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# PROPELLANES AS SUBSTRATES FOR STEREOCHEMICAL STUDIES

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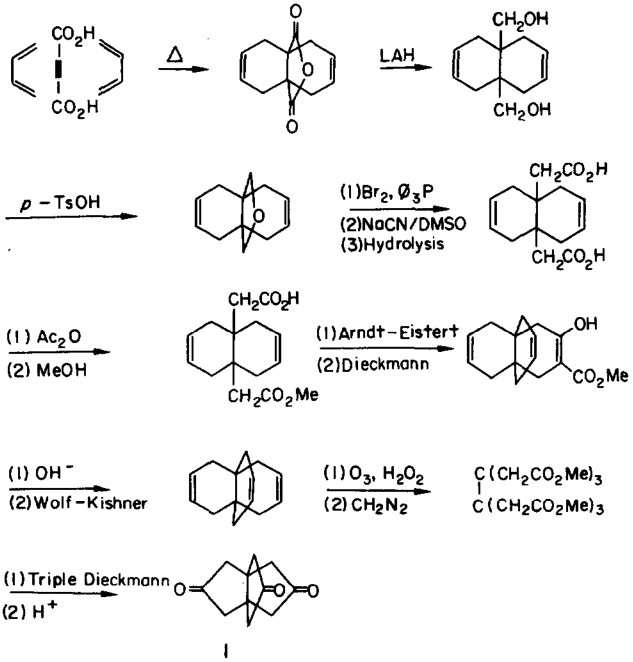
**Abstract**—Various reactions are described in which the behavior of configurationally-different propellanes may be correlated with the respective configurations.

Perhaps enigmas concerning the chronology of appearance of certain classes of compounds should be relegated to the realm of psychology. Yet I still marvel at the fact that the first results of attempts directed at the synthesis of tricyclic compounds conjoined in a carbon–carbon single bond were first published only within this last decade of the van't Hoff–le Bel centenary. And when these results appeared, they stemmed independently from three laboratories.[1-3] In our own case the chronology arose from a long interest in analgesics. It was hoped that certain easily synthesized nitrogen-containing tricyclic compounds might exhibit analgesic activity. When these had been prepared,[4] it occurred to us to synthesize alicyclic analogs and a literature search at that time disclosed that no attempts has been reported concerning syntheses of such compounds. When we considered synthetic methods this fact appeared even stranger. Often a certain class of compounds appears in the literature as a result of the discovery of a new reaction which enables its synthesis. However, in this case the fundamental first step for the synthesis of simple members of the series is the Diels–Alder reaction, a reaction which had been known for more than three decades. Other reactions used in synthetic elaboration were nearly as old or older. Consider, for example, the synthetic sequence for the preparation of 3,7,10-propellanetrione, **1** (Scheme 1).[3,5,6]

The sequence in preparing two tetraenic compounds **2** and **3** whose reactions will be discussed below in detail, began from the same starting materials (Scheme 2).[5,7]

Further, it is difficult to understand the delay in becoming acquainted with propellanes in view of the tremendous interest in conformational analysis



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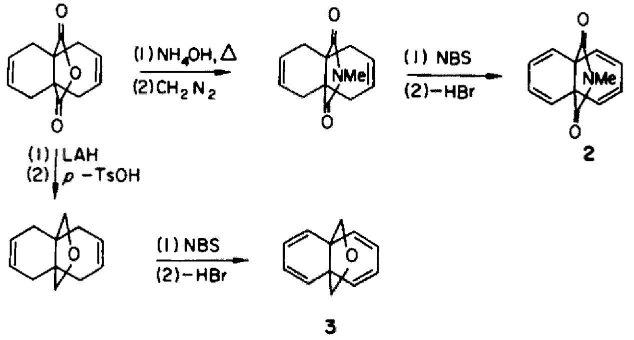
SCHEME 1



SCHEME 2

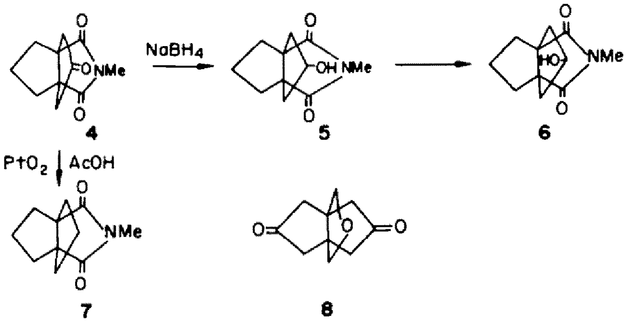
and in proximity effects in the preceding two decades.

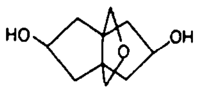
Certain results owing to proximity effects between different rings in a given propellane became evident early on. Thus, for example,[3] catalytic reduction of **4** led not to alcohol **5** or **6** but to the hydrocarbon **7**. Sodium borohydride reduction of **4** led to the hydrogen bonded epimer **5** of the two possible alcohols that may be expected. Inversion of its tosylate afforded the epimer **6**. These two alcohols could therefore be independently subjected to the same hydrogenolytic conditions used for the ketone **4**. No hydrogenolysis occurred. Hydrogenolysis of **4** recalls that of ketones in the α-position to an aromatic nucleus or to a ferrocene nucleus. Perhaps hydrogenolysis in these cases as well as that of **4** involves formation of a loose complex between the carbonyl group and the metal catalyst followed by hydrogenolysis of a carbon–O–metal bond rather than that of a carbon–OH bond and perhaps the presence of the imide ring in **4** assists in stabilizing such a hypothetical (unproved and unisolated) loose carbonyl-metal intermediate. This was chronologically perhaps the first case in which an unexpected proximity effect was observed. It was expected *a priori* and later it became clear that many interesting reactions could be planned in view of the very nature of propellanes. You simply cannot have three rings arrayed as they are in this system without interesting consequences. Whether these are foreseen or not is a measure of the calibre of the investigator rather than the calibre of propellanes as substrates in stereochemical studies.

Reduction of the diketone **8** with sodium borohydride led to a mixture of diols, isolated by elution with chloroform from a column of basic alumina in the order **9**, **10**, **11** and in the ratio 5:9:1 (isolated), respectively.

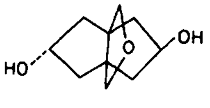
It is often simpler when representing the consequences of symmetry in these compounds to represent them as the "silhouette" of the molecule as one peers down along the axis of the conjoining bond (*cf* **9a**, **10a**, **11a**).

The protons α- to the ether O atom in the three diols serve as a convenient NMR probe for determination of their symmetry. This unfortunately is not always foolproof as, through coincidence, a singlet is sometimes exhibited by these protons even when they are not disposed towards an identical environment. Yet when all possible isomers are actually isolated, as in the above cases, **9–11**, reasonable deductions may be made. Thus, **9** and **11** exhibit singlets for the pertinent protons whilst **10**, as expected, exhibits an AB quartet. The reduction of **8** obeys the Robinson dictum that when one carries out a reaction leading to several possible epimers one always obtains less of the more desired epimer. Only one part in fifteen was obtained of **11**. It may be readily seen from **11a** that this is the epimer one wants in order to produce the cyclic carbonate **12**. Despite its availability in short

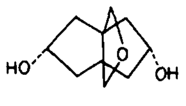




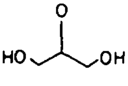
**9**



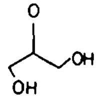
**10**



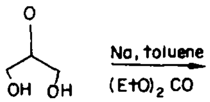
**11**



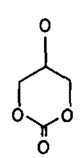
**9a**



**10a**



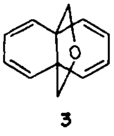
**11a**



**12**

supply **11a** afforded **12**, thus establishing the configuration of its hydroxyl groups; the structure of **9** then follows.[8]

A similar exercise in symmetry stemmed from a study of the reaction of the tetraenic ether **3** with $Fe(CO)_5$ and $Fe_2(CO)_9$, respectively.[6,9] Since there are two substituted *cis*-butadienes in **3**, in principle one should be able to obtain mono- or *bis*-irontricarbonyl complexes. Iron pentacarbonyl afforded only one of these, a presumably symmetrical *bis*-derivative since the protons adjacent to the ether oxygen atom exhibited a singlet in the NMR spectrum. With $Fe_2(CO)_9$, however, veritable riches of ironclad compounds were obtained. All of the possible products, two mono-$Fe(CO)_3$ complexes **13** and **14**, and the three possible *bis*-complexes **15**–**17** were isolated after laborious chromatography of the reaction mixture on alumina.



**3**

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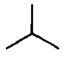
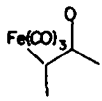
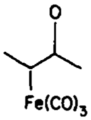
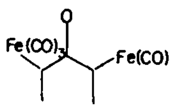


**3a**

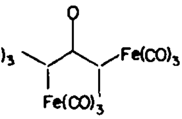




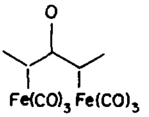
13* 14*



15[9,10]



16[11]

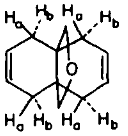


17*

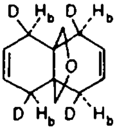
Again the protons $\alpha$- to the ether oxygen permitted selection of the unsymmetrical *bis* complex **16** since an AB quartet was exhibited in its NMR spectrum whilst **15** and **17** exhibited singlets for their respective protons. Since the structure of **15** was established by X-ray crystallography,[9,10] that of **17** follows. It was found that it is possible to effect stepwise removal of each of the two $Fe(CO)_3$ groups in **15**. Removal of the first gave **13**, established its configuration.[9] More interesting is the fact that similar stepwise reaction using **16** afforded **14**. An explanation of this fact is readily afforded by noting that the $Fe(CO)_3$ group on the "top" face of **16** is less hindered towards the approach of ceric ion than that attached to the bottom face, as clearly shown by the X-ray-crystallographically determined structure of **16**.[11] The distance between the ether oxygen and the cyclohexadiene boat attached to the "bottom" $Fe(CO)_3$ group is such as to suggest that as the latter withdraws electrons from the diene the lone pairs on oxygen afford some replenishment of charge to the same diene. Thus the envelope conformation exists in the 5-membered ether ring of **16**. This is not found in **15**, albeit the X-ray structure found for this ring in **15** may result from the averaging of the equal number of conformers in which both possible envelopes exist.

Evidently, when $Fe(CO)_5$ is used and only **15** is obtained, there must be some loose precoordination between the metal carbonyl and the ether oxygen and thus $Fe(CO)_3$ is delivered only to the top face of each cyclohexadiene ring. When $Fe_2(CO)_9$ is used, it is known[13] that $Fe(CO)_4$ is the reactive species and this apparently attacks with much less discrimination.

A similar explanation has been invoked for the steric course of homogeneous hydrogenation of **3**, employing an arenechromium tricarbonyl as catalyst. The major product is **18**. The atoms marked $H_a$ (on the "top" faces) are closer to the ether oxygen



**18**



**19**

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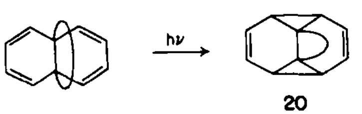
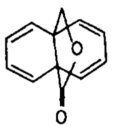
*The structures **15** and **16** are ironclad twice over as they were established by X-ray crystallography.[9-11] Structures **13**, **14** and **17** are represented by *analogy* to the above findings and others[12] in which cyclohexadienes have been shown to attain a boat-like conformation when complexed to $Fe(CO)_3$. See also additional evidence for such conformations below, in the discussion of the steric course of the Diels–Alder reactions of **15**.

atom than those marked $H_b$, no matter what conformation obtains for each cyclohexene ring. Since the only anchor for a lanthanide shift reagent in **18** or **19** is the O atom it is possible to assign the pertinent lines to $H_a$ and $H_b$ in **18** and to $H_b$ in **19**. The relative slopes of the straight lines obtained by plotting $\delta\Delta\nu$ *vs* the concentration ratio of $[Eu(DPM)_3]/[Diene]$ were determined, leading to the unequivocal deduction that deuterium (and therefore hydrogen as well) is delivered from the top face of each cyclohexadiene ring in **3**.[14]

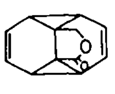
Let us now discuss electrocyclic reactions of **2** and **3** which have shed some light on the steric course of these reactions. Their photochemical behavior is perhaps less interesting from this point of view as it parallels that of the bicyclic system, *cis*-9,10-dihydronaphthalene which may, after all, be considered their parent. The irradiation of these compounds led to intermediates of type **20**.[15] When the token ring in **20** was that of a 5-membered imide or N-methyl-imide, both of these compounds of type **20** were stable enough so as to permit their isolation, in contradistinction to the parent of **20** where H atoms replaced the termini of this added ring. For an ether, lactone or anhydride ring, all 5-membered, the analogous derivatives were less stable than the corresponding imides, but they could be observed by low temperature NMR. Most interesting of these was the lactone **21** where the thermal fluxional isomerism in its photochemical product **22** could be observed by variable temperature NMR. The analysis of the 100 MHz and 220 MHz spectra together with variable temperature studies which revealed (27–180°) a drastic but completely reversible temperature dependence permitted assignment of the different types of $H_a$, $H_b$, $H_c$ and $H_d$ to the set of fluoxional isomers **22**–**24**.[16] The reaction **22**$\rightleftharpoons$**23** is considerably faster than **22**$\rightleftharpoons$**24**. At room temperature the mixture contains **22**, **23**, **24** in the ratio 23:45:32.



**20**

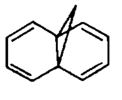


**21**

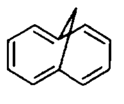


**22**

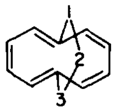
Since we have already discussed the interesting case of fluxional isomerism in the $(CH)_{10}$ series, in particular in the case of its propellane offspring[15–17] let us now use propellane substrates directly, in thermal electrocyclic reactions. We had hoped that heating of tetraenic propellanes such as **2** and **3** might follow a course analogous to that of **25**. When the synthesis of the latter was attempted, the much more interesting methano[10]annulene, **26**, was obtained.[18] In the case of **2** or **3**, the [10]annulene system would be bridged by a 3-atom chain, as in **27**, rather than by a single atom unit. When **2** was heated just above its m.p., at 160°, we watched it melt and soon after, resolidify. The product isolated in 85% yield had m.p. 309–310° and it was not immediately apparent why the "open chain" analog **27** of **2** should differ so in m.p. Our elation was shortlived as the mass spectrometer soon indicated that **2** had dimerized.[19] Since the dimer is not obtained upon heating **2** under reflux in dibutyl ether but is obtained under these conditions in the presence of $Cr(CO)_6$ we feel that it may be that **2** does give some of the [10]annulene, tenuously stabilized as its $Cr(CO)_3$ complex (a stable chromiumtricarbonyl complex of **26** has been prepared[20]), but since even the latter cannot be isolated, the series of equilibria afford the dimer in this case as well.



**25**

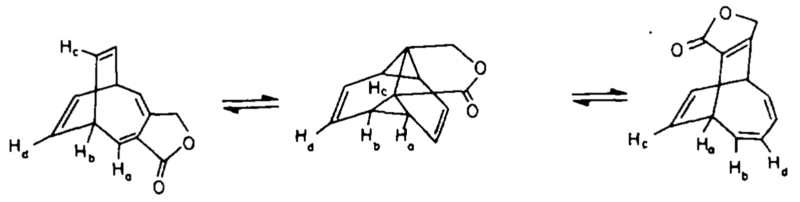


**26**



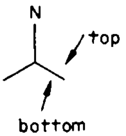
**27**

Indor spectroscopy was employed in order to elucidate of structure of the dimer **28** after chemical means failed. To be sure, reduction of the dimer afforded an *octa*hydro-derivative although two moles of **2** contain a total of eight double bonds. Had one mole of **2** behaved as a diene and another as a dienophile, a Diels–Alder adduct should be formed capable of undergoing reduction to a dodecahydro-derivative. Since only four moles of hydrogen were absorbed and the product exhibited no vinylic protons in its NMR spectrum, a second, *intra*molecular Diels–Alder addition must have fol-

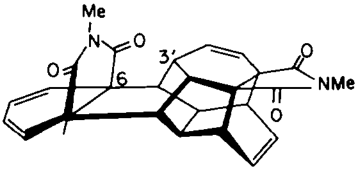


**23** **22** **24**

lowed the first *inter*molecular step. The dimer **28** must therefore be a cage compound. Its degradation by oxidative means led to irreproducible results along with copious amounts of expected $CO_2$. Thus, this was the first case where indor spectroscopy was used successfully in the elucidation of the structure of a rather complex molecule.[19] Here too as discussed above with respect to the approach of metal carbonyls, the dienophile **2** may approach the diene **2** from the top face or the bottom face. Two possible structures are possible for **28**, differing in configuration at the 1,6-junction. That the structure shown in **28** is correct was proved through the NOE. Irradiation at the N-Me (at left of structure) frequency enhanced the integral of the proton at position 3′ by 20%.



2



28

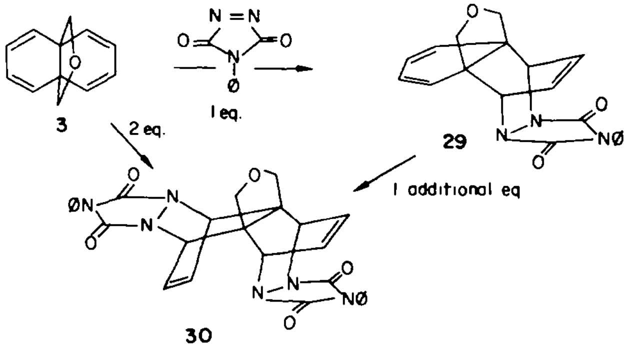
Whilst Dr. Sciacovelli was carrying out his indor measurements in Zürich Messrs. Tatarsky and Korat were studying the Diels–Alder reactions of **2** and **3** with dienophiles simpler than **2**.

Here these substrates can clearly be used to study whether dienophiles would approach the diene system (and react with it) from above or from below.[21] We preferred to start with the ether **3** rather than with the methylimide **2** because the former had the 4 protons adjacent to oxygen as a built-in NMR probe for determining the symmetry of the product. It soon became apparent that for most of the dienophiles studied this probe was unnecessary. Only one mole of dienophile could be caused to react with **3** and no conditions were found to convince a second mole to follow and to give a 2:1 adduct. Thus an unsymmetrical product was necessarily formed and the probe was completely unnecessary. We believe that the dienophiles react from below but this has not been proven unequivocally. Other cases have been reported regarding the direction of attack of a propellane in a Diels–Alder cycloaddition but generally the authors assume the structure of the product and support it by means of NMR data alone; this is a dangerous procedure (even when the result turns out to be correct), since only one of the two possible isomers was available to them.[22a,31] In many of our cases, therefore, we did not prove the configuration of the 1:1 adducts unequivocally. We did, however, by interrelation of e.g. the adducts of **3** with maleic anhydride, with maleate, with fumarate, show that all of these belonged to the same family of adducts. The dienophiles all reacted with **3** from the same direction.

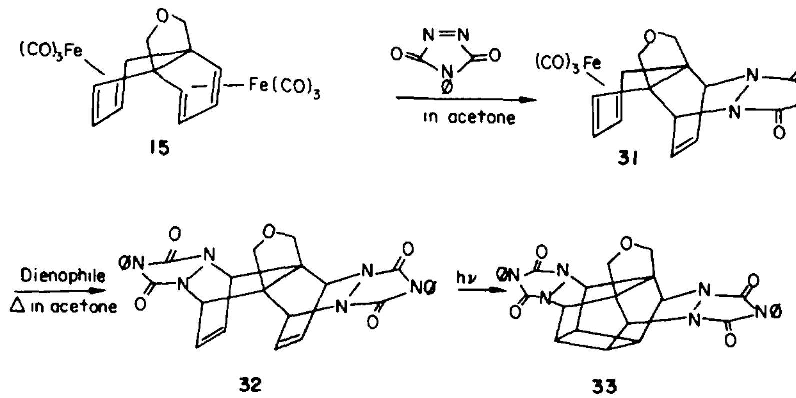
2:1-Adducts could be obtained only when **3** reacted with 4-phenyl-1,2,4-triazoline-3,5-dione. When the 1:1 adducts described above were reacted with the same extremely reactive dienophile, mixed 2:1-adducts were obtained.

This dienophile gave a 1:1 adduct **29** with the ether **3**. With an additional mole of dienophile **29** afforded the unsymmetrical *bis*-adduct **30** (AB quartet for the protons adjacent to the ether oxygen). The latter was obtained directly from **3** by adding two moles of dienophile without intermediate isolation of **29** (Scheme 3).

Since we had available in good yield **15**, the *bis*-irontricarbonyl complex of **3**, and since the triazolinedione was such a reactive dienophile, we thought we might be successful in employing it to displace the irontricarbonyl group from its attachment to the diene systems. Thus two sigma bonds would be formed in a Diels–Alder reaction of the diene system with the reactive dienophile (equivalent to four electrons) whilst displacing the metal ligand attached to the pi system of the diene (equivalent to four electrons). If the dienophile attacked from below one could *formally* picture this as a quasi (4 electron) $S_N$-2 reaction in the sense that this could be represented as back-side attack. However, the dienophile is far from being a potent nucleophile. It is much better described as an electrophile and thus one may imagine that it would first complex to the iron atom displacing CO. If the com-



Scheme 3



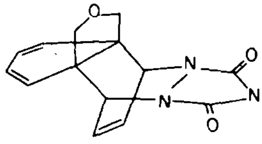
SCHEME 4

plex thus obtained is less stable than the original one, the whole metal ligand would be removed leaving a diene system to react with additional dienophile in the heterogeneous reaction mixture which indeed contained an excess of dienophile. Thus the reaction may be represented as front-side attack but it would not be certain at this stage whether the unclad diene system would react with retention or with inversion of configuration.

In the first place, the hoped-for reaction did occur and it was possible to carry it out stepwise, as shown in Scheme 4, or without isolation of the intermediate 31.

Both irontricarbonyl groups were displaced with *retention* of configuration. This was proved in an ironclad manner, despite the removal of iron. After irradiation of 32 four vinylic protons exhibited in the NMR spectrum of 32 disappeared and 4 cyclobutane protons appeared in the NMR spectrum of 33. Such a [2 + 2] cycloaddition could only occur in a compound having the structure 32. (Similar irradiation of 30 was nonetheless carried out but the material was completely recovered, unchanged).

An important observation was made upon removal of the metal ligand by treating 31 with ceric ion. A 1:1 adduct of 3 with the triazoline, 34, was thus obtained, isomeric with 29 obtained from the same precursors 3 and the triazoline, *without* the intervention of iron.

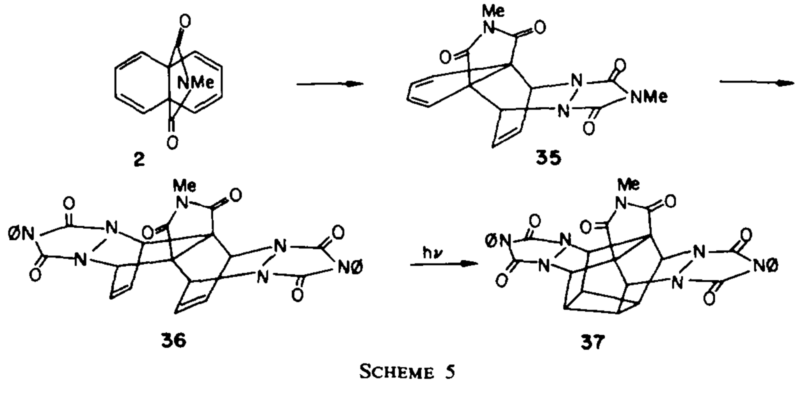


34

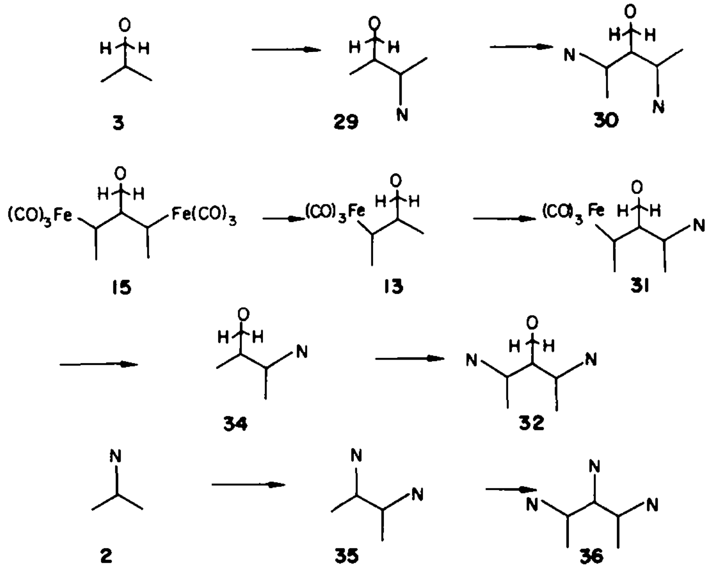
Since 32 was obtained in which both moles of dienophile reacted from the top of the cyclohexadiene rings, then the first mole of dienophile also reacted from the top face (giving 31 and then 34). Hence, 29, the isomer of 34, was formed by the dienophile reacting with 3 from the *bottom* face. The chronology in the formation of the unsymmetrical *bis*-adduct 30 is therefore first attack from below and then the second mole of dienophile attacks from above.

The course of the reaction of 2 with the same dienophile was now easily discerned (Scheme 5). The 2:1 adduct 36 behaved similarly to 32 upon irradiation, affording 37, the analog of 33. The monoadduct 35 must therefore have the configuration shown.

The explanation for the difference in behavior of



SCHEME 5



Scheme 6

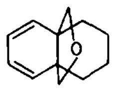
the first mole of dienophile towards 2 and 3 is based on steric grounds (Scheme 6).

There are H atoms adjacent to the ether oxygen in 3 and in 15 as well as in all of their derivatives. The dienophile prefers to approach 3 from below where there are no such hydrogens to exert steric hindrance. Once 29 has been formed however, the second equivalent of triazoline follows the mode of the lesser of two evils. Approach from above is hindered by two hydrogens but approach from below is hindered by a boat portion of the diazabicyclo[2.2.2]octane. Thus approach is from above.

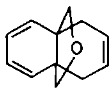
In 15 there are already two boats as shown by X-ray crystallography,[9,10] hindering approach from below. The triazoline, in any event, electronically, prefers to approach the Fe atom. Once one of the $Fe(CO)_3$ groups is removed one gets a molecule which may be represented as 13 (although its X-ray structure has not been determined). The lesser of two evils for the dienophile is still the top face approach (two hydrogens) rather than from the bottom face (boat hindering) and 31 is obtained. When 34 is present in the reaction mixture after the second irontricarbonyl group has been removed by its interaction with the triazoline we again have the choice between a (covalently constituted) boat hindering from below *vis à vis* two hydrogens hindering from above; above it is—leading to 32!

In 2 there are carbonyl groups and no hydrogens are available to hinder approach of the dienophile from above. The reason for exclusive attack from above stems from the equilibrium nature of the Diels–Alder reaction thus permitting formation of the thermodynamically most stable product. A second order orbital effect has been invoked to explain the relatively higher stability of the transition state for attack from above as compared to that from below.[21]

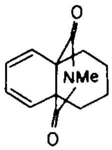
In the cases of the dienic and trienic ethers related to 3 and the corresponding dienic and trienic methylimides related to 2 the course of reaction is similar to that of 3 and 2, respectively. Here only one conjugated diene is present and only a mono-adduct can be obtained.



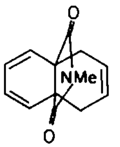
Tetrahydro-3



Dihydro-3

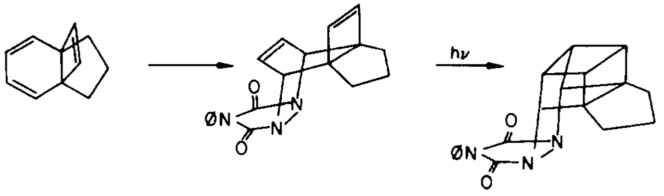


Tetrahydro-2



Dihydro-2

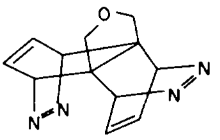
The monoadduct in the case of the ethers was reduced to the perhydro-derivative of 29 indicating that here too the dienophile attacked from below. Since reduction of the monoadduct of 2, its corresponding diene and triene each afforded the same perhydro-derivative it is clear that in all of these cases the dienophile attacked from above.[7] It happens that the same dienophile was added to [4.3.2]propell-2,4,10-triene.[22b] That it added from below was shown unequivocally by photocyclization to the open cubane system (Scheme 7).



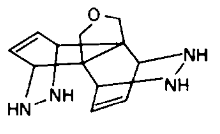
SCHEME 7

Since compounds such as **29**, **30**, **32** and **34** were available to us, clearly they were excellent substrates to convert into azopropellanes so that these could be studied thermally and photochemically.[23] Thus far by design and forethought. We shall soon see that because of proximity affects in these and similar molecules there was added serendipity in the grand manner.[*]

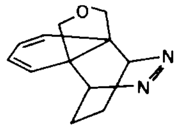
There would be no point in attempting to prepare an azopropellane such as **38** as at this oxidation level, a retro-Diels–Alder reaction would be sure to occur and the starting point **3** would be regained. However, at the oxidation level of **39**, the material which would result from alkaline hydrolysis of **30**, would be stable. Thus **30** was hydrolyzed under such conditions. However, **39**, was not isolated. Rather, **40** was obtained. Undoubtedly **39** is formed but because of the proximity of one hydrazine residue to a double bond, an intramolecular hydrogen transfer occurs in a reaction reminiscent of (the intermolecular) diimide reduction. The azocyclohexene thus obtained in one portion of the molecule undergoes a thermal retro-Diels–Alder reaction leading to a cyclohexadiene whilst the hydrazine portion remaining in the molecule is oxidized by air to the azo-derivative **40**.



**38**

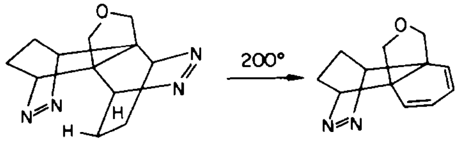


**39**

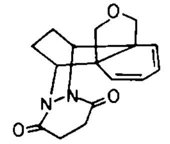


**40**

Even more peculiar is the thermal treatment of **41**, the tetrahydro-derivative of **38**. At 200°, nitrogen in evolved and **42**, an isomer of **40** is isolated. In this case, a paraffinic chain –CH$_2$–CH$_2$– intramolecularly reduces the proximate azo group to the corresponding hydrazine. The azocyclohexene portion of the molecule again loses nitrogen and gives a cyclohexadiene. That this is so was shown by heating **41** at 200° in the presence of succinic anhydride; **43** was isolated, clearly proving that a hydrazine group was obtained in the portion of the molecule *anti*-to the ether ring.

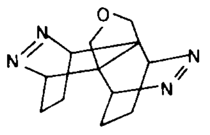


**41** **42**

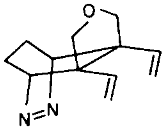


**43**

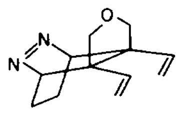
We had available for photochemical studies the monoazo compounds **40** and **42** as well as the *bis*-azo compounds **41** and **44**.



**44**



**45**



**46**

Irradiation of **41** for 20 min caused evolution of nitrogen and formation of **45** whilst similar treatment of **44** which must necessarily lose nitrogen from an upper face of the molecule afforded a configurationally isomeric product **46**.

Upon further irradiation **45** and **46** in turn give the same mixture of products **47** and **48**.

Thus, although a concerted photochemical $\sigma 2s + \sigma 2s$ process is allowed, the photolysis of **45**

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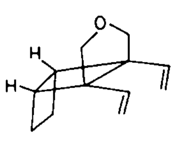
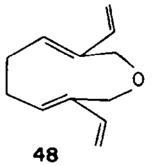
[*] One would not cavil that "serendipity" was first used in the chemical literature by R. B. Woodward who is responsible, *inter alia*, for enriching the vocabularies of his confreres.



**47**



**48**

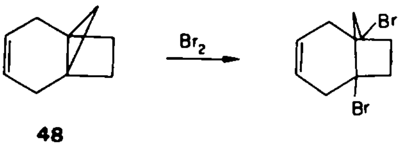
proceeds with inversion of configuration so that presumably there is a 1,4-biradical intermediate which undergoes inversion in this case, to afford **47**. The latter is obtained from **46** with retention of configuration but this does not necessarily mean that its photolysis does not occur through a biradical intermediate as well[23] (Scheme 8).

We were indeed interested in these reactions from the point of view of synthesis of small ring propellanes containing cyclobutene rings. The steric points more directly germane to this review are related to the possible inverted tetrahedral geometry in such compounds.[24,25]* But the chemical reactivity of such systems which cannot be divorced from the special steric situation at the conjoining bond affords us an exotic case in which bromine addition occurs across a carbon–carbon single bond in a compound **48** which contains a carbon–carbon olefinic bond.[26]

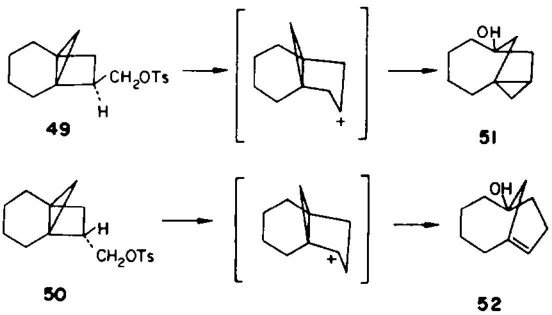
Perhaps the most interesting case of a steric effect in small ring propellanes has been reported by Gassman for the solvolysis of two epimeric tosylates **49** and **50** (Scheme 9).[27] When these solvolyses were carried out in aqueous acetone two completely different products were obtained, **51** and **52**, respectively, as the major products.

In the former case the cation obtained is well disposed for stabilization by the neighboring cyclopropyl ring.

We have noted some time ago certain abnormalities in the UV spectra of certain propellanes. A methylimide chromophore in a compound such as **53** is not expected to exhibit a high extinction value

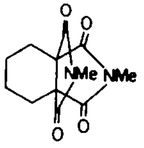


**48**

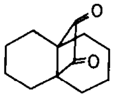


SCHEME 9

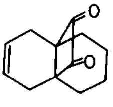
but its UV spectrum as those of similar type clearly exhibit interaction between the imide rings.[3] Similarly the hyposochromic shift in tetraenic propellanes such as **3** is peculiar[5] but thus far no explanation has been forthcoming although the PE spectra of two series of compounds related to **2** and to **3** (containing from zero to four double bonds) have been measured.[28] It has not been possible to assign with certainty the various electronic transi-



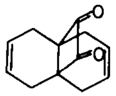
**53**



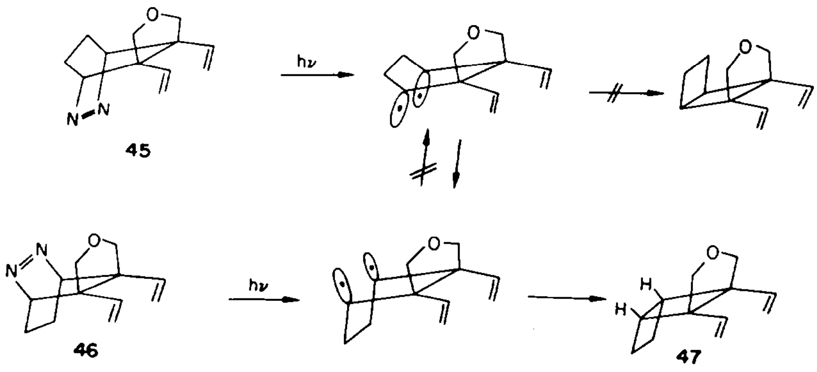
**54**



**55**



**56**



SCHEME 8

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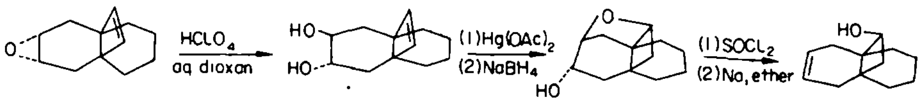
*I daresay that van't Hoff and le Bel would accept this qualification in the tetrahedrality of the C atom, since an extension of their original concept is involved.



SCHEME 10

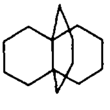
tions involved. The PE spectra of another series of propellanes have been reported.[29]

The unusual visible spectral properties of the series of [4.4.2]propellenediones **54–56** have been reported[30a] and interpreted.[30b]

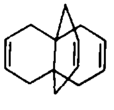
We have begun in our laboratory a series of chemical investigations designed to discover the importance of steric proximity of the rings to one another in the course of electrophilic attack upon one or more rings. Results of this type have already been published[31] (Scheme 10).

We shall report our results in due course.

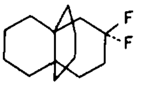
Finally we should mention work that has been done employing X-ray crystallography and NMR spectroscopy in order to determine conformations of certain propellanes in the crystal or in solution. The X-ray work on certain irontricarbonyl complexes of **3** has already been mentioned. The structures of [4.4.4]propellane, **57**, and the corresponding triene **58** have been determined.[32] The cyclohexane rings are flattened out chairs and half-chairs, respectively. An NMR study in solution has been reported for triene **58** and for the difluoropropellane **59**.[33]



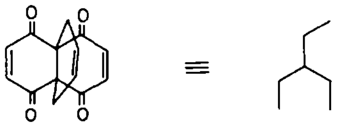
**57**



**58**



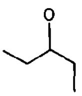
**59**



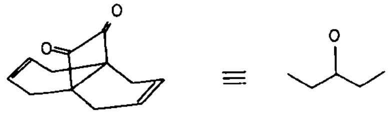
**60**

An ESR study of a free radical prepared from **60** led to the conclusion that the rings are boats as shown.[34] Perhaps this is also the reason for the copper color of the crystals of **60**. ESR spectra of the semidiones derived from **54–56** have been reported.[30]

The conformation which evidently is most stable in solution for the semidione from **56** is **61**[30c] but the X-ray structure of the crystalline dione is **62**.[30b]



**61**



**62**

We also have several cases in which lanthanide shift reagents have been used to cast light upon conformations of certain propellanes. Our results will be reported elsewhere.[7]

## REFERENCES

[1] G. Snatzke and G. Zanati, *Liebigs Ann.* **684**, 62 (1965)
[2] F. Nerdel, K. Janowsky and D. Frank, *Tetrahedron Letters* 2979 (1965)
[3] J. Altman, E. Babad, J. Itzchaki and D. Ginsburg, *Tetrahedron* Suppl. **8**, Part I, 279 (1966)
[4] S. Welner and D. Ginsburg, *Israel J. Chem.* **4**, 39 (1966)
[5] J. Altman, E. Babad, J. Pucknat, N. Reshef and D. Ginsburg, *Tetrahedron* **24**, 975 (1968)
[6] J. Altman, E. Cohen, T. Maymon, J. B. Petersen, N. Reshef and D. Ginsburg, *Ibid.* **25**, 5115 (1969)
[7] C. Amith, unpublished results
[8] E. Cohen, unpublished results
[9] K. B. Birnbaum, J. Altman, T. Maymon and D. Ginsburg, *Tetrahedron Letters* 2051 (1970)
[10] K. B. Birnbaum, *Acta Crystallog.* B. **28**, 161 (1972)
[11] G. I. Birnbaum, *J. Am. Chem. Soc.* **94**, 2455 (1972)
[12] M. R. Churchill and R. Mason, *Proc. Roy. Soc.* A, **301**, 433 (1967)
[13] A. Z. Rubezhov and S. P. Gupin, *Adv. Organometallic Chem.* (Edited by F. G. A. Stone and R. West) vol. 10, p. 374. Academic Press, N.Y. (1972); *cf.* G. F. Emerson, K. Ehrlich, W. P. Giering and D. Ehntholt, *Transac. N.Y. Acad. Sci.* **30**, 1001 (1968)
[14] C. Amith, M. Cais, D. Fraenkel and D. Ginsburg, *Heterocycles* **1**, 39 (1973)
[15] J. Altman, E. Babad, D. Ginsburg and M. B. Rubin, *Israel J. Chem.* **7**, 435 (1969) and refs given
[16] W. von Philipsborn, J. Altman, E. Babad, J. J. Bloomfield, D. Ginsburg and M. B. Rubin, *Helv. Chim Acta* **53**, 725 (1970)
[17] D. Ginsburg, *Accounts Chem. Res.* **2**, 121 (1969)
[18a] E. Vogel and H. D. Roth, *Angew Chem.* **76**, 145 (1964); [b] E. Vogel, W. Maier and J. Eimer, *Tetrahedron Letters* 655 (1966)
[19] O. Sciacovelli, W. von Philipsborn, C. Amith and D. Ginsburg, *Tetrahedron* **26**, 4589 (1970)
[20] P. E. Baikie and O. S. Mills, *J. Chem. Soc.* A, 328 (1969)
[21] M. Korat, D. Tatarsky and D. Ginsburg, *Tetrahedron* **28**, 2315 (1972)
[22a] L. A. Paquette, T. Kakihana, J. F. Hansen and J. C. Philips, *J. Am. Chem. Soc.* **93**, 152 (1971); [b] L. A. Paquette, R. E. Wingard, Jr. and R. K. Russell, *Ibid.* **94**, 4739 (1972)
[23] M. Korat and D. Ginsburg, *Tetrahedron* **29**, 2373 (1973)
[24a] K. B. Wiberg and G. J. Burgmaier, *J. Am. Chem. Soc.* **94**, 7396 (1972); [b] K. B. Wiberg, G. J. Burgmaier, K. Shen, S. J. La Placa, W. C. Hamilton and M. D. Newton, *Ibid.* **94**, 7402 (1972)
[25] D. Ginsburg, *Accounts Chem. Res.* **5**, 249 (1972)
[26] P. Warner and R. La Rose, *Tetrahedron Letters* 2141 (1973)
[27] P. G. Gassman and E. A. Armour, *J. Am. Chem. Soc.* in press, personal communication

[28] E. Heilbronner, personal communication

[29] R. Gleiter, E. Heilbronner, L. A. Paquette, G. L. Thompson and R. E. Wingard, Jr., *Tetrahedron* **29**, 565 (1973)

[30a] J. J. Bloomfield and R. E. Moser, *J. Am. Chem. Soc.* **90**, 5625 (1968); [b] S. C. Neely, R. Fink, D. van der Helm and J. J. Bloomfield, *Ibid.* **93**, 4903 (1971); [c] J. M. Fritsch and J. J. Bloomfield, *Spectroscopy Letters* **1**, 277 (1968)

[31] L. A. Paquette and G. L. Thompson, *J. Am. Chem. Soc.* **94**, 7118 (1972)

[32] O. Ermer, R. Gerdil and J. D. Dunitz, *Helv. Chim. Acta* **54**, 2476 (1971)

[33] H. Gilboa, J. Altman and A. Loewenstein, *J. Am. Chem. Soc.* **91**, 6062 (1969)

[34] R. Bar-Adon, S. Schlick, B. L. Silver and D. Ginsburg, *Tetrahedron Letters* 325 (1972)