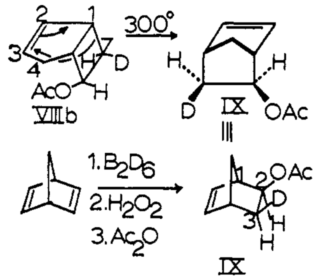
and hydroboration is *cis*[9]) and by the retention of virtually all of the label in the sequence from IV. It is confirmed by the nmr spectra of VIIIb and VIb, which are interpreted with the aid of double- and triple-resonance[10] spectra at 100 Mhz of the undeuterated substances (VIa and VIIIa) and their 5-*d* and 5,7,7-d_3 analogs. The absorptions due to the 7-*exo* protons in VIa and VIIIa disappear in VIb and VIIIb.

Heating VIIIb in decalin solution at 307° under conditions previously shown to cause intramolecular,[5,6] 1,3-sigmatropic[6] rearrangement to *exo*-norbornenyl acetate gives that compound with the deuterium and acetoxy groups both *exo* and hence *cis* (IX). The stereochemistry of IX is established by the nmr spectrum. The spectrum of undeuterated *exo*-norbornenyl acetate shows[6] the absorption of the 3-*exo* proton as a multiplet at δ 1.35 downfield from internal tetramethylsilane. This pattern is missing from the spectrum of the pyrolysis product IX. The geminal coupling (J = 12 cps) in the pattern of the 3-*endo* proton of undeuterated *exo*-norbornenyl acetate disappears in IX, and the doublet of doublets due to the 2-*endo* proton of undeuterated material ($J_{2,3\text{-}exo}$ = 2.8 cps, $J_{2,3\text{-}endo}$ = 7 cps) collapses to a doublet ($J_{2,3\text{-}endo}$ = 7 cps). The entire spectrum is virtually indistinguishable from that of authentic[11] IX, synthesized by deuterioboration–oxidation–acetylation of norbornadiene. From time-averaged repeated-scan observation of the δ 1.35 region of the spectrum and comparison with that of authentic 3-*endo*-deuterio-2-*exo*-norbornenyl acetate independently synthesized,[12] the amount of the latter substance present as contaminant in the pyrolysis product IX can be estimated to be less than 5%. Control experiments show that (1) a mixture of synthetic IX and the undeuterated analog does not fractionate under the pyrolysis conditions; (2) prolonged pyrolysis converts IX to a mixture containing both *endo*- and *exo*-norbornenyl acetate, but the *exo*-acetate recovered is still IX (3-*exo*-*d*); (3) starting material VIIIb recovered from pyrolysis is still exclusively VIIIb (7-*exo*-*d*).



The VIIIb → IX rearrangement, necessarily suprafacial, thus occurs with highly specific inversion of the migrating group, C-7. This result is difficult to rationalize in terms of a stepwise mechanism passing over an intermediate in which the C-7–C-1 bond is broken but no significant bonding of C-7–C-3 exists. Such a process would be expected to result in retention or randomization of configuration. Apparently, the preferred approach to the transition state is by compression of the C-2–C-1–C-7 angle and torsion about the C-5–C-6 and C-6–C-7 bonds until *opposite faces* of C-7 can bond simultaneously to C-1 and C-3, as in II. That progress along the reaction coordinate should consist of this complex set of motions demonstrates the predictive power of orbital symmetry considerations.[13]

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(9) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

(10) We are indebted to Professor P. Bender and Mr. L. Sims for expert advice on these techniques and to Miss Martha Petrie for a number of the spectra.

(11) *Cf.* S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *J. Org. Chem.*, 31, 2726 (1966).

(12) As the minor component from the sequence: exchange of one (mostly *exo*) deuterium of norbornenone-3,3-d_2, hydride reduction, acetylation, and vpc separation.

(13) Since a transition state with the geometry of II places the migrating group substituents in a plane perpendicular to that of the allyl system, steric repulsions when the substituents are large may be so severe as to prohibit this mechanism.

(14) National Institutes of Health Predoctoral Fellow, 1966–1967.

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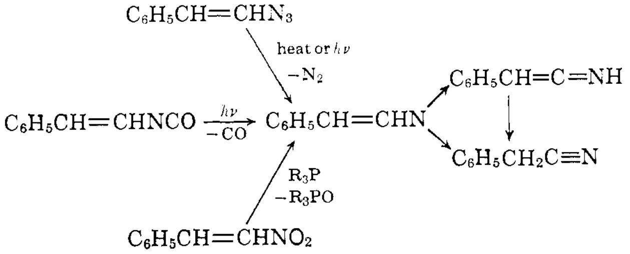
β-Styrylnitrene

Sir:

Both β-styryl azide and β-styryl isocyanate undergo photochemical transformation into phenylacetonitrile, a product also obtained from the former by pyrolysis. A previous report that deoxygenation of β-nitrostyrene by triethyl phosphite affords the same nitrile in low yield[1] has been confirmed by glpc analysis. β-Styrylnitrene, a proposed intermediate for the deoxygenation reaction,[1] may be common for all three reactions; however, other mechanisms, such as fragmentation concerted with rearrangement, have not been eliminated.[2] To our knowledge, this is the second recorded example of the probable formation of an organic nitrene from an isocyanate by photolysis.[3]



Other reactions of β-styrylnitrene have not been elucidated. Cyclization to indole was not observed.[4] Neither abstraction from nor insertion with *n*-heptane C–H bonds during photolysis of either β-styryl azide or isocyanate has been established. By comparison with the formation of 2-phenylazirine from either pyrolysis or photolysis of α-styryl azide,[5] the formation of 3-phenylazirine could be expected from both β-styryl azide and isocyanate. Firm evidence for its presence is not avail-

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(1) R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, 64, 165 (1964), reported a private communication from J. Weinstock.

(2) For a discussion of nitrene formation from azides, see P. A. S. Smith, "Open-Chain Nitrogen Compounds," Vol. 2, W. A. Benjamin, Inc., New York, N. Y., 1966, p 216; from nitro compounds, see J. I. G. Cadogan and M. J. Todd, *Chem. Commun.*, 178 (1967), and earlier papers.

(3) D. A. Bamford and C. H. Bamford, *J. Chem. Soc.*, 30 (1941), reported $CH_3NCO + h\nu \longrightarrow CH_3N + CO$. After the present paper was submitted for publication, J. S. Swenton, *Tetrahedron Letters*, 2855 (1967), reported the formation of carbazole and phenanthridone during the photolysis of *o*-biphenyl isocyanate.

(4) A positive, but unspecified, indole test was reported for a product from the deoxygenation of β-nitrostyrene.[1]

(5) G. Smolinsky, *J. Org. Chem.*, 27, 3557 (1962); L. Horner, A. Christmann, and A. Gross, *Chem. Ber.*, 96, 399 (1963).

able, nevertheless, the possibility of an equilibrium between 3-phenylazirine and β-styrylnitrene prior to rearrangement to phenylacetonitrile is recognized.[6] Formation of the nitrile requires migration of hydrogen either from carbon to nitrogen, followed by tautomerization, or from α- to β-carbon. Initial formation of a ketenimine follows the established pattern of 1,2 migration of hydrogen from carbon to nitrogen for primary and secondary alkyl nitrenes.[7]

Styrene azidohydrin, obtained from phenacyl azide by reduction with sodium borohydride,[8] was transformed into styrene azidochloride. At −25° potassium *t*-butoxide in ether removes both hydrogen chloride and hydrogen azide from styrene azidochloride. The major portion of the product was an oil from which known α-chlorostyrene (17%) could be separated by distillation, bp 28–32° (0.6 mm), n^{25}D 1.5606. By chromatographic purification of the pot residue over alumina, β-styryl azide (44%) was isolated, infrared absorption (cm^{-1}) at 2100 (s) (N_3), 1645 (s) (C=C), nmr (ppm) 7.14 (five phenyl protons), 6.32 and 6.11 (a pair of doublets representing two vinyl protons (probably *trans*), J = 14.0 cps). The azide could not be distilled and decomposed at about 70°. This low temperature for elimination of nitrogen probably reflects assistance through participation by the adjacent olefinic bond.

Neat β-styryl azide was pyrolyzed in the injection port of an Aerograph Autoprep Model 700 gas chromatograph. Two products accounted for 90% of the total peak area on the chromatogram, and the remaining 10% represented impurities known to be present and traces of unidentified material. The major product (74%) was collected after elution from a 20-ft 20% SE-30 silicone gum on Chromosorb W column and identified by comparing its infrared absorption, refractive index, and glpc retention time with authentic phenylacetonitrile.

A *n*-heptane solution of β-styryl azide in a quartz vessel was photolyzed overnight in a Rayonet photochemical reactor with light at 2537 A supplied by 16 35-w low-pressure mercury lamps. An unidentified solid (74%), apparently polymeric, was separated. The concentrated filtrate gave a dark oil containing phenylacetonitrile whose presence was indicated by nmr (ppm) centered at 7.21 and 3.50, corresponding to absorption at 7.19 and 3.48 for authentic material, and by glpc retention time. From the chromatogram a maximum of 8% yield was indicated.

Under similar conditions, photolysis of *trans*-β-styryl isocyanate[9] produced an unidentified, apparently polymeric, solid, judged by infrared absorption to be identical with a product, described above, from β-styryl azide. Analysis of the filtrate by glpc indicated the presence of two components whose chromatographic peaks corresponded with peaks similarly obtained not only from β-styryl azide but also from phenylacetonitrile after comparable photolytic treatment. The component with the longer retention time represented a maximum of 20% yield of phenylacetonitrile from β-styryl isocyanate, as determined from the chromatogram and further identified by comparison of its infrared spectrum with that of a known sample.

Acknowledgment. Financial assistance was received from NASA Grant NGR 14-012-004.

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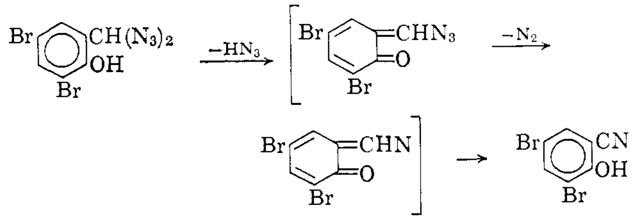
(6) Cadogan and Todd discuss the possible equilibrium between a bicyclic azirine and phenylnitrene.[2]

(7) Five terminal vinyl azides have been reported either in fact or implication: A. N. Nesmeyanov and M. I. Rybinskaya (*Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 816 (1962); *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 761 (1962); *Chem. Abstr.*, **58**, 3408 (1963)) reported $C_6H_5COCH{=}CHN_3 + HCl \longrightarrow C_6H_5COCH_2CN$ + other products. J. H. Boyer and F. C. Canter (*Chem. Rev.*, **54**, 34 (1954)) explain the pyrolysis of 3,5-dibromo-2-hydroxybenzaldiazide (H. Lindemann and H. Thiele, *Ber.*, **61**, 1529 (1928)) in terms of an intermediate terminal vinyl azide.



F. W. Fowler, A. Hassner, and L. A. Levy (*J. Am. Chem. Soc.*, **89**, 2077 (1967)) have reported the preparation of $(CH_3)_3CCH{=}CHN_3$. J. S. Meek and J. S. Fowler (*ibid.*, **89**, 1967 (1967)) reported the isomerization of β-azidovinyl *p*-tolyl sulfone to 4(5)-*p*-toluenesulfonyltriazole. R. H. Wiley and J. Moffat (*J. Org. Chem.*, **22**, 995 (1957)) reported the preparation and polymerization of vinyl azide.

(8) J. H. Boyer and S. E. Ellzey, Jr., *ibid.*, **23**, 127 (1958).

(9) L. W. Jones and J. P. Mason, *J. Am. Chem. Soc.*, **49**, 2528 (1927).

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Sulfur Trioxide in the Oxidation of Alcohols by Dimethyl Sulfoxide

Sir:

Following the discovery of Kornblum and coworkers[1] that halides or tosylates may be oxidized with dimethyl sulfoxide (DMSO) to carbonyl compounds, the intermediacy of dimethylsulfoxonium ions was hypothesized[2] and, quite recently, has been substantiated by Torssell.[2d] On this basis, Barton, *et al.*,[3] described a procedure involving the formation of the intermediate dimethylsulfoxonium ions by the action of DMSO on alkyl chloroformates and a novel catalysis of their decomposition with triethylamine.[2d]

Agents such as dicyclohexylcarbodiimide (DCC),[4] acetic anhydride,[5] and phosphorus pentoxide[6] in combination with DMSO have also been reported to effect oxidation of alcohols.[7] The function of dicyclohexylcarbodiimide has been elegantly elucidated and a di-

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(1) N. Kornblum, J. W. Powers, G. J. Anderson, W. J. Jones, H. O. Larson, O. Levand, and W. M. Weaver, *J. Am. Chem. Soc.*, **79**, 6562 (1957); N. Kornblum, W. J. Jones, and G. J. Anderson, *ibid.*, **81**, 4113 (1959).

(2) (a) S. G. Smith and S. Winstein, *Tetrahedron*, **3**, 317 (1958); (b) I. M. Hunsberger and J. M. Tien, *Chem. Ind.* (London), **88** (1959); (c) N. R. Nace and J. J. Monagle, *J. Org. Chem.*, **24**, 1792 (1959); (d) K. Torssell, *Tetrahedron Letters*, 4445 (1966); *Acta Chem. Scand.*, **21**, 1 (1967).

(3) D. H. R. Barton, B. J. Garner, and R. H. Wightman, *J. Chem. Soc.*, 1855 (1964).

(4) K. E. Pfitzner and J. G. Moffatt, *J. Am. Chem. Soc.*, **85**, 3027 (1963); *ibid.*, **87**, 5661 (1965); **87**, 5670 (1965).

(5) J. D. Albright and L. Goldman, *ibid.*, **87**, 4214 (1965); **89**, 2416 (1967).

(6) K. Onodera, S. Hirano, and N. Kashimura, *ibid.*, **87**, 4651 (1965).

(7) See recent reviews by (a) N. Kharasch and B. S. Thyagarajan, *Quart. Rept. Sulfur Chem.*, 1, 16 (1966); (b) W. W. Epstein and F. W. Sweat, *Chem. Rev.*, **67**, 247 (1967).