Vogel for a delightful year at the University of Köln, where a part of this work was accomplished. The author thanks Mr. Donald Tomalia for the initial synthesis of 1-phenylthiocarbonylaziridine and for an experiment of this material in moist acetone containing sodium iodide.

The Oxymercuration of Olefins. I. A General Method for Determination of the Stereochemistry of Oxymercuration

BY T. G. TRAYLOR AND A. W. BAKER

The addition of mercuric salts to olefins in water produces hydroxymercurials, $HOCR_2CR_2HgX$, whose OH stretching frequency differs from that of the parent alcohol, $HOCR_2CR_2H$, by an amount which depends on the mercury-oxygen distance. The frequency difference, $\Delta\nu$, amounts to 6–10 cm.$^{-1}$ for either open chain or trans-hydroxymercurials; cis-hydroxymercurials show a $\Delta\nu$ of 18–22 cm.$^{-1}$. Consequently, it is possible to deduce the stereochemistry of oxymercuration from the OH stretching frequency of the product. Using this technique, and other methods for corroboration, we have confirmed our previous conclusion that, although cyclopentene and cyclohexene form trans-oxymercuration products, norbornene is oxymercurated exclusively cis-exo. Because the latter result is anomalous on two counts, we have extended this finding to dicyclopentadiene and benznorbornene, concluding that such strained olefins generally add mercuric salts without rearrangement to afford exclusively exo-cis products. These findings are incorporated into previously proposed mechanisms of electrophilic addition. Structural effects responsible for changes in stereochemistry of addition are discussed.

Introduction

The similarity of oxymercuration to other electrophilic olefin addition reactions is well established.[1]

$$HgX_2 + \quad C=C \quad + ROH \longrightarrow \quad C-C \quad + HX \quad (1)$$
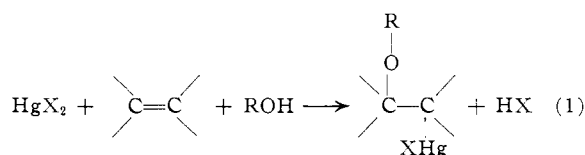
The addition is first order in mercuric salt, first order in olefin, and is stereospecific.[1] The products of this addition to cyclopentene and cyclohexene have been demonstrated to have trans configurations by their elimination rates,[2,3] dipole moments,[4] and nuclear magnetic resonance spectra.[5] Therefore, the recent observation that norbornene adds mercuric salts to give the exo-cis configuration[6] seems to warrant further investigation of olefin oxymercuration, especially the oxymercuration of strained and bicyclic olefins. We have consequently undertaken the tasks of establishing the generality of the cis addition in 2.2.1-bicyclic olefins and of determining whether this change from complete trans-oxymercuration to complete cis-oxymercuration with change in olefin structure is due to olefin angle strain or some more specific property of bicyclic systems. This paper reports our progress on the former along with some conclusions concerning the mechanisms of ionic additions to olefins.

In order to pursue efficiently the stereochemistry of the addition reaction with a variety of olefins it was necessary to develop a simple, general method of structure proof. This proof must establish the skeletal structure, the –OR configuration, and the position and configuration of the mercury atom. The first of these can usually be accomplished by reducing the mercurial with sodium amalgam[7] or sodium borohydride[8,9] to replace mercury by hydrogen. Typical reductions are illustrated in eq. 2 and 3 for the norbornene adduct.
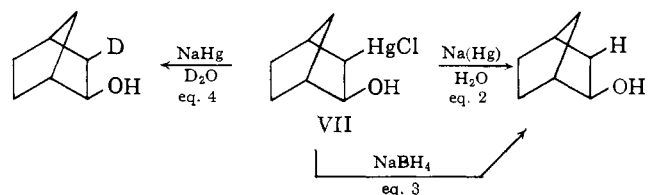
We have occasionally employed sodium borodeuteride or sodium amalgam in D_2O to afford additional stereochemical evidence (eq. 4). Identification of the resulting alcohol with a known alcohol establishes the skeletal structure and configuration of the OH (or OR) group. The position of the mercury atom can be ascertained by the deuterium replacement shown in eq. 4, by the n.m.r. spectrum of the mercurial,[5] or by a less equivocal process of oxidizing the alcohol with permanganate to a ketone[10] in which the mercury is enolizable only if it is α to the ketone group[11] (eq. 5).


$$ (5) $$
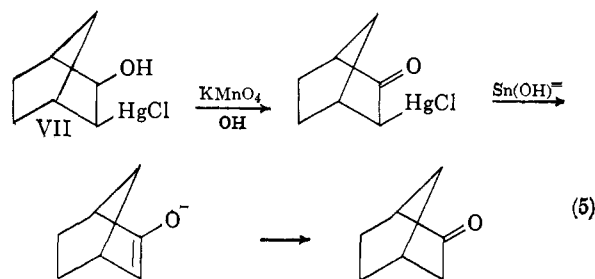
We have employed all three methods.

The configuration of the mercury atom relative to the OH group can be inferred from rates of elimination in acid[2] or from dipole moment measurement.[4a,b] This configuration can be established in some cases (e.g., in VII) from the n.m.r. coupling constant between protons attached to the carbon atoms in question.[5] But the most general and convenient method for demonstrating the stereochemical relationship of these two groups is the infrared method presented here.

(1) J. Chatt, Chem. Rev., 48, 7 (1951).

(2) M. M. Kreevoy and F. R. Kowitt, J. Am. Chem. Soc., 82, 739 (1960).

(3) T. G. Traylor and S. Winstein, Abstracts, 135th National Meeting of the American Chemical Society, Boston, Mass., April, 1959, p. 82-O.

(4) (a) A. G. Brook, R. Donovan, and G. F. Wright, Can. J. Chem., 31, 536 (1953); (b) although these authors interpret their dipole moment results as indicating cis addition, they are clearly more consistent with trans.

(5) M. M. Anderson and P. M. Henry, Chem. Ind. (London), 2053 (1961).

(6) T. G. Traylor and A. W. Baker, Tetrahedron Letters, No. 19, 14 (1959).

(7) (a) J. Sand and F. Singer, Ber., 35, 3170 (1902); (b) Ann., 329, 181 (1903).

(8) J. H. Robson and G. F. Wright, Can. J. Chem., 38, 21 (1960).

(9) H. B. Henbest and B. Nicholls, J. Chem. Soc., 227 (1959).

(10) I. F. Lutsenko and R. I. Sivkova, Zh. Obshchei Khim., 29, 1182 (1959).

(11) O. A. Reutov and L. T. Chzhu, Dokl. Akad. Nauk S.S.S.R., 110, 575 (1956).

Results

I. Methods of Oxymercuration.

Both the rate of oxymercuration (k_1)[1] and the rate of solvolytic decomposition of the oxymercurial[12a] increase with increasing ionic character in the Hg–X bond (eq. 6 and 7).


$$\text{(6)}$$

$$\text{(7)}$$
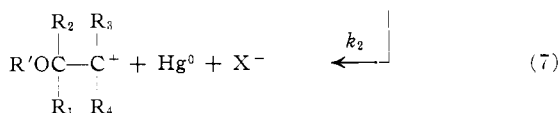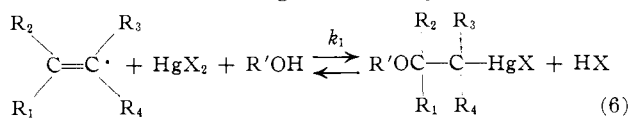
Reaction 7 occurs readily when R_3 and R_4 are groups which stabilize the carbonium ion and X is the anion of a strong acid. For example, norbornadiene reacts with mercuric trifluoroacetate or mercuric perchlorate in methanol to produce large amounts of mercury but reacts smoothly with mercuric chloride in methanol, affording the methoxymercurial in good yield.

$$\text{(8)}$$

$$\text{(9)}$$
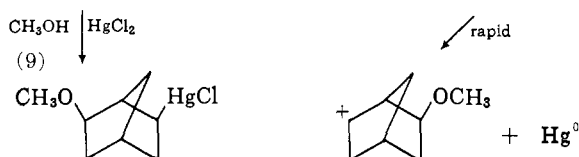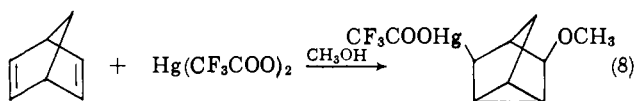
Mercuric chloride reacts extremely slowly with cyclic or acyclic olefins, whereas these olefins react quite rapidly with mercuric acetate or mercuric nitrate without subsequent decomposition.

An additional complication which occurs with all the bicycloheptenes studied is the competition of anions such as acetate with solvent in the addition reaction[13] as illustrated in eq. 10.

$$\text{(10)}$$
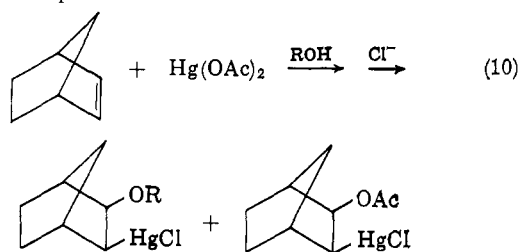
Such acetate-containing products are not obtained with unstrained olefins.

Therefore, the conditions employed in oxymercuration reactions must be varied to accommodate these variations in olefin reactivities.

We have employed the standard procedure[1] of mixing the olefin with a mercuric salt in a hydroxylic solvent. If water was used, an equal volume of acetone was added to increase solubilities. Based on the above considerations the mercuric salts were varied as follows: 1. Mercuric acetate was used with rather unreactive olefins whose addition product does not give a stable carbonium ion by loss of HgX^- (eq. 7). 2. Olefins which are very reactive but whose addition product is not a precursor of a stable carbonium ion by eq. 7 were oxymercurated using one mole of mercuric oxide and one equivalent of a strong acid such as perchloric or toluene-

(12) (a) F. R. Jensen and R. J. Ouellette, *J. Am. Chem. Soc.*, **83**, 4479 (1961); (b) F. R. Jensen and L. H. Gale, *ibid.*, **81**, 6337 (1959).

(13) M. J. Abercrombie, A. Rodgman, K. R. Bharucha, and G. F Wright, *Can. J. Chem.*, **37**, 1328 (1959). The configurational assignments in this paper are incorrect.[3,5]

sulfonic acid. 3. If the addition product can form a stable carbonium ion by HgX^- loss, then either mercuric chloride or a mixture of mercuric chloride and mercuric oxide were employed. For example, method 1 was used for cyclohexene, method 2 for norbornenes, and method 3 for norbornadiene and some norbornenes. In most cases the oxymercurials were stored as halide salts because the more ionic salts slowly decompose to metallic mercury and tar, presumably by the reaction of eq. 7.

II. The Infrared Method for Configurational Assignment.

β-Hydroxymercurials in dilute solution show single sharp peaks in contrast to α-hydroxyferrocenes which exhibit doublet peaks.[14,15] This indicates the absence of hydrogen bonding to metal such as that to which the above doublet was attributed.
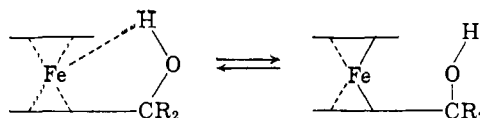
Consequently, the shift to lower hydroxyl stretching frequencies upon substitution of mercury for hydrogen β to the hydroxyl group must be attributed to other interactions, such as electrostatic interactions, between mercury and oxygen.
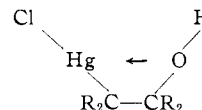
The frequency shift varies with relative configurations of the hydroxyl and chloromercuri groups and this variation forms the basis of our method of configurational assignment. Such direct interaction between mercury and oxygen reasonably increases with decreasing mercury–oxygen distance or torsional angle. This is illustrated in Fig. 1 where it can be seen that the interac-
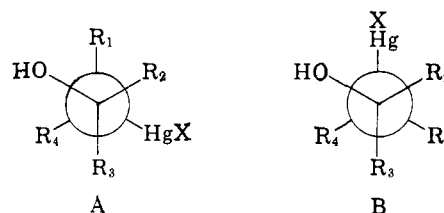
Figure 1.

tion and thus the frequency shift should be greater for B than for A. This consideration predicts a larger frequency decrease by substituting mercury for a hydrogen which is *cis* to a hydroxyl group (B) than by making the corresponding *trans* substitution (A).
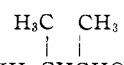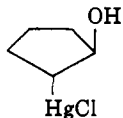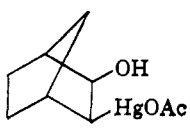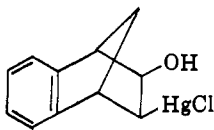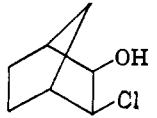
The experimental basis for this generality is seen in Table I. Compounds V and VI have been demonstrated by other means[2-6] to have *trans* configurations of the two groups; the frequency shifts are -6 and -7 cm.$^{-1}$. Compounds VII, VIII, IX, and X have been assigned *cis* configurations from n.m.r.[5] and dipole moment[6] data as described in the following section; they have frequency shifts of -18 to -20 cm.$^{-1}$. Acyclic hydroxymercurials show frequency shifts of -8 to -10 cm.$^{-1}$, presumably the result of a slight preference for *cis* conformation. The greater frequency shift in *o*- (XIII) than in *p*-chloromercuriphenol (XII) is also attributable to direct Hg–O interaction, although these shifts are consistent with inductive effects as well.

It is possible that this technique would not differentiate between *cis*- and *trans*-2-chloromercuricyclohexa-

(14) D. S. Trifan and R. Bacskai, *J. Am. Chem. Soc.*, **82**, 5010 (1960).

(15) E. A. Hill and J. H. Richards, *ibid.*, **83**, 3845 (1961).

TABLE I

HYDROXYL STRETCHING FREQUENCIES FOR *cis*- AND *trans*-HYDROXYMERCURIALS[a] (CM.$^{-1}$)

Compound		OH frequency	OH frequency of parent alcohol	$\Delta\nu$, cm.$^{-1}$
I	ClHgCH$_2$CH$_2$OH	3627.4	3636.4	− 9.0
		3610.4[b]	3618.7[b]	− 8.3
II	AcOHgCH$_2$CH$_2$OH	3627.2	3636.4	− 9.2
		3609[b]	3618.7[b]	− 9.7
III	IHgCHCHOH (*threo*)	3118	3628.0	−10
IV	Same (*erythro*)	3118	3628.0	−10
V[e]		3617.7	3623.7	− 6.0
VI		3620.0	3627.0	− 7.0
VII[e]		3603.0	3621.2	−18.2
VIII		3603.5	3621.2	−17.7
IX[e]		3601.5[c]	3621.2	−19.7
X[e]		3605	3625.0	−20
XI		3601.5	3624.1	−22.6
XII	ClHg-*p*-C$_6$H$_4$OH	3576.2[b]	3584.8[b]	− 8.6
XIII	ClHg-*o*-C$_6$H$_4$OH	3572.5[b]	3584.8[b]	−12.3
XIV		3631.2[d]	3621.2	10

(For III: H$_3$C CH$_3$ substituents shown on structure)

[a] All frequencies determined in carbon tetrachloride and corrected by using phenol in carbon tetrachloride at 3612.5 cm.$^{-1}$ as standard. [b] Measured in dichloromethane. [c] Broad peak at 3310 cm.$^{-1}$. [d] The bonded ·OH was at 3592 cm.$^{-1}$ and was smaller than the 3631.2 cm.$^{-1}$ peak. [e] See text for structures not included in table.

nols (Va and Vb) owing to the similarity of the Hg–O distances in the favored conformations shown in Fig. 2. However, because the A-values for hydroxyl and chloro-
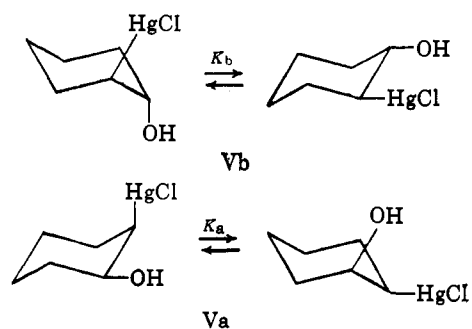
Figure 2.

mercuri groups are ∼0.5 and zero,[12b] respectively, K_b should be only ∼2 to 3 as written, resulting in a considerable contribution of the Vb axial–axial conformation and a smaller average frequency shift in Vb than in Va. Furthermore, the chloromercuri group, possessing a small A-value, does not introduce extra conformational effects on the hydroxyl stretching frequency.

We are therefore assigning *trans* configurations to β-hydroxymercurials whose hydroxyl stretching frequencies differ from the parent alcohol by less than 10 cm.$^{-1}$ and *cis* configurations to those whose frequencies differ by more than 18 cm.$^{-1}$.

III. Structures of the Mercurials in Table I.— The structures of compounds I–VIII have been established[1–6] and the remaining structures may be assigned by using the methods described above.

Quantitative conversion of IX to VII with mercuric chloride constitutes a complete structure proof of IX because this reaction is known to proceed with complete retention of configuration.[12b,16] The occurrence of an intramolecular hydrogen bond as shown in the infrared spectrum is also evidence for the *cis,cis* configuration of IX.
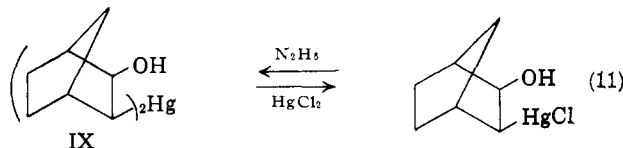
The 20 cm.$^{-1}$ difference between the hydroxyl stretching frequency of IX and that of norborneol provides additional confidence in the use of hydroxyl stretching frequencies for the structural assignments.

Both n.m.r. and infrared spectra indicate that oxymercuration of *endo*-dicyclopentadiene gives the mixture of *cis* products X indicated below, with no addition to the less strained five-membered ring.
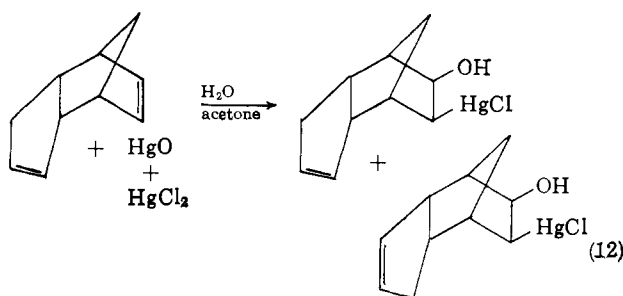
The n.m.r. spectrum of the acetate related to X has a broad vinyl proton absorption at 4.55 τ corresponding to a cyclopentene and no absorption at ∼4.1 τ which would indicate a norbornene structure. Thus, the mercuration occurred on the norbornene double bond and not on the cyclopentene ring. The doublet at 6.4 τ shows that only one hydrogen is in the position β to the hydroxyl group and the coupling constant, $J = 6$ c.p.s., for this doublet indicates that the hydrogens α and β to the hydroxyl are *cis*.[5] The 20 cm.$^{-1}$ shift in the hydroxyl frequency confirms this assignment.

The position of the mercury is also indicated by the n.m.r. spectrum of the alcohol obtained on reducing the mercurial X with sodium amalgam in D$_2$O.
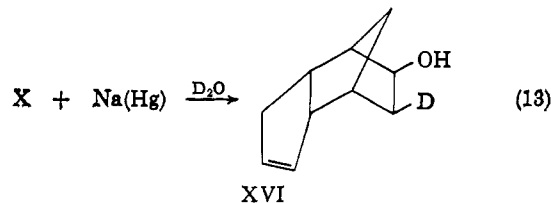
As in the mercurial itself, the vinyl proton at 4.55 τ and the doublet at 6.40 τ with $J = 6$ c.p.s. indicate the structure XVI.

The structure of XI was established by a comparison of the hydroxyl stretching frequency of the mercurial

(16) S. Winstein, T. G. Traylor, and C. S. Garner, *J. Am. Chem. Soc.*, **77**, 3741 (1955).

with that of the alcohol which was obtained by sodium amalgam reduction of XI (Table I). This alcohol had an over-all infrared spectram identical to the published spectrum of *exo*-benznorborneol.[17] Although no experiments were carried out to exclude the possibility of rearrangement, it seems unlikely in this system in view of the results described above; *trans* addition is definitely excluded.
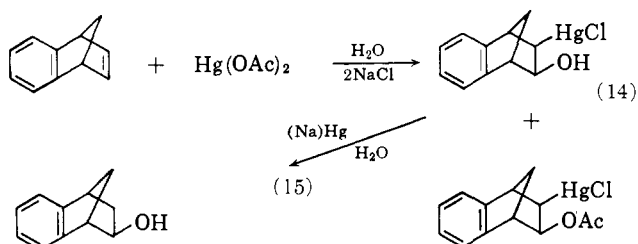
It can therefore be concluded that the three 2,2,1-bicycloheptenes studied undergo *cis* oxymercuration and it is tempting to generalize this stereochemistry for the bicycloheptene system.[18]

Discussion

The additions of most ionic reagents including mercuric salts to simple olefins proceed by second-order kinetics to give products of *trans* addition. For this reason and because certain metals such as platinum are known to form stable π-complexes wih olefins,[1] the mercurinium ion[19] formulation XVII for the intermediate in oxymercuration reactions is quite generally accepted.[1] This intermediate is analogous to the well known bromonium ion.[20]

When these reactions are applied to norbornenes, all the ionic addends save mercuric salts give similar results. Whereas bromine,[21a] hypochlorous acid,[22] sulfenyl chlorides,[21b] and peracids[23] add to norbornene with the usual *trans* stereochemistry accompanied by various amounts of rearrangement, mercuric salts add completely *cis* and without rearrangement.
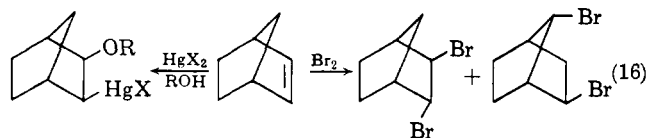
The predominance of rearrangement in bromination, etc., is attributed in part to steric hindrance by the 5- and 6-*endo* hydrogens to backside nucleophilic attack on the bromonium.[21a] This cannot account for the complete absence of *trans*-oxymercuration products in both norbornene and benznorbornene. Nor can the *cis*-oxymercuration be attributed to a free-radical reaction which, in a few cases, does give *cis-exo* addition to norbornenes.[24] Previous stereochemical and kinetic re-

(17) P. D. Bartlett and W. P. Giddings, *J. Am. Chem. Soc.*, **82**, 1240 (1960).

(18) Similar results have been obtained by Professor Saul Winstein. We are grateful for disclosure of his results and for helpful discussions concerning our own work.

(19) H. J. Lucas, F. R. Hepner, and S. Winstein, *J. Am. Chem. Soc.*, **61**, 3102 (1939).

(20) I. Roberts and G. E. Kimball *ibid.*, **59**, 947 (1937).

(21) (a) H. Kwart and L. Kaplan, *ibid.*, **76**, 4072 (1954); (b) H. Kwart and R. K. Miller, *ibid.*, **78**, 5678 (1956).

(22) W. G. Woods, R. A. Carboni, and J. D. Roberts, *ibid.*, **78**, 5653 (1956).

(23) H. M. Walborsky and R. D. Loncrini, *ibid.*, **76**, 5397 (1954).

(24) J. A. Berson and R. Swidler, *ibid.*, **76**, 4060 (1954).
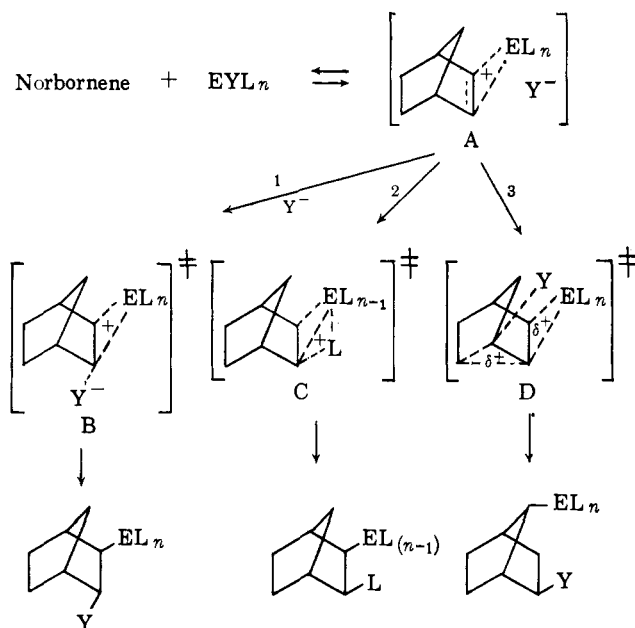
Figure 3.

sults[1,13] make free-radical oxymercuration very unlikely.

A four-center molecular oxymercuration of strained olefins similar to that proposed for hydroboration[25] or permanganate hydroxylation[26a] must still be considered. In the case of acyclic and unstrained cyclic olefins, a molecular oxymercuration is ruled out by the stereochemical results.

Because norbornene and cyclopentene both form 1:1 complexes with silver ion,[26b] it seems logical to assume a similarity in their initial reaction with mercuric ions also. The striking differences in oxymercuration of these two olefins can then be attributed to subsequent reactions of the respective mercurinium ion intermediates. Participation of a neighboring hydroxyl group in norbornene oxymercuration[9]
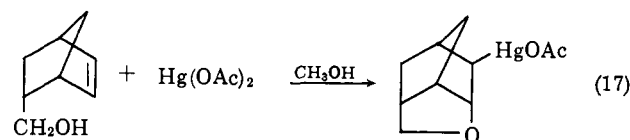
as in the oxymercuration of the acyclic olefin shown below[7b]
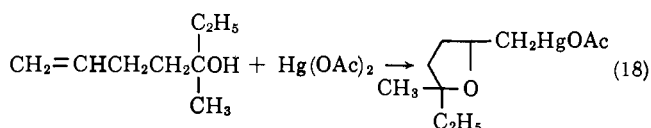
agrees with this postulate.

We therefore propose that one of the ligands on mercury is displaced by norbornene to form a π-complex which is opened from the front by ligand migration or ion pair collapse. This formulation explains the *cis* addition and the production of the two kinds of products shown in eq. 19. In unstrained olefins where the mercurinium ion is opened by backside nucleophilic attack, acetate ion is present in insufficient concentration to compete with solvent as a nucleophile and none of the acetoxyalkylmercurial corresponding to B is obtained.

(25) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

(26) (a) J. G. Traynam, *Chem. Ind.* (London), 1142 (1958); (b) J. G. Traynam and J. R. Olechowski, *J. Am. Chem. Soc.*, **81**, 571 (1959).

$$(19)$$
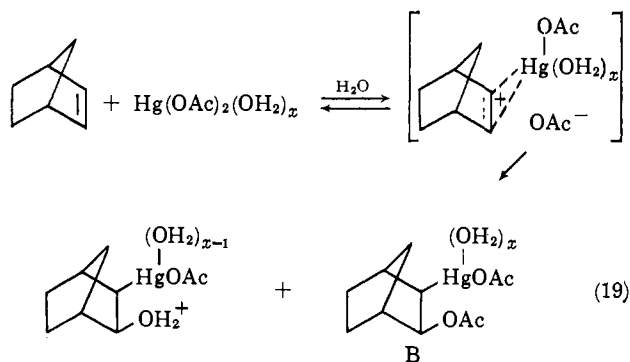
All the electrophilic additions to strained olefins such as norbornene are compatible with the π-complex mechanism in which the fate of the intermediate is determined by the electrophilicity of the addend and the olefin strain and rigidity. The general mechanistic scheme in which EYL_n represents the reagents $Hg(OAc)_2$, $ClOH$, Br_2, $RSCl$, etc., is shown below; E is the electrophile, Y the anion, and L other ligands. This scheme is similar to that proposed by Kaplan, Kwart, and Schleyer[27] except that their mechanism did not take account of ionic *cis* addition because their configuration of the norbornene oxymercuration product, taken from the work of Wright,[13] was incorrect.

The π-complex A is assumed to be in rapidly established equilibrium with the olefin. Normal behavior of unstrained olefins toward all the reagents mentioned is *trans* addition through path 1 because backside nucleophilic displacement is ordinarily much more favorable than frontside displacement. However, it is apparent from Fig. 4 that transition state B for this process re-
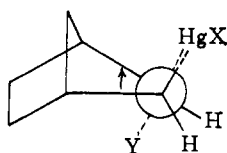
Figure 4.

quires an approximately 30° twist about the C–C bond. Such a twist is easily accomplished in simple acyclic or medium ring cyclic olefins. But an increase in rigidity of the olefin markedly increases the energy of B by preventing this twist. Although the reactivity of an olefin toward π-complex formation increases with increasing strain, the over-all activation energy in going to B would increase.

An increase in olefin strain should lower the activation energy for processes 2 and 3 because the strain energy, which is largely retained in the π-complex, is relieved in going to the activated complexes C and D. Therefore, increasing strain and rigidity in the olefin would favor processes 2 and 3 over 1.

The electrophile E^+ places a charge on the α-carbon by virtue of the electronegativity of E. The charge density on the α-carbon then controls the extent of rearrangement. This effect is clearly seen in Table II where the extent of rearrangement is directly relatable to electronegativities of the various E.

An alternative statement of this electronegativity effect is that increasing the potential C–E bond strength increases the tendency toward an unsymmetrical π-complex or open carbonium ion formation.
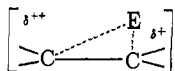
(27) L. Kaplan, H. Kwart, and P. von R. Schleyer, *J. Am. Chem. Soc.*, **82**, 2341 (1960).

TABLE II

REARRANGEMENT DURING THE ADDITION OF VARIOUS ELECTROPHILES TO NORBORNENE

Addend E[+]	Electronegativity of E	C–E bond strength, kcal.	Rearrangement,[a] %
OH[+]	3.5	84	100
Cl[+]	3.0	78.5	63
Br[+]	2.8	65.9	26
RS[+]	2.5	62	0
XHg[+]	1.9	56	0

[a] Data summarized in ref. 27.

Thus rearrangement decreases as electronegativity of E decreases until RS^+ and XHg^+ are reached where no rearrangement occurs. The choice is then front- or backside ring opening (paths 1 and 2). The completely different stereochemistry obtained in the RSCl and HgX_2 additions cannot be explained on the basis of olefin rigidity and electronegativity difference alone, although the greater charge on carbon in the sulfonium ion should assist in overcoming the steric hindrance and twist strain in backside displacement.

The principal difference between these two reagents is the greater ability of mercury to carry other ligands such as water, acetate, etc. It is the presence of such ligands which makes the ordinarily unfavorable frontside ring opening competitive with backside attack in these rigid systems.

On this basis we conclude that reactions of norbornenes and similarly strained olefins with electronegative addends lead to rearrangement; less electronegative addends which do not carry several ligands add *trans;* and less electronegative addends carrying several ligands add *cis.*

By this classification the acid-catalyzed addition of water to norbornenes would result in *cis* addition because the proton has a low electronegativity and is highly solvated. The recent observation that the products of acid-catalyzed addition of alcohols to dicyclopentadiene differ from the products of solvolysis of the corresponding tosylate is consistent with this view.[28]

$$(20)$$

$$+$$

$$H_2\overset{+}{O}CH_3$$
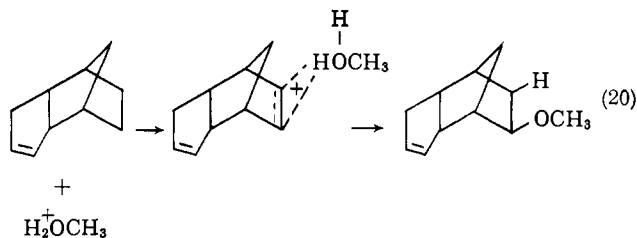
In this reaction the π-complex lacks the stability of those discussed above because the proton lacks the extra bonding orbitals of the larger atoms. For this reason some collapse to open carbonium ion is the expected and frequently observed result.

The mechanism of oxymercuration presented here predicts that as the olefin strain is decreased from that in norbornene to a value between norbornene and cyclopentene, front- and backside opening of the mercurinium ion will become competitive, and the stereochemistry of oxymercuration will be a function of solvent nucleophilicity. Such systems are the subject of the next paper in this series.

Experimental

Infrared Measurements.—The fundamental hydroxyl stretching frequencies of alcohols and hydroxymercurials were determined on a Beckman IR-7 spectrophotometer using 1-cm. silica cells and about 1 mg. of compound per ml. of solvent. Scale expansion and slow scanning speeds were used to get large

(28) S. J. Cristol, W. K. Seifert, D. W. Johnson, and J. B. Jurale, *ibid.*, **84**, 3918 (1962).

symmetrical peaks. The frequencies were corrected by measuring the phenol hydroxyl frequency in the same solvent immediately after the sample measurement and using 3612.5 cm.$^{-1}$ as the phenol stretching frequency in carbon tetrachloride. The hydroxyl peaks were sharp and single in this region. Some of the measurements have been checked on Beckman IR-9 and Perkin–Elmer 421 spectrophotometers.[29] The data, in which $\Delta\nu$ is known to ±0.5 cm.$^{-1}$, are given in Table I.

Nuclear Magnetic Resonance Spectra.—The spectra reported here were taken on a Varian A-60 n.m.r. spectrometer and reported in units of τ relative to tetramethylsilane as an internal standard.

2-Hydroxyethylmercuric chloride (I) was supplied by Dr. R.R. Grinstead of the Dow Chemical Co.

2-Hydroxyethylmercuric acetate (II) was prepared by the method of Sand[7a] and recrystallized from ethyl acetate–pentane.

3-Hydroxy-2-butylmercuric Iodides.—The *threo*-(III) and *erythro*-(IV) mercurials were supplied by Professor Maurice Kreevoy, Chemistry Department, University of Minnesota.

trans-2-Hydroxycyclohexylmercuric acetate (V) was obtained along with other products by treating cyclohexene with aqueous mercuric acetate as described by Nesmeyanov.[30] After recrystallization from ethyl acetate, it melted at 112–113°.

trans-2-Hydroxycyclopentylmercuric Chloride (VI).—Cyclopentene (6.0 ml., 0.068 mole) (Aldrich) was added to 15 g. (0.047 mole) of mercuric acetate in 600 ml. of 50 volume % aqueous acetone. After 10 min. 56.7 ml. of 0.1 N sodium hydroxide (0.057 mole) and 7 g. (0.12 mole) of sodium chloride were added and the solution evaporated to ~150 ml. on a rotary evaporator, then cooled. The precipitate was filtered off and dried; yield 9.5 g. Evaporating the filtrate afforded more product. After recrystallizing from water, the product melted at 112–113°. *Anal.* Calcd. for C$_5$H$_9$OHgCl: C, 18.59; H, 2.82. Found: C, 18.49; H, 2.82.

exo-cis-3-Hydroxy-2-norbornylmercuric Chloride (VII).—To a mixture of 94 g. (1 mole) of norbornene and 1 mole of perchloric acid in 1600 ml. of water was added 216.6 g. (1 mole) of mercuric oxide in several portions. The mixture was warmed to 50° to melt the small amount of remaining olefin. (This is more conveniently carried out if the solvent contains 50% acetone.) The end of the reaction was evidenced by disappearance of mercuric oxide and by failure of the solution to precipitate HgO in base. This mixture was decanted from a small amount of oil into 2 moles sodium chloride in 1 l. of water. The precipitate was filtered and dried; yield 300 g. (86%), m.p. 124–126°. Two recrystallizations from ethyl acetate–heptane gave a material, m.p. 131–131.5°.

exo-3-Chloromercurinorcamphor (XIX).—Solid potassium permanganate (53.8 g., 0.3 mole) was added slowly to a stirred mixture of 34.7 g. (0.1 mole) of VII and 0.3 mole of sodium hydroxide in 675 ml. of water at 0°. After the 20 min. required for the addition and another half-hour stirring, the mixture was treated slowly with gaseous sulfur dioxide, keeping the temperature below 10°, until the mixture was light pink (pH ~ 1). After addition of 7.5 g. of sodium chloride, the solid was filtered off and dried; yield 25.3 g. (68%), m.p. 187–191°. Recrystallization from dioxane–water raised the m.p. to 200–200.5°. *Anal.* Calcd. for C$_7$H$_9$OHgCl: C, 24.35; H, 2.63; Hg, 58.0. Found: C, 24.77; H, 2.69; Hg, 58.5.

This compound in carbon tetrachloride had a carbonyl peak in the infrared at 1731 cm.$^{-1}$ and that of norcamphor was 1749 cm.$^{-1}$. Stirring 3.46 g. (0.01 mole) of the chloromercurinorcamphor (XIX) with excess (0.045 mole) aqueous sodium stannite[11] for 24 hr., extracting the mixture with ether, evaporation of the ether, and vacuum sublimation of the residue afforded 0.51 g. (47%) of norcamphor, m.p. 93–94°, having an infrared spectrum identical with that of an authentic sample.

exo-cis-3-Hydroxy-2-norbornylmercuric Acetate (VIII).[13]—A mixture of 9.4 g. (0.1 mole) of norbornene, 0.05 mole each of mercuric oxide and mercuric acetate in 250 ml. of water was stirred 30 hr., evaporated to dryness, and the solid extracted with ethyl acetate, diluted with heptane, and cooled to give 23 g. (61%) of product. This compound decomposed very slowly to a gray-brown tar.

Di-*exo*-3-hydroxy-*exo*-2-norcamphanylmercury (IX).—To a solution of 5.6 g. (0.016 mole) of VII in 72 ml. of absolute methanol was added 1.28 g. of sodium hydroxide in 4 ml. of water and 1.09 g. of 95% hydrazine. Mercury separated immediately. The solution was refluxed 6 hr. and decanted from the mercury into 300 ml. of ether. The mercury was washed successively with methanol, water, and acetone, dried, and weighed; yield 1.814 g. (56.2%). The ether solution was washed with two 200-ml. portions of distilled water, dried over sodium sulfate, evaporated to ~20 ml., and cooled to precipitate IX. After washing with cold ether and drying, the product weighed 1.243 g. (37% of norborneol residues, 19% of mercury),

m.p. 152–152.5° dec. It gave no precipitate in hot ethanolic silver nitrate solution. *Anal.* Calcd. for C$_{14}$H$_{22}$O$_2$Hg: C, 39.75; H, 5.24; Hg. 47.4. Found: C, 40.13; H, 5.36; Hg, 48.5.

The infrared spectrum of this compound differed from that of VII especially in the hydroxyl stretching region. Besides the sharp peak at 3601.5 cm.$^{-1}$ it possessed a very strong broad peak at 3310 cm.$^{-1}$ which remained even in dilute solution indicating strong intramolecular hydrogen bonding. This and the single unbonded stretching frequency indicates *cis-cis* structure. This structure is confirmed by the following cleavage reaction. Treating 0.1014 g. of IX in 20 ml. of ether with 0.066 g. of mercuric chloride and evaporating the solvent produced 0.160 g. of VII, m.p. 122–129°, which showed only one sharp peak at 3603.5 cm.$^{-1}$ in the hydroxyl region and was identical with VII in other parts of the infrared spectrum.

exo-Norborneol.—The filtrate from the precipitation of IX was evaporated to dryness; yield of residue 0.6685 g. (38%), m.p. 115–127°. The infrared spectrum was identical with that of authentic *exo*-norborneol.

Mercuration of Dicyclopentadiene.—For n.m.r. structure determination: To 200 mg. of mercuric acetate in 0.2 ml. of D$_2$O and 0.2 ml. of acetone-d_6 (Merck) in an n.m.r. tube was added 75 µl. of dicyclopentadiene. After shaking for a few minutes and allowing the mixture to stand overnight an n.m.r. spectrum was taken. The product had a small peak at 4.48 τ, a large peak at 4.55 τ which in combination were rather broad, a singlet at 5.7 τ (probably H$_2$O), a doublet centered at 6.4 τ with $J = 6$ c.p.s., a resplit doublet centered at 7.1 τ, $J = 6$ and 2 c.p.s., a very large peak at 8.1 τ, and other unresolved peaks at 7–9 τ. Dicyclopentadiene has singlets at 4.14 and 4.55 τ in addition to peaks from 7–9 τ.

Preparation of X.—A solution of 2.64 g. (0.02 mole) of commercial dicyclopentadiene, 2.16 g. (0.01 mole) of mercuric oxide, and 2.72 g. (0.01 mole) of mercuric chloride in 30 ml. of 50 volume % aqueous acetone was stirred overnight. A light yellow precipitate remained. Acetone was evaporated and the resulting solid filtered off and recrystallized from aqueous acetone, then from carbon tetrachloride to give colorless crystals melting at 100–103.2°. *Anal.* Calcd. for C$_{10}$H$_{13}$OHgCl: C, 31.18; H, 3.40. Found: C, 31.05; H, 3.46. The hydroxyl frequency in carbon tetrachloride was 3605.2 cm.$^{-1}$. This mercurial (X, 0.65 g.) was shaken with 15 g. of 2% sodium amalgam in 2.5 ml. of D$_2$O for 5 hr. and the mixture extracted with 5 ml. of carbon tetrachloride. Infrared spectrum of this solution showed a hydroxyl frequency of 3625.1 cm.$^{-1}$. The n.m.r. spectrum displayed a rather broad peak at 4.55 τ, a doublet centered at 6.40 τ, $J = 6$ c.p.s., a large broad absorption at 7.9 τ, and smaller peaks at 8.3, 8.65, and 8.8 τ.

cis-exo-3-Hydroxybenz-2-*exo*-norbornylmercuric Chloride (XI). —A mixture of 1.534 g. (1.07 mmoles) of benznorbornene, 1.175 g. (0.50 mmole) of mercuric oxide, and 1.718 g. (0.54 mmole) of mercuric acetate in 75 ml. of water was stirred 24 hr. The mercuric oxide had disappeared and was replaced by a thick oil. The supernatant liquid was decanted into aqueous excess sodium chloride and the precipitate collected. The oil was dissolved in 95% ethanol, filtered, and poured into about three volumes of water containing 2 g. of sodium chloride. An oil separated and slowly crystallized. This was combined with the first precipitate to give a total of 2.2 g. (50% yield). A large band at 5.78 µ in the infrared indicated that much of the product was *exo*-3-acetoxybenz-2-*exo*-norbornylmercuric chloride. The product was recrystallized from 95% ethanol containing a trace each of sodium chloride and sodium hydroxide to produce a carbonyl-free product, m.p. 193–195°. *Anal.* Calcd. for C$_{11}$H$_{11}$OHgCl; C, 33.40; H, 2.81. Found: C, 33.22; H, 2.89. The infrared spectrum had the following peaks in chloroform: *2.72*, 2.90, *3.33, 6.43, 6.87*, 7.37, 7.69, 7.92, 8.77, *9.68*, 9.95, 10.30, 10.52. The hydroxyl frequency in carbon tetrachloride was 3601.5 cm.$^{-1}$.

Benznorborneol.—The crude oxymercurial XI (0.6 g.) was shaken 6 hr. with 9 g. of 2% sodium amalgam and 3 ml. of 2 N sodium hydroxide. This mixture was extracted with 3 ml. of carbon tetrachloride, the extract dried over sodium sulfate, and examined in the infrared. The hydroxyl frequency was 3624.1 cm.$^{-1}$; the spectrum was identical with that published for *exo*-benznorborneol.[17] The *endo* isomer is known to have a very different spectrum.[17]

Chloromercuriphenols.—The *o*- and *p*-chloromercuriphenols were prepared according to the method in ref. 31a; m.p. *ortho* 157–157.5°, *para* 219–224° (lit.[31b] 152° and 219–220°). Carbon-hydrogen analysis indicated the presence of some dimercuriated product in the *para* compound. This did not dissolve in the solvent used for infrared measurements and thus does not affect such measurements.

(29) We are grateful to the Beckman Instrument Co. and to Mr. Donald Steele of the Chemistry Department, U.C.L.A., for these measurements.

(30) A. N. Nesmeyanov and K. Freidlina, *Ber.*, **69**, 1631 (1936).

(31) (a) "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 161; (b) F. C. Whitmore, "Organic Compounds of Mercury," ACS Monograph, New York, N. Y., 1921, pp. 256–257.

Oxymercuration of Norbornadiene.—Whereas the reaction of mercuric chloride with norbornadiene in acetic acid[32a] or in methanol[32b] produces oxymercuration products and no metallic mercury, the reaction of mercuric trifluoroacetate (0.05 mole) with norbornadiene (0.1 mole) in 35 ml. of water produced a

large quantity of metallic mercury and an oil which was not identified. Similar treatment with mercuric acetate also yielded mercury, but at a slower rate.

(32) (a) S. Winstein and M. Shatavsky, *Chem. Ind.* (London), 56 (1956); (b) R. A. Alexander, N. C. Baenziger, C. Carpenter, and J. R. Doyle, *J. Am. Chem. Soc.*, **82**, 535 (1960). We have repeated their reaction with similar results.

Azo Compounds.[1] Dipole Moments and Spectral Data

By C. G. Overberger, Jean-Pierre Anselme,[2] and J. R. Hall

The dipole moments, the ultraviolet, infrared, and n.m.r. spectra of 1-azo-bis-1-phenylpropane and of cyclic azo compounds (I, $n = 1, 3, 4$) have been determined. It is concluded that the cyclic compounds I have a *cis*-azo linkage and that the 3,5-substituents of the 1-pyrazolines are *trans* to each other.

Introduction

The study of the rates of the thermal decomposition of cyclic azo compounds of types I and II have indicated that they can be classified in two groups: *trans*-azo compounds, including the large cyclic compounds (II, $n = 6, 8, 10$) and the acyclic compounds such as 1-azo-bis-1-phenylpropane, and *cis*-azo compounds such as I ($n = 1, 2, 3$)[3–6] which were found to decompose considerably faster than the *trans* compounds. Surprisingly, 3,8-diphenyl-1,2-diaza-1-cyclooctene(I, $n = 4$) proved to be much more stable than either the *cis* or *trans* compounds[7]; the rate of decomposition was one-

I, $n = 1$–4   II, $n = 6, 8, 10$
Ar = C_6H_5, p-C_6H_4

thousandth that of the six- and seven-membered rings (I, $n = 2, 3$) and one-one hundred eightieth that of 1-azo-bis-1-phenylpropane. It was concluded that the eight-membered ring had a *cis*-azo linkage but that steric effects prevented the phenyl groups from being co-planar with the C—N=N—C system in the transition state, thereby reducing the labilizing effect of the phenyl substituents on the C–N bonds.[7] The *trans* structure could not be ruled out completely, however, in view of its anomalous ultraviolet spectrum, λ_{max} 368 mμ; the *trans*-azo compounds had maxima at 359–360 mμ while the six- and seven-membered rings absorbed at 387 and 390 mμ, respectively. Furthermore, it was possible that the eight-membered ring could accommodate a

(1) This is the 42nd in a series of papers concerned with the preparation and decomposition of azo compounds. For the previous paper in this series, see C. G. Overberger, M. Tobkes, and A. Zweig, *J. Org. Chem.*, **28**, 620 (1963).

(2) This paper comprises a portion of a thesis submitted by Jean-Pierre Anselme in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn.

(3) C. G. Overberger and J-P. Anselme, *J. Am. Chem. Soc.*, **84**, 869 (1962).

(4) C. G. Overberger and J. G. Lombardino, *ibid.*, **80**, 2317 (1958).

(5) C. G. Overberger, I. Tashlick, M. Bernstein, and R. G. Hiskey, *ibid.*, **80**, 6556 (1958).

(6) S. G. Cohen, S. Hsiao, E. Saklad, and C. H. Wang, *ibid.*, **79**, 4400 (1957).

(7) C. G. Overberger and I. Tashlick, *ibid.*, **81**, 217 (1959).

trans —N=N— bond since the *trans* isomer of cyclooctene had been isolated.[8]

While the decomposition of the seven- and eight-membered rings (I, $n = 3, 4$) had resulted in the formation of a mixture of the *cis* and *trans* isomers of the corresponding cycloalkane and olefin, it was found that 3,5-diphenyl-1-pyrazoline (I, $n = 1$, Ar = C_6H_5) decomposed stereoselectively to *trans*-1,2-diphenylcyclopropane.[3] No trace of the *cis* isomer or of the corresponding olefin could be detected. This was the first authenticated case of the thermal decomposition of a pyrazoline resulting in the formation of only one isomer of the coupled product. Subsequently, 3,5-bis-(p-chlorophenyl)-1-pyrazoline (I, $n = 1$, Ar = p-ClC$_6$H$_4$) was synthesized and again *trans*-1,2-bis-(p-chlorophenyl)-cyclopropane was the sole product of decomposition.[9] The mode of formation of 1-pyrazolines from diazoalkanes and activated olefins has been viewed as a *cis* addition.[10] Therefore it was assumed that the present pyrazolines were the *trans* isomers. However, since these were the first and only cases of thermal stereoselective decomposition, more evidence was necessary to support our claim.

In order to shed some light on the configuration of those cyclic azo compounds, we have determined their dipole moments, their ultraviolet, infrared, and n.m.r. spectra.

Results and Discussion

The dipole moments were calculated from the dielectric constants measured in benzene solutions at 25° and are shown in Table I with the ultraviolet maxima. The

Table I
Dipole Moments and Ultraviolet Maxima

	μ, D.[a]	λ_{max}, mμ[b]
1-Azo-bis-1-phenylpropane	0.50	359
I, $n = 1$, Ar = C_6H_5	2.23	329[c]
I, $n = 1$, Ar = p-ClC$_6$H$_4$	2.32	327[c]
I, $n = 3$, Ar = C_6H_5	2.42	390
I, $n = 4$, Ar = C_6H_5	2.33	368
II, $n = 8$	..	360

[a] Probable error ±0.05 D.   [b] In chloroform unless otherwise noted.   [c] In ethanol.

n.m.r. spectra were taken in deuteriochloroform with tetramethylsilane as an internal standard. The τ-values, along with the infrared frequency of the —N=N— bond, are given in Table II.

(8) A. C. Cope, R. A. Pike, and C. F. Spencer, *ibid.*, **75**, 3212 (1953).

(9) C. G. Overberger and J-P. Anselme, unpublished results.

(10) For an excellent discussion, see T. V. Van Auken and K. L. Rinehart, *J. Am. Chem. Soc.*, **84**, 3736 (1962).