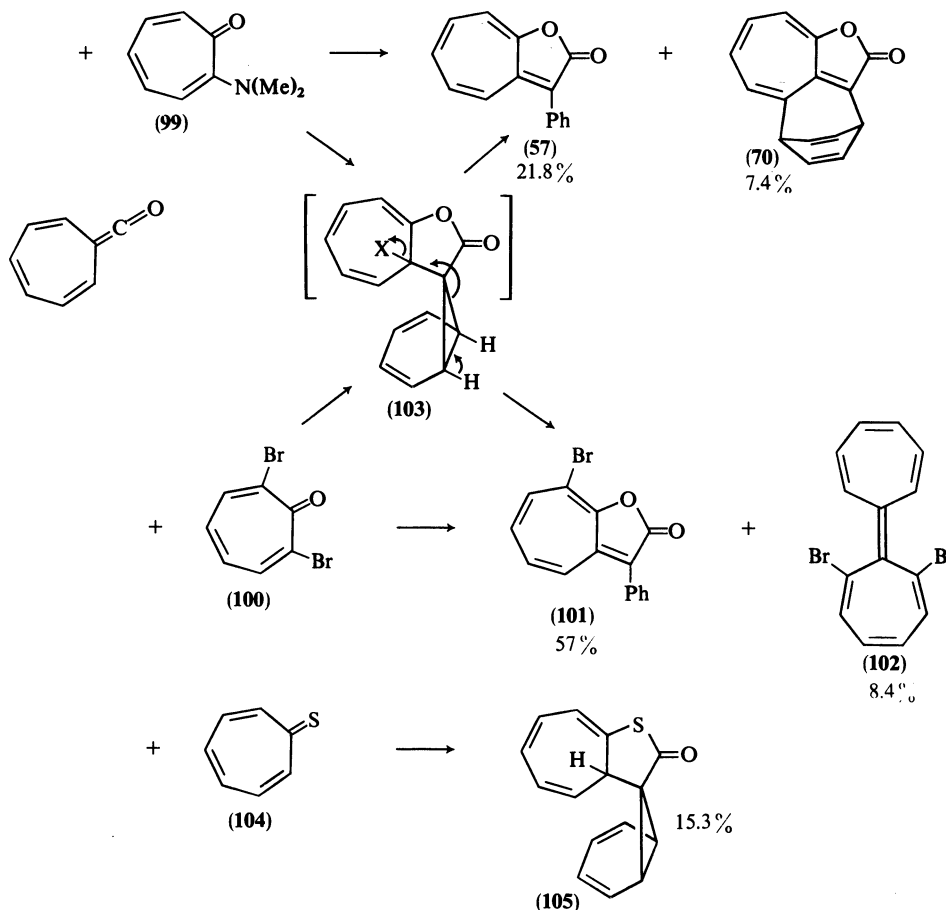


The pattern of the reaction of 2-dimethylaminotropone (99) with (1) was found to be completely different from those of (92) and (95), and the reaction gave 3-phenyl-1-oxaazulan-2-one (57) (21.8 per cent) and the cage molecule (70)<sup>51</sup>.

The direct formation of (57) is the first example in the reaction of tropones with (1), and the mechanism can be explained by the elimination of dimethylamine involving a cleavage of cyclopropane ring from the [8 + 2] cycloadduct (103) which is formed by the cycloaddition between the C-2 and carbonyl oxygen of 2-dimethylaminotropone (99) with (1) as shown in the scheme<sup>51</sup>.

2,7-Dibromotropone (100) yielded 1,6-dibromoheptafulvalene (102) and 8-bromo-3-phenyl-1-oxaazulan-2-one (101)<sup>51</sup>.

The reaction of tropone thione with (1) afforded only the [8 + 2] cycloadduct (105)<sup>51</sup>.



As a conclusion of the reaction of 8-oxoheptafulvene with tropone, at first [2 + 2] cycloaddition might occur in all cases, and four subsequent processes must follow. First of all is decarboxylation to heptafulvalene, second is [1, 7] carbon migration to give norcaradiene compounds, third is [1, 7] oxygen migration followed by Cope rearrangement to oxazulanone with cyclohexa-1,4-diene moiety, and last of all is [1, 7] carbon migration to give another norcaradiene intermediate which easily eliminate hydrogen halide to afford phenyl-1-oxaazulanone.

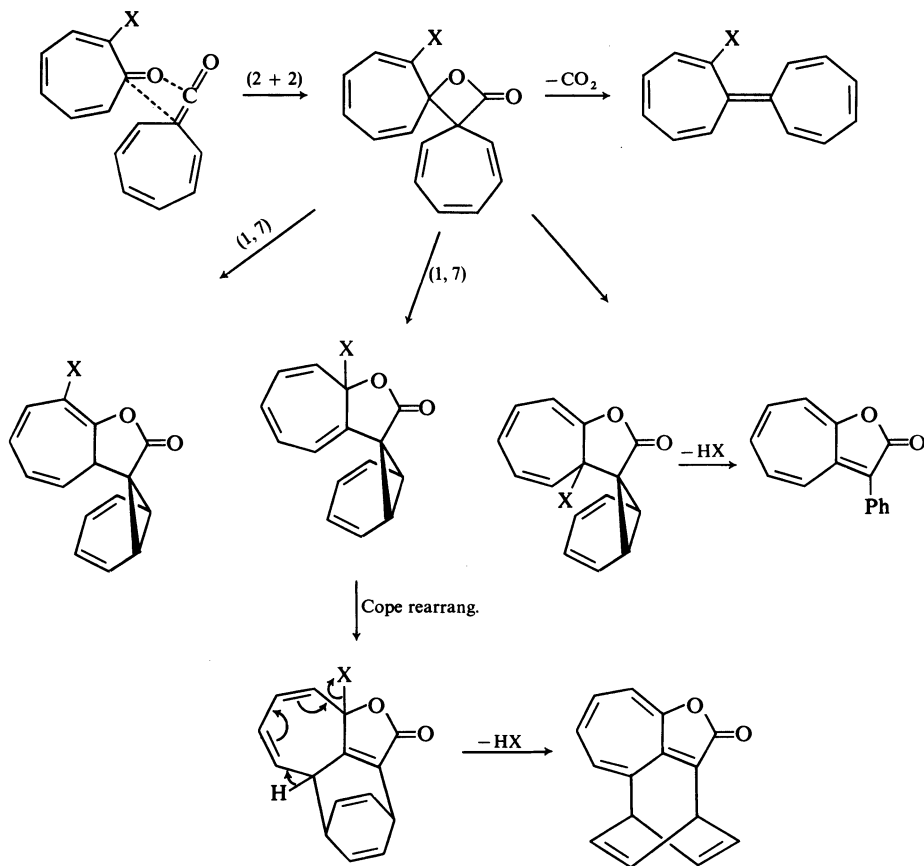
### ACKNOWLEDGEMENTS

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Mechanism of reactions with tropones



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