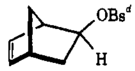
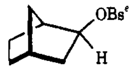
Table I. Kinetic Data for Solvolysis in Buffered (NaOAc) Acetic Acid

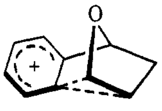
Compd	T, °C	k, sec^{-1}	k(exo)[a]/k(endo)	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	k_{rel}[a]
exo-**4**	25	1.6×10^{-9} [b]	5,700	28.9	−1.9	5.7×10^{3}
	79.91	3.79×10^{-6}				
	100.05	3.67×10^{-5}				
	109.95	1.04×10^{-4}				
endo-**4**	25	2.8×10^{-13} [b]	5,700	33.6	−3.3	1
	142.85	3.62×10^{-6}				
	158.95	1.60×10^{-5}				
	173.25	6.22×10^{-5}				
exo-**1**[c]	25.03	7.47×10^{-6}	15,000	24.1	−1.2	2.7×10^{7}
endo-**1**[c]	25	5.1×10^{-10}	15,000	27.85	−7.0	1.8×10^{3}
 [d]	25.00	4.5×10^{-5}	8,000			1.6×10^{8}
 [e]	24.98	1.22×10^{-4}	350[f]			4.4×10^{8}

[a] At 25°. [b] Data obtained by extrapolation using the activation parameters. [c] Taken from ref 2. [d] S. Winstein, H. M. Walborsky, and K. C. Schreiber, *J. Amer. Chem. Soc.*, **72**, 5795 (1950); S. Winstein and M. Shatavsky, *ibid.*, **78**, 592 (1956). [e] S. Winstein and D. Trifan, *ibid.*, **74**, 1154 (1952). [f] S. Winstein, E. Clippinger, A. H. Fainberg, and G. C. Robinson, *Chem. Ind.* (*London*), 664 (1954).

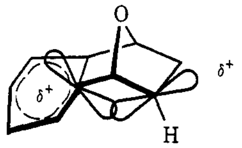
Measured first-order rate constants for acetolysis of **4** are summarized in Table I along with additional relevant data. Because the acetolysis mixtures were found to be sensitive to air at the requisite elevated temperatures, the reactions were performed under an atmosphere of nitrogen. Despite this precaution, the formation of a dark precipitate in the late stages of the solvolysis of *endo*-**4** did occur and the resulting sample inhomogeneity necessitated the use of calculated infinity titers for the rate constant calculations.

The kinetic data reveal clearly that the oxygen bridge in *exo*- and *endo*-**4** exerts a very large decelerative effect when compared to the respective carbocyclic congeners (**1**). Calculated rate retardations at 25° are 4.7×10^3 and 1.8×10^3, respectively, for the two epimers. These values compare very closely to that calculated for the inductive deceleration caused by the heteroatom in **5** ($2\text{–}6 \times 10^3$);[5] consequently, the purely inductive contribution of the oxygen is a constant affecting the exo and endo derivatives about equally.

Also, the exo/endo reactivity ratio of **4** is of the same order of magnitude as that observed for **1** (2.5-fold difference) and the simpler norbornenyl brosylate (Table I). The absence of a significant increase in σ participation for *exo*-**4** which one might have predicted from the behavior of **6** can be attributed in part to the presence of an extra driving force in **6** provided by ionization to a stabilized tertiary species. The 7-oxa derivatives **4** and **5** do not possess this additional driving force.[15] More importantly, the results reveal that charge delocalization to the 1 position in the exo isomer does not gain significance since resonance interaction with the heteroatom is not operative. Nor is it possible that σ-delocalized intermediates intervene without n orbital involvement from the oxygen, for on this basis marked rate retardation in exo solvolyses should result from adverse inductive effects and these are not encountered. In our opinion, the development of positive charge at C_1 would have been readily detected due to the well-aligned stereoelectronic overlap of the nonbonding electrons on oxygen with the developing p orbital at the 1 position and the apparent inapplicability of Bredt's rule restrictions.



7



8

Consequently, it may be concluded that *exo*-**4** and, by analogy, *exo*-**1** do not experience initial ionization *via* anchimeric assistance by σ participation with charge dispersal to the bridgehead position. Although the data are inconsistent with the involvement of the σ-delocalized cation **7** during rate-determining ionization of *exo*-**4**, it is entirely possible that p–π participation (*cf.* **8**) operates since delocalization of positive charge into the aromatic ring by this mechanism seemingly would not affect the electronic character of C_1 to an extent sufficiently large to be detected. Dissection of the exo/endo rate ratio of **4** into its p–π and steric components is not yet possible.

Acknowledgment. We acknowledge the financial support (in part) of the National Science Foundation and helpful discussions with Professor H. C. Brown.

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Received December 18, 1972

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[15] The acetolysis of *exo*- and *endo*-**4** is accompanied by structural rearrangement. Although the acetates of retained structure were stable to the reaction conditions up to at least 110°, the rearranged products underwent polymerization and full characterization was thereby precluded. Additional evidence that rearrangement *via* an oxonium ion follows upon generation of a carbonium ion at C_2 in this ring system is afforded by the recent studies of Sasaki, *et al.*, wherein the oxonium ion was trapped intramolecularly upon addition of certain uniparticulate electrophiles to benzo-7-oxabicyclo[2.2.1]heptadiene.[16]

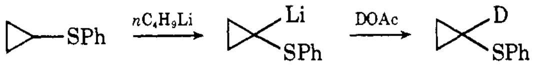
[16] T. Sasaki, K. Kanematsu, and M. Uchide, *Tetrahedron Lett.*, 4855 (1971).

1-Lithiocyclopropyl Phenyl Sulfide. A New Spiroannelating Reagent

Sir:

We recently reported a facile method for synthesizing oxaspiropentanes and cyclobutanones employing diphenylsulfonium cyclopropylide.[1,2] The limitations of the method appeared to be the preferred conjugate addition reaction with formation of spiropentanes instead of carbonyl addition with α,β-unsaturated carbonyls and the sluggishness of reaction with very hindered ketones. With a view to expanding the utility of the reaction because of the multifaceted applications of the cyclobutanones in synthesis,[3,4] we have developed a new reagent for effecting this transformation of a carbonyl group into a cyclobutanone.

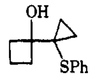
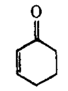
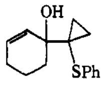
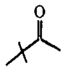
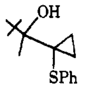
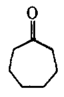
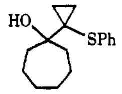
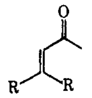
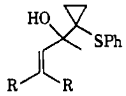
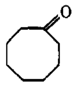
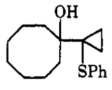
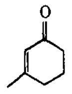
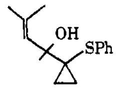
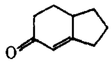
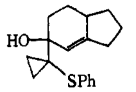
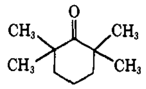
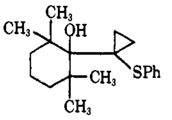
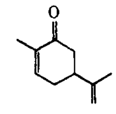
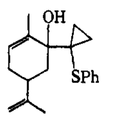
Whereas lithiation of thioanisole proceeds well to produce phenylthiomethyllithium,[5] lithiation of the higher alkyl aryl sulfides normally leads to preferential reaction at the aryl group with no subsequent rearangement to metalation at the side chain.[6] The enhanced acidity of cyclopropyl over normal secondary hydrogens suggested that, in contrast to this fact, metalation at the alkyl rather than the aryl group would predominate, at least in a thermodynamic sense. Indeed, treatment of cyclopropyl phenyl sulfide[7] with *n*-butyllithium in tetrahydrofuran at 0° for 2 hr followed by quenching with deuterioacetic acid revealed formation of 1-deuteriocyclopropyl phenyl sulfide with greater than 95% deuterium incorporation. Addition of a ketone at 0° to the solution of **1**, stirring for 30 min, quenching with water, and normal extraction work-up led to the desired alcohols in high yields in most cases (see Table I).[8] In the case of simple saturated ketones, starting material is recovered even when a twofold excess of lithiocyclopropyl phenyl sulfide (**1**) is employed, suggesting some problem of enolization. Enones react smoothly and by complete carbonyl condensation. Even the highly hindered 2,2,6,6-tetramethylcyclohexanone reacted smoothly to give the adduct in essentially quantitative yield.



1

Conversion of the adducts to cyclobutanones was envisioned to require ionization of the hydroxyl group to the tertiary carbonium ion followed by cyclopropylcarbinyl to cyclobutyl rearrangement facilitated by the electron releasing sulfur. Simple hydrolysis of the sulfur-stabilized carbonium ion would complete the conversion. Indeed, treatment of an ethereal solution of adduct **2** or **3** with aqueous fluoboric acid at room temperature for 25 min led to cyclobutanones **6** or **7** in 84 or 100% yields, respectively (Table II). These products were characterized by carbonyl absorptions at 1778–1780 cm^{-1} and absorptions for the methylene α to the carbonyl at around δ 2.5–3.0 as an approximate triplet (J = 8.5 Hz). Adducts **4** and **5** were examined to exemplify the applicability of the new spiroannelation to conjugated ketones. In both cases, rearrange-

Table I. Addition of Lithiocyclopropyl Phenyl Sulfide (**1**) to Ketones[a,c]

Ketone	Product	% yield	Ketone	Product	% yield
		81		 **5**	85[b]
		92			
	 **2**	51[b]	 R = H R = CH$_3$	 **4**	83 89
	 **3**	67[b]		 **4**	89
					84
		98			98

[a] All yields represent isolated material based on total amount of starting ketone. [b] This yield increases to essentially 100% if based on recovered ketone. [c] All new compounds have been characterized by nmr, ir, and mass spectroscopy as well as elemental composition.

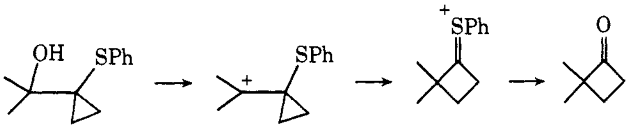
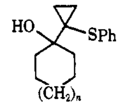
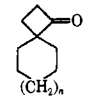
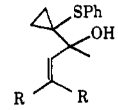
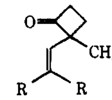
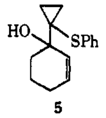
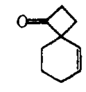


Table II. Rearrangement of Cyclopropylcarbinols[a,b]

Starting compound	Product	% yield
 **2**, n = 2 **3**, n = 3	 **6** **7**	84 100
		R = H 89% R = CH$_3$ 47%
 **5**	 **9**	64

[a] All yields represent isolated material. Optimization of yields has not been made in most cases. [b] All new compounds have been characterized by nmr, ir, and mass spectroscopy as well as elemental composition.

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(1) B. M. Trost and M. J. Bogdanowicz, *J. Amer. Chem. Soc.*, **93**, 3773 (1971); M. J. Bogdanowicz and B. M. Trost, *Tetrahedron Lett.*, 887 (1972). This communication forms part II of our series on new synthetic reactions.

(2) For an alternative approach, see C. R. Johnson, G. F. Katekar, R. F. Huxol, and E. R. Janiga, *J. Amer. Chem. Soc.*, **93**, 3771 (1971). For other related work also see J. R. Salaün and J. M. Conia, *Chem. Commun.*, 1579 (1971); J. R. Wiseman and H. F. Chan, *J. Amer. Chem. Soc.*, **92**, 4749 (1970); J. R. Salaün and J. M. Conia, *Tetrahedron Lett.*, 2849 (1972); H. H. Wasserman, R. E. Cochoy, and M. S. Baird, *J. Amer. Chem. Soc.*, **91**, 2375 (1969).

(3) For leading references, see J. M. Conia and J. R. Salaün, *Accounts Chem. Res.*, **5**, 33 (1972); D. Seebach, S. Beckmann, and H. Geiger, "Methoden der Organischen Chemie (Houben-Weyl)," Vol. IV/4, E. Müller, Ed., Georg Thieme Verlag, Stuttgart, 1971.

(4) B. M. Trost and M. J. Bogdanowicz, *J. Amer. Chem. Soc.*, **94**, 4777 (1972); B. M. Trost and M. J. Bogdanowicz, *ibid.*, **95**, 2038 (1973).

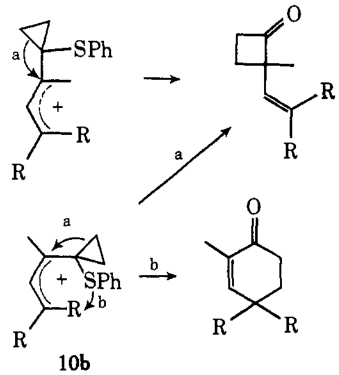
(5) E. J. Corey and D. Seebach, *J. Org. Chem.*, **31**, 4097 (1966); R. L. Sowerby and R. M. Coates, *J. Amer. Chem. Soc.*, **94**, 4758 (1972).

(6) D. A. Shirley and B. J. Reeves, *J. Organometal. Chem.*, **16**, 1 (1969).

(7) W. E. Truce, K. R. Hollister, L. B. Lindy, and J. E. Parr, *J. Org. Chem.*, **33**, 43 (1968).

(8) Typically a 30% excess of **1** was employed.

ment generated the cyclobutanones **8** and **9** demonstrating the feasibility of the spiroannelation of conjugated ketones. The cyclobutanone structures are firmly established spectroscopically by the presence of the carbonyl frequency at 1779 and 1776 cm^{-1} and the presence of the methylene group α to the carbonyl group in the nmr spectrum at approximately 2.9–3.1 as an apparent triplet ($J \sim 9$ Hz). Interestingly, in the case of **4**, rearrangement may be envisioned to give either a cyclobutanone or a cyclohexenone—the latter to the extent that a cisoid allyl cation **10b** is formed. The fact that only cyclobutanone can be seen in the infrared spectrum of a crude mixture is indicative of either the exclusive formation of the transoid allyl cation **10a** or high preference for a 1,2 shift compared to a 1,4 shift. Thus, the method nicely complements the sulfonium ylide technique and allows spiroannelation for virtually every type of carbonyl compound.[9,9a]



10b

Acknowledgment. We wish to thank the National Science Foundation and the National Institutes of Health for their generous support of our programs.

(9) For related use of sulfide stabilized anions as sulfur ylide substitutes, see T. Durst, R. Viaw, R. Van Den Elzen, and C, H. Nguyen, *Chem. Commun.*, 1334 (1971); T. Durst, R. Viaw, and M. R. McCloy, *J. Amer. Chem. Soc.*, **93**, 3077 (1971); C. R. Johnson and C. W. Schroek, *ibid.*, **93**, 5303 (1971); M. Yashimini and M. J. Hatch, *ibid.*, **89**, 5831 (1967).

(9a) NOTE ADDED IN PROOF. A recent report describes the generation and rearrangement of cyclopropylallyl cations in which cyclobutyl derivatives were not found; see K. Rajeswari and T. S. Sorensen, *J. Amer. Chem. Soc.*, **95**, 1239 (1973).

(10) Camille and Henry Dreyfus Teacher-Scholar Grant Recipient.

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Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Received February 21, 1973

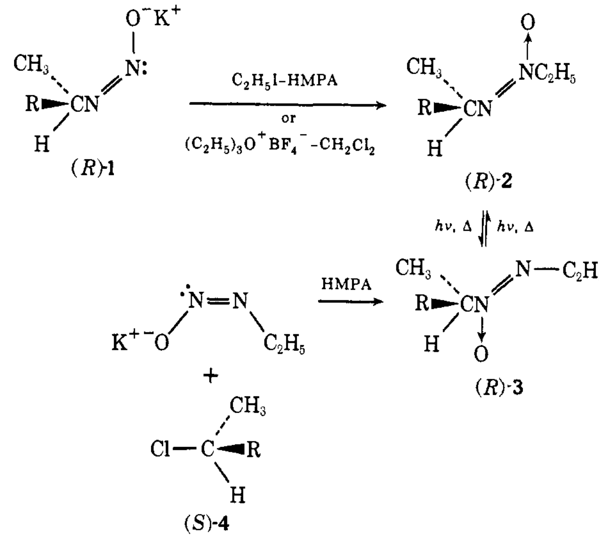
Stereospecific Synthesis of Azoxyalkanes[1]

Sir:

Successful synthesis of the naturally occurring and biologically potent chiral azoxyalkanes elaiomycin[2] and LL-BH872α[3] will probably require a novel method of construction of the azoxy functionality.[4] The alkylation of alkane diazotates[1,5] could be that method. It is flexible, or applicable to the synthesis of many unsymmetrical azoxyalkanes, directed, affording one structurally predictable azoxyalkane, and utilizes common precursors.[1]

Now we show that this method satisfies the final basic requirement for a general synthesis; it accommodates chirality at the carbon atoms α or α' to the azoxy function. We report the first *stereospecific* syntheses of such azoxyalkanes, by *two* independent, albeit related methods. The basic reactions are outlined in Scheme I, in which the key step is the "photothermal" interconversion[6] of isomeric azoxyalkanes **2** and **3**.

Scheme I



R = n-C$_6$H$_{13}$

Irradiation of d,l-**2**[1] in hexane at 254 nm gave a photostationary mixture of **3** and **2** (1.28:1 by gc). The **3**:**2** distribution did not change upon extended photolysis,[7] and the same distribution was obtained by photolysis of **3**. The new azoxyalkane, **3**, was isolated by gas chromatography.[8] It showed characteristic[9] ir bands at 1490 and 1290 cm^{-1} (neat) and λ_{max} 218 nm (log ϵ 3.82) and 285 (1.89) indicative of a *trans*-azoxyalkane.[6,9] The nmr (CCl$_4$) revealed a quartet, δ 3.39 (J = 7 Hz, 2 H), for =NCH$_2$–, and a multiplet centered at δ 4.23 (1 H) for =N(O)CH<. The remaining protons appeared as a multiplet from $\sim$2.0 to 0.6. The chemical shifts of the methylene and methine protons are consistent with structure **3**,[1,10] particularly in comparison with those of *sec*-C$_4$H$_9$N(O)=N-n-C$_8$H$_{17}$.[1] A satisfactory elemental analysis was obtained.

l-2-Aminooctane[11] was converted to the l-urethane, α^{25}D −3.25°,[12] 72.6% optically pure,[13] and thence, by

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(1) Alkyl Diazotates. XII. Part XI: R. A. Moss, M. J. Landon, K. M. Luchter, and A. Mamantov, *J. Amer. Chem. Soc.*, **94**, 4392 (1972).

(2) C. L. Stevens, B. T. Gillis, and T. H. Haskell, *ibid.*, **81**, 1435 (1959), and references therein.

(3) W. J. McGahren and M. P. Kunstmann, *ibid.*, **92**, 1587 (1970); **91**, 2808 (1969).

(4) Discussions of the inadequacy of older synthetic methods and of the biological properties of azoxyalkanes appear in ref 1.

(5) R. A. Moss and M. J. Landon, *Tetrahedron Lett.*, 3897 (1969).

(6) K. G. Taylor and T. Riehl, *J. Amer. Chem. Soc.*, **94**, 250 (1972); J. Swigert and K. G. Taylor, *ibid.*, **93**, 7337 (1971).

(7) However, leakage to several unidentified minor products (total $\sim$30%) did occur.

(8) 10 ft × 0.25 in., 10% TCEP on 40/60 Gas-Chrom R, at 163°.

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

(10) J. P. Freeman, *J. Org. Chem.*, **28**, 2508 (1963); B. Korsch and N. V. Riggs, *Tetrahedron Lett.*, 523 (1964); F. D. Greene and S. S. Hecht, *J. Org. Chem.*, **35**, 2482 (1970).

(11) F. G. Mann and J. W. G. Porter, *J. Chem. Soc.*, 456 (1944).

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