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Captodative substituent effects in radical chemistry (ref. 1)

Heinz G. Viehe*, Robert Merényi and Zdenek Janousek

Laboratoire de Chimie Organique, Université de Louvain, Place L. Pasteur, 1348 Louvain-la-Neuve, Belgium

Abstract - Polar substituents are generally more efficient for the stabilisation of ions than for radicals. These last species are more and more recognised as important intermediates in chemistry and in biochemistry. The cumulative effect of two substituents of the same polarity shows antagonism for radical stabilisation whereas captodative (cd) substituents show synergy. Synthetic applications of the cd-effect use the breaking of adjacent weak "proradical" C-H and C-C bonds. Further, cd-double bonds are useful as radical traps and as partners in cycloaddition reactions. cd-N-vinyl substitution induces with complete stereocontrol the epoxy-epimination rearrangement of chiral oxazines and opens a new route to inosite and streptamine derivatives.

Making and breaking chemical bonds is the essence of our profession. The understanding of substituent effects (ref. 2) on bond energies is therefore of prime importance. We all know that the incorporation of multiple bonds or of polar substituents generally increases the reactivity of molecules and more specifically that of particular bonds.

Whenever C-C bonds arise or break via any pathway - by molecular addition or elimination, via ions, radicals or radical ions - the scene may always be influenced by substituents. Naturally captor (electron withdrawing) substituents stabilise carbanions, the dative ones stabilise carbocations and according to the captodative (cd) postulate (ref. 3) the simultaneous substitution of a radical center by a captor and a dative group leads to particular stabilisation (Fig. 1).

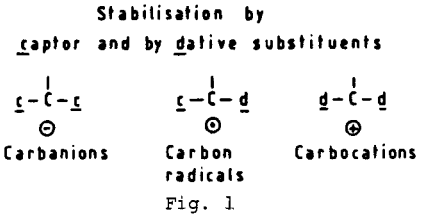
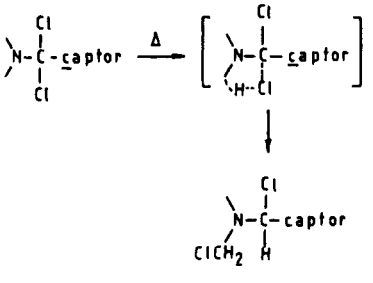


Fig. 1

Today it appears that our cd-postulate which was formulated ten years ago stimulated much work and discussion. Similar ideas (ref. 4) had been advanced before we entered this field with the discovery of a new rearrangement reaction (ref. 5, 6a, 6b). For years we had been working with iminium-chlorides but only when we introduced α-capto-substituents we encountered this rearrangement as a non ionic and unimolecular reaction which could be explained by the weak C-Cl-bond because of the cd-nature of the dichloromethylene group between the dimethylamino and the captor group. cd-Substitution makes adjacent bonds weak toward homolysis and we call them proradical. It is mechanistically and synthetically interesting that both the π and σ-acceptors permit the rearrangement (Fig. 2).



captor	Temp (°C)	Ea (Kcal/mole)
$-\overset{+}{C}=N$	-60	
$-C\equiv N$	-20	
-COOMe	0-20	21.3
$-CF_3$	60-100	28.9
$-CCl_3$	60-100	

Fig. 2

The iminium salt is not involved : it can be obtained by Cl^- complexation, with HCl or with PCl_5 and then is stable and does not rearrange.

cd-Dichloromethylene compounds with aminosubstituents as dative group have little ionic character but do display it in substitution reactions with nucleophiles if the rearrangement is avoided, for example, by temperature control. With the CF3-group as captor group potential α-trifluoromethyl-cations are available both before and after the rearrangement which takes place around 100°C (ref. 6) (Fig. 3).

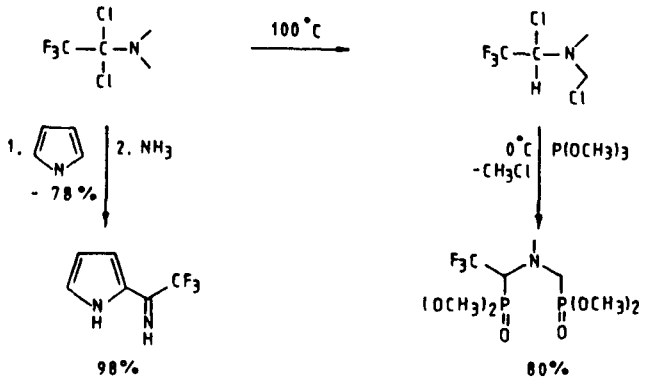


Fig. 3

The stabilisation of ions by polar groups is generally much more efficient than that of radicals (ref. 7). Radical stabilisation enthalpy only attains up to 10 Kcal/mol per polar substituent whereas allylic, benzylic or propargylic groups reach about 12-15 Kcal/mol (ref. 3c).

The cumulative effect of two polar substituents becomes evident from the comparison of interaction parameters Δ_{XY} derived from the experimental substituent parameters Δ_X, Δ_Y, A_{XY} and A_{HH} (ref. 8). These are obtained either from ESR (or muon) coupling constants or from activation energies. Positive Δ_{XY} values indicate synergy of the two substituents in all cases for cd-substitution thereby fully supporting the cd postulate. In contrast antagonism is found with negative Δ_{XY} values for substituents of like polarity (Fig. 4).

SUBSTITUENT INTERACTION PARAMETER $(\Delta_{XY} \cdot 100)$ $A_{XY}/A_{HH} = (1-\Delta_X)(1-\Delta_Y)(1-\Delta_{XY})$

X/Y	X-C(Me)(CN)• [a]	X-C(COOEt)• [b]	X-C(H)(Mu)-Y• [c]	H-C(X)-Y• [d]	X-≡-C(H)-Y• [d]
CN/CN	- 2.4			- 12,5	
COOMe/CN	- 2.1			- 12.0	
COOR/COOR		- 0.8		- 12,0	
SOMe/COOEt		- 0.6			
SO_2Me/COOEt		- 0.6			
OMe/OMe			- 3.4	-13.6	
Me/NH_2					- 7.7
Me/OH					- 3.3
OMe/CN	+ 1.0		+ 5.17	+ 16.0	
CN/OMe			+ 6.96		
SR/CN	- 0.3			+ 13.0	
NH_2/CN	+ 4.2			+ 9.6	
COOEt/N(SiMe3)					+ 12.8
COOEt/OH					+ 7.4
OMe/COOEt		+ 2.6			
SMe/COOEt		+ 0.8			

a) meso to dl isomerisation ($\Delta G^{\neq}$) ref 3c, 9
b) methylenecyclopropane isomerisation ($\Delta G^{\neq}$) ref 10
c) Muon addition to 1,3 substituted benzenes (A^{Mu}) ref 8
d) ESR hyperfine coupling constants (a^H) ref 11

Fig. 4

C-C-Bond-homolysis of radical dimers is strongly influenced by proximity effects such as by steric effects and σ-interactions. This makes very difficult the quantitative comparison of radical stabilisations based on Bond Dissociation Energies of systems with different polar substituents X,Y (ref. 12) (Fig. 5a).

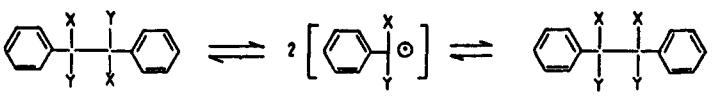


Fig. 5a

Tetramethoxyethane (X,Y = OMe) derivatives are examples of ground-state stabilisation by about 14 Kcal through the anomeric effect (ref. 13), whereas tetracyanoethane appears to be destabilised by up to 30 Kcal (ref. 7a).
In order to minimise such proximity effects for dl-meso-isomerisations of benzylic radical dimers we chose the variation of para-substituents in Fig. 5b thereby avoiding benzylic substitution variation such as in Fig. 5a. Expectedly in this phenylogous system the cd-effect is confirmed (ref. 3d, 9) (Fig. 4).

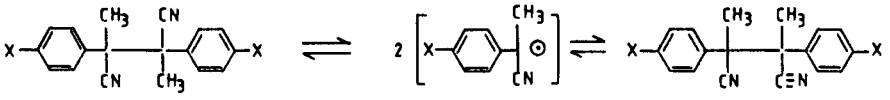


Fig. 5b

Cis-trans isomerisations of tetra-substituted cyclopropane derivatives (ref. 14) and also the dissociation energies of 1.3 tetra-substituted allylic radical dimers (ref. 15) show in support of the cd concept again better stabilisation of cd radicals than do their dicapto analogs (Fig. 6).

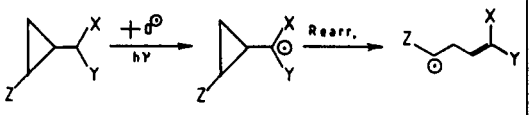
Sequence of radical stabilisation

X,Y = NMe_2, CN > SMe, CN > OMe, CN > COOMe, CN > COOMe, COOMe

Fig. 6

α-cyclopropyl centers are well known radical clocks because of the occurrence of low temperature homoallylic rearrangement (ref. 16) : cd-substitution stops that clock ! Whereas the cyclopropylmethyl radical itself is only observable below -120°, cd-analogous systems are so much stabilised that according to ESR measurements no homoallylic rearrangement is observed even at room temperature (ref. 17, 18) (Fig. 7).

It appears of preparative interest that cd-substitution on the cyclopropyl group of vinyl cyclopropanes facilitates the thermal rearrangement to cyclopentenes more than does the cc-substitution (ref. 18a) (Fig. 8).



X	Y	Z	Cyclopropane stable until
$(CH_3)_3SiO$	CN	H	+ 32°C *
$(CH_3)_3SiO$	CO_2Me	H	+ 135°C *
Et_2N	CN	CO_2Me	+ 20°C
Et_2N	CO_2Me	CO_2Me	+ 20°C
+S	CN	CO_2Me	+ 20°C
+S	CO_2Me	CO_2Me	+ 20°C

Fig. 7

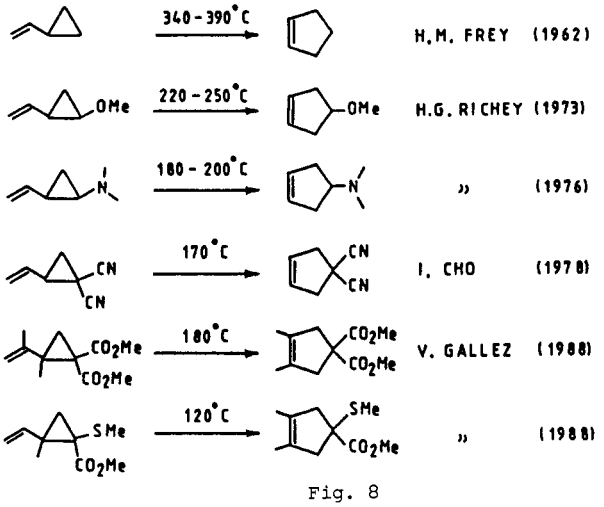


Fig. 8

The **cd** effect on carbocations and on carbanions is expected to destabilise them in favour of a one electron transfer leading to the corresponding **cd**-radicals. The example of **cd**-indene anions (ref. 19a) could be cited as complementary to other **cd** cases (ref. 19b) : in support of a radical reaction besides about 65 % t-butylation 10-13 % dehydrodimerisation is observed (Fig. 9).

cd-Substitution on double bonds is particularly interesting !

For the geminal arrangement of substituents with opposite polarity in cd-olefins MNDO and FMO calculations agree well with photoelectron and UV spectroscopy as well as with ^{13}C NMR shifts

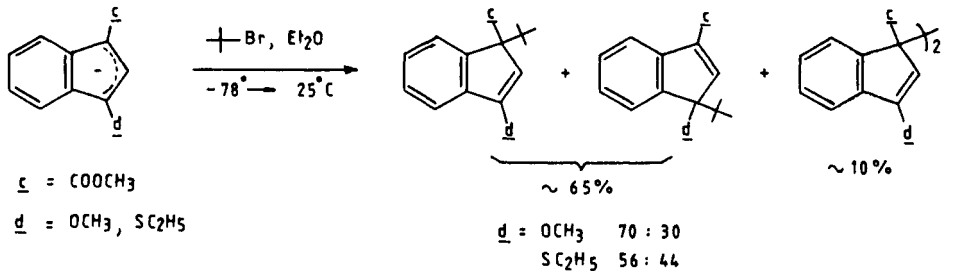


Fig. 9

to convey the picture that cd-olefins still retain reactivity both as nucleophiles and as electrophiles. Their HOMO-LUMO-gap is reduced and the reactivity in the β-position is enhanced (ref.3b,c, 20). This explains their radicophilic nature and leads to reactions with an unsymmetrical transition state and with radical intermediates as the limiting case (Fig. 10).

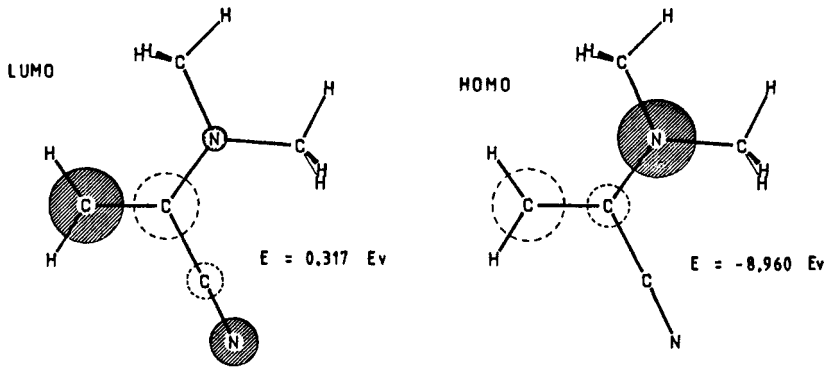


Fig. 10

Radical additions to cd-olefins conform well to this image with rates higher than expected from polar effects only (ref. 21). Furthermore radical adducts deriving from cd-olefins are sufficiently cd-stabilised to avoid chain reactions or disproportioning in most cases and they rather dimerise or trap a second radical.
Hydrogen abstraction with tert-butoxy-radicals in neat phase from alkanes, ethers, amines, amides, ketones and aldehydes, for example, is known as the Kharash-reaction and leads generally in good yields to coupling products (ref. 22). These are, however, completely suppressed in the presence of intercepting cd-olefins such as α-thio-tert-butylacrylonitrile and radical adduct dimers are generally formed in high yield (ref. 23) (Fig. 11).

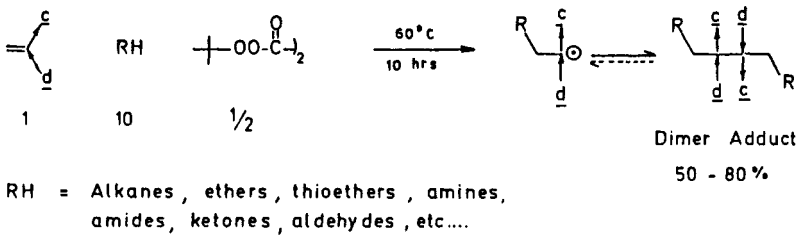


Fig. 11

Applied to crown ethers the coupling and the "bridged dehydrodimers" can be obtained (Fig. 12) (ref. 23c).

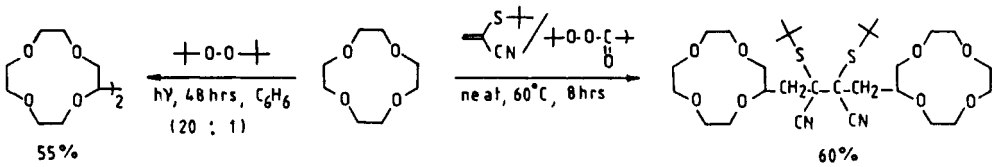


Fig. 12

Contrary to previsions based on polar effects hydrogen abstraction from cd or other proradical alkane derivatives is also accelerated (ref. 24).

cd-olefins and cd-1.3 dienes are particularly valuable as partners in (2+2) and (4+2) cycloaddition reactions as schematically summarised (ref. 25, 26) (Fig. 13).

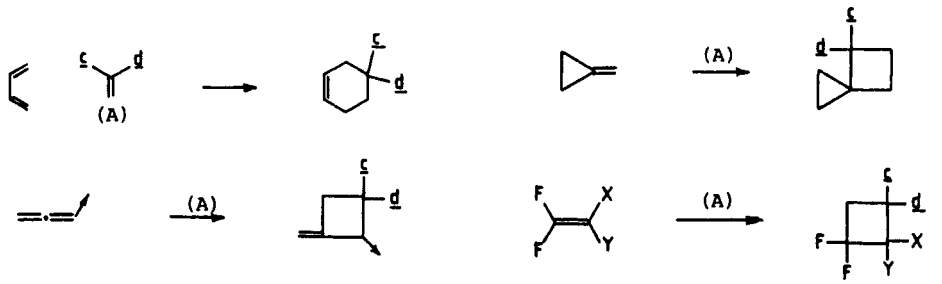


Fig. 13

The most striking and oldest example for the head-to-head cyclodimerisation of a cd-olefin is that of acrylonitrile-α-thioethers at room temperature (ref. 27) (Fig. 14). Expectedly analogous seleno-ethers give this cyclodimerisation also but around 60° (ref. 26a).

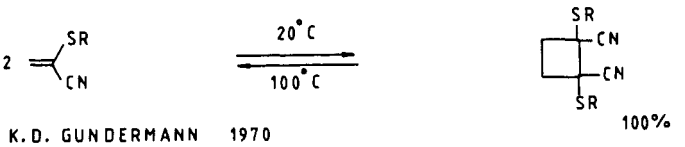
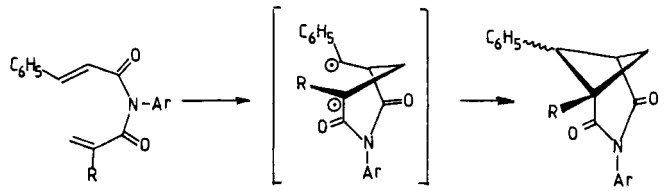


Fig. 14

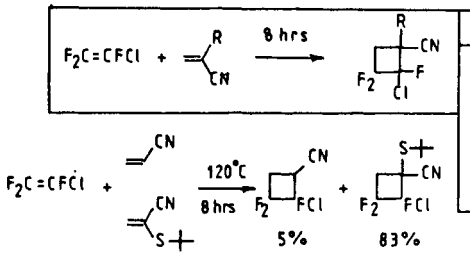
Intramolecular thermal (2+2) cyclodimerisations occur well at the lowest temperatures and in highest yields with cd-olefins (ref. 28) (Fig. 15).



R	Cdts	yield (%)
CH_3	140°C, 4 hrs	75
SCH_3	140°C, 5 min	91
SCH_3	40°C, 3 days	90

Fig. 15

Various 1,1-difluoroethenes, including the liquid 1,1-difluoro-2-alkylthioethylenes undergo (2+2) cycloadditions to cd-olefins (ref. 26a) (Fig. 16).



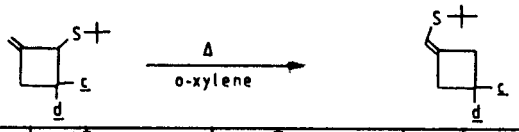
R	Temp °C	Yield %
H	160	65
Cl	120	72
SePh	120	70
SEt	120	83
SPh	120	85
S+	120	90

Fig. 16

Expectedly allenes are also good partners for (2+2) cycloadditions to cd-olefins. The following adduct rearrangement shows the substituent effect of different cd-couples on the stabilisation of the intermediate diradical (ref. 26c,d) (Fig. 17).

cd-dienes may present different substitution patterns either in 1,1- or 1,3 positions. 1,1-cd butadiene and 1-capto-3-dative butadienes have been prepared and applied usefully in radical trapping and in cycloaddition reactions (ref. 29). In contrast, 3-capto-1-dative butadienes are very unstable but the dimer of the 3-cyano-1,1-dithioether butadiene derivative could be obtained at room temperature in quantitative yield as a formal Diels-Alder adduct, possibly via biradicals and intermediate (2+2) adducts (ref. 30) (Fig. 18).

Generally 2-cyano-substituted butadienes are thermally unstable and even the related α-cyano-styrene is known since a long time to dimerise at room temperature (ref. 31) and the p-methoxy analogue follows this example (ref. 32) (Fig. 19).



c	d	ΔH‡ kcal mole	ΔS‡ cal K mole	$\Delta G^{\ddagger}_{300}$ kcal mole
-CN	-N O	28.6 ± 1.8	+ 7.9 ± 6.9	26.2 ± 3.8
-CN	-S+	24.9 ± 1.5	- 5.1 ± 5.8	26.4 ± 3.2
-CN	$-OCH_3$	44.2 ± 0.6	+ 36.1 ± 2.2	33.4 ± 2.8
-CN	-Cl	39.9 ± 2.0	+ 18.0 ± 4.5	34.5 ± 3.3

Fig. 17

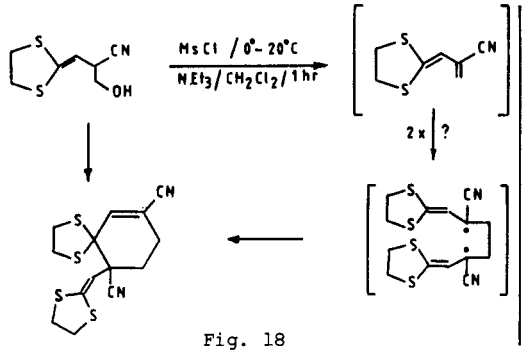


Fig. 18

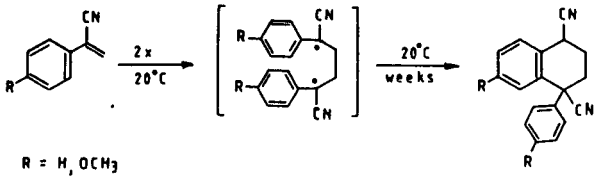


Fig. 19

Figure 20 describes the most remarkable case of a 3-capto-1-dative diene for which the cyclobutane intermediate has been proven. Dimerisation occurs at a temperature as low as -40°C in a reversible (2+2) head-to-head cycloaddition and then leads already at -20° to the formal Diels-Alder adduct (ref. 33). Because of the head-to-head cyclobutane-dimer, in agreement with the Woodward-Hoffmann-Rules a biradical two-step mechanism was discussed. Today this particular reactivity can be attributed to stabilised 1,3-allylic cd-radical intermediates. The fragile cyclobutane becomes understandably stable upon protonation and reduction of the double bond (ref. 33). The final Diels-Alder-adduct, however, with N-butenyl substitution instead of methyl, shows the cd-influence of its substituents when refluxed in toluene. The Diels-Alder dimer undergoes cycloreversion to the then intramolecularly intercepted cd-diene (ref. 34) (Fig. 21).

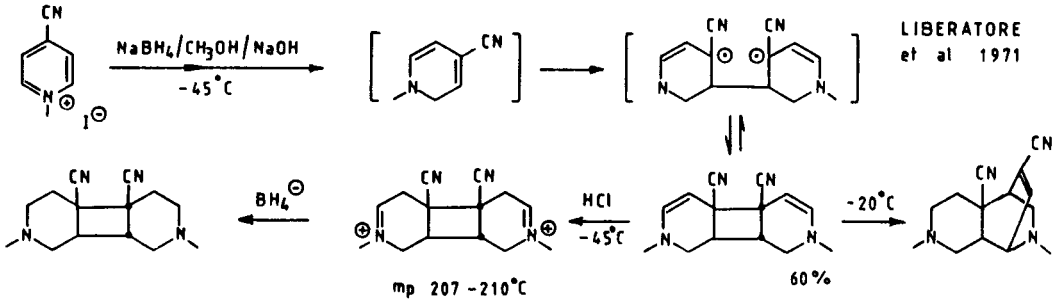


Fig. 20

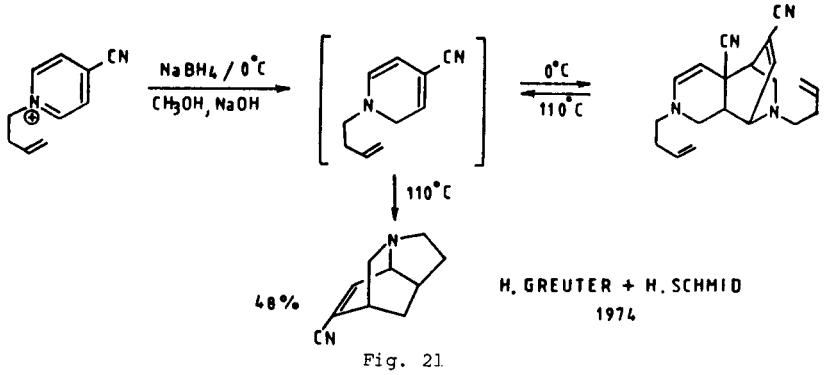


Fig. 21

cd-activation leading to selective bond breaking became useful in developing complete stereocontrol for the functionalisation of all four sp2 carbon atoms in cyclodienes, for example, from cyclohexadiene to inosamines, i.e. amino-cyclohexane-polyols. These are constituents of amino-glycoside antibiotics such as streptomycine and its mutasynthetic variations.
Our entry into this field started with the discovery of a substituent induced rearrangement of oxazine derivatives from nitrosoolefin adducts to cyclodienes (ref. 35). This reaction is aza-analogous to the well known rearrangement of endoperoxides to bis-epoxides (ref. 36).

The driving force for these rearrangements under the influence of adequate substituents arises from both the ground state destabilisation of these N-substituted oxazines and stabilisation of intermediates or transition states such as biradicals or biradicaloids (Fig. 22).

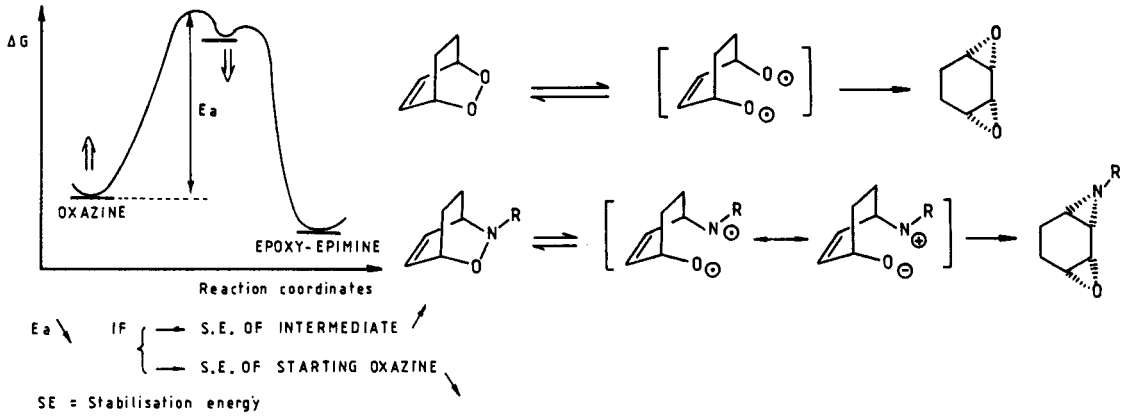


Fig. 22

The influence of strain becomes evident by the finding that the trichlorovinylnitroso adduct to cyclopentadiene rearranges at room temperature whereas the less strained cyclohexadiene adduct requires 60°C (ref. 37) (Fig. 23).

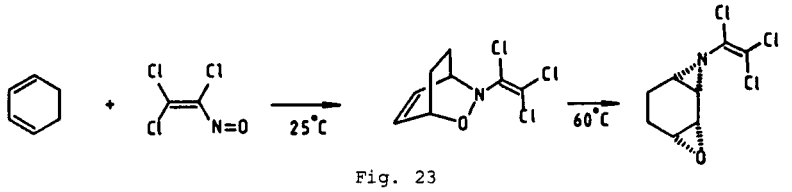


Fig. 23

The new epoxy-epimination prompted us to study the effect of substituents and led us to the synthesis of nitrosoethylenes with substituent variation in the vinyl group and subsequent trapping of these fragile compounds by cyclopentadiene. The scope of that approach remained limited (ref. 38) (Fig. 24).

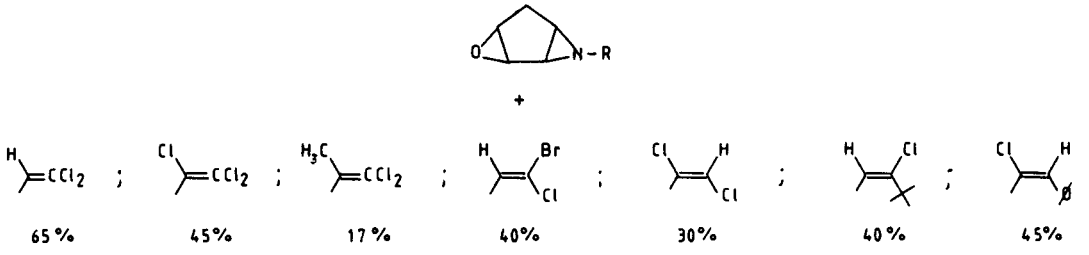


Fig. 24

Variation of N-substituents in oxazine derivatives became facile by N-substitution of the readily accessible N-H precursors which are prepared from α-chloronitroso compounds in a one-pot reaction (ref. 39a,b,c) (Fig. 25).

N-acylation, sulfonation and 2,4-dinitrophenylations produced derivatives which failed to undergo the epoxy-epimination rearrangement (ref. 40). For that purpose proradical character

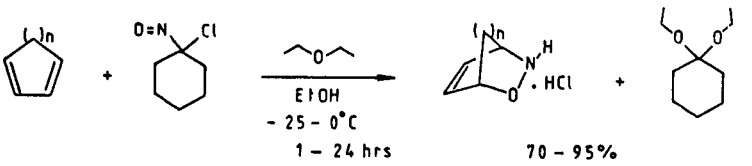


Fig. 25

of the N-O-bond was imparted by N-substitution with a cd-vinyl group.
Indeed, cd-vinyl substitution expectedly induces the weakening of the N-O-bond leading to a smooth epoxy-epimination which contrasts with the thermally stable β,β-dicapto-vinyl-derivatives (ref. 40, 41) (Fig. 26).

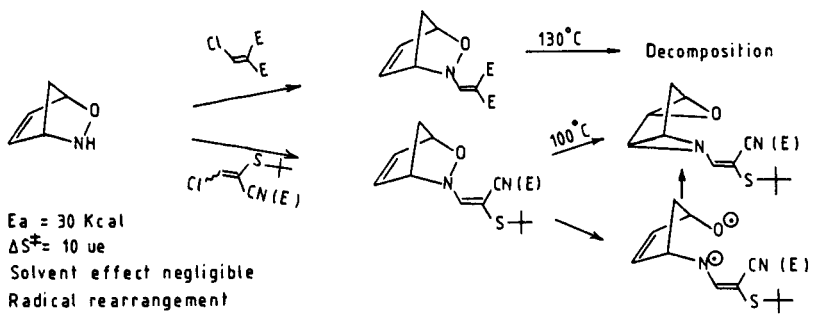


Fig. 26

The assumption of homolytical N-O bond breaking is supported by the following experiments : Diimide reduction of the CC-double bond to saturated oxazine derivatives prevents of course the epoxy-epimination but not the N-O bond breaking. Thus heating in xylene leads to ring opening and hydrogen abstraction for the cd-vinyl derivative while the N-acyl compound remains unchanged (ref. 40, 42) (Fig. 27).

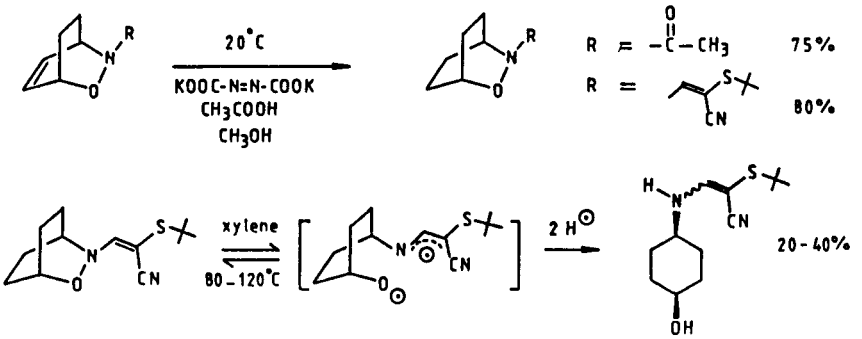


Fig. 27

According to photoelectron spectra of both the reduced and the unsaturated oxazine it can be concluded that N-O and C=C bond do not interact in the last compound (ref. 43). If therefore the cd-vinyl substituent on nitrogen induces the rearrangement it occurs most probably also via biradicals.
A collaboration with G. Kresze and his group has shown furthermore that the oxazine derivative from cis-1,2 diacetoxycyclohexadiene produced the desired epoxy-epimination in high yield together with traces of the N-O hydrogenolysis product as indication of prior N-O homolysis (ref. 42) (Fig. 28).

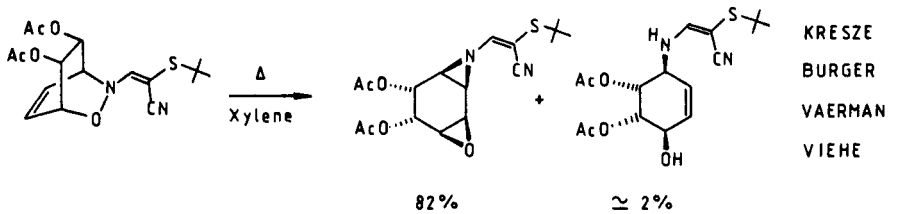


Fig. 28

Beyond these mechanistic questions lies the potential of these reactions for use in synthesis. The epoxy-epimination is strain dependent and applicable to cyclopenta-, hexa- and heptadiene but not to cyclooctadiene or to open chain butadiene adducts (ref. 41).
The three cyclodienes of use for the epoxy-epimination lead to chiral oxazines in high optical yields (ref. 40) (Fig. 29).

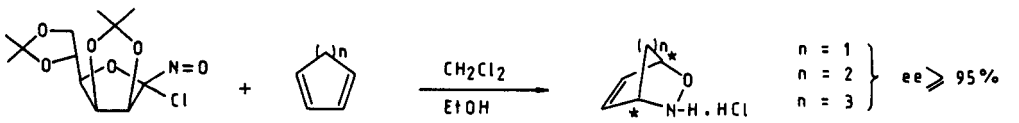


Fig. 29

From readily available 1,2-dioxy-cyclohexadiene derivatives (ref. 42) an efficient stereocontrolled synthesis of inosamine derivatives becomes possible (Fig. 30).

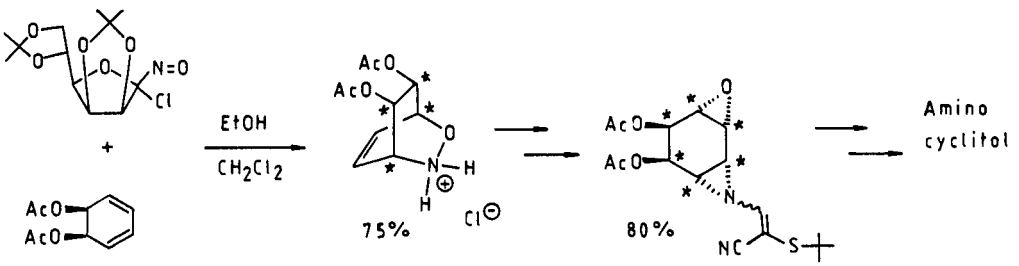


Fig. 30

In conclusion, it appears that the cd-postulate has been stimulating and useful in synthesis and it promises many perspectives.

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REFERENCES

1. Captodative Substituent Effect Part 45; Part 44 see H.G. Viehe, Z. Janousek, R. Merényi in "Free Radicals in Synthesis and Biology" NATO ASI Series 1988, in print.
2. Substituent Effects in Radical Chemistry, H.G. Viehe, Z. Janousek, R. Merényi, Eds NATO ASI Series C 189, D. Reidel, Dordrecht (1986).
3 a) L. Stella, Z. Janousek, R. Merényi and H.G. Viehe, Angew. Chem. 90, 741 (1978); Int. Ed. Engl. 17, 691 (1978); b) H.G. Viehe, R. Merényi, L. Stella, Z. Janousek, Angew. Chem. 91, 982 (1979); Int. Ed. Engl. 18, 917 (1976); c) H.G. Viehe, Z. Janousek, R. Merényi, L. Stella, Acc. Chem. Res. 18, 148 (1985); c) R. Merényi, Z. Janousek, H.G. Viehe, in ref. 2, p. 301.
4. a) M.J.S. Dewar, J. Am. Chem. Soc. 74, 3353 (1952); b) A.T. Balaban, Rev. Roum. Chim. 16, 725 (1971); c) R.W. Baldock, P. Hudson, A.R. Katritzky, F. Soti, J. Chem. Soc. Perkin Trans. 1, 1422 (1974).
5. a) F. Huys, R. Merényi, Z. Janousek, L. Stella, H.G. Viehe, Angew. Chem. 91, 650 (1979); Int. Ed. Engl. 18, 615 (1979); b) M. Rover-Kevers, L. Vertommen, F. Huys, R. Merényi, L. Stella, Z. Janousek, H.G. Viehe, Angew. Chem. 93, 1091 (1981); Int. Ed. Engl. 20, 1023 (1981); c) Z. Janousek, F. Huys, L. René, M. Masquelier, L. Stella, R. Merényi, H.G. Viehe, Angew. Chem. 91, 651 (1979); Int. Ed. Engl. 18, 615 (1979).
6. a) M. Rover-Kevers, Ph.D. Thesis, Louvain-la-Neuve (1980); b) Ph. Dellis, Ph.D. Thesis, Louvain-la-Neuve (1987); c) M.A. Decock-Plancquaert, Ph.D. Thesis in preparation.
7. a) G. Leroy, Adv. Quantum Chem. 17, 1 (1985); b) G. Leroy, C. Wilante, D. Peeters, M.M. Uyewa, J. Mol. Struct. (Theochem) 124, 107 (1985).
8. Ch.J. Rhodes, E. Roduner, Tetrah. Lett. 29, 1437 (1988).
9. a) R. Merényi, V. Daffe, J. Klein, W. Masamba, H.G. Viehe, Bull. Soc. Chim. Belg. 91, 456 (1982); b) R. Merényi, J. Klein, H.G. Viehe, to be published.
10. a) X. Creary, M.E. Mehrsheikh-Mohammadi, J. Org. Chem. 51, 2664 (1986); b) X. Creary in ref. 2, p. 245.
11. a) H.G. Korth, P. Lommes, R. Sustmann, L. Sylvander, L. Stella, New J. of Chem. 11, 365 (1987); b) I. MacInnes, J.C. Walton, J. Chem. Soc. Perkin Trans. II, 1077 (1987).
12. H. Birkofer, J. Hädrich, N.D. Beckhaus, C. Rüchardt, Angew. Chem. 99, 592 (1987); Int. Ed. Engl. 26, 573 (1987).

13. N.M. Gutner, N.D. Lebedeva, S.L. Dobychin, N.N. Kiseleva, Zhur. Prikl. Khim. 53, 2061 (1980); Engl. Transl. p. 1523.
14. a) A. De Mesmaeker, L. Vertommen, R. Merényi, H.G. Viehe, Tetrah. Lett. 23, 69 (1982); b) R. Merényi, A. De Mesmaeker, H.G. Viehe, Tetrah. Lett. 24, 2765 (1983).
15. M. Van Hoecke, A. Borghese, J. Penelle, R. Merényi, H.G. Viehe, Tetrah. Lett. 27, 4569 (1986).
16. J.K. Kochi, D.J. Krusic, D.R. Eaton, J. Am. Chem. Soc. 91, 1877 (1969).
17. D. Laurie, E. Lucas, D.C. Nonhebel, C.J. Suckling, J.C. Walton, Tetrah. 42, 1035 (1986).
18. a) V. Gallez, Ph.D. Thesis in preparation; b) W. Masamba, Ph.D. Thesis, Louvain-la-Neuve (1987).
19. a) D. Vereecke, Ph.D. Thesis in preparation; b) D. Grierson, M. Urrea, H.P. Husson, J. Chem. Soc. Chem. Commun., 891 (1983).
20. R. Sustmann, W. Müller, S. Mignani, R. Merényi, Z. Janousek, H.G. Viehe, in preparation.
21. a) F. Lahousse, R. Merényi, J.R. Desmurs, H. Allaime, A. Borghese, H.G. Viehe, Tetrah. Lett. 25, 3823 (1984); b) S.U. Park, S.K. Chung, M.I. Newcomb, J. Am. Chem. Soc. 108, 240 (1986).
22. H. Naarman, M. Beaujean, R. Merényi, H.G. Viehe, Polym. Bull. 2, 363, 417 (1980).
23. a) S. Mignani, M. Beaujean, Z. Janousek, R. Merényi, H.G. Viehe, Tetrah. 37, Suppl. 1, 111 (1981); b) S. Mignani, Z. Janousek, R. Merényi, H.G. Viehe, Bull. Soc. Chim. France, 1267 (1985); c) M. Beaujean, S. Mignani, Z. Merényi, Z. Janousek, H.G. Viehe, M. Kirch, J.M. Lehn, Tetrahedron 40, 4395 (1984).
24. a) L.Vertommen, M. Beaujean, R. Merényi, Z. Janousek, H.G. Viehe, in ref. 2, p. 329; b) B. Giese, G. Kretzschmar, Chem. Ber. 116, 3267 (1983).
25. a) J.L. Boucher, L. Stella, Tetrah., 3871 (1986); b) L. Stella in ref. 2, p. 361; c) D. Döpp in ref. 2, p. 383 and D. Döpp, M. Pies, J. Chem. Soc. Chem. Commun. 1734 (1987).
26. a) Ch. De Cock, S. Piettre, F. Lahousse, Z. Janousek, R. Merényi, H.G. Viehe, Tetrah. 41, 4183 (1985); b) A. De Meijere, H. Wenck, F. Seyed-Mahdavi, H.G. Viehe, V. Gallez, I. Erden, Tetrah. 42, 1291 (1986); c) G. Coppe-Motte, Ph.D. Thesis, Louvain-la-Neuve (1986); d) G. Coppe-Motte, A. Borghese, Z. Janousek, R. Merényi, H.G. Viehe, ref. 2, p. 371.
27. K.D. Gundermann, A. Losler, Liebigs Ann. Chem. 758, 155 (1972).
28. A. Alder, D. Bellus, J. Am. Chem. Soc. 105, 6712 (1983).
29. a) N. Stévenart-De Mesmaeker, Ph.D. Thesis, Louvain-la-Neuve (1983); b) N. Stévenart-De Mesmaeker, R. Merényi, H.G. Viehe, Tetrah. Lett. 28, 2591 (1987); c) O. Vandevelde, Ph.D. Thesis, Louvain-la-Neuve (1984).
30. Y. Morizawa, H.G. Viehe, unpublished results.
31. J. Colonge, J. Dreux and J.P. Regeaud, Bull. Soc. Chim. France, 1244 (1959).
32. H. Allaime, Ph.D. Thesis, Louvain-la-Neuve (1984).
33. J. Liberatore, A. Casini, V. Cavelli, A. Arnone, R. Mondelli, Tetrah. Lett. 26, 2381 (1971) and 26, 2829 (1971).
34. H. Greuter, H. Schmid, Helv. Chim. Acta 57, 1204 (1974).
35. a) H.G. Viehe, R. Merényi, E. Francotte, M. Van Meerssche, G. Germain, J.P. Declercq, J. Am. Chem. Soc. 99, 2340 (1977); b) E. Francotte, R. Merényi, B. Vandenbulcke-Coyette, H.G. Viehe, Helv. Chem. Acta 64, 1208 (1981).
36. For a review see M. Balci, Chem. Rev. 81, 91 (1981).
37. E. Francotte, R. Merényi, H.G. Viehe, Angew. Chem. 90, 911 (1978); Int. Ed. Engl. 17, 936 (1978).
38. E. Francotte, Ph.D. Thesis, Louvain-la-Neuve (1978); B. Vandenbulcke-Coyette, Ph.D. Thesis, Louvain-la-Neuve (1982).
39. a) Y.A. Arbusov, A. Markovskaya, Izv. Akad. Nauk. SSSR, Otdel., Khim. Nauk., 363 (1952); C.A. 47, 33168 (1953); b) K. Iida, Y. Watanabe, C. Kibayashi, J. Org. Chem. 50, 1818 (1981); c) D. Ranganathan, S. Ranganathan, C.B. Rao, K. Raman, Tetrah. 37, 629 (1981).
40. J.L. Vaerman, Ph.D. Thesis, Louvain-la-Neuve (1988).
41. H.G. Viehe, J.L. Vaerman, J. Prakt. Chem., submitted.
42. a) W. Burger, Ph.D. Work, München, in preparation; b) G. Kresze, W. Dittel, H. Melzer, Liebigs Ann. Chem., 224 (1981).
43. R. Sustmann, unpublished results.