Mechanism of α-Elimination by Hydroxide Ion on p-Nitrobenzylsulfonium Ion in Aqueous Solution[1,2]
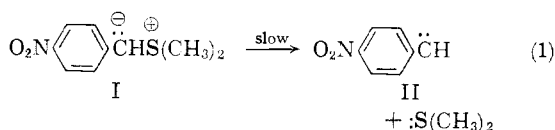
BY C. GARDNER SWAIN AND EDWARD R. THORNTON

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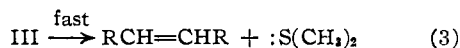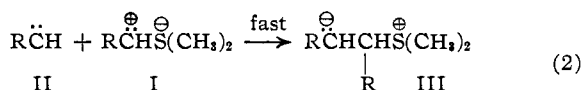Sodium hydroxide reacts with p-nitrobenzyldimethylsulfonium p-toluenesulfonate in water at 60° to form p,p'-dinitrostilbenes in high yield. The reaction is first order in hydroxide ion and first order in sulfonium ion. The rate-determining step cannot be formation of carbanion I because of infrared evidence for rapid deuterium exchange into the salt, and is therefore formation of carbene II from I. The over-all sulfur isotope effect k_{32}/k_{34} is 1.0066 ± 0.0008, too low for subsequent dimerization of carbenes, but reasonable if II reacts predominantly with I.

The product of reaction of sodium hydroxide with p-nitrobenzyldimethylsulfonium p-toluenesulfonate (tosylate) in water at 60° is a mixture of cis- and trans-p,p'-dinitrostilbenes in 99% yield. The reaction is first order in each reactant. A red color, believed due to a low concentration of carbanion I (a dipolar ion with positive charge on sulfur), forms rapidly relative to the rate of disappearance of base when the reactants are mixed. Sulfonium salt isolated after partial reaction in D_2O has CD bonds, showing that carbanion formation is reversible.

The kinetic order excludes rate-determining reaction between carbanion and sodium salt, but is consistent with rate-determining formation of carbene II

$$\underset{I}{O_2N\!\!-\!\!\langle\;\rangle\!\!-\!\!\overset{\ominus}{C}H\overset{\oplus}{S}(CH_3)_2} \xrightarrow{\text{slow}} \underset{II}{O_2N\!\!-\!\!\langle\;\rangle\!\!-\!\!\ddot{C}H} \quad (1)$$
$$+ :S(CH_3)_2$$

The sulfur isotope effect k_{32}/k_{34} is 1.0066 (with a standard deviation of ± 0.0008). This seems too low for reaction 1 followed by rapid dimerization of II because the first-order solvolysis of t-butyldimethylsulfonium iodide in water at 59° has a sulfur isotope effect of 1.0177 ± 0.0014.[3] One expects a large isotope effect when forming a highly unstable intermediate (like a carbene or carbonium ion) because the transition state is then close to the intermediate, with a weak C–S bond. For formation of either carbene or carbonium ion, the same change in carbon hybridization occurs, from sp^3 to a vacant p-orbital. However, it is consistent with reaction 1 followed by rapid attack of carbene II on carbanion I

$$\underset{II}{R\ddot{C}H} + \underset{I}{R\overset{\oplus}{C}H\overset{\ominus}{S}(CH_3)_2} \xrightarrow{\text{fast}} \underset{R \quad III}{R\overset{\ominus}{C}HCH\overset{\oplus}{S}(CH_3)_2} \quad (2)$$

$$III \xrightarrow{\text{fast}} RCH=CHR + :S(CH_3)_2 \quad (3)$$

The second-order reaction of sodium hydroxide with β-phenylethyldimethylsulfonium bromide in water at 59° has a sulfur isotope effect of only 1.0015 ± 0.0009.[3] One expects a small isotope effect

for decomposition of an unstable carbanion (like III) to give stable products because the transition state will then be close to the reactant, with a still strong C–S bond. For formation of olefin from either the carbene or the E2 elimination reaction, the same change in carbon hybridization occurs, from sp^3 to an occupied π-bonding p-orbital. If step 2 is reversible so that the sulfur isotope effect is determined in steps 1 and 3, one expects it to approximate the mean of the isotope effects for these models for reactions 1 and 3 (1.0177 and 1.0015), as 1.0066 does. If step 2 is irreversible or if 2 and 3 are concerted, one expects it to approximate the mean of the isotope effects for steps 1 and 2 (1.0177 and 1.0000), since reaction 2 should have an even smaller isotope effect than reaction 3.

Experimental

p-Nitrobenzyldimethylsulfonium tosylate was prepared by reaction of p-nitrobenzyl p-toluenesulfonate[4] with excess dimethyl sulfide in acetonitrile at room temperature. The salt crystallized slowly from solution, m.p. 138.5–139.2°.

Anal. Calcd. for $C_{16}H_{19}NO_5S_2$: C, 52.01; H, 5.18; N, 3.79; S, 17.36. Found: C, 51.38; H, 4.76; N, 4.09; S, 17.34.

Product Analysis.—A mixture of cis- and trans-p,p'-dinitrostilbenes was isolated in 99% yield by neutralization and filtration of the reaction mixture obtained by heating 0.1 M sulfonium salt with 0.2 M sodium hydroxide in water at 59.95 ± 0.05° for 18 hours, which melted over a large range (150° to above 255°). The infrared spectrum, taken in a Nujol mull on a Perkin–Elmer model 21 infrared spectrophotometer, showed no significant OH stretching band, and was in agreement with the assigned structure.

Anal. Calcd. for $C_{14}H_{10}N_2O$: C, 62.22; H, 3.73. Found: C, 61.88; H, 4.03.

A small amount of product was heated at reflux in nitrobenzene (210°) with a trace of iodine. Pure trans-p,p'-dinitrostilbene was isolated, m.p. 304–306° (cor.), lit.[5] 296–305°.

Kinetics.—Runs with 0.04 M sodium hydroxide, 0.02 M sulfonium salt and 0.3 M sodium perchlorate for constant ionic strength were carried out in water at 59.95 ± 0.05°. Reaction was followed by quenching 10-ml. aliquots with 2 ml. of 0.2 M standard hydrochloric acid and back-titrating with 0.2 M standard sodium hydroxide. Second-order rate constants were constant to < 5% up to 84% reaction; k_2 was 2.52 ± 0.11 × 10^{-3} M^{-1} sec.$^{-1}$ from two runs. A similar run but without perchlorate gave 4.28 × 10^{-3} M^{-1} sec.$^{-1}$, constant to < 5% up to 66% reaction.

Intermediate I.—When a pellet of potassium hydroxide was added to a slightly orange solution of the sulfonium salt in aqueous sodium hydroxide, a deep crimson color formed in the solution near the pellet as it dissolved. This great deepening of color demonstrates that the red species was in very low concentration in the orange solution.

A solution of 0.2 M sodium deuteroxide and 0.1 M sulfonium salt in D_2O was allowed to react for only 5 min. at

(1) Supported in part by the National Institutes of Health through Research Grant RG-3711 and by a postdoctoral fellowship to E. R. T. from the Division of General Medical Sciences, U. S. Public Health Service.

(2) Cf. C. G. Swain and E. R. Thornton, *J. Org. Chem.*, in press.

(3) W. H. Saunders, Jr., and A. Aśperger, *J. Am. Chem. Soc.*, 79, 1612 (1957).

(4) H. Gilman and N. J. Beaber, *ibid.*, 47, 518 (1925).

(5) I. Heilbron, "Dictionary of Organic Compounds," Vol. 2, Oxford University Press, New York, 1953, p. 390.

25°, then neutralized dropwise with concd. hydrochloric acid until the red color disappeared and filtered to remove stilbene. Excess sodium perchlorate was added to precipitate the insoluble sulfonium perchlorate, which was removed by filtration and dried. The infrared spectrum had two major C–D stretching bands, at 2210 and 2130 cm.$^{-1}$, which were not present in the spectrum of the (undeuterated) sulfonium perchlorate isolated by precipitation from H_2O solution with sodium perchlorate. Therefore the

formation of the carbanion is reversible. Similar results have been obtained with p-nitrobenzyl chloride in 50% aqueous dioxane at 30°.[6]

Isotope effects were measured as described previously.[2] Two separate runs gave 1.00601 and 1.00713.

(6) S. B. Hanna, S.M. Thesis in Chemistry, Alexandria University, Egypt, 1957; S. B. Hanna, Y. Iskander and Y. Riad, *J. Chem. Soc.*, 217 (1961); S. B. Hanna, Y. Iskander and A. Salama, *ibid.*, 221 (1961).
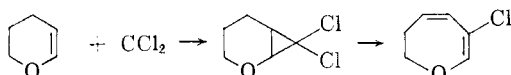

The Reaction of Dichlorocarbene with 2H-1-Benzothiopyran and 4H-1-Benzothiopyran[1]

BY WILLIAM E. PARHAM[1] AND ROBERT KONCOS[2]

The reaction of 2H-1-benzothiopyran (I) with dichlorocarbene gives the insertion products 2-dichloromethyl-2H-1-benzothiopyran (II) and 4-dichloromethyl-4H-1-benzothiopyran (III). There was no evidence for formation of the expected cyclopropane IV. The reaction of dichlorocarbene with the isomeric 4H-1-benzothiopyran gives only the cyclopropyl adduct XIV. Thermal decomposition of XIV in hot quinolines gives 2-chloronaphthalene.

We previously observed[3] that halocarbenes react with dihydropyran to give cyclopropyl adducts, which afford dihydroöxepines, in high yield, by subsequent ring expansion and elimination of hydrogen chloride. This reaction sequence

appears to offer considerable promise as a synthetic method for oxepin, thiepin and azepine, or derivatives of these unsaturated heterocycles, and experiments directed toward these objectives are in progress. We now wish to report studies of the reaction of dichlorocarbene with 2H-1-benzothiopyran (I) and 4H-1-benzothiopyran (X).

Dichlorocarbene was generated by reaction of ethyl trichloroacetate[4] and sodium methoxide, and was allowed to react with 2H-1-benzothiopyran (I) in petroleum ether at 0 to 25°. The products
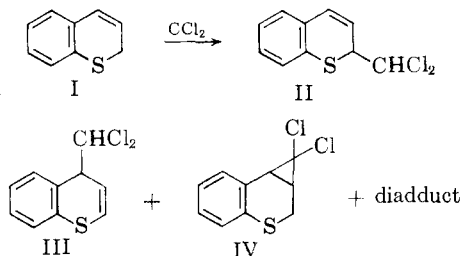
isolated from the reaction mixture were: (1) recovered I, when one equivalent of ethyl trichloroacetate was employed, (2) an oil (b.p. 108–115° (0.65 mm.), 31% yield) with the composition calculated for a monoadduct (II, III or IV), and (3) a solid (m.p. 125°, 8.4% yield) diadduct derived apparently from one equivalent of I and two equivalents of dichlorocarbene.

(1) This work was supported by a grant from the National Science Foundation (NSF-G14458), and by a grant (1959–1960) from the Office of Ordnance Research (Contract No. DA-11-022-ORD-2616).

(2) NSF predoctoral fellow, 1960–1961.

(3) E. E. Schweizer and W. E. Parham, *J. Am. Chem. Soc.*, **82**, 4085 (1960).

(4) W. E. Parham and E. E. Schweizer, *J. Org. Chem.*, **24**, 1733 (1959).

The monoadduct partially crystallized, and the solid fraction (m.p. 57–58°) was subsequently identified as II. Nuclear magnetic resonance studies of this solid established its structure to be II or III,[5] furthermore, nuclear magnetic resonance studies of the oil, obtained subsequent to the removal of II, established that this product was a mixture of II and III (approximately 40 and 60%, respectively). Thus, the ratio of II to III in the crude monoadduct was approximately 2.4/1 (22% yield and 9.1% yield, respectively). There was no evidence for the formation of the expected cyclopropane IV.

The structure of the solid monoadduct, and the composition of the mixed monoadducts, were further confirmed by their reduction with Raney nickel in ethanol. The solid (II) gave n-butylbenzene (72.5% yield), while the mixture obtained subsequent to removal of solid II afforded nearly equal amounts of n-butylbenzene and sec-butylbenzene (37 and 40.5%, respectively). The products in each case were analyzed by vapor phase chromatography.

Although insertion reactions are common for methylene,[6] this is the first reported example of preferential insertion involving a halocarbene. The distribution of products in the allylic system suggests, of course, that a resonance ion is involved, and the reaction may occur as shown in the accompanying equation. It is reasonable, however,
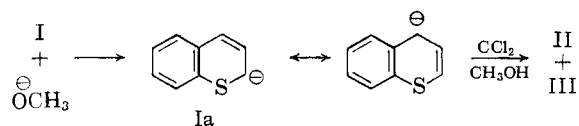
to assume that the sulfur atom in I can compete as a nucleophilic site with the conjugated double bond for the electrophilic carbene, and we are inclined to believe that the reaction is more properly

(5) A variety of structures with an expanded ring, derivatives of benzothiepin, also were considered; however, the n.m.r. spectrum was incompatible with such assignment.

(6) Cf. (a) W. von E. Doering, R. G. Buttery, R. G. Laughlin and N. Chaudhuri, *J. Am. Chem. Soc.*, **78**, 3224 (1956); (b) D. B. Richardson, M. C. Simmons and I. Dvoretzky, *ibid.*, **82**, 5001 (1960).