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).

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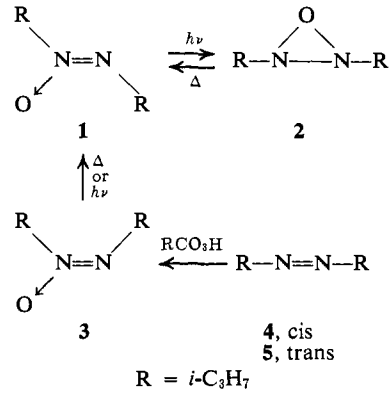
Aliphatic Azoxy Compounds. I. Photolytic Isomerization of Azoxyalkanes[1]

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]

	Proton			
Compd	$CH_3CN=$	$CH_3CN(O)$	$HCN=$	$HCN(O)$
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**.

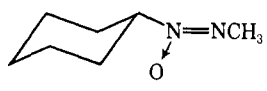
Table II. Results of 22° Thermolysis of **2**

Solvent	$\sim t_{1/2}$, hr	**1**:**3** ratio[a]
Neat	23	80:20
CCl_4	27	74:26
CD_3OD	14	70:30
DMSO-d_6	14	68:32

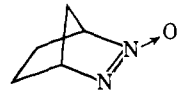
[a] Determined by nmr and corroborated by vpc.

established by alternate synthesis (in 72% yield) *via* peracid oxidation of *cis*-azoisopropane (**4**).[9] Elemental analysis and thermal isomerization (>100°) to **1** substantiated the assigned structure of **3**. Compound **3**, representing the first documented example of an acyclic *cis*-azoxyalkane, had the following absorption spectral features: uv, λ_{max} 232 (ϵ 7900), 280 nm (sh); ir_{CCl_4}, $\nu_{N=N}$ 1480 cm^{-1} plus ν_{NO} 1275 cm^{-1}, with intensity reduced relative to the ν_{NO} of the trans isomer **1**. The nmr of **3** (see Table I) shows the methine H signals downfield relative to those of the *cis*-azoalkane **4**, as predicted by Freeman.[10] In contrast, the methine H signals of cyclic *cis*-azoxyalkanes are superimposed, and upfield, relative to their azoalkane counterparts.[11] Finally, **3** can be photoisomerized completely to **1** (ratio, 97/3 at 9 hr) under conditions which yield no **2** (3500 Å, Pyrex filter, pentane).

The above results indicate that, despite the event of a highly unfavorable cis–trans photoequilibrium, *cis*-azoxyalkanes should be synthesizable, if not by direct photoisomerization,[3] then by the photolysis–thermolysis sequence which converted **1** to **3**. The extension of the results of Scheme I to the synthesis of the unsymmetrical *cis*-azoxyalkane **6**[12] (35% yield, mp 98–98.5°; uv, λ_{max} 232 nm (ϵ 6000); elemental analysis, within limits) from



6, cis
7, trans



8 (λ_{max} 228 nm)

7 give an indication of the generality of the approach. Incidentally, the uv spectra of **3**, **6**, and cyclic azoxy compounds such as **8**[13] indicate a λ_{max} range of about 230 ± 3 mμ for *cis*-azoxyalkanes (trans range, 220 ± 3 mμ) which permits the assignment of cis geometry to the azoxy compound (λ_{max} 237) isolated by Hortmann and Youngstrom.[14]

The formation of **3** from the ring opening of **2** finds analogy in the reported formation of *cis* (as well as *trans*) nitrones from the thermolysis of *trans*-oxaziridines.[15] As can be seen from Table II both the rate of isomerization of **2** and the yield of *cis*-azoxyalkane show a modest increase with increasing dielectric constant of the reaction solvent. Thus, it would seem that the developing higher dipole moment of the cis isomer is, as would be expected, more stabilized in the transition state by highly polar solvents.

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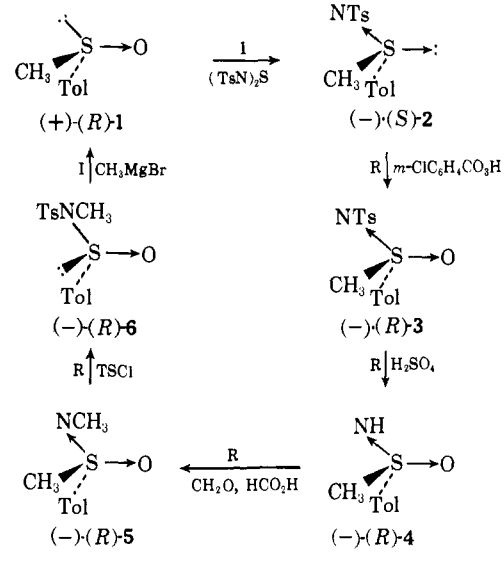
James Swigert, K. Grant Taylor*
Department of Chemistry, University of Louisville
Louisville, Kentucky 40208
Received September 23, 1971

Three New Organosulfur Reactions and the First Example of a Monoligostatic Stereochemical Cycle[1]

Sir:

Recently the properties of stereochemical reaction cycles were described[2] and a literature search revealed no example of a stereochemical reaction cycle in which only a single ligand of a chiral tetrahedron was common to all chiromers (optically active compounds of the cycle). We now wish to report completion of such a *monoligostatic* cycle which contains two new reactions (Chart I). In addition we report a third new reaction

Chart I



Tol = p-$CH_3C_6H_4$; Ts = p-$CH_3C_6H_4SO_2$

which completes a new four-reaction diligostatic cycle.

In the cycle of Chart I the single ligand common to all chiromers is the *p*-tolyl group, and the chiral center is sulfur. Replaceable ligands are O, electron pair, NTs, NH, CH_3, NCH_3, and $TsNCH_3$. The cycle involves six reactions and six chiromers, none of which are enantiomerically related (podal). Two of its reactions occur with inversion, four with retention of configuration, and the cycle contains no ligand metathesis.

The stereochemical courses of the reactions (+)-(*R*)-**1** → (−)-(*S*)-**2** → (−)-(*R*)-**3** → (−)-(*R*)-**4** have been es-

(9) I. I. Abram, G. S. Milne, B. S. Solomon, and C. Steel (*J. Amer. Chem. Soc.*, **91**, 1220 (1969)) report the preparation of **4** by photoisomerization of **5**. Interestingly, mercuric oxide oxidation of symmetrical diisopropylhydrazine affords **4** (4%) as well as **5** (96%) and the cis compound can be isolated by distillation of large-scale oxidations.
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(12) K. G. Taylor and S. Isaac, unpublished results.
(13) F. D. Greene and S. S. Hecht, *Tetrahedron Lett.*, 575 (1969).
(14) A. G. Hortman and R. E. Youngstrom, *J. Org. Chem.*, **34**, 3392 (1969).
(15) J. S. Splitter, T-M. Su, H. Ono, and M. Calvin, *J. Amer. Chem. Soc.*, **93**, 4075 (1971).

(1) This investigation was supported by the U.S. Public Health Service, Research Grant No. GM 12640-07 from the Department of Health, Education, and Welfare.
(2) D. C. Garwood and D. J. Cram, *J. Amer. Chem. Soc.*, **92**, 4575 (1970).