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Aromatic Nulceophilic Substitution. I. Preparation of Spiro Meisenheimer Complexes of Arenes

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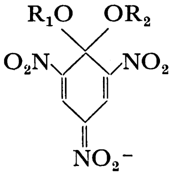
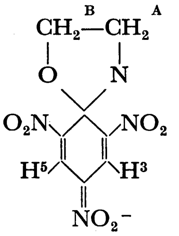
Since Jackson and Gazzolo,[1] and Meisenheimer[2] synthesized the so-called Meisenheimer Complex I (R_1, R_2; alkyl), a large number of the complexes have been prepared.[3] We have recently found that the spiro Meisenheimer complexes (II, III) having the $N-C_1-O$ bond could be isolated at room temperature (*ca.* 20°C) in the reaction of 1-[*N*-methyl-(2′-hydroxy)ethylamino]-2,4,6-trinitrobenzene (IV) or 1-[*N*-methyl-(2′-hydroxy)ethylamino]-2,4-dinitronaphthalene (V) with sodium methoxide.


I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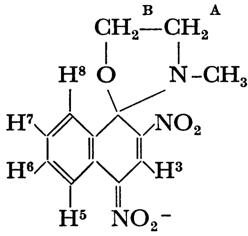
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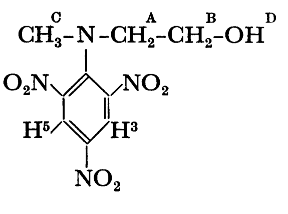
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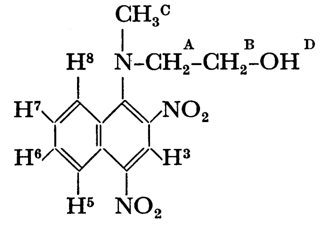
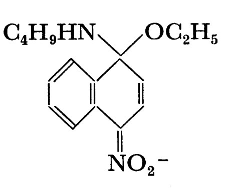

V

Preparation of II. When IV was treated with sodium methoxide in methanol at room temperature, II was formed. In the IR spectrum of V, the strong broad bands at 1220 and 1516 cm^{-1} could be assignable as the nitro group carrying the increased negative charge,[7] whereas these bands appeared at 1340 and 1516 cm^{-1} in that of IV. In the visible spectrum of II (3.47×10^{-5} mol/l), there are double maxima: λ_{max} 421 nm (ε 26100); λ_{max} 490 nm (sh, ε 16800). Not only the shape, but also the positions and intensities are similar to those of well-characterized Meisenheimer complexes.[3] In the NMR spectrum of II, the proton resonances at τ 1.41 (s, 2H), 5.77 (t, 2H), 6.62 (m, 2H), and 7.82 (s, 3H) are assignable as H^3 and H^5 (ring protons), H^B, H^A, and H^C ones, respectively, whereas H^3 and H^5 ones appeared at τ 1.17 (s, 2H) in that of IV. In the spectrum, a resonance appeared at τ 8.87 as a triplet. This resonance was due to the methyl group of diethyl ether, which was used for purification of II (see Experimental Section). The resonances of the methylene group of diethyl ether and the *N*-methylene one of II (or H_A resonance) overlapped each other at τ 6.62.

Preparation of III. Under the similar reaction condition to II, III was produced from V. In the IR spectrum of III, strong broad bands appeared at 1487 and 1150 cm^{-1}, assignable as the asymmetric and symmetric stretching absorptions of the nitro group,[8] whereas these bands appeared at 1510 and 1300 cm^{-1} in that of V. The visible spectrum of III (4.373×10^{-5} mol/l) has double maxima [λ_{max} 502 nm (ε 19400); λ_{max} 344 nm (ε 14200)], characteristic of 1,1-disubstituted 2,4-dinitronaphthalene σ-complexes.[4] Its shape, positions, and intensities are similar to those of VI, the presence of which was confirmed by Orvik and Bunnett.[9] The postulated structure of III was supported by its NMR spectrum. For III, H^3 and H^8 resonances appeared at τ 0.75 (s, 1H) and 1.18 (d, 1H), respectively, and H^5, H^6, and H^7 resonances overlapped at τ about 2.60 (m, 3H). These chemical shifts are different from those of V, in the NMR spectrum of which H^3 resonance appeared at τ 1.32 (s, 1H), H^5 and H^8 ones centered at τ 1.38 (m, 2H), and H^6 and H^7 ones centered at τ 2.07 (m, 2H).


VI

Acid Decomposition of Meisenheimer Complexes (II and III). Acid decomposition of various Meisen-

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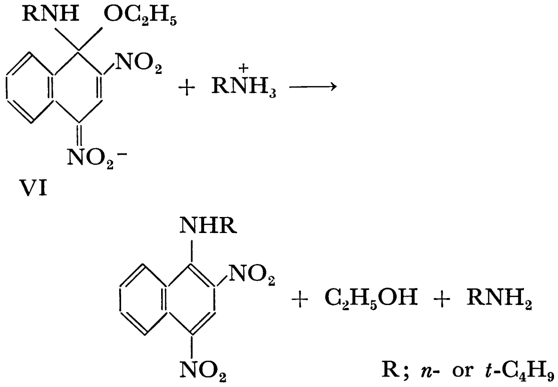
9) J. A. Orvik and J. F. Bunnett, *J. Amer. Chem. Soc.*, **92**, 2147 (1970).

heimer complexes have been reported.[10,11] Bunnett and Zahler[12] stated the formation of an anion by dissociation of a complex to depend upon the stability of the anion. The ease of anion seperation decreases in the order of alkoxide ions>amide ions. The decomposition of II and III with methanolic hydrochloric acid quantitatively gave IV and V, respectively. Our results are very consistent with the above order. Orvik and Bunnett[9] studied the nucleophilic substitution reaction of 2,4-dinitro-1-naphthyl ethyl ether (DNEE) with *n*- and *t*-butylamines in dimethyl sulfoxide solution, during the course of which VI, produced in the initial stage, was acid-catalyzed with butylammonium ion to seperate the alcohol. Our results are similar to those of Orvik and Bunnett.[9]



R; *n*- or *t*-C_4H_9

Experimental

Elemental analyses were performed in the Microanalytical Center of the University of Gunma. NMR spectra were recorded in DMSO-d_6 on a Varian A-60D spectrometer. IR spectra were measured in nujol mull on a Jasco DS-301 spectrophotometer. Visible spectra were recorded in methanol on a Hitachi-124 UV-VIS spectrophotometer. All melting points were uncorrected. The solvents and reagents were purified by the usual methods.

1-[N-*Methyl-(2′-hydroxy)ethylamino*]*-2,4,6-trinitrobenzene (IV).* To a stirred solution of 3.2 g (0.043 mol) of *N*-methylethanolamine (NMEA) in 100 ml of acetone was added at room temperature 5.0 g (0.020 mol) of picryl chloride in 30 ml of acetone. After an additional 4 hrs' stirring at 40°C, the mixture was poured into 200 ml of ice-water, filtered, and dried. Recrystallization from methanol yielded 5.0 g of IV (86%, based on picryl chloride), mp 138.0—139.0 °C. IR (Nujol): ν_{OH} 3570, 3400 cm^{-1}, ν_{NO_2} 1516, 1332 cm^{-1}, ν_{Ar-N} 1352 cm^{-1}. NMR: τ_{Me_4Si} 5.46 (s, 1H, H^D).

The formation of 1-[2′-(*N*-methylamino)ethoxy]-2,4,6-trinitrobenzene was excluded by the evidence that in the IR spectrum of IV the band attributable to the ether bond [C(sp^2)-O-C(sp^3)] was not found by comparison of the spectrum of picryl ethyl ether.[13]

1-[N-*Methyl-(2′-hydroxy)ethylamino*]*-2,4-dinitronaphthalene (V).* To a stirred solution of 3.2 g (0.043 mol) of NMEA in 50 ml of acetone was added at room temperature 5.0 g (0.020 mol) of 2,4-dinitro-1-naphthyl chloride (DNC) in 50 ml) of acetone. After the temperature had been raised to 40°C, the mixture was stirred for 8 hr. Then, the mixture was poured into 300 ml of ice-water. The aqueous mixture was extracted with three 50 ml portions of benzene. After drying of the benzene solution over calcium chloride, the distillation of benzene produced crude V. Further, chromatographic separation was carried out on a column of sicila gel. Recrystallization from diethyl ether-petroleum ether yielded 4.0 g (69%, based on DNC), mp 77.0—77.5°C. IR (Nujol): ν_{OH} 3518 cm^{-1}, ν_{NO_2} 1510, 1305 cm^{-1}, ν_{Ar-N} 1305 cm^{-1}. NMR: τ_{Me_4Si} 5.18 (s, 1H, H^D). Found: C, 53.33; H, 4.66%. Calcd for $C_{13}H_{13}N_3O_5$: C, 53.61; H, 4.50%.

The formation of 1-[2′-(*N*-methylamino)ethoxy]-2,4-dinitronaphthalene was excluded by comparison of IR spectra of IV and DNEE.[9]

Preparation of spiro Meisenheimer Complexes (II and III). A typical procedure is noted below in the case of III. When 7 ml (0.0045 mol) of methanolic sodium methoxide (0.638 mol/l) was added to a stirred solution of 1.310 g (0.0045 mol) of V in 30 ml of methanol at room temperature under nitrogen stream, the solution became red immediately. After an additional 30 mins' stirring, the solution was concentrated by evaporation of methanol at 30°C under reduced pressure. Further, the precipitate was filtered, washed with three 20 ml portions of diethyl ether in a dry box. After that, the precipitate was dried. Yield 1.0 g (71%, based on V). The complex (II) was obtained by the same method in a 65% yield. Found: C, 50.22; H, 3.62; N, 13.22%. Calcd for $C_{13}H_{12}N_2O_5Na$ (III): C, 49.84; H, 3.86; N, 13.41%. Found: C, 38.62; H, 4.01; N, 16.46%. Calcd for $C_9H_9O_7N_4Na \cdot \frac{1}{2}(C_4H_{10}O)$ (II): C, 38.26; H, 4.08; N, 16.23%.

Acid decomposition of spiro Meisenheimer Complexes (II and III). When an equimolar amount of hydrochloric acid in 10 ml of methanol was added to a stirred solution of 0.50 g (0.0014 mol) of II in 15 ml of methanol at room temperature, the mixture became immediately yellow. This mixture was poured into 200 ml of ice-water, filtered, and dried. Thin layer chromatography and mixed melting point test proved this compound to be IV. Yield 0.40 g (98%) for crude IV. The same treatment of 0.5 g (0.0016 mol) of III yielded 0.45 g (97%) of crude V.

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