

Similarly,⁵ Va gave retained unrearranged acetate Vb, while the *exo* epimer Vc solvolyzed with rearrangement to give VI. The 5,6-dihydro analogs reacted similarly. Again there was no rate enhancement with the isomer undergoing replacement with retention.

These investigations were conducted with bicyclo-[2.2.1]heptane derivatives while ours were conducted with derivatives of dibenzobicyclo[3.2.1]octadiene (VII) where one can test for π participation from benzene rings at different angles to the departing group (IX). To summarize briefly, when a carbonium ion was formed at C-8 from a *syn* epimer (substituent Z) either by solvolysis or by deamination, the product was the unrearranged retained acetate VII (Z = OAc); when the carbonium ion came from an *anti* epimer (substituent Y), the product was the rearranged acetate VIII (Y = OAc). Examples follow.

Treatment of *syn*-8-iodo-*exo*-2-dibenzobicyclo[3.2.1]-octadienol acetate VIIa, m.p. 141–142°, with silver acetate in refluxing acetic acid gave the known⁶ unrearranged retained diacetate VIIb (92%). Deamination of the amine VIId, m.p. 178.5–179.5°, followed by acetylation also gave VIIb (37%), as did nitrosation of the amide VIIc, m.p. 174°, followed by decomposition of the N-nitrosamide (80%) (procedure of White⁷). On the other hand, deamination of the nitrosamide of the epimeric VIIe, m.p. 290°, proceeded with rearrangement, giving *anti*-*cis*-*anti*-dibenzobicyclo[3.3.0]octadiene-2,6-diol diacetate VIIa (85%), m.p. 131°. This was synthesized from *cis*-dibenzobicyclo[3.3.0]octadiene-2,6-dione (VIIe).⁸ Reduction of VIIe with lithium aluminum hydride followed by acetylation with acetic anhydride and pyridine gave a mixture of isomeric diacetates from which VIIb⁸ could be isolated. Equilibration of the mixture with acetic acid–sulfuric acid or acid-catalyzed acetylation of the diol mixture gave only the more stable VIIa, m.p. 131°. The configurations of the acetoxy groups in each isomer were readily established from n.m.r. data.

Solvolysis of chloride VIIf, m.p. 121.5–122.5°, in glacial acetic acid, assisted by silver acetate, produced the rearranged compound VIIId (71%), m.p. 105–106°. The structure of VIIId was demonstrated by hydrogenolysis over 10% palladium-on-charcoal to the known hydrocarbon VIIIf,⁹ m.p. and m.m.p. 101–103°. The configuration of the acetoxy group in VIIId was assigned on the basis of n.m.r. studies. Attempted solvolysis of the epimeric VIIg failed. In refluxing glacial acetic acid, and in the presence of equimolar quantities of silver acetate, compound VIIg failed to react after 20 days. In an equivalent length of time, isomer VIIf reacted completely.

The results of this work clearly indicate that the carbonium ion intermediates formed from these epimeric pairs cannot be identical and are not interconverted. Heterolysis of groups in the *anti* position results in rearrangement rather than the retention of structure and configuration observed with groups in the *syn* position. This may reflect the fact that ring B (*anti* to Y) is not broadside to the developing cationic center (as is the case with ring A, *anti* to Z) or more probably the fact that the competitive rearrangement to the [3.3.0] system involves both the formation of a benzylic cation and a less strained ring system *accompanying heterolysis*, while Wagner–Meerwein rearrangement of the *syn* epimers *accompanying heterolysis* would lead to a non-stabilized highly strained [4.2.0] cation. As suggested

for *anti*-7-norbornenyl tosylate² and for the benzo analog,¹⁰ the retention of structure and configuration with the *syn* isomers may be due to participation of π -electrons.

A striking difference between our work and that of Winstein^{2,3} is that our solvolysis–rearrangement appears to be much faster than solvolysis of the epimer (compare results with VIIf and VIIg). As the [3.3.0] cation may thus be presumed to be more stable than the unrearranged cation, there must be a large energy barrier between the two cations to preclude interconversion.

It appears that there is a large preference for migration of the bond to the benzene ring rather than that to the aliphatic carbon atom, although both are *anti* to Y. Further work on these dibenzobicyclooctyl and the analogous dibenzobicycloheptyl systems is in progress.

Acknowledgments.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Air Force Office of Scientific Research, and the National Science Foundation for support of this research.

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DEPARTMENT OF CHEMISTRY
UNIVERSITY OF COLORADO
BOULDER, COLORADO

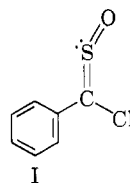
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DONALD E. FLORDE
KURT SCHWARZENBACH

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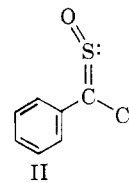
Geometrical Isomerism about a Carbon–Sulfur Double Bond¹

Sir:

We have recently reported that the action of triethylamine on benzylsulfonyl chloride in cyclohexane yields oxythiobenzoyl chloride.² We have now isolated a second component from the crude oxythiobenzoyl chloride mixture and wish to describe our observations which show that the two compounds are the geometrical isomers, *cis*- and *trans*-oxythiobenzoyl chloride (I and II).



I



II

The cyclohexane-soluble material obtained after mixing triethylamine (15 mmoles) with benzylsulfonyl chloride (10.0 mmoles) in cyclohexane at room temperature was separated by chromatography on silica gel into two major components: **A**, the previously described material (1.9 mmoles, eluted with benzene) which after recrystallization from ether–pentane melts at 38–39°, and **B**, a new material (0.9 mmole, eluted with petroleum ether–benzene 3:1) which after recrystallization from cold pentane melts at 5°. Analytical and physical data are summarized in Table I.

B is transformed into **A** on heating, the half-life of **B** being about 0.75 hr. in refluxing toluene and about 8 hr. in refluxing carbon tetrachloride. The conversion is faster in polar solvents but is complicated by a higher proportion of side reactions, e.g., hydrolysis.² Ultraviolet irradiation of a cyclohexane solution of **A** or **B** very rapidly yields benzoyl chloride (>60%); the

(5) C. H. DePuy, I. A. Ogawa, and J. C. McDaniels, *J. Am. Chem. Soc.*, **82**, 2397 (1960).

(6) S. J. Cristol and R. K. Bly, *ibid.*, **82**, 6160 (1960).

(7) E. H. White and C. A. Aufdermarsch, *ibid.*, **83**, 1179 (1961).

(8) K. Brand and W. Hennig, *Chem. Ber.*, **81**, 382 (1948).

(9) W. Roser, *Ann.*, **247**, 152 (1888).

(1) Presented to the 46th Annual Canadian Chemical Conference, Toronto, Ontario, June, 1963.

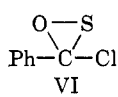
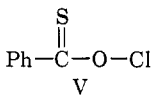
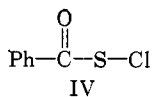
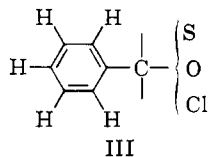
(2) J. F. King and T. Durst, *Tetrahedron Letters*, 585 (1963).

TABLE I

	Isomer A (m.p. 39°)	Isomer B (m.p. 5°)
<i>Anal.</i> Calcd. for C_7H_5SOCl : C, 48.70; H, 2.92; S, 18.54; Cl, 20.55	Found: C, 48.59; H, 3.02; S, 18.67; Cl, 20.81	Found: C, 48.88; H, 3.07; S, 18.85; Cl, 20.44
Molecular weight (cryoscopic, in cyclohexane) Calcd.: 172.6	170, 178	165, 170
Molecular weight (mass spectrometer)		172 (+174)
Refractive index, n_D^{20}	1.605	1.657
Density, d_4^{20}	1.205	1.285
Molar refractivity, R_D	49.1	49.3
Ultraviolet (in cyclohexane)	229 $m\mu$ (ϵ 8000), 323 $m\mu$ (ϵ 9000)	226 $m\mu$ (ϵ 8000), 328 $m\mu$ (ϵ 14,000)
Infrared (0.6 <i>M</i> in CCl_4 , values around 750 cm^{-1} determined in CS_2)	1446 (m), 1145 (vs), 1100 (m), 1025 (s), 920 (m), 753 (s), 688 (s) cm^{-1}	1445 (m), 1269 (s), 1188 (m), 1120 (vs), 1005 (s), 910 (m), 758 (s), 683 (s) cm^{-1}
H^1 n.m.r. (TMS, $\delta = 0$)	$\delta \sim 7.5$ (multiplet)	$\delta \sim 8.3$ and ~ 7.5 (multiplets, ratio 2:3)
C^{13} n.m.r.	$\delta_c = 12$ (singlet, nonaromatic C), and ~ 65 (complex absorption, aromatic C's) ³	$\delta_c = 12$ (singlet, nonaromatic C), and ~ 67 (complex absorption, aromatic C's) ³
Dipole moment, μ	3.97 D.	2.63 D.

reaction apparently belongs to the family of photochemical oxygen-transfer rearrangements discussed by Amin and Mayo.⁴

The chemical transformations, together with the presence of only aromatic absorption in the proton n.m.r. spectra and the infrared bands around 755 and 685 cm^{-1} , require that both compounds have partial



structure III. Structures IV, V, and VI are the only covalent structures, in addition to I and II, which can be derived by completing III without involving electron-deficient species or placing a formal positive charge on either carbon, oxygen, or chlorine. Structure IV, however, would require a carbonyl band in the infrared, V would be expected to absorb at longer wave lengths in the ultraviolet spectrum⁵ than is observed, and VI would not account for the ultraviolet maxima around 325 $m\mu$ found in both **A** and **B**. Structure VI would also not be compatible with the C^{13} n.m.r. spectra; the observed chemical shift of the nonaromatic

(3) Determined at 15.1 Mc./sec. in CCl_4 solution using enriched CH_3I as an external standard and given in p.p.m. relative to CS_2 ($\delta_c = 0$): P. C. Lauterbur, *J. Am. Chem. Soc.*, **83**, 1838 (1961).

(4) J. H. Amin and P. de Mayo, *Tetrahedron Letters*, in press.

(5) Allyl thionbenzoates show a maximum at 420 $m\mu$ (ϵ 97): S. G. Smith, *J. Am. Chem. Soc.*, **83**, 4285 (1961). **A** and **B** even in 0.1 *M* solutions show no sign of a maximum around 420 $m\mu$; at this wave length $\epsilon < 4$ for both **A** and **B**.

carbon (12 p.p.m. from CS_2 in both **A** and **B**) is close to that observed for carboxylic acids and some other functions in which the carbon atom is doubly bonded but is at substantially lower field than that reported for any saturated carbon.⁶ Furthermore, if one isomer were IV, V, or VI, then the other isomer would have to have a completely different structure from the first, since neither IV, V, or VI is capable of geometrical isomerism or diastereoisomerism. However, the striking feature of the data summarized by Table I is the close similarity of many of the properties of **A** and **B**. The molar refractivities and the ultraviolet and C^{13} n.m.r. spectra are very similar, and the three strongest bands in the infrared spectrum of **A** (excluding those due to the phenyl group) at 1145, 1025, and 920 cm^{-1} , respectively, have counterparts of comparable intensity in the spectrum of **B** at 1120, 1005, and 910 cm^{-1} . We therefore assign structures I and II to the isomers.

Assuming that the S-O and C-Cl bonds are polarized so that the oxygen and chlorine atoms are each partially negatively charged, the dipole moment of I should be greater than that of II. On this basis we propose structure I for **A** ($\mu = 3.97$ D.) and II for **B** ($\mu = 2.63$ D.).

Geometrical isomerism about carbon-carbon, carbon-nitrogen, and nitrogen-nitrogen double bonds has been known for many years, and recently geometrical isomerism about a boron-nitrogen bond has been suggested.⁷ I and II apparently represent the first case of geometrical isomerism about a double bond to an element outside the first short period of the periodic table.

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(6) P. C. Lauterbur, Chapter 7 in "Determination of Organic Structures by Physical Methods," Vol. II, ed. by F. C. Nachod and W. D. Phillips, Academic Press, New York and London, 1962; also P. C. Lauterbur, *Ann. N.Y. Acad. Sci.*, **70**, 841 (1958).

(7) M. F. Lappert and M. K. Majumdar, *Proc. Chem. Soc.*, **88** (1963).

(8) Holder of National Research Council of Canada Scholarships, 1961–1963.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WESTERN ONTARIO
LONDON, ONTARIO, CANADA

J. F. KING
T. DURST⁸

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A New, Stereospecific Olefin Synthesis from 1,2-Diols Sir:

In the field of complex molecular synthesis, especially in the area of organic natural products, there is a need for new and general methods for position-specific and stereospecific introduction of carbon-carbon double bonds. We report here a new reaction which gives promise of broad practical application in stereospecific synthesis. Because the new method allows complete control of both the stereochemistry and the position of unsaturation, it possesses definite advantages in many synthetic problems over any of the presently known approaches.^{1–10}

(1) G. Wittig and U. Schöllkopf, *Ber.*, **87**, 1318 (1954); this synthesis is both general and position-specific, but does not allow control of stereochemistry.

(2) R. C. Brandon, J. M. Derfer, and C. E. Boord, *J. Am. Chem. Soc.*, **72**, 2120 (1950), and preceding papers there listed.

(3) J. W. Cornforth, R. H. Cornforth, and K. K. Mathew, *J. Chem. Soc.*, 112 (1959).