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CYCLOHEPTA[b][1,4]BENZOXAZINE AND RELATED COMPOUNDS —— SOME NOVEL ASPECTS IN TROPONOID CHEMISTRY

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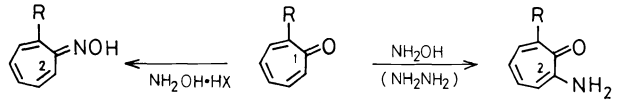
Abstract - Monocyclic troponoids bearing a good leaving group at C-2 ("reactive troponoids") are highly sensitive towards various nucleophiles, whereas those fused with benzene or heteroaromatic rings tend to lose such characteristic reactivities of troponoids owing to the overwhelming aromatic characters of the fused system. Cyclohepta[b][1,4]benzoxazines, a heteroaromatic-fused troponoid, have been shown to possess a reactive tropylium system analogous to the cyclohepta[b]furan-2-ones and -imines. The 6- and 8-bromo-cyclohepta-benzoxazines react with o-aminophenol and its analogues to give many interesting products, most of which were isolated and characterized. The courses of this condensation reaction dramatically alter when subjected to only slightly different conditions. The oxidation of S- and N-analogues of the title compounds has also been examined.

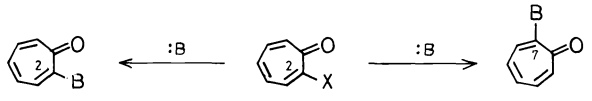
INTRODUCTION

Chemistry of troponoid compound emerged unexpectedly about 40 years ago during the study of a certain kind of natural products and since then, it has grown up rapidly into the main part of a new area of organic chemistry, which is now commonly called "chemistry of nonbenzenoid aromatic compounds". (Ref. 1) It has been generally recognized that as compared with usual compounds the courses of many reactions of troponoids are far more dramatically altered by a slight difference of the inner and outer environement of the molecule, such as structure of the substrate, kind of reagents, catalysts, and solvents, or even concentration and temperature of reactants. The following few examples are of unique reactions of monocyclic



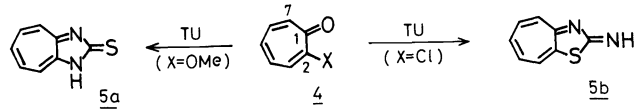
2 1 3

troponoids: 1) Tropone 1 gives its oxime 2 and azines with mineral acid salt of hydroxyamine and hydrazine, whereas treatment of tropone with their free bases produces 2-aminotropone 3 quantitatively (Ref. 1). 2) Troponoid compounds bearing a good leaving group at C-2 (usually called "reactive troponoids" 4) are highly sensitive towards various nucleophiles to yield normal substitution products at C-2 or cine substitution products at C-7, or various benzenoid products after rearrangement, depending on the reaction



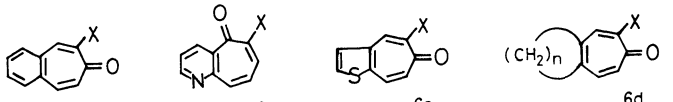
"normal" 4 "cine"

conditions (Ref. 1). 3) These reactive troponoids readily condense with bifunctional nucleophiles such as guanidine, thiourea, malonate and acetoacetate, directly providing tropylium compounds fused with heteroaromatic rings: e.g. 2-methoxy- (4a) and 2-chloro-tropone (4b) easily react with thiourea (TU) to afford cyclohepta-imidazol (5a) and -thiazol (5b) respectively in excellent yields. In contrast, no such reactions are generally observed with those fused troponoids 6a-d. This has been explained in terms of the diminished aromatic character of the troponoid ring caused by the overwhelming aromaticity of the fused aromatic



5a 4 5b

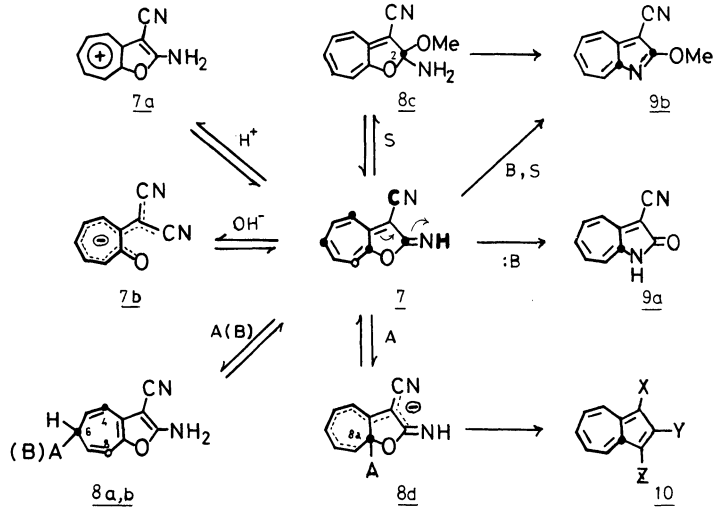
or heteroaromatic nucleus, or by the ring strain of the fused cycloalkane ring (Ref. 1).



6a 6b 6c 6d

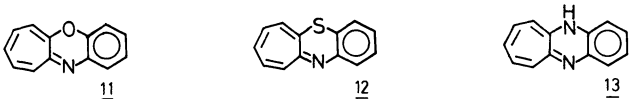
However, we have found recently a number of troponoids fused with a heteroaromatic ring which exhibit unique characters based on a tropylium system. For example, as illustrated in Scheme 1, cyclohepta[b]furan-2-imine (7) (and the corresponding lactone) reversibly forms stable cation (7a) with acid, the anion (7b) with alkali, and the covalent addition products 8a or 8b with active methylene compounds (A) and the catalyst amines (B), or 8c with solvent methanol (S), sometimes accompanied by the irreversible ring transposition to afford 1-azaazulenes 9a and 9b.

Scheme 1



7a 8c 9b 7b 7 9a 8a,b 8d 10

Moreover, polysubstituted azulenes (10) are directly and almost quantitatively available from 7 under appropriate conditions (Ref. 2). This kind of complex reactions were very rare and attributed to the large polarizability of the fused ring system and relatively facile ring-opening character of furan ring compared with other heterocycles. As will be described herein, cyclohepta[b][1,4]benzoxazine (11) and its S- and N-analogs (12 and 13) were found to be another type of interesting reactive compounds possessing a tropylium system (Refs. 3, 4).



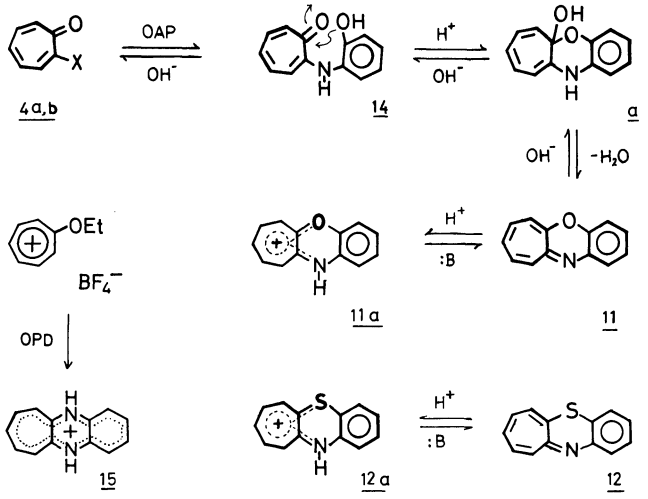
11 12 13

CYCLOHEPTA[b][1,4]BENZOXAZINES

Condensation of 4a,b with o-aminophenol (OAP) in ethanol produced o-hydroxyanilinotropone (14), which readily cyclized to the parent compound 11 upon heating with acetic acid containing a trace of conc. sulfuric acid; without

sulfuric acid the cyclization was incomplete (Scheme 2). Upon treatment with alkali 11 reproduced 14, which subsequently further hydrolyzed to tropolone and OAP on heating with excess alkali. On the other hand compound 11 was stable in strong acid and confirmed by NMR to exist as the red colored cation 11a stabilized by delocalized 6π tropylium (or acyclic 10π) system (Ref.3). The similar cation 12a was also derived from the S-analog 12 which had been prepared earlier from 4 and o-aminothiophenol (OAT)(Ref. 4)

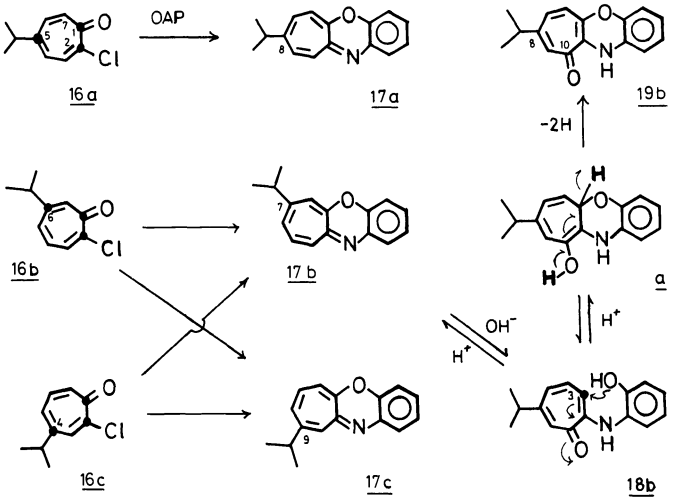
Scheme 2



These cations appear to be different from the dark greenish cation 15 which was obtained by Fukunaga from ethoxytropylium tetrafluoroborate and o-phenylenediamine (OPD) and suggested to possess 16 π periferal delocalization system (Ref. 5)

On refluxing with OAP in acetic acid, 5-isopropyl-2-chlorotropone (16a) provided 17a as a single product, whereas both isomeric tropones 16b and 16c gave almost a 1 : 1 mixture of 17b and 17c (Scheme 3). This suggested that the amino group of OAP was almost equally attacking C-1 and C-2 of 16 but the cine substitution at C-7 was not detected in this condensation reaction. Besides these main products 17a-c, a trace amount of minor products

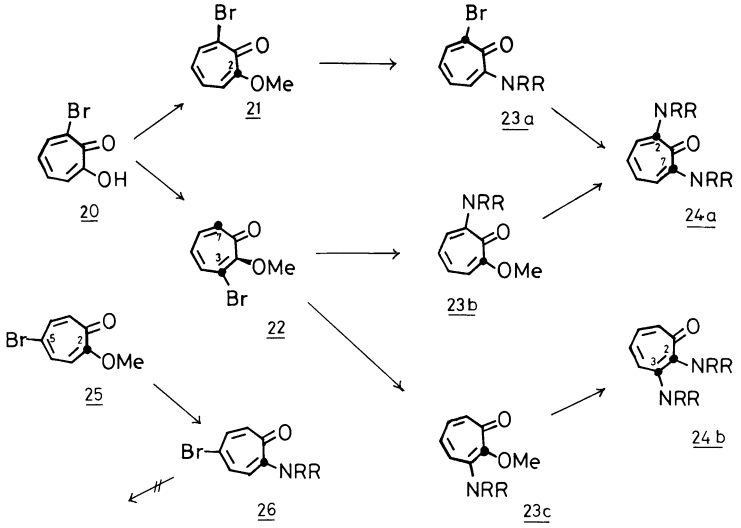
Scheme 3



19a-c were isolated in all cases; e.g. 19b was formed from 16b probably via 18b, followed by air oxidation of the intermediate a as shown in Scheme 3. This unusual ring-transposition accompanied by dehydrogenation takes place only to a small extent (less than 1% yield) in the present case, but it becomes significant for other types of active troponoids as will be described later (Ref. 3).

About 30 years ago we prepared two isomeric methyl ethers 21 and 22 from 3-bromotropolone (20) with diazomethane and noticed that these two methyl ethers showed very different reactivities towards alkali (Ref.1). The dipole moment and X-ray study indicated that the 2-methoxy group of 22 is forced to stay out of plane of the seven-membered ring because of the steric repulsion by the bulky bromine and carbonyl group (Ref. 5). Therefore, the nucleophilic displacement at C-2 of 22 is expected to be retarded or slow. (Ref. 1). Therefore we took up the study of condensation of 21 and 22 with OAP. Meanwhile, Takase, et al. have recently reported that the treatment of 21 with a mono-functional nucleophile such as morpholine or pyrrolidine first gave the 2-substituted product 23a exclusively, then the disubstituted tropone 24a, whereas 22 first afforded 3- and 7-substituted products 23c and 23b, which eventually yielded 24b and 24a, respectively.
5-Bromo-2-methoxytropone (25) on the other hand has been known to afford the mono-substituted product 26 but no disubstituted derivative (Scheme 4) (Ref. 7). One might expect similar reactivities, at least in the initial stage, when OAP is used as a nucleophile.

Scheme 4



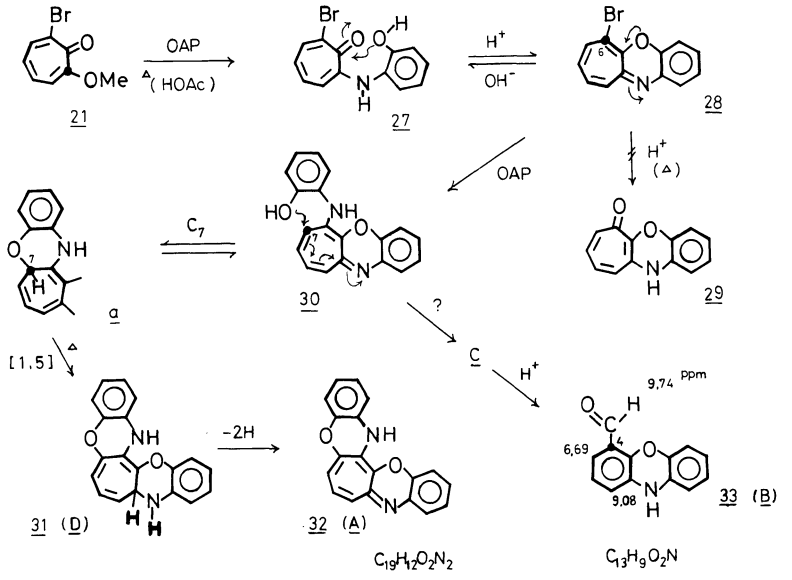
Throughout our present study the reaction was followed periodically by the reversed phase HPLC equipped with a stopped-flow UV measurement apparatus for product analysis in order to establish complete reaction pathways, and also the same reaction was repeated at least two or three times to confirm the reproducibility.

Condensation of 21 and OAP in refluxing acetic acid mainly gave 2-(2-hydroxyanilino)-7-bromotropone 27 in 70% yield by normal substitution at C-2 as in the case of 23a. In addition to this, 4.7% yield of yellowish orange substance B and 0.5% of a dark violet pigment A were also isolated. The major product 27 readily cyclized to give 28 upon heating with acetic acid containing a trace of sulfuric acid as was obseved in the case of the parent compound 11. Compound 28 reverts to 27 and eventually to 3-bromotropolone and OAP in alkali. Treatment of 28 with another equivalent of OAP in acetic acid produces a mixture of A and B, whereas the same treatment in alcohol yields mainly B. (Ref.3)

The elementary analysis of substances A and B and their spectral data led us to assign the structures 32 and 33 for these products respectively (Scheme 5). Compound A is produced presumably via intermediate 30 and its cyclized form a, followed by [1,5]-hydrogen shift to 31 (D) and dehydrogenation.

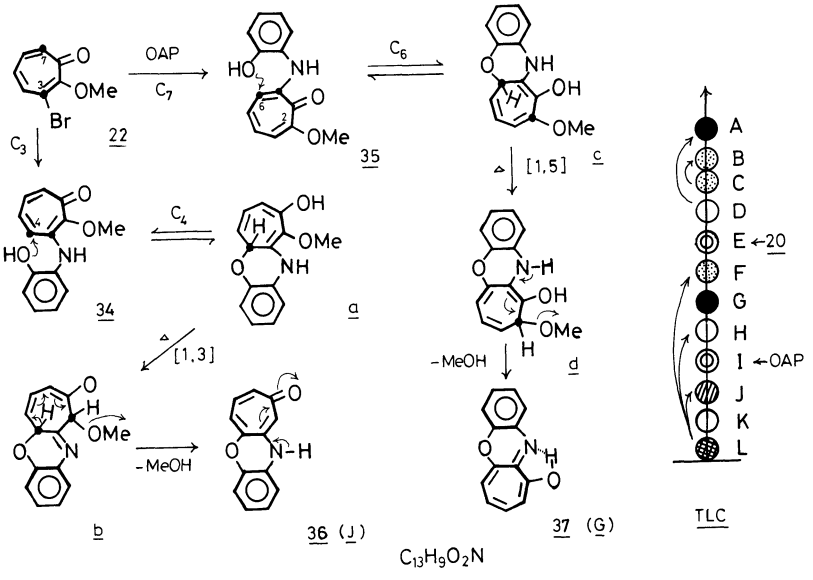
The formation of these unexpected minor products prompted us to examine the

Scheme 5



condensation reaction of isomeric 22 and OAP. On checking with silicagel TLC using 10% methanol-benzene as an eluent, the reaction products were nicely separated into at least twelve, colorful spots which were referred to as A, B, C, - - - and L according to the Rf values (Scheme 6). The two-dimentional development showed that substance D readily changed to A, and C gradually decomposed to B and OAP on heating in methanol. Substances F, H, and J were slowly produced when the most polar spot L was again developed with acetone, suggesting that L contained precursors of these spots. The structures of compounds G and J were assigned to 37 and 36 respectively on

Scheme 6



the basis of the elementary analysis and spectral data, and the possible reaction pathways for the formation of these products are shown in Scheme 6. The normal and cine substitution of the bromine atom of 22 with the amino group of OAP should give the unstable intermediates 34 and 35 (probably in spot K) which subsequently produces the 1 : 1 condensation products J and G respectively after the ring-closure and hydrogen shift, then removal of a molecule of methanol (Ref. 3).

An example of the reversed phase HPLC chromatogram of the reaction mixture is shown in Fig. 1 after heating 22 and OAP in acetic acid at 100°C for 30 minutes. Each peak was characterized by the stopped-flow UV spectra and TLC, also by MS after separation, if necessary. The assignment of the major peaks 3 (OAP), 4 (J), 7 (22) and 9 (G) thus made are shown in Fig. 1. The peaks 1 and 2 are due to the more polar species L and K mentioned earlier.

When the heating was continued several hours peaks 10 to 14 began to appear at 20 to 30 minutes of retention time, their amplified figures being shown in the right half of Fig. 1. The peaks 11, 12 and 13 were identified to be of substances C, D and B, respectively, by the stopped-flow UV measurement and TLC (Ref. 8).

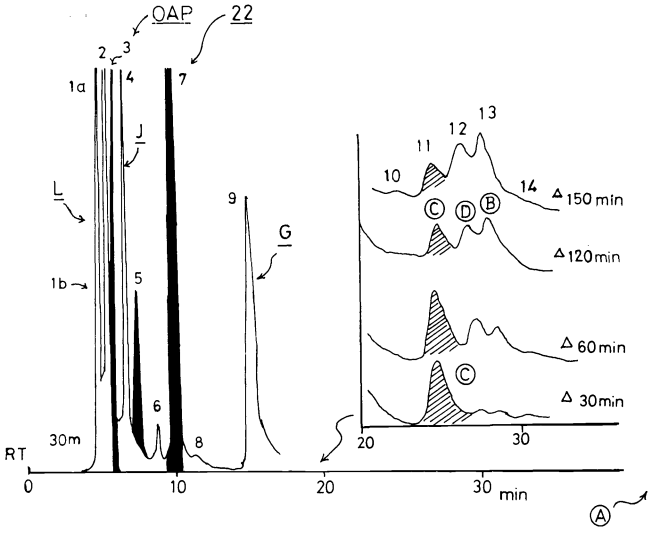


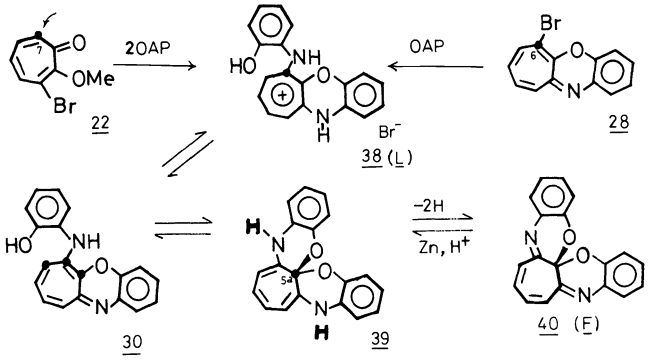
Fig. 1 The reversed-phase HPLC chromatogram of the reaction products from 22 and OAP in AcOH at 100°C after 30 minutes.

The polar substance L was isolated as dark reddish brown crystals from the reaction mixture of 22 and excess OAP by using preparative silicagel column chromatography or in better yield from the combination of 28 and OAP. The elementary analysis showed the composition $C_{19}H_{15}O_2N_2Br$ and the structure 38 (hydrobromide salt of 30) was assigned for L from the spectral data. This salt was found to be the key intermediate for various products such as A, C, and F, depending on the position of the subsequent ring closure as shown in Scheme 6 and 7. When L was allowed to stand in methanol containing a trace of alkali or purified by alumina chromatography, compound F was mainly obtained as orange yellow crystals, and its structure 40 was established by elementary analysis ($C_{19}H_{12}O_2N_2$) and spectral data. Compound F, an isomer of the dark reddish violet pigment A, contains an interesting chiral center in the molecule and formed very likely through the ring-closed tautomer 39 of the key intermediate 30, followed by air-oxidation (Scheme 7). It should be noted that F reproduced the salt L (as acetate) by zinc dust reduction in acetic acid, whereas A gave a different, unidentified product.

Although substances C and D were identified by TLC and HPLC as the unstable precursors of the products B and A respectively, these intermediates were formed only limited quantities under the above conditions (i.e. in refluxing acetic acid). Thus we tried to optimize the reaction conditions to prepare these compounds for structural assignment, and found that C was formed as an almost single product when 1 : 3 mixture of 28 and OAP was simply kept in the refrigerator. Substance C was found by the elementary analysis and spectra to be a Schiff base 41 of the rearranged product B (33) and confirmed to be hydrolyzed rapidly to B and OAP by the addition of a trace of dilute sulfuric acid via a deep reddish purple colored intermediate (the iminium salt d).

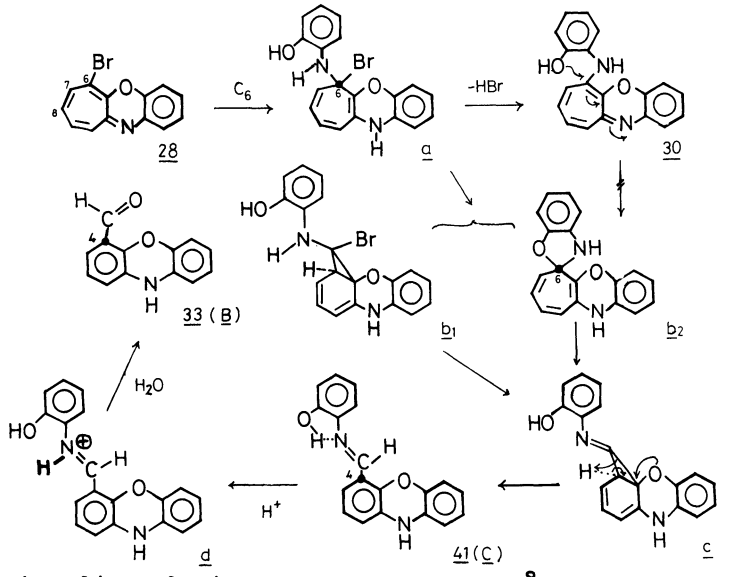
Although the exact course of this interesting but unusual rearrangement has not been clarified, a plausible mechanism for the formation of C from 28 is shown in Scheme 8. We thought at first the rearrangement would proceed through the normal substitution product 30 and its spiro-tautomer b_2, then

Scheme 7

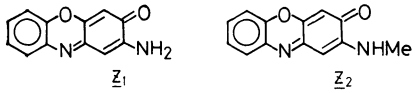


the norcaradiene intermediate c. However, compound L (HBr salt of 30) mainly gives F by air oxidation (Scheme 7), and C is readily produced on

Scheme 8



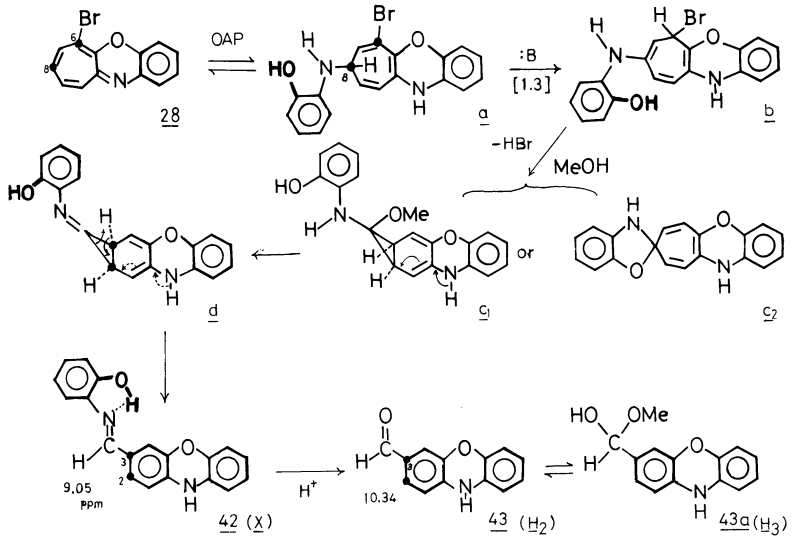
standing a methanolic solution of 28 and OAP at 5°C as described above. These facts suggest that the Meisenheimer-type intermediate a may directly give rise to c via b_1 (or b_2). It is known that tropone-imines are generally stable and do not rearrange. Accordingly we speculate at the moment that a combination of the instability of the π-excessive ethylenic 1,4-oxazine system of a or b_2 and an electron releasing effect of the heterocyclic O-atom of b or c is considered to be the most likely driving force to result in this irreversible ring contruction to yield C. In an attempt to clarify the exact mechanism of this rearrangement, the condensation of 28 and OAP (1 : 2) in methanol was carried out in the presence of base such as Dabco (Ref. 9). In this case a new compound X predominantly formed among the minor products H_1 and H_2. H_1 was found to be 2-aminophenoxazine-3(3H)-one (Z_1) produced by the air-oxidation of



OAP itself under these basic conditions. Curiously a trace of N-methyl derivative Z_2 was also isolated from the polar part of the reaction mixture (Ref. 8). Compound X almost completely changed into a mixture of H_2, H_3 and OAP, when a trace of sulfuric acid was added into a methanolic solution of X. Thus these compounds were isolated by preparative HPLC and characterized by elementary analysis and spectral data, and also chemical

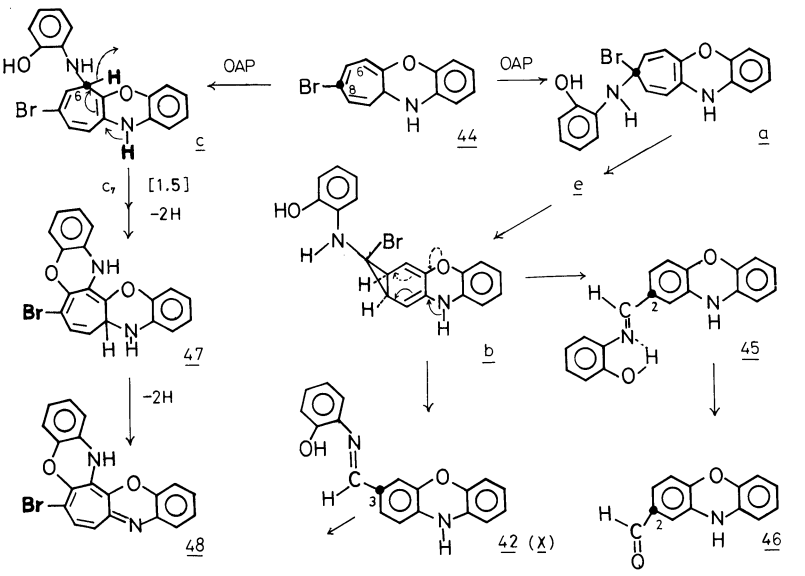
transformation. Compounds X and H_2 turned out to be the positional isomers 42 and 43 of the rearranged compounds C and B respectively (Scheme 9). Because the UV spectra of H_3 resembled closely that of colorless phenoxazine itself, and H_3 readily regenerated H_2 in benzene or chloroform, the structure of H_3 was tentatively assigned to the hemiacetal (43a) of H_2.

Scheme 9



In this type of rearrangement, probably a kinetically more favorable, reversible addition of OAP to 28 is taking place at C-8 (instead of the bromo-substituted C-6) to produce eventually a cine substituted intermediate c_1 or c_2 after the consecutive base catalyzed 1,3-prototropic shift and dehydrobromination. The rearrangement of c through the norcaradiene form d similar to the case of the formations of c in Scheme 8 would produce the Schiff base X; the position of the azomethine substituent of X was tentatively assigned at C-3 because of the apparently more favorable ring-opening of the three-membered ring in the norcaradiene intermediate assisted by the enamine group of the phenoxazine ring under the basic conditions.

Scheme 10

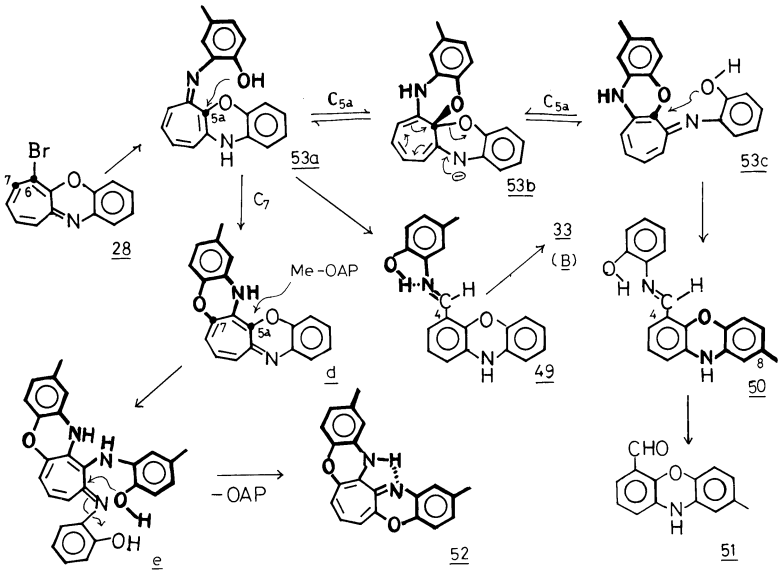


It became apparent that the courses of the condensation reactions of two isomeric tropones 21 and 22 with OAP readily altered to a great extent when subjected to only a slightly different reaction conditions. This is most likely caused by the presence of many reactive centers within the relatively polarized, complex troponoid molecule fused with a benzoxazine ring, thus facilitating many kinds of competitive paths.

5-Bromo-2-methoxytropone (25) and OAP likewise furnished the 8-bromo-derivative 44 under acidic conditions. When 44 was subjected to the similar condensation reaction with OAP as in the case of 6-bromo isomer 28, various products including violet and even blue pigments were formed simultaneously. Among them the following four main new products were isolated besides 42 and 43: 2-formylphenoxazine 45 and its Schiff-base 46, 8-bromo-derivatives of D and A (47 and 48)(Scheme 10). It is interesting to note that a mixture of isomeric Schiff base were formed in this case by the opening of the cyclopropane ring of norcaradine form d in both directions owing to the different reaction conditions (Scheme 10). The bromo compounds 47 and 48 were obviously formed through the similar pathway to that of the formation of A from 28. It should be noted however, that the intermediate did not gave D and A by dehydrobromination (cine substitution) but produced bromo derivative 47 and 48 by twice dehydrogenation (Ref. 9).

When 4-methyl-2-aminophenol (MeOAP) was used for the condensation with 6-bromo compound 28 in methanol at 45°C, two major products 49 and 50 were

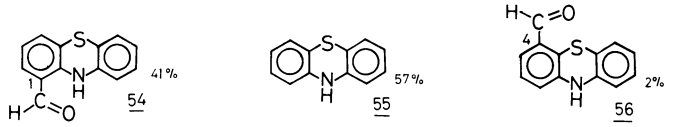
Scheme 11



produced, which were readily hydrolyzed with dilute sulfuric acid to give 33 (B) and 4-formyl-8-methylphenoxazine (51), respectively. A small amount of dark purple crystals were also isolated and identified to be 52 of the symmetrical structure on the evidence of UV, NMR and mass spectra. The formation of these products can be rationalized in terms of the competitive reaction pathways of the key intermediate 53a-c formed by the normal nucleophilic substitution as illustrated in Scheme 11. On the other hand, the addition of Dabco to the above condensation reaction exclusively produced Schiff base of the type X through a cine subsititution intermediate, then 43 (H_2) after hydrolysis in the same manner as in the case of 28 and OAP. It was also found that the Schiff base of the X was the major product, when 28 was condenced with arylamine bearing no ortho-hydroxy group (e.g. p-aminophenol, p-toluidine, and o- and p-anisidine) in methanol with or without Dabco, although a minor amount of 6-arylamino derivative of 28 was produced in some cases apparently by the normal substitution. These facts suggest that the o-hydroxy group of the arylamine exerts considerable interaction with the benzoxazine ring of 28, thus preferably facilitating the normal substitution of C-6 as illustrated in Scheme 8. Alternatively the irreversible [1,3] prototropic shift to give the intermediate b in Scheme 9 may be effected by Dabco and other excess basic aryl amines but not by a weaker base such as OAP (or MeOAP). However, more precise mechanistic study is required with regard to this rearrangement.

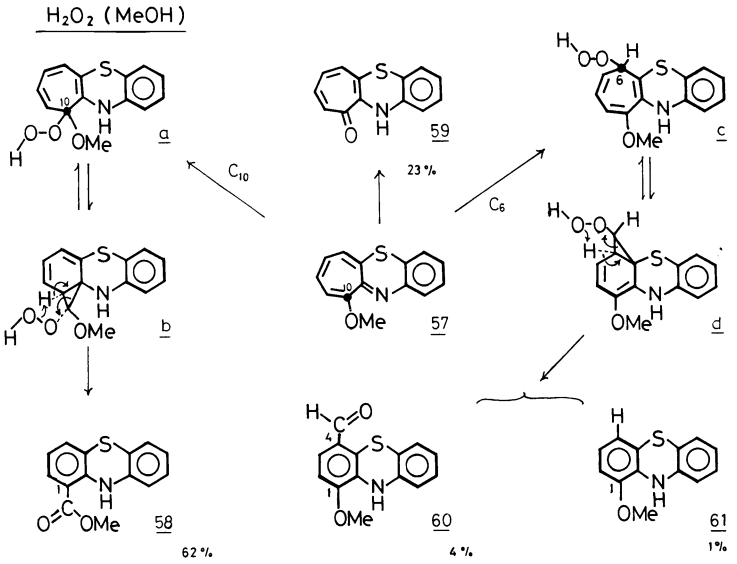
CYCLOHEPTA[b][1,4]BENZOTHIAZINES

In order to compare with the cycloheptabenzoxazines, we studied some reactivities of the S-analogs (e.g. 12) readily prepared from the reactive troponoid and OAT (Ref. 4). First it was found that 12 entirely resisted ring opening reactions under the acidic and alkaline conditions, whereas the O-analog 11 produced various ring opening products as was mentioned above. Therefore we examined oxidation reactions of these compounds with air or hydrogen peroxide. When 12 was oxidized with hydrogen peroxide in methanol, 41% of the rearranged product 54 and 57% of deformylated 55 were formed besides 2% of the 4-isomer 56. Prolonged oxidation gradually converted these products into the corresponding S-monoxides and the dioxides.



In contrast with these rearranged products the same oxidation of benzoxazine 11 exclusively afforded 37 (G) together with less than 1% of 33(B). In both cases the oxidation appears to be initiated by the preferencial nucleophilic addition of a hydroperoxide anion at C-10 of 11 and 12. This was

Scheme 12



confirmed by the same oxidation of 10-methoxycycloheptabenzothiazine 57 readily prepared from 21 and OAT; the isolated products were more than 62% yield of 10-methoxycarbonylphenothiazine 58 and its S-oxide, 23% yield of tropone 59 and its S-oxide, and only a small amount of 1-methoxyphenothiazine derivatives 60 and 61 and their S-oxides. Since 59 is presumably produced by the hydrolysis of the starting material 57, the oxidative rearrangement to the main product 58 very likely proceeds through the intermediate a and b, whereas 60 and 61 are formed by the oxidation at C-6 via c and d as illustrated in Scheme 12. The periodical checking of the reaction mixture by HPLC the rearrangement was found to precede to the S-oxidation. It should be noted that this type of ring contraction readily takes place with the cyclohepta-benzothiazines whereas almost no rearrangement is observed with the cyclohepta-benzoxazine, the reason for which however has not been clarified (Ref. 9).

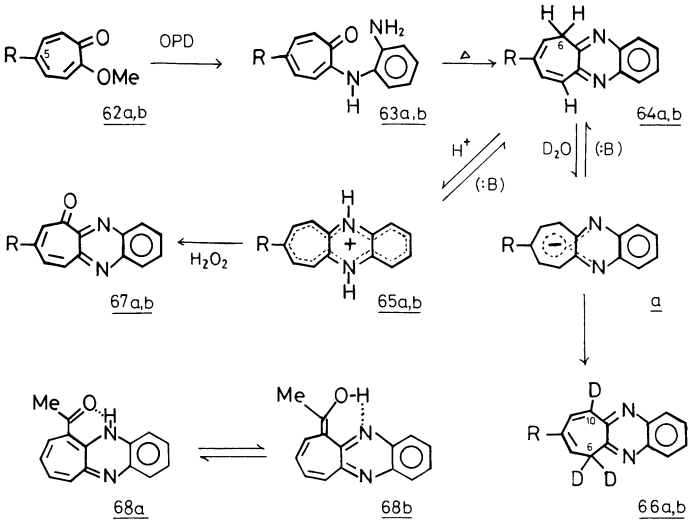
CYCLOHEPTA[b][1,4]BENZODIAZINES

More than twenty years ago we reported the condensation product of tropolone methyl ether 62a with OPD and presented the structure 13 analogous to 11 and 12 (Ref. 10). Later, Fukunaga obtained 15 (Scheme 2) which was converted to the quinoxalotropylidene 64a upon neutralization; the structures of those

products were established by proton NMR (Ref. 5). Thus we took up first closer reexamination of these products in connection with the clarification of the diversity of chemical reactions of troponoid system, particularly of 11 and 12.

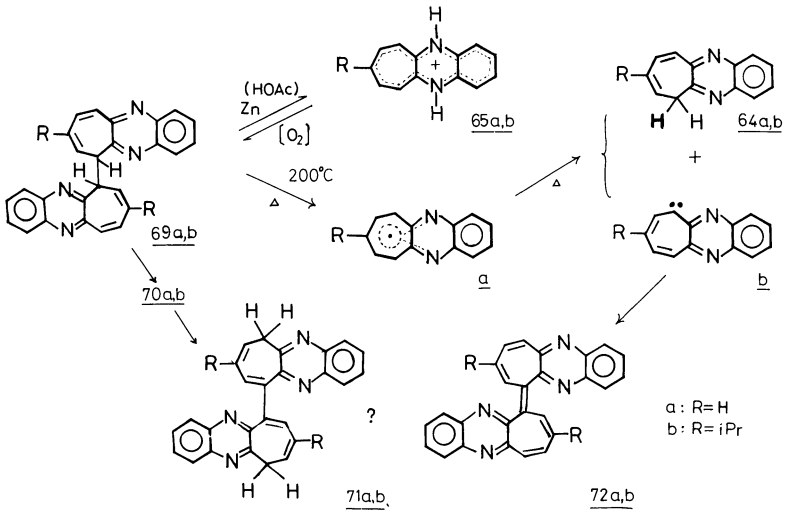
The condensation of methyl ethers of tropolone and 5-isopropyl homolog 62a and 62b with OPD in hot alcohol gave good yields of o-aminoanilinotropones 63a and 63b, which readily cyclized at higher temperature in a seeled tube to afford a quantitative yield of 64a and 64b, respectively. Compound 64 afforded stable, dark green cations 65a and 65b, which reproduced 64 upon basification under nitrogen (Scheme 13). The NMR spectra confirmed the structures 64 and 65, proposed earlier by Fukunaga. The diazines 64a,b were found to be stable in alkali and did not revert to 63 or tropolone. Thus, when 64a,b were basified with sodium carbonate in D_2O under nitrogen, 6,6,10-trideuterio derivatives 66 were formed presumably via symmetrical anions a as shown in Scheme 13. Meanwhile, Imafuku recently reported an interesting example of a tautomeric mixture of the cycloheptabenzoxazine systems 68a and 68b in various solvents (Ref. 11).

Scheme 13



However, if the cations 65 were basified with sodium carbonate in methanol

Scheme 14



without protection against air, it was found by HPLC that the oxidative dimerization took place to give initially 69a,b, which partly changed to 70a,b and 71a,b after hydrogen shift (Scheme 14). The reduction of 69a,b with zinc powder in acetic acid reproduced the cations 65, whereas heating 69a without solvent at 200°C yielded the disproportionation products 64a,b and 72a,b, the latter being formed probably via dimerization of the carbene b as illustrated in Scheme 14 (Ref. 9).

On the other hand, the hydrogen peroxide oxidation of the cations 65a,b in methanol gave the quinoxaline derivatives of ortho-tropoquinones 67a,b, besides the dehydro-dimers 69-71 (see Scheme 13 and 14). In this case the oxidation took place at C-6 and 8 on the tropylium nucleus and no ring contraction is observed. These oxidative processes of the benzodiazines were again entirely different from those of O- and S-analogs (Ref. 9).

CONCLUSION

Although some of the topics are still under investigation particularly with regard to the reaction mechanism, a wide range of our experimental results were presented here in hope of demonstrating a part of the diversity of chemical reactions and intricate characters of troponoid compounds.

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REFERENCES

1. (a) T. Nozoe in Non-benzenoid Aromatic Compound, Editor, D. Ginsburg, p.239, Interscience, New York, 1959; (b) F. Pietra, Accounts Chem, Res., 132 (1979); (c) T. Nozoe et al., in Dai Yuki Kagaku (Comprehensive Organic Chemistry), Editor, M. Kotake, Vol.13, pp.1-608, Asakura Shoten Tokyo, (1960)
2. (a) T. Nozoe, Croat. Chem. Acta, 29, 207 (1957); (b) T. Nozoe, Pure Appl. Chem. 28, 239 (1971); (c) T. Nozoe, K. Takase, T. Nakazawa and S. Fukuda, Tetrahedron 27, 3357 (1971); (d) T. Nozoe, K. Takase, M. Kato and T. Nogi, ibid, 27 6023 (1971)
3. (a) T. Nozoe, H. Okai and T. Someya, Bull. Chem. Soc. Jpn., 51, 2185 (1978); (b) T. Nozoe and T. Someya, ibid., 51, 3316 (1978); (c) T. Nozoe, T. Someya and H. Okai, ibid., 52, 1156 (1979); (d) T. Someya, ibid., 52, 1156 (1979)
4. T. Nozoe, T. Asao and K. Takahashi, Bull. Chem. Soc. Jpn. 34 146 (1961); T. Nozoe, T. Asao and K. Takahashi, ibid., 39, 1980 (1966)
5. T. Fukunaga, Private Communication. Presented at the 23rd IUPAC Congress, Boston, 1971
6. (a) Y. Kurita, T. Nozoe and M. Kubo, Bull. Chem. Soc. Jpn., 26, 242 (1953); (b) K. Furukawa, Y. Sasada, A. Shimada and T. Watanabe, ibid., 37, 1871 (1964)
7. K. Takase, Y. Sasakawa and M. Yasunami, in preparation
8. T. Someya, H. Okai, H. Wakabayashi and T. Nozoe, in preparation
9. K. Shindo, S. Ishikawa, H. Wakabayashi, H. Okai and T. Nozoe, in preparation
10. T. Nozoe, Y. Kitahara, K. Takase, M. Sasaki, Proc. Japan Acad., 32, 349 (1956)
11. K. Imafuku, A. Yamane and H. Matsumura, J. Heterocycl. Chem., 17, 1293 (1981)