raphy which indicated formation of *ca.* 1% of hexachlorocylopropane (t_R = 6.6).[11] The chromatograms showed peaks due to several other minor components, one of which was collected (t_R = 2.7) and found to have a strong band at 1763 cm.$^{-1}$ but which was not characterized further.

In a similar experiment, the gas evolved during the reflux period was collected and analyzed by infrared spectroscopy which indicated that the sample consisted of carbon dioxide that did not contain more than a small amount (< 5%) of carbon monoxide. This result apparently precludes significant reaction of dichlorocarbene with trichloroacetate ion to give, over-all, carbon monoxide, trichloroacetyl chloride, and chloride ion by a reaction path formally similar to that described[12] for the reaction of dichlorocarbene with alkoxide ions. In other control experiments it was found that the thermal decomposition of sodium trichloroacetate in 1,2-dimethoxyethane did not produce significant quantities of materials with retention times greater than that of the solvent.

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[11] Retention time relative to tetrachloroethylene, t_R = 1.00; 1,2-dimethoxyethane, t_R = 0.33 on silicone oil at 150°.

[12] P. S. Skell and I. Starer, *J. Am. Chem. Soc.*, **81**, 4117 (1959).

Addition Reactions of *m*- and *p*-Nitronitrosobenzene[1]

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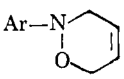
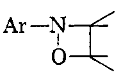
The addition reactions of aromatic nitroso compounds to conjugated dienes are well known.[2] The reaction products I, dihydroöxazines, generally are isolated in high yields. Side products of the reaction have not been reported.

o-Nitronitrosobenzene[2] conforms to this pattern, but for the reaction of *m*- or *p*-nitrosobenzene with 2,3-dimethyl-1,3-butadiene, we have found two reaction products. One of these reaction products was found to be the expected adduct I. The second reaction product II showed an elemental analysis and molecular weight corresponding to an adduct consisting of one mole of diene and two moles of nitroso compound.

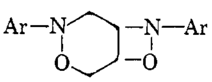
Aromatic nitroso compounds have been reported to react smoothly with suitably substituted alkenes,[3] yielding oxazetidines III. Product II, therefore, might be the result of the normal 1,4-addition of nitroso compound to diene, followed by a 1,2-addition of the nitroso compound to the dihydroöxazine, yielding compound IV or its isomer.



I



III



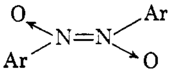
IV

In order to test this hypothesis, we attempted to treat the normal 1,4-adduct of *p*-nitronitrosobenzene and 2,3-dimethyl-1,3-butadiene with the equivalent amount of *p*-nitronitrosobenzene. We were unable to detect a reaction with the aid of infrared spectra. Unsuccessful attempts were also made to prepare an oxazetidine from *p*-nitronitrosobenzene and the following alkenes: cyclohexene, cyclopentene, isobutylene, *cis*- and *trans*-2-butene.

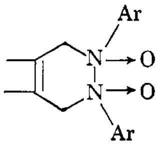
Considering the evidence, this hypothesis concerning the structure of product II was then rejected. It was also considered unlikely that the conjugated diene would add two moles of the nitroso compound in a 1,2-fashion.

It is well established that many aromatic nitroso compounds are in a state of equilibrium between monomer and dimer in solution.[4] The monomeric state is generally favored by electron-donating groups. The electron-withdrawing nitro group will cause a considerable fraction of the nitronitrosobenzenes to be in the dimeric state V. It is also well known that electron-poor azo groups are excellent dienophiles in Diels–Alder reactions.[5]

The formation of the products II may then be accounted for by a reaction between the diene and the electron-poor N═N group of the dimeric nitronitrosobenzene, to form a tetrahydro-1,2-diazine-N,N-dioxide VI. Steric hindrance may explain the failure of *o*-nitronitrosobenzene to give an adduct of this type, while the low yield of this adduct for *m*-nitronitrosobenzene may be ascribed to the decreased resonance effect.



V



VI

The infrared absorption band at about 1050 cm.$^{-1}$ associated with the oxazine ring,[2] was absent from the spectra of products II. Although the spectra of a small number of tertiary amine oxides have been reported[6], we have not been able to assign bands in the 970–950-cm.$^{-1}$ region unequivocally to the amine oxide. The insolubility of products II in suitable solvents ruled out the determination of an nuclear magnetic resonance spectrum.

Conclusive evidence for the assertion that products II have structure VI was furnished by the deoxygenation of the N,N-dioxide IIa by Ochai's method,[7] employing phosphorus trichloride as the deoxygenation agent. The known substance 4,5-dimethyl-1,2-bis-(*p*-nitrophenyl)-1,2,3,6-tetrahydropyridazine[8] was obtained as the deoxygenation product.

Experimental[9]

***m*-Nitronitrosobenzene,** m.p. 89–90°, and ***p*-nitronitrosobenzene,** m.p. 118°, were prepared by oxidation with Caro's acid from the corresponding amines.[10]

Adducts of *p*-Nitronitrosobenzene.—*p*-Nitronitrosobenzene, 0.50 g. (3.3 mmoles), and 2,3-dimethyl-1,3-butadiene, 0.37 g. (4.5 mmoles), were dissolved in 20 ml. of nitromethane at 0°. The green color of the solution, caused by the monomeric nitroso compound, changed in about 15 min. to orange, indicating the

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[1] This work was supported by the Petroleum Research Fund; it was presented at the 14th Southeastern Regional Meeting, Gatlinburg, Tenn., November 3, 1962.

[2] J. Hamer and R. E. Bernard, *Rec. trav. chim.*, **81**, 734 (1962).

[3] C. K. Ingold and J. D. Weaver, *J. Chem. Soc.*, **125**, 1146 (1924).

[4] B. G. Gowenlock and W. Luetkke, *Quart. Rev.* (London), **12**, 321 (1958).

[5] A. Rodgman and G. F. Wright, *J. Org. Chem.*, **18**, 465 (1953).

[6] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 308.

[7] E. Ochai, *J. Org. Chem.*, **18**, 550 (1953).

[8] P. Baranger, J. Levisalles, and M. Vuidart, *Compt. rend.*, **236**, 1365 (1953).

[9] All melting points are uncorrected. Analysis by Galbraith Microanalytical Laboratories, Knoxville, Tenn. Infrared spectra measured in potassium bromide with a Beckman IR-5.

[10] E. Bamberger and E. Huebner, *Ber.*, **36**, 3803 (1903).

termination of the reaction. Upon cooling in a salt–ice bath, dark orange crystals of product IIa precipitated, m.p. 199–201°, yield, 0.3 g. Calculated for a 2:1 adduct $C_{18}H_{18}N_4O_6$: mol. wt., 386. Found (Rast method): mol. wt., 420.

Anal. Calcd. for $C_{18}H_{18}N_4O_6$: C, 55.89; H, 4.67; N, 14.51. Found: C, 55.80; H, 4.46; N, 15.02.

The filtrate was concentrated further at 0°, and the formed precipitate isolated. This product, Ia, was also orange, m.p. 119–120°, yield, 0.3 g. It was identified as the normal 1,4-adduct by its infrared spectrum.[2]

Anal. Calcd. for $C_{12}H_{14}N_2O_3$: C, 61.54; H, 5.98; N. 11.96. Found: C, 61.34; H. 6.09: N. 12.00.

Product Ia, 0.19 g. (0.8 mmole), was mixed with *p*-nitronitrosobenzene, 0.75 g. (5 mmole). An infrared spectrum in potassium bromide was taken from some of this mixture. The rest was dissolved in nitromethane at 0°, and allowed to stand for 24 hr. The solvent was then evaporated, and an infrared spectrum in potassium bromide was made of the residue. The two spectra were identical.

Product IIa, 0.39-g. (1 mmole), was suspended in 20 ml. of ice-cold chloroform, to which was added phosphorus trichloride, 2 ml. The suspension was allowed to reach room temperature and left overnight. The liquids were then removed under reduced pressure until a solid remained, which was the recrystallized from ethanol. The yield of 4,5-dimethyl-1,2-bis(*p*-nitrophenyl)-1,2,3,6-tetrahydropyradizine was 0.26 g. (74%), yellow crystals, m.p. 271–273° (lit.,[8] m.p. 272–272.5°).

Adducts of *m*-Nitronitrosobenzene.—*m*-Nitronitrosobenzene, 0.30 g. (1.9 mmoles), reacted with 2,3-dimethyl-1,3-butadiene, 0.22 g. (2.7 mmoles), in 35 ml. of dichloromethane at 0°. The solvent was evaporated, and a yellow solid was isolated. This solid was dissolved in anhydrous ether, and filtered through a column a column (12 × 10 cm.) packed with alumina. The first fraction yielded bright yellow crystals, m.p. 94–99°, yield, 0.26 g. It was identified as the normal 1,4-adduct (product Ib) by its infrared spectrum.[2]

Anal. Calcd. for $C_{12}H_{14}N_2O_3$: C, 61.54; H, 5.98; N, 11.96. Found: C, 61.34; H, 5.93; N, 11.91.

The second fraction yielded 25 mg. of bright yellow crystals, product IIb, m.p. 161.5–163°.

Anal. Calcd. for $C_{18}H_{18}N_4O_6$: C, 55.98; H, 4.67; N, 14.51. Found: C, 55.01; H, 4.37; N, 14.02.

Displacement Reactions of Neopentyl-type Sulfonate Esters[1]

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During the course of an investigation involving synthesis of derivatives of pentaerythritol, we observed that *O*-benzylidenepentaerythritol dibenzenesulfonate reacted with sodium iodide in acetone to form *O*-benzylidene-*O*-benzenesulfonylpentaerythritol iodide in high (89%) yield. A previous investigation[3] demonstrated that *O*-isopropylidenepentaerythritol di-*p*-toluenesulfonate reacted with potassium thiolacetate to give the product of monosubstitution in good yield. The high degree of selectivity at one of the two functional groups prompted a study directed towards a better understanding of this type of reaction.

A series of sulfonate esters of *O*-benzylidene- and *O*-isopropylidenepentaerythritol was prepared (Table I), and their reactivities with sodium iodide in acetone determined by varying reaction time and temperature (Table II). Although the monosubstitution product could be isolated in high yield from *O*-benzylidenepentaerythritol dibenzenesulfonate, this intermediate could then be converted into *O*-benzylidenepentaerythritol diiodide in high (85%) yield by a second reaction for a longer period of time and at a higher temperature. As expected, *O*-benzylidenepentaerythritol di-*p*-bromobenzenesulfonate reacted to allow isolation of essentially the same high yields of mono- and di-substitution products under somewhat milder conditions. In the experiment in which the monodisplacement compound was isolated as the principal product, a small amount (5%) of the diiodide was also separated. The di-*p*-toluenesulfonate was found to yield less of the monosubstitution product under conditions comparable to that applied with the dibenzenesulfonate. *O*-Isopropylidenepentaerythritol dibenzenesulfonate and di-*p*-toluenesulfonate were found to yield products of mono- and di-substitution under milder conditions than required for the corresponding *O*-benzylidene compounds.

A variety of displacement reactions has also been studied using cyanide ion as the nucleophilic reagent. Because of complications attending this type of reaction, several acyclic substrates were included in the study (Table III). 2,2-Dimethyl-1-propanol benzenesulfonate was found to react with sodium cyanide in a *N,N*-dimethylformamide (DMF) solution to give 3,3-dimethylbutyronitrile in a yield of 56%, and 1,3-propanediol dibenzenesulfonate gave glutaronitrile in a yield of 81%, accompanied by varying amounts of polymeric materials depending upon the reaction conditions employed. Nelson, Maienthal, Lane, and Benderly[4] reported that no products were isolable from the reactions of di-*p*-toluenesulfonates of 1,3-propanediol and 2-methyl-1,3-propanediol with potassium cyanide in ethylene glycol. 2,2-Dimethyl-1,3-propanediol dibenzenesulfonate reacted with sodium cyanide in a dimethylformamide solution to give 3,3-dimethylglutaronitrile, isolated in a yield of 28%, and 2,2-dimethylcyclopropanecarboxylic acid, separated from the reaction mixture following base-catalyzed hydrolysis in a yield of 28%. Its precursor, 2,2-dimethylcyclopropanecarbonitrile, was undoubtedly formed in a somewhat larger amount, but undoubtedly less than the 63% previously reported[4] from the reaction of 2,2-dimethyl-1,3-propanediol di-*p*-toluenesulfonate and potassium cyanide in ethylene glycol.

Displacement reactions of *O*-benzylidenepentaerythritol derivatives with sodium cyanide gave a single crystalline compound in all instances. The structure of this compound was assigned to be *O*-benzylidene-2,2-bis(hydroxymethyl)cyclopropanecarbonitrile (I) on the basis of a variety of observations. Alkaline hydrolysis gave a crystalline compound, with analysis agreeing with *O*-benzylidene-2,2-bis(hydroxymethyl)-cyclopropanecarboxamide (II). Acid hydrolysis with hydrochloric acid gave a liquid in low yield, presumed to be 2-chloromethyl-2-hydroxymethylcyclopropanecarboxylic acid lactone (III) on the basis of elemental analysis and of the nuclear magnetic resonance spec-

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(1) Abstracted from portions of the Ph.D. theses of Donald L. Schmidt and Samuel M. Dorrence and of the M.S. thesis of Vincent D. Calbi.

(2) An Air Force Officer on an Air Force Scholarship.

(3) P. Bladon and L. N. Owen, *J. Chem. Soc.*, 585 (1950).

(4) E. R. Nelson, M. Maienthal, L. A. Lane, and A. A. Benderly, *J. Am. Chem. Soc.*, **79**, 3467 (1957).