

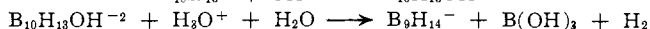
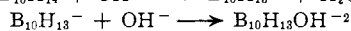
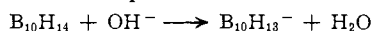
Salts prepared by metathesis include cesium, triphenylmethylphosphonium, alkylammonium, and quaternary ammonium tetradehydroborates(1-). For example, $\text{CsB}_9\text{H}_{14}$ was obtained in 65% yield (*Anal.* Calcd. for $\text{B}_9\text{CsH}_{14}$: B, 39.83; H, 5.77; mol. wt., 244. Found: B, 40.21; H, 5.17; mol. wt., 244) and $(\text{CH}_3)_4\text{NB}_9\text{H}_{14}$ in 85% yield (*Anal.* Calcd. for $\text{C}_4\text{H}_{26}\text{B}_9\text{N}$: C, 25.89; H, 14.12; B, 52.44; N, 7.55. Found: C, 25.39; H, 13.63; B, 52.24; N, 7.91).

A structural similarity between the B_9H_{14} anion and members of the B_9H_{13} (ligand) series of compounds³ was demonstrated by the following transformations: Heating a suspension of $(\text{CH}_3)_3\text{NHB}_9\text{H}_{14}$ in benzene resulted in the elimination of hydrogen and the formation of $\text{B}_9\text{H}_{13}[(\text{CH}_3)_3\text{N}]$ in 67% yield. Similarly, treatment of $(\text{CH}_3)_4\text{NB}_9\text{H}_{14}$ with a solution of anhydrous hydrogen chloride in acetonitrile gave a 66% yield of $\text{B}_9\text{H}_{13}(\text{CH}_3\text{CN})$.

Both inorganic bases such as sodium, potassium, and ammonium hydroxides as well as weak organic bases such as N-methyl- and N,N-dimethylformamide effectively degrade decaborane to the B_9H_{14} anion in aqueous solution. The course of the reaction, however, depends both on the quantity and the type of base used. Only reactions in aqueous hydroxide are summarized here. More detailed information will be reported at a later date.

When decaborane is stirred with one molar equivalent of aqueous sodium or potassium hydroxide for a period of about 12 hr., hydrogen is gradually evolved and the $\text{B}_9\text{H}_{14}^-$ ion is formed by way of an apparently complex series of reactions. With two molar equivalents of hydroxide, decaborane is quickly converted to a colorless, reasonably stable intermediate with no gas evolution. This intermediate undergoes very slow hydrolysis to $\text{B}_9\text{H}_{14}^-$. Acidification, however, effects the conversion rapidly and in high yield.

The second procedure has been studied in some detail and has been found to proceed in three discernible steps: (1) Decaborane first reacts with hydroxide to yield a yellow solution containing the $\text{B}_{10}\text{H}_{13}$ anion, identified by its ultraviolet absorption maxima at 265 and 330 $\text{m}\mu$.² (2) Further reaction with hydroxide yields the intermediate anion which absorbs at 227 and 262 $\text{m}\mu$. This ion has not been fully characterized but is believed to be a dianion of the composition $\text{B}_{10}\text{H}_{13}\text{OH}^{2-}$, resulting from the addition of OH^- to $\text{B}_{10}\text{H}_{13}^-$. Analogous ions have been reported.⁴ (3) The intermediate finally undergoes acidolysis to produce the B_9H_{14} anion ($\lambda_{\text{max}}^{\text{H}_2\text{O}}$ 271 $\text{m}\mu$, ϵ 3980), boric acid, and hydrogen. The reaction sequence is shown in the equations



The stoichiometry of the over-all process was ascertained by quantitative determination of the products and found to be in agreement with the sum of the above equations.

Acknowledgment.—This research was supported by the Advanced Research Projects Agency, Propellant Chemistry Office, and was monitored by the Bureau of Naval Weapons, RMMP, under Contract No. NOrd 18728.

(3) B. M. Graybill, A. R. Pitochelli, and M. F. Hawthorne, *Inorg. Chem.*, **1**, 626 (1962).

(4) W. H. Knott and E. L. Muetterties, *J. Inorg. Nucl. Chem.*, **20**, 66 (1961); B. M. Graybill, A. R. Pitochelli, and M. F. Hawthorne, *Inorg. Chem.*, **1**, 622 (1962).

AMERICAN CYANAMID COMPANY
STAMFORD LABORATORIES
STAMFORD, CONNECTICUT

LAWRENCE E. BENJAMIN
STANLEY F. STAFIEJ
EDWARD A. TAKACS

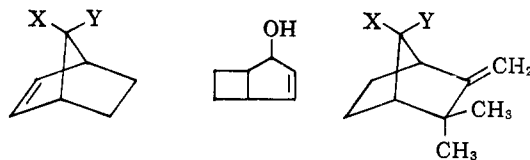
RECEIVED JUNE 7, 1963

Bridged Polycyclic Compounds. XXIII. Some Carbonium Ion Reactions in Dibenzobicyclo[3.2.1]octadiene Systems¹

Sir:

Several examples are known demonstrating that the course of carbonium ion reactions of epimeric homoallylic compounds may be significantly different. In one system,^{2,3} acetolysis of Ia resulted in complete retention of structure and configuration, forming acetate Ib, while its epimer Ic underwent Wagner-Meerwein rearrangement on hydrolysis in aqueous sodium bicarbonate, forming II. Ia solvolyzes 10^7 times faster than Ic. The reactivity and retention observed with Ia has been ascribed^{2,3} to anchimeric assistance by the π -electrons of the double bond. The driving force for the solvolysis rearrangement was attributed to the formation of an allylic cation.

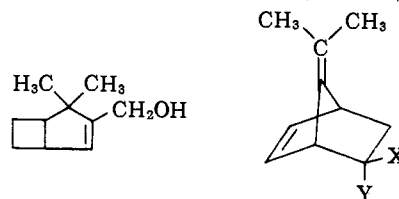
Similarly, it has been observed⁴ that acetolysis of IIIa or deamination of IIIb led to unrearranged and retained IIIc or IIIId, while the *syn-p*-toluenesulfonate IIIe solvolyzed with rearrangement to IV. No rate enhancement was observed with the *anti*-tosylate IIIa.



Ia, X = H, Y = OTs
Ib, X = H, Y = OAc
Ic, X = OTs, Y = H

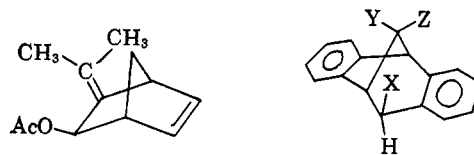
II

IIIa, X = OTs, Y = H
IIIb, X = NH₂, Y = H
IIIc, X = OAc, Y = H
IIId, X = OH, Y = H
IIIe, X = H, Y = OTs



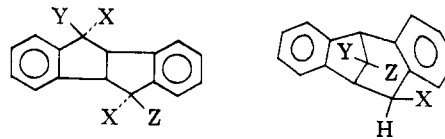
IV

Va, X = H, Y = OTs
Vb, X = H, Y = OAc
Vc, X = OTs, Y = H



VI

VIIa, X = OAc, Y = H, Z = H
VIIb, X = OAc, Y = H, Z = OAc
VIIc, X = OAc, Y = H, Z = NHAc
VIId, X = OH, Y = H, Z = NH₂
VIIe, X = OAc, Y = NHAc, Z = H
VIIf, X = H, Y = Cl, Z = H
VIIg, X = H, Y = H, Z = Cl



VIIIa, X = H, Y = Z = OAc
VIIIb, X = OAc, Y = Z = H
VIIIc, X = Y = Z = H
VIId, X = H, Y = OAc, Z = H
VIIIe, X + Y = O, X + Z = O

IX

(1) Previous paper in series: S. J. Cristol and J. K. Harrington, *J. Org. Chem.*, **28**, 1413 (1963).

(2) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Am. Chem. Soc.*, **77**, 4183 (1955).

(3) S. Winstein and E. T. Stafford, *ibid.*, **79**, 505 (1957).

(4) E. E. van Tamelen and C. I. Judd, *ibid.*, **80**, 6305 (1958).

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 VIIIa (85%), m.p. 131°. This was synthesized from *cis*-dibenzobicyclo[3.3.0]octadiene-2,6-dione (VIIIE).⁸ Reduction of VIIIE with lithium aluminum hydride followed by acetylation with acetic anhydride and pyridine gave a mixture of isomeric diacetates from which VIIIb⁸ 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 VIIIa, 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 VIIIE,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.

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

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF COLORADO
BOULDER, COLORADO

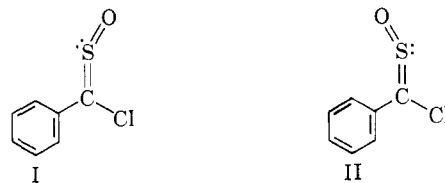
STANLEY J. CRISTOL
JERRY R. MOHRIG
FARN PWU PARUNGO
DONALD E. FLORDE
KURT SCHWARZENBACH

RECEIVED MAY 6, 1963

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).



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. Braud 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).