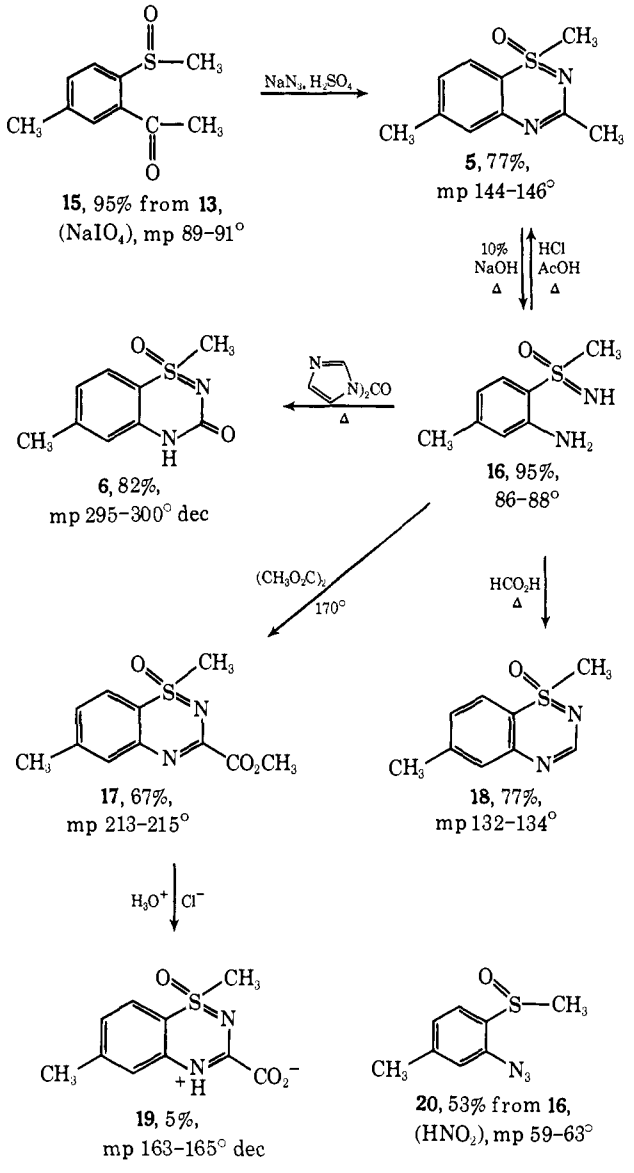
Chart III



erated **4**. The stretching frequency of the C=O of **4** in chloroform absorbs at 1655 cm^{-1}, and thus has less double bond character than the four-membered lactam, **1**. The double oxidation of keto sulfide **13** to sulfoxide acid **14** is without analogy, to our knowledge.

Chart III contains a triple reaction in the combined imidation–Schmidt rearrangement–ring closure to produce **5** from **15**. The open-chain hydrolysis product of **5**, amino sulfoximide **16**, served as a starting material for the preparation of the new heterocyclic system **6**, as well as a number of interesting derivatives of **5**, *e.g.*, **19**. Treatment of **16** with nitrous acid produced sulfoxide azide **20**, probably passing through still another new heterocyclic system in the process, one that contains an N=N—N=S linkage. Attempts to isolate this system failed.

Although heterocycles **3**, **11**, and **18** formally contain six π electrons, the nmr chemical shifts of their ring protons are unlike those of aromatic models, *e.g.*, quinazoline as a model for **18**.[8] The chemical shifts (δ) are as follows: quinazoline[8] (CCl_4), proton 2, 9.29; compound **3** ($CDCl_3$), proton 4, 5.90, proton 6, 6.70; compound **11** ($CDCl_3$), proton 4, 6.10, proton 6, 6.60; compound **18** ($CDCl_3$), proton 3, 8.15.

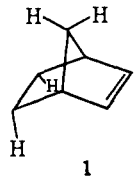
(8) P. J. Black and M. L. Heffernan, *Aust. J. Chem.*, **18**, 707 (1965).

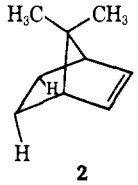
Todd R. Williams, Donald J. Cram*
Contribution No. 2900, Department of Chemistry
University of California at Los Angeles
Los Angeles, California 90024
Received September 29, 1971

Relative Rate of Exo Addition to Norbornene and 7,7-Dimethylnorbornene. A New Criterion for Distinguishing between Cyclic and Noncyclic Addition Processes

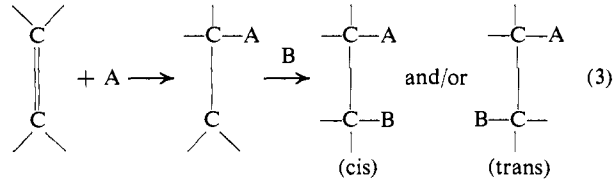
Sir:

The ratio, $k_{exo\text{-norbornyl}}/k_{7,7\text{-dimethyl-}exo\text{-norbornyl}}$, of rates of exo addition to norbornene (**1**) and 7,7-dimethylnorbornene (**2**) is relatively high for additions involving cyclic transition states or intermediates (cyclic addition), and is relatively low for additions not involving cyclic transition states or intermediates (noncyclic addition). Consequently, this phenomenon provides a valuable criterion for exploring the mechanisms of addition reactions.[1,2]


1


2

Generally speaking, there are two categories of addition reactions, cyclic and noncyclic, according to the structure of the transition state or intermediate. In cyclic addition a cyclic transition state or intermediate is involved, and the stereochemistry of the product may either be cis or trans dependent upon whether the reaction proceeds *via* one stage or two (eq 1 and 2). For example, hydroboration gives cis adduct,[3] whereas the addition of benzenesulfenyl chloride is trans.[4] On the other hand, the transition state or intermediate for noncyclic addition is "open," and the stereochemistry is governed by the steric features of the specific system and the nature of the addend (eq 3). For instance,

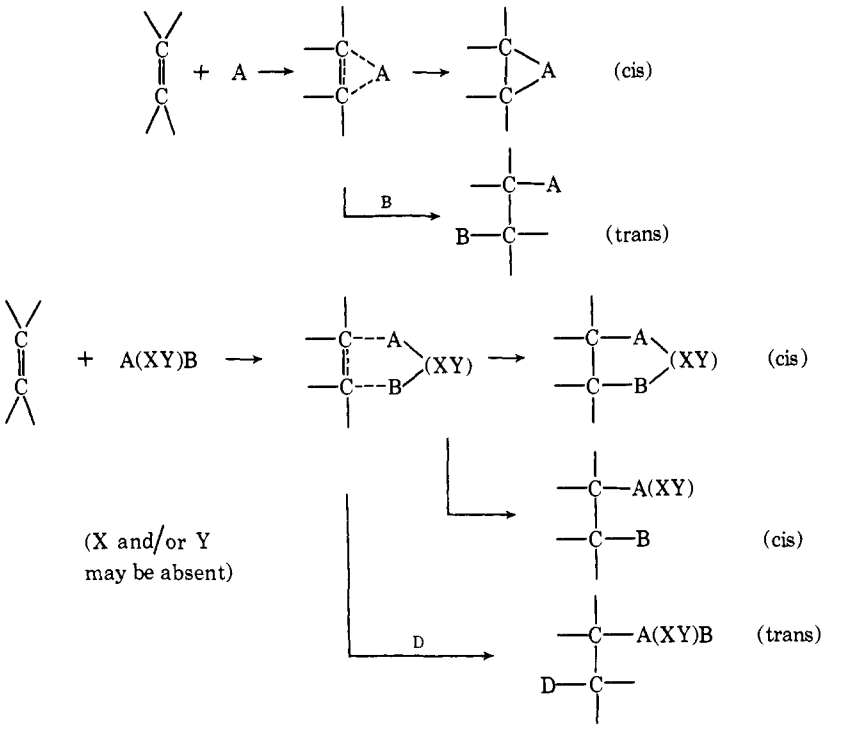


(3)

cis hydrochlorination has been observed with both **1**[5] and cyclohexene,[6] whereas oxymercuration is cis with **1** and trans with cyclohexene.[7]

It is generally accepted that the preference for exo addition in the reactions of norbornenes results from

(1) H. C. Brown and J. H. Kawakami, *J. Amer. Chem. Soc.*, **92**, 201 (1970).
(2) H. C. Brown and K.-T. Liu, *ibid.*, **92**, 3502 (1970).
(3) H. C. Brown, "Hydroboration," W. A. Benjamin, New York, N. Y., 1962.
(4) W. H. Mueller, *Angew. Chem., Int. Ed. Engl.*, **8**, 482 (1969).
(5) H. C. Brown and K.-T. Liu, *J. Amer. Chem. Soc.*, **89**, 3900 (1967).
(6) R. C. Fahey and M. W. Monahan, *ibid.*, **92**, 2816 (1970).
(7) For review see W. Kitching, *Organometal. Chem. Rev.*, **3**, 61 (1968).



the large steric hindrance of the endo side arising predominantly from the endo hydrogens at the C-5 and C-6 positions.[8-10] In the case of **2**, the approach of the addend from the endo side is as hindered as in **1**. Moreover, the exo approach would also be hindered by the bulky *syn*-7-methyl substituent. The relative importance of the *syn*-7-methyl *vs.* the endo 5,6-hydrogens depends upon the reaction type. Indeed, in cyclic additions the *syn*-7-methyl group gives rise to comparable or even greater steric hindrance to exo addition as compared with endo addition. Thus, epoxidation and hydroboration go preferentially exo with **1** but endo with **2**.[1] Phenyl azide adds readily to **1** but fails to add to **2**.[11] Furthermore, an enormous rate retardation (*ca.* 1000) on exo epoxidation of **2** has been observed.[12] For noncyclic additions, such as the addition of acetic acid and trifluoroacetic acid,[13] the stereochemistry is exo-cis with both **1** and **2**. Introduction of 7,7-dimethyl substituents causes only a small (2.8) retardation of exo addition of acetic acid.

The observed difference in the effect of 7,7-dimethyl substituents on the rate of exo addition suggested that such rate data might provide an unambiguous diagnosis of the mechanism of these two types of additions. Therefore, we undertook to examine the comparative behavior of **1** and **2** in other representative addition reactions: diimide reduction, addition of benzenesulfenyl chloride, hydroboration with 9-BBN, radical addition of thiophenol, oxymercuration in aqueous tetrahydrofuran, and hydrochlorination.

All these reactions were carried out under standard conditions. A limited amount of addend was allowed to react with a mixture of **1** and **2**, both in excess. Hydroboration with 9-BBN showed a much higher selectivity with **2**, 97% endo and 3% exo, than hydroboration with borane, 78% endo and 22% exo, although the selectivity was about the same toward **1**.[14] Addition of benzenesulfenyl chloride gave exclusively *exo*-phenylthio-*endo*-chloro adduct with **1**, but a 96:4 ratio of *endo*-phenylthio-*exo*-chloro to *exo*-phenylthio-*endo*-chloro adduct with **2**.[2] These adducts were reduced with triphenyltin hydride to the corresponding phenyl sulfides in order to facilitate glpc analysis. The hydrochlorination products were hydrolyzed to the corresponding alcohols for the same reason. Other adducts were analyzed directly with glpc using appropriate columns. The relative rate ratio for exo addition, $k_{exo\text{-norbornyl}}/k_{7,7\text{-dimethyl-}exo\text{-norbornyl}}$, can thus be calculated (Table I). Oxymercuration in aqueous tetrahydrofuran yielded a mixture of exo alcohol and exo acetate, 83% *exo*-norbornanol and 17% *exo*-norbornyl acetate from **1**, and 37% 7,7-dimethyl-*exo*-norbornanol and 63% 7,7-dimethyl-*exo*-norbornyl acetate from **2**. Consequently, the relative rate is 130 for the formation

Table I. Relative Rate of Exo Addition to Norbornene and 7,7-Dimethylnorbornene

Type of addition	Addend	Rate ratio, $k_{exo\text{-norbornyl}}/k_{7,7\text{-dimethyl-}exo\text{-norbornyl}}$
Cyclic	PhSCl	1820
	$ArCO_3H$	1000[a]
	N_2H_2	950
	9-BBN	480
Noncyclic	$Hg(OAc)_2$, H_2O	58
	PhSh (*hν*)	30
	HOAc	2.8[b]
	HCl	2.2

[a] Reference 12. [b] Reference 13.

(8) R. C. Fahey, *Top. Stereochem.*, **3**, 253 (1969).
(9) T. G. Traylor, *Accounts Chem. Res.*, **2**, 152 (1969).
(10) Although there are no endo 5,6 hydrogens in benzonorbornadiene, the π cloud may be equally effective in hindering endo approach.
(11) K. Alder and G. Stein, *Justus Liebigs Ann. Chem.*, **501**, 1 (1933); **515**, 185 (1935).
(12) H. C. Brown, S. Ikegami, and J. H. Kawakami, *J. Amer. Chem. Soc.*, **92**, 6914 (1970).
(13) H. C. Brown, J. H. Kawakami, and K.-T. Liu, *ibid.*, **92**, 3816, 5536 (1970).
(14) E. F. Knights and H. C. Brown, *ibid.*, **90**, 5281 (1968).

of exo alcohols and is 16 for the formation of exo acetates.

These data make it clear that introduction of 7,7-dimethyl substituents to norbornene causes large rate retardations (480–1820) for those reactions believed to proceed through cyclic processes, whereas the effect on reactions involving noncyclic additions is much smaller. It is likely that in noncyclic additions the addend approaches from the exo side at the end of the double bond, away from the bulky *syn*-7-methyl group, whereas in cyclic additions, the addend must approach the double bond symmetrically, bridging it under the *syn*-7-methyl group. According to this picture 7,7-dimethyl substituents would exert much smaller steric effects on noncyclic additions than on cyclic additions, provided the addend is of modest steric requirements. The hindrance could become larger for bulkier addends, such as associated water molecules, and this might account for the relatively high ratio (130) observed in the alcohol fraction of the oxymercuration products.

The present results clearly demonstrate that the relative rate of exo addition to **1** and **2** is closely related to the mechanism of additions. The ratio, $k_{exo\text{-norbornyl}}/k_{7,7\text{-dimethyl-}exo\text{-norbornyl}}$, is high, 480–1820, for cyclic additions and is low, below 58, for noncyclic additions. This distinct difference is capable of providing a new criterion, in addition to the stereochemistry of reaction,[1,2] to distinguish between cyclic and noncyclic mechanisms. The low ratio, 16, in the acetate fraction of oxymercuration suggests that a cyclic mechanism, molecular addition of mercuric acetate[8] or formation of mercurinium ion,[9] is probably not involved.[15]

(15) The unimportance of the mercurinium ion under the usual oxymercuration conditions is indicated in a number of recent studies: kinetic,[16] ^{13}C nuclear magnetic resonance,[17] oxymercuration of optically active olefin,[18] trapping experiments,[19] and the earlier stereochemical data.[1]

(16) J. Halpern and H. B. Tinker, *J. Amer. Chem. Soc.*, **89**, 6427 (1967).

(17) R G Parker and J. D. Roberts, *ibid.*, **92**, 743 (1970).

(18) V. I. Sokolov, L L Troitskaya, and O. A. Reutov, *J. Organometal. Chem.*, **17**, 323 (1969).

(19) S. Bentham, P. Chamberlain, and H. Whitham, *Chem. Commun.*, 1528 (1970).

(20) Postdoctoral Research Associate (1968–1970) on a grant (GP 492X) provided by the National Science Foundation.

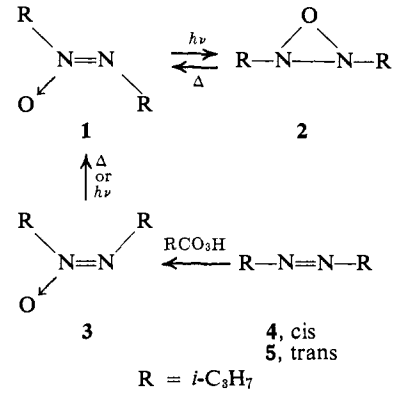
Herbert C. Brown,* Kwang-Ting Liu[20]
Richard B. Wetherill Laboratory
Purdue University, Lafayette, Indiana 47907
Received September 16, 1971

Aliphatic Azoxy Compounds. I. Photolytic Isomerization of Azoxyalkanes[1]

Sir:

The potent carcinogenic properties of naturally occurring and synthetic members of the title class of compounds[2] have stimulated our interest in their chemistry. We have been examining the potential of photolytic isomerization of the azoxy function as a synthetic route to new azoxyalkanes[3] and have based our approach on the previous results of Jaffe[4] and Greene.[5] In this communication we wish to report, in preliminary form, the chemistry outlined in Scheme I, results which appear to

Scheme I



form a general base for the synthesis of the heretofore unknown (or unrecognized) acyclic, *cis*-azoxyalkanes.

A preparative scale photolysis[6] of an 8% pentane solution of **1**[7] gave, after 17 hr, a reaction mixture containing 52% **2**, 20% **1**, and 28% other products (including **5**) as evidenced by vpc. Oxidiaziridine **2** could be isolated in 38% yield (85–90% purity; based on recovered **1**) by rapid fractional distillation (pot temp, 40° (200–15 mm)), or by preparative vpc.[8]

The principal spectral data supporting structure **2** were the relatively high-field locations of the methyl and methine proton signals (see Table I). In addition, both

Table I. Nmr Chemical Shifts (δ) of Compounds **1–5**[a,b]

Compd	Proton: $CH_3CN=$	$CH_3CN(O)$	HCN=	HCN(O)
1	1.11	1.42	4.12	4.38
2		1.13		2.15
3	1.25	1.41	4.10	4.96
4	1.23		4.05	
5	1.37		3.56	

[a] In CCl_4. [b] Methyl signals were doublets and methine signals were symmetrical septets, J = 6.5–7 Hz.

ir and uv spectra indicated the absence of the azoxy function in **2**. As expected,[5b] **2** rapidly oxidized iodide ion, and, at 52° in CCl_4, was isomerized to **1**.

However, thermolysis of **2** at 22° yielded, contrary to expectations based on the literature,[5b] the *cis*-azoxyalkane (**3**), as well as **1**, in preparatively useful ratios (see Table II). The structure of **3** was definitively

(1) Partial support of this work from NIH Grant No. NS07119 is acknowledged with appreciation.

(2) See, for example: (a) H. Druckrey, S. Ivankovic, and A. V. Hodenberg *Ann. N.Y. Acad Sci.*, **163**, 697 (1969); (b) M. Spatz, *ibid.*, **163**, 848 (1969)

(3) K. G. Taylor and T. Riehl, *J. Amer. Chem. Soc.*, in press.

(4) D. Webb and H. H. Jaffe, *Tetrahedron Lett.*, 1875 (1964): photoisomerization of azoxybenzenes. See also R. Tanikaga, *Bull. Chem. Soc. Jap.*, **41**, 2151 (1968).

(5) (a) S. S. Hecht and F. D. Greene, *J. Amer. Chem. Soc.*, **89**, 6761 (1967); (b) F. D. Greene and S. S. Hecht, *J. Org. Chem.*, **35**, 2482 (1970): photoisomerization of azoxyalkanes.

(6) Photolysis conditions: 450-W Hanovia medium-pressure lamp, Vycor filter, in air; reaction temperature reached 38° during photolysis.

(7) B. W. Langley, B. Lythgoe, and L. S. Rayner, *J. Chem. Soc.*, 4191 (1952).

(8) Preparative vpc conditions: 8 ft × 1/4 in. 20% Dow-Corning 710 silicone oil on silanized Chromosorb W; column temp, 27°, injection port, 80°; detector (thermal conductivity), 85°; flow rate, 200 ml/min. For analytical work, a 3 ft × 1/8 in. column was used with appropriate flow rate; appropriate temperature programming of analytical samples allowed the successive elution of **5**, **2**, **4**, **1**, and **3**.