Cyclobutyltriphenylphosphonium Bromide[1a]

KIRBY V. SCHERER, JR., AND ROBERT S. LUNT, III[1b]

Department of Chemistry, University of California, Berkeley, California 94720

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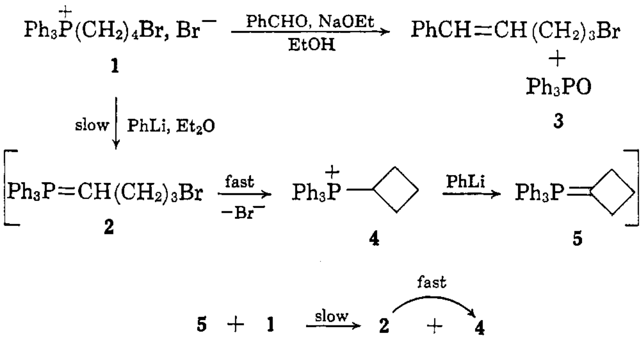
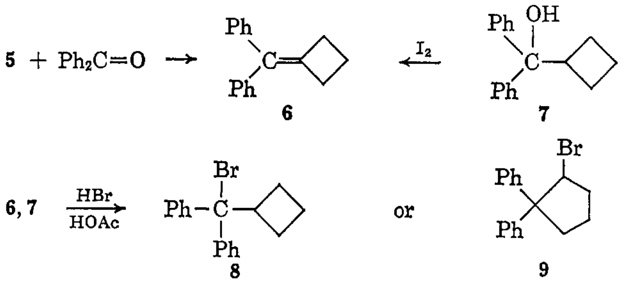
Monden, in 1957, examined the use of 4-bromobutyltriphenylphosphonium bromide (**1**) in the Wittig reaction and made several observations which lead to the following interpretation.[2] Thus, although reaction of **1** with base in the presence of benzaldehyde led to a bromo olefin (**3**), **1** with phenyllithium in ether gave a red solution, which in turn reacted with carbonyl compounds to give bromine-free products (apparently not further characterized), or slowly deposited a precipitate from which a new phosphonium salt could be isolated. Although Monden's investigation largely concerned bisylides, he did purify and analyze the new salt, found that it was not hydrogenated over Adams catalyst, and suggested for it structure **4**. Recently, however, Bestmann and Häberlein reported that they could not confirm Monden's suggestion, apparently because they failed to isolate cyclobutanone following autoxidation of **5**.[3,4] We have repeated the preparation of Monden's salt in connection with another problem and verified his structural assignment; because **4** and **5** are potentially valuable intermediates for the synthesis of cyclobutane derivatives, we report here our evidence and some observations incident thereto.



Reaction of **1** with 1 equiv. of phenyllithium in ether (the reported procedure[2]) gave an intractable crude product,[5] but with excess phenyllithium almost all the original **1** dissolved giving a red solution of ylide. Introduction of dry hydrogen bromide precipitated the new phosphonium salt as a white gum, but this time one recrystallization from water gave colorless crystals in 76% yield. We were also unable to isolate crystalline product when the phenyllithium was replaced by butyllithium or by methylsulfinylsodium in dimethyl sulfoxide.[6] When the recrystallized **4** was suspended in ether and treated with phenyllithium, a clear red solution formed. Addition of benzophenone and work-up gave diphenylmethylenecyclobutane (**6**), identical with authentic material,[7] in 57% isolated yield.

Having prepared both **6** and its precursor, cyclobutyldiphenylcarbinol (**7**), we examined the structure of the bromide derivable from either of them through the action of hydrogen bromide.[7,8] Graham and Williams suggested that this bromide probably has the unrearranged structure **8**, rather than the alternative **9**, even though it failed to liberate more than traces of bromide ion on prolonged boiling with potassium hydroxide in aqueous dioxane, and despite the fact that **6** and **7** rearrange readily under acidic conditions.[7,8] We prepared the bromide as described and determined its proton magnetic resonance spectrum. The significant feature of the spectrum is a somewhat broadened triplet ($J \cong 4.5$ c.p.s.) at τ 5.0, indicating a hydrogen on a carbon bearing bromine and pointing to structure **9**.[9] The methine hydrogen of **7**-O-*d* appears as a complex multiplet at *ca.* τ 6.8; the methylene region is complex in both **7** and the bromide but presents a quite different appearance in the two spectra, again supporting structure **9**.



Experimental

Infrared spectra were recorded on a Perkin–Elmer Model 237 Infracord, n.m.r. spectra on a Varian A-60 spectrometer in carbon disulfide with tetramethylsilane as internal reference, and ultraviolet spectra on a Cary Model 14 spectrophotometer. Microanalyses were carried out by Mr. V. Tashinian and Mrs. D. James.

Cyclobutyltriphenylphosphonium Bromide (4).—To a stirred suspension of 9.5 g. (20 mmoles) of 1[2] in 75 ml. of dry ether, under nitrogen, was added a solution containing slightly over 2 equiv. of phenyllithium (prepared from 0.6 g. of Li and 7.8 g. of C_6H_5Br, or purchased from Foote Mineral Co.) in 100 ml. of ether. Nearly all the salt dissolved, and the resulting red solution was stirred overnight. Hydrogen bromide gas passed into the solution discharged the red color immediately and caused precipitation of a gummy white solid, which was separated and digested with 150 ml. of hot water. The filtered aqueous solution deposited, on cooling, 6.0 g. (76%) of colorless crystals, m.p. 275–279° (lit.[2] 271°). One recrystallization from acetonitrile gave an analytical sample, m.p. 278.5–279.5°.

Anal. Calcd. for $C_{22}H_{22}PBr$ (397.31): C, 66.50; H, 5.58; Br, 20.12. Found: C, 65.95, 66.38; H, 5.61, 5.47; Br, 20.52, 21.32.

Diphenylmethylenecyclobutane (6).—To a stirred suspension of 2.00 g. of 4 in 100 ml. of dry ether (under N_2) was added 4.0 ml. of a 20% solution (Foote) of phenyllithium. The salt dissolved over 2 hr. to give a red solution, and 1.58 g. (70% excess) of benzophenone dissolved in a little ether was then added.

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[1] (a) Supported in part by a grant from the Petroleum Research Fund, administered by the American Chemical Society; grateful acknowledgment is made to the donors of the fund. (b) NSF Predoctoral Fellow.

[2] A. Monden, *Ann.*, **603**, 115 (1957).

[3] H. J. Bestmann and H. Häberlein, *Z. Naturforsch.*, **17B**, 787 (1962).

[4] P. T. Keough and M. Grayson, *J. Org. Chem.*, **29**, 631 (1964).

[5] Preliminary experiments carried out by Mr. James Aubry.

[6] E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 866 (1962).

[7] S. H. Graham and A. J. S. Williams, *J. Chem. Soc.*, 4066 (1959).

[8] N. Kishner, *J. Russ. Phys.-Chem. Soc.*, **42**, 1228 (1910); *Chem. Zentr.*, [5] **15**, 544 (1911).

[9] Compare with bromocyclopentane, τ 5.61, noting that the shielding of a 2-*cis*-phenyl just compensates for its inductive effect (methine C–H of cumene τ 7.13 *vs.* 7.11 for *trans*-1,2-diphenylcyclopentane) while a 2-*trans*-phenyl causes a downfield shift (*cis*-1,2-diphenylcyclopentane, τ 6.71): L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959, pp. 54, 126, and references therein.

A dark green color formed and faded slowly with formation of a white precipitate. The mixture was stirred overnight, water was added, and the separated ether phase was taken to dryness. Crystallization of the crude product from aqueous ethanol gave 0.63 g. (two crops, 57%) of **6** as colorless plates, m.p. 57.8–58.0° (lit.[7] 57–58°), $\lambda_{\max}^{\text{cyclohexane}}$ 257 μ (ε 17,000), identical (infrared and ultraviolet spectra, gas chromatography) with authentic material.[7]

2-Bromo-1,1-diphenylcyclopentane (**9**) was prepared by the action of hydrogen bromide on **7** according to the published procedure[7]; our product was obtained in 83% yield with m.p. 91–93° (lit.[7] 93–94°) and $\lambda\lambda_{\max}^{\text{cyclohexane}}$ 255 μ (ε 510), 262 (550), and 270 (370).

Evidence for a Radical Process in the Dark Cyclization Reaction of Aliphatic Alcohols with Silver Oxide and Bromine

Gerald Smolinsky and Bernice I. Feuer

Bell Telephone Laboratories, Inc., Murray Hill, New Jersey 07971

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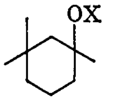
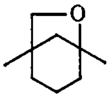
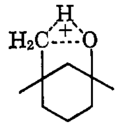
In 1958 Corey and White[1] reported that treatment of peroxide Ib with *p*-nitrobenzenesulfonyl chloride in cold pyridine–methylene chloride produced some bicyclic ether II. They suggested that the transformation, Ib → II, proceeded *via* a cationic transition state such as III. More recently, Sneen and Matheny[2a] have published a rather extensive study of this cyclization reaction under a variety of conditions and have speculated on the several mechanisms involved. The most useful procedure described for use in synthesis was the conversion, Ia → II, employing silver oxide and bromine in pentane in the dark. Indeed, using these conditions, 2-methylpentanol-2 (IV) could be converted in reasonable yield to 2,2-dimethyltetrahydrofuran (V).[2]



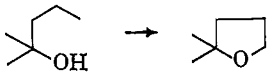
Ia, X = H
b, X = OH
c, X = Br
d, X = OTs
e, X = O-*p*-NB



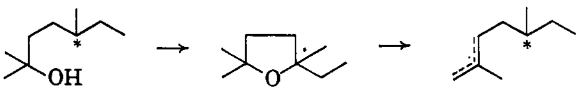
II



III

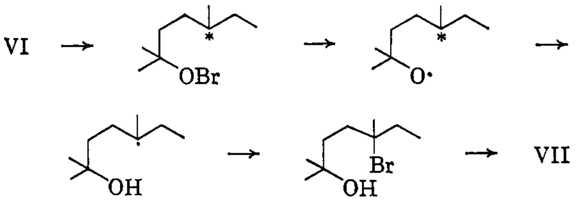


IV V



VI VII VIII

In this note, we concern ourselves with the mechanism of this dark cyclization reaction. We found that treating a pentane solution of (+)-(*S*)-2,5-dimethylhexanol-2 (VI) in the dark with silver oxide and bromine[2a] gave an approximately equal mixture of *optically inactive* 2-ethyl-2,5,5-trimethyltetrahydrofuran (VII) and optically active olefins VIII, as well as about 70% recovered alcohol VI. We believe that the formation of optically inactive VII is inconsistent with a concerted cyclization mechanism.[1,2] This result cannot readily be explained by a process involving the intermediacy of a monovalent cationic oxygen species[3] which abstracts a hydride ion from the δ-carbon atom to form a carbonium ion, and then lives long enough in pentane solution to rotate about a C–C bond before reacting with the nearby hydroxyl group. We feel a mechanism such as the following multiple-step process (eq. 1) to be more reasonable.[5] Indeed, Sneen and Matheny[2a] showed that formation of hypobromite Ic from alcohol Ia is possible by the action of bromine in the presence of a base such as silver oxide, and further showed that light-induced rearrangement of Ic to bromohydrin IX, which cyclized to ether II, on reaction with silver oxide.



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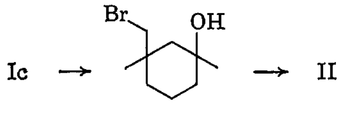

IX

The results from the silver oxide–bromine induced cyclization reaction should be compared with the findings from three similar substitution reactions at unactivated carbon atoms: reaction of lead tetraacetate with optically active alcohol X gave inactive ether XI[7]; photoinduced cyclization of optically active N-iodoamide XII gave inactive imine XIII[8]; and, finally, nitrene (XIV and XVI) cyclizations at optically active

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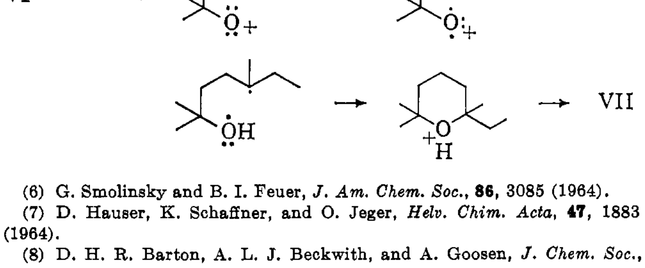
[1] E. J. Corey and R. W. White, *J. Am. Chem. Soc.*, **80**, 6686 (1958).

[2] (a) R. A. Sneen and N. P. Matheny, *ibid.*, **86**, 5503 (1964); (b) *ibid.*, **86**, 3905 (1964).

[3] Sneen and Matheny[2a] concluded that the silver oxide–bromine cyclization, Ia → II, in the dark, was not a radical process mainly on the basis that, when this reaction was carried out in the presence of thiophenol, no diphenyl disulfide formation could be detected by infrared analysis. However, when the light-induced rearrangement of hypobromite Ic to bromohydrin IX was run with thiophenol present, again no diphenyl disulfide could be detected, yet this rearrangement is very likely a radical-like process.[4]

[4] C. Walling and A. Padwa, *J. Am. Chem. Soc.*, **85**, 1597 (1963).

[5] An alternative, but we feel less likely explanation for the loss of optical activity during this reaction, would be to invoke the triplet state of the supposed cationic oxygen intermediate. (For a discussion of triplet-state nitrene and carbene reactions see ref. 6 and W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964.)



[6] G. Smolinsky and B. I. Feuer, *J. Am. Chem. Soc.*, **86**, 3085 (1964).

[7] D. Hauser, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **47**, 1883 (1964).

[8] D. H. R. Barton, A. L. J. Beckwith, and A. Goosen, *J. Chem. Soc.*, 181 (1965).