ml of isopropyl alcohol was added 0.5 g of sodium borohydride, and the solution was stirred for 0.5 hr and diluted with water, and the solid crystallized from alcohol: mp 124–125° dec; λ_{max} ($\epsilon \times 10^{-3}$) 250 (22.8) and 360 nm (1.8); mass spectrum *m/e* 388 (15), 357 (100), 327 (23), 313 (13), 311 (14), 271 (10), 165 (8), and 57 (30).

Anal. Calcd for $C_{21}H_{28}N_2O_5$: C, 64.9; H, 7.3; N, 7.2. Found: C, 64.9; H, 7.0; N, 7.0.

2′,6′-Diphenyl-3-hydroxy-1-methoxyspiro[indoline-2,4′-[4′*H*]-pyran] (**12c**).—Compound **9c** was reduced with sodium borohydride as described for **12b** giving **12c**: mp 127–130°; mass spectrum *m/e* 383 (20), 252 (100), 322 (47), 246 (12), 233 (13), 218 (8), 217 (9), and 105 (36).

Anal. Calcd for $C_{25}H_{21}NO_3$: C, 78.3; H, 5.5; N, 3.7. Found: C, 77.9; H, 5.2; N, 3.5.

2′,6′-Di-*tert*-butyl-6-nitro-3-oxospiro[indoline-2,4′-[4′*H*]pyran] (**13b**).—A solution of 0.5 g of **12b** in 25 ml of degassed chloroform was acidified with 0.5 ml of acetic acid and concentrated under vacuum. The residue was recrystallized from alcohol giving 0.4 g of **13b**: mp 238–239°; λ_{max} ($\epsilon \times 10^{-3}$) 247 (21.6), 273 (15.2), and ~305 nm (11.1); mass spectrum *m/e* 356 (12), 327 (100), 315 (62), 313 (29), 282 (10), 281 (9), 271 (42), 267 (9), 266 (9), 225 (5), and 57 (13).

Anal. Calcd for $C_{20}H_{24}N_2O_4$: C, 67.4; H, 6.8; N, 7.9. Found: C, 67.1; H, 6.7; N, 7.9.

2′,6′-Diphenyl-3-oxospiro[indoline-2,4′-[4′*H*]pyran] (**13c**).—Compound **12c** was allowed to react as described for the preparation of **13b** giving **13c**: yield 65%; mp 208–209° from alcohol; mass spectrum *m/e* 351 (14.3), 324 (6), 323 (35), 322 (100), 246 (11), 218 (13), 217 (17), 216 (8), and 105 (20).

Anal. Calcd for $C_{24}H_{17}NO_2$: C, 82.0; H, 4.9; N, 4.0. Found: C, 81.8; H, 5.0; N, 4.0.

2,′6′-Diphenylspiro[indoline-2,4′-[4′*H*]pyran] (**14**).—A solution of 0.2 g of **13c** in 10 ml of ether was treated with 0.1 g of lithium aluminum hydride. After the mixture had been stirred for 15 min, an nmr spectrum was determined on a sample (for results see discussion of nmr spectrum).

4-(2-Aminobenzylidene)-2,6-diphenyl-4*H*-pyran (**15**). **Method A.**—A solution of 0.5 g of **2c** in 50 ml of hot alcohol was treated with 2 g of sodium sulfide, refluxed overnight, and filtered; the hot filtrate was diluted with water and chilled. The solid was collected and crystallized from aqueous alcohol giving 0.3 g of **15**: mp 107–108°; mass spectrum *m/e* 337 (100), 336 (52), 232 (19), 230 (14), 168.5, 115 (7), 105 (26), and 77 (24).

Anal. Calcd for $C_{24}H_{19}NO$: C, 85.4; H, 5.6; N, 4.1. Found: C, 85.3; H, 5.5; N, 4.2.

Method B.—The ether solution of **14** was allowed to stand for 1 hr, and the nmr spectrum was identical with that of **15** prepared by method A.

Acknowledgment.—We wish to acknowledge the assistance of Mr. D. P. Maier for the mass spectral data and of Dr. T. H. Regan for the low-temperature nmr spectra.

Registry No.—**1**, 17539-77-4; **2a**, 40576-44-1; **2b**, 40576-45-2; **2c**, 40576-46-3; **3a**, 40576-47-4; **3b**, 40576-48-5; **3c**, 40576-49-6; **4**, 40576-50-9; **5**, 40576-51-0; **6a**, 40576-52-1; **6b**, 40576-53-2; **6c**, 40576-54-3; **7a**, 40576-55-4; **7b**, 40576-56-5; **7c**, 40576-57-6; **8**, 40576-58-7; **9a**, 40576-59-8; **9b**, 40576-60-1; **9c**, 40576-61-2; **11a**, 40576-62-3; **11b**, 40576-63-4; **12b**, 40576-64-5; **12c**, 40576-65-6; **13b**, 40576-66-7; **13c**, 40576-67-8; **14**, 40576-68-9; **15**, 40576-69-0; 2,6-di-*tert*-butyl-4-methylpyrylium perchlorate, 14604-52-5; *o*-nitrophenylacetic acid, 3740-52-1; 2,4-dinitrotoluene, 121-14-2; 2,4-dinitrochlorobenzene, 97-00-7.

Intermediates in Nucleophilic Aromatic Substitution. X.[1] Synthesis of *N*-Methyl-β-aminoethyl Nitroaryl Ethers *via* an Unusual Smiles Rearrangement

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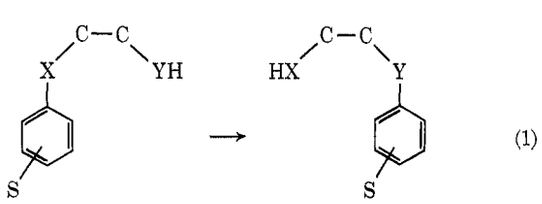
N-Methyl-β-aminoethyl nitroaryl ethers undergo a Smiles rearrangement into *N*-methyl-*N*-β-hydroxyethylnitroarylamines so readily that the aryl ethers cannot be prepared by obvious methods. However, when the aromatic system is sufficiently activated so that in the presence of base the aryl amine can be converted into a cyclic Meisenheimer complex, the Smiles rearrangement can be reversed and the ether obtained by rapidly acidifying the Meisenheimer complex. The aryl ether is the kinetically controlled product of the ring opening of the complex and can be trapped and isolated in the form of its ammonium salt.

Intramolecular rearrangements of the type shown in eq 1 are known as Smiles[3] rearrangements. The reaction is in fact an intramolecular activated (S = activating substituent) nucleophilic aromatic substitution. In most cases the displacement is by Y^- rather than by YH and thus the presence of a strong base is usually required. When YH is NH_2 or NHR a base may or may not be necessary for the reaction to proceed. The carbon chain joining X and Y may be saturated or be part of an aromatic system. The field has been reviewed recently.[4]



(1)

In this paper we are concerned with X = O, YH = NH_2 or NHR, and in particular with the inverse combination X = NH or NR, YH = OH. Most examples from the early literature[5] involve compounds where the C–C chain is part of an aromatic ring.[6]

More recently examples where the C–C chain is saturated have been reported by Kleb;[7] reaction 2 is representative. The rearrangement of **1** to **2** occurs so rapidly that **1** and a variety of similar β-aminoalkyl 4-nitrophenyl ethers could not be prepared from obvious starting materials. In fact the occurrence of reaction 2

(1) Part IX: C. F. Bernasconi and R. G. Bergstrom, *J. Amer. Chem. Soc.*, **95**, 3603 (1973).

(2) Alfred P. Sloan Fellow, 1971–1973.

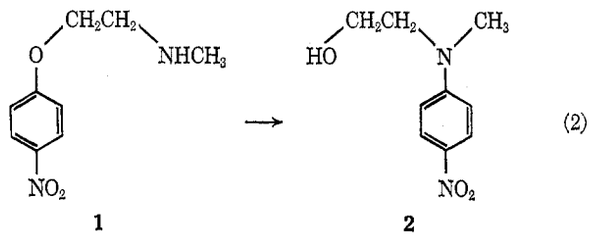
(3) (a) L. A. Warren and S. Smiles, *J. Chem. Soc.*, 956 (1930); (b) W. J. Evans and S. Smiles, *ibid.*, 181 (1935).

(4) (a) W. E. Truce, E. M. Kreider, and W. W. Brand, *Org. React.*, **18**, 99 (1970); (b) H. J. Shine, "Aromatic Rearrangements," Elsevier, New York, N. Y., 1967, p 307.

(5) J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, **49**, 275 (1951).

(6) K. C. Roberts and C. G. M. de Worms, *J. Chem. Soc.*, 737 (1934).

(7) K. G. Kleb, *Angew. Chem., Int. Ed. Engl.*, **7**, 291 (1968).



(2)

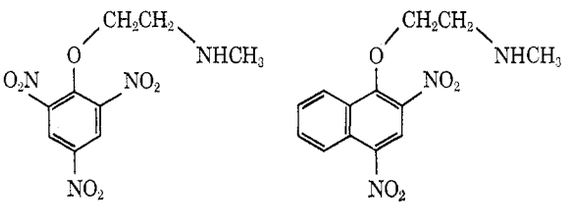
1 2

had to be inferred indirectly from a sequence where **1** was an intermediate.[7]

That reactions such as 2 are strongly favored thermodynamically in the direction indicated is in agreement with observations on a large number of *inter*molecular aromatic nucleophilic displacements of oxygen bases by amines.[8] We now report three examples in which, by judicious choice of conditions, the reaction can be forced into the reverse direction and the aryl ether can be isolated as the amine hydrochloride.

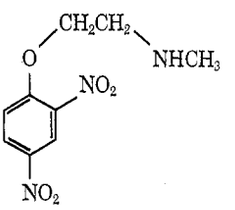
Results

***N*-Methyl-β-aminoethyl Picryl Ether (4a).**—Despite considerable effort, we were unable to synthesize *N*-methyl-β-aminoethyl picryl ether (**4a**), in an unreactive form such as the amine hydrochloride, by straightforward methods.[9] *N*-Methyl-*N*-β-hydroxyethyl picramide (**5a**) and/or other unidentified products formed instead.



4a

4b



4c

On the other hand, the following procedure starting with *N*-methyl-*N*-β-hydroxyethyl picramide (**5a**) makes the picryl ether **4a** easily available. When base is added to a solution of **5a** either in a hydroxilic or a dipolar aprotic solvent, the cyclic Meisenheimer complex **7a** is formed immediately according to sequence 3. **7a** is very stable and can readily be isolated from ethanol, as was shown earlier by Hünig and Fleckenstein.[11] The spectra in Figure 1, taken in aqueous solution, of **5a** show the gradual conversion of **5a** into

(8) For recent reviews see (a) C. F. Bernasconi, *MTP Int. Rev. Sci., Org. Chem. Ser. 1*, **3**, 33 (1973); (b) F. Pietra, *Quart. Rev., Chem. Soc.*, **23**, 504 (1969); (c) J. Miller, "Aromatic Nucleophilic Substitution," Elsevier, New York, N. Y., 1968; (d) T. J. de Boer and I. P. Dirkx in "The Chemistry of the Nitro and Nitroso Groups," part I, H. Feuer, Ed., Interscience, New York, N. Y., 1969, p 487.

(9) These included the reaction of picryl chloride with *N*-methylethanolamine under protection of the amino group by the *tert*-butylcarbonyl group[10] in basic solution under a variety of conditions, the attempted nitration of *N*-methyl-β-aminoethyl phenyl ether, and some others.

(10) B. Iselin and R. Schwyzer, *Helv. Chim. Acta*, **44**, 169 (1961).

(11) S. Hünig and E. Fleckenstein, private communication (1970).

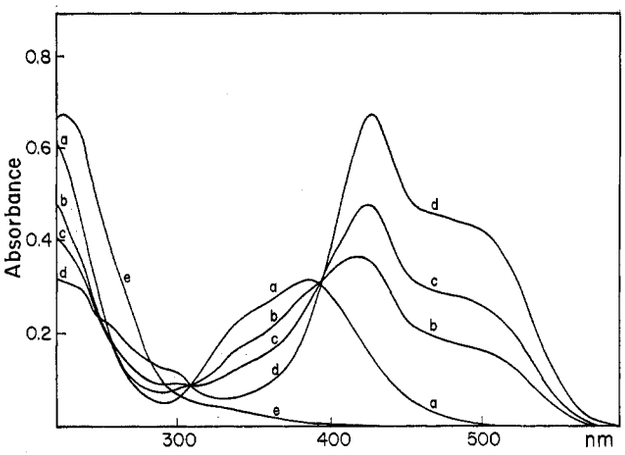
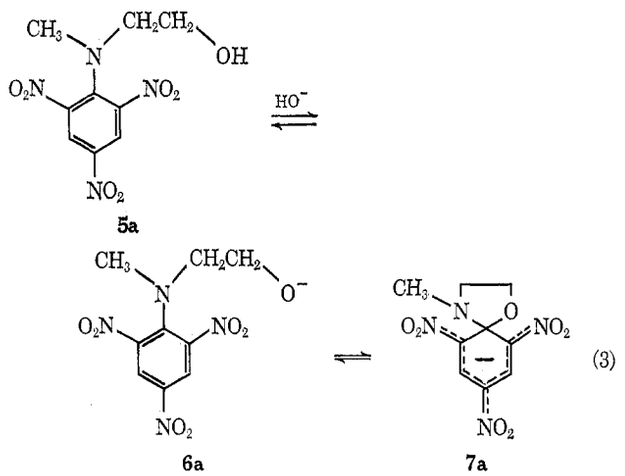


Figure 1.—Absorption spectra in the picryl system in aqueous solution at 25°: a–d, **5a** as a function of pH, $[\mathbf{5a}]_0 = 3 \times 10^{-5}$ *M*; a, pH 6.00; b, pH 9.40; c, pH 9.80; d, pH 12.00 (conversion to **7a** is complete at pH 12.00); e, after acidification of a solution of **7a**, spectrum of **8a** (3×10^{-5} *M*) in 1 *M* HCl.



5a **6a** **7a**

(3)

7a as the pH is increased. At pH ≥12 the conversion is virtually quantitative.

When a dilute aqueous solution (~10^{-4} *M*) of **7a** is added to a large enough volume of a 0.01 *M* HCl solution so that after neutralizing of all the base the pH is ≤3, the ether **4a** is formed quantitatively judging by uv spectroscopy; it is trapped as the corresponding ammonium ion. With minor modifications the procedure is conveniently carried out on a preparative scale in ethanolic solution from which the hydrochloride of **4a** is isolated in good yield.

Below pH 5 the ether solution is quite stable; above pH 5 it is gradually converted into the original starting material **5a**, the more rapidly the higher the pH.

***N*-Methyl-β-aminoethyl 2,4-Dinitronaphthalene Ether (4b).**—The reactions affording the picryl ether **4a** apply equally for the 2,4-dinitronaphthyl system. In fact *N*-methyl-*N*-β-hydroxyethyl 2,4-dinitronaphthyl amine (**5b**) is about as readily converted to the cyclic Meisenheimer complex **7b** as **5a** is converted to **7a**. In aqueous solution containing 2% DMSO (v/v) (added for solubility reasons) the conversion is complete at pH ≥12. Spectra of solutions of **5b** at various pH values are shown in Figure 2.

Acidification of **7b** with acid of the same concentration as for **7a** affords the ammonium salt of **4b** in quantitative yield (**8b**). As in the case of **4a** an increase in

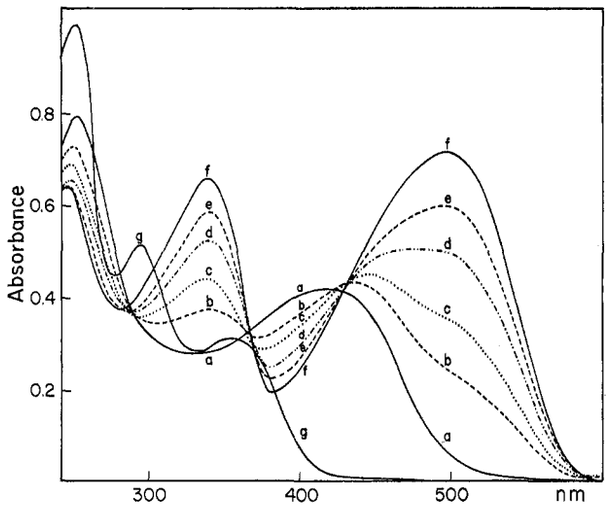
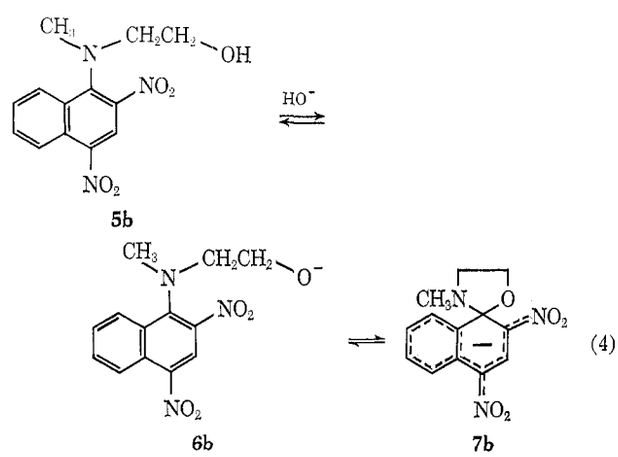
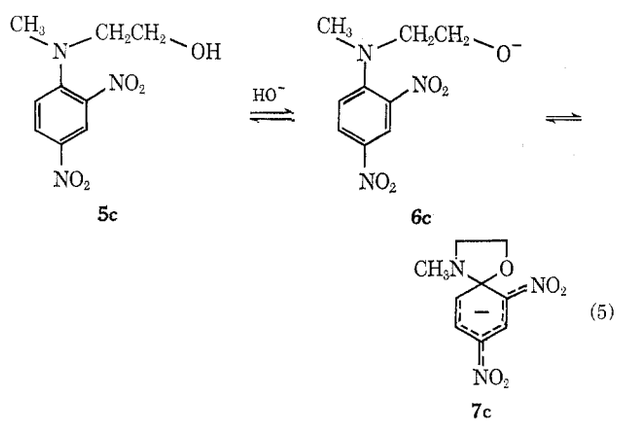


Figure 2.—Absorption spectra in the 2,4-dinitronaphthyl system in 2% DMSO–98% H_2O (v/v) at 25°: a–f, **5b** as a function of pH, $[\mathbf{5b}]_0 = 5.5 \times 10^{-5}$ *M*; a, 0.01 *M* HCl; b, pH 9.085; c, pH 9.375; d, pH 9.780; e, pH 10.115; f, 0.01 *M* NaOH (conversion to **7b** is complete in 0.01 *M* NaOH); g, after acidification of a solution of **7b**, spectrum of **8b** (5.5×10^{-5} *M*) in 0.01 *M* HCl.



pH above 5 leads to gradual conversion of **4b** to **5b**, which becomes more rapid as the pH is increased. Ethanol is again a convenient solvent for preparative work.

N-Methyl-β-aminoethyl 2,4-Dinitrophenyl Ether (4c).—As has been shown recently,[12] conversion of **5c** to **7c** is insignificant in strongly alkaline aqueous solutions but extensive in aqueous solutions containing ≥80% (v/v). In 85% DMSO (v/v) and 0.01 *M* $(CH_3)_4$-NOH the conversion into **7c** is quantitative.



Attempts to transform **7c** quantitatively into **8c**, *i.e.*, the ammonium salt of **4c**, by acidifying the solution of **7c** in 90% DMSO (v/v) with aqueous acid were only successful when ≥1 *M* HCl was used. Significant amounts of **5c** were formed in more dilute acid. The yields of **4c** (**8c**), which tended to be variable when dilute HCl was employed, could be improved by adding the solution of **7c** dropwise to the acid under vigorous stirring; with such efficient mixing the product distribution was about 75% **4c** (**8c**) and 25% **5c** in 0.02 *M* HCl, end pH ~2.

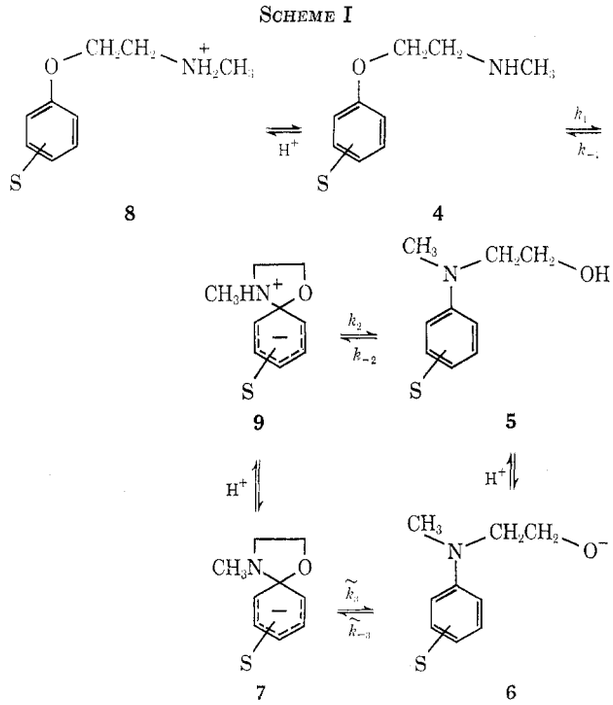
When the Meisenheimer complex was acidified with a ≥0.02 *M* HCl solution in 90% DMSO (v/v) instead of aqueous acid, **8c** was formed quantitatively, as determined spectrophotometrically.

From a preparative point of view the necessity to generate **7c** in the solution containing DMSO is a drawback since it is difficult to isolate the product. The possibility of generating **7c** in the dioxane–methanol–methoxide ion system[13] was explored. Acidifying the complex with 1.2 *M* HCl in 90% dioxane–10% water (v/v) yields about 20% of **8c**.

Discussion

Our approach to the synthesis of **4a**, **4b**, and **4c** and the experimental observations reported under Results are best discussed with reference to Scheme I, which includes the species believed to play a significant role in our reaction system.[14]

SCHEME I



The behavior of the picryl and the 2,4-dinitrona-

(12) C. F. Bernasconi and R. H. de Rossi, *J. Org. Chem.*, **38**, 500 (1973).

(13) E. J. Fendler, J. H. Fendler, W. E. Byrne, and C. E. Griffith, *J. Org. Chem.*, **33**, 4141 (1968).

(14) The symbols for the rate coefficients are consistent with the ones used in representing the mechanism of nucleophilic aromatic substitution reactions by amines.[8a]

phthyl systems can be rationalized as follows. Upon acidifying an alkaline solution of **7a** (**7b**), there must be a rapid protonation of **7a** (**7b**) to form **9a** (**9b**). Following that, **9a** (**9b**) may decompose either toward **4a** (**4b**) and/or toward **5a** (**5b**). It is to be noted that step **9a** (**9b**) → **5a** (**5b**) is practically irreversible, whereas the reaction **4a** (**4b**) ⇌ **9a** (**9b**) is reversible. Formation of **4a** (**4b**) apparently occurs faster than the irreversible transformation into **5a** (**5b**). This is not unexpected, since frequently $k_{-1} \gg k_2$ in similar *inter*molecular substitutions involving secondary amines as nucleophiles.[8]

By keeping the pH low enough the kinetically favored product **4a** (**4b**) is converted into its unreactive from **8a** (**8b**) and formation of **5a** (**5b**) is prevented altogether.

If the conversion of **9a** (**9b**) to **4a** (**4b**) is carried out in a less acidic medium or if the pH of a solution containing **8a** (**8b**) is raised, the system is gradually drained off into the thermodynamically more stable form **5a** (**5b**), or, at high pH (~12), into **7a** (**7b**).

Similar considerations apply to the 2,4-dinitrophenyl system. However, the observation of increased yields of **8c** under vigorous stirring and/or when more concentrated acid was used indicates that under certain conditions the events are not only controlled by chemical rate processes but also by the rate at which the solutions becomes homogeneous (on the microscopic level) after mixing.

Thus in the early stages of the mixing process the pH of the microenvironment around **7** is still rather high and therefore little of **9**, which could decompose to **8** *via* **4**, is formed. On the other hand **5** may form *via* **6** as soon as the pH of the microenvironment has dropped low enough as to make the process **7** ⇌ **6** → **5** thermodynamically favorable, but not yet low enough to form significant amounts of **9**. Since we have indications that the pK_a's of **9** are around 6–7,[15] this situation must indeed arise: **5a** and **5b** become favored over their respective complexes **7a** and **7b** at pH <9.4 (see Figures 1 and 2), **5c** is always thermodynamically favored over **7c** in aqueous solution,[12] whereas in 90% DMSO **5c** is estimated to become favored when $[HO^-] < 10^{-5}\ M$.

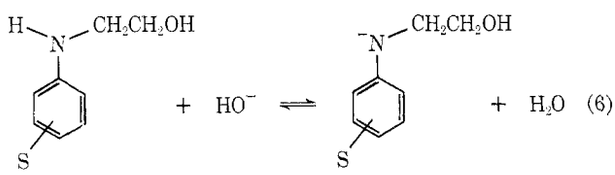
Whether there is sufficient time for a significant amount of **5** to form *via* **6** before the pH drops further (now favoring process **7** ⇌ **9** ⇌ **4** → **8**) depends on the magnitude of $\tilde{k}_3$.

In the case of **7a** and **7b** $\tilde{k}_3 < 10^{-2}$ sec^{-1} in aqueous solution;[15] this is much too low for the reaction **7a** (**7b**) ⇌ **6a** (**6b**) → **5a** (**5b**) to make any significant progress during the mixing process. For **7c** in 90% DMSO, $\tilde{k}_3 < 9$ sec^{-1},[12] which apparently is also too low and explains why no **5c** is formed upon acidification of a basic solution of **7c** in 90% DMSO with an acid solution in 90% DMSO.

For **7c** in more highly aqueous DMSO $\tilde{k}_3$ has been determined as follows: 923, 650, 332, 116, 53, and 9 sec^{-1} in 2, 20, 50, 65, 80, and 85% DMSO,[12] respectively. The magnitude of $\tilde{k}_3$ in solutions with a not too high DMSO content, say 65% or less, is quite high and appears sufficient for the reaction **7c** ⇌ **6c** → **5c** to make some progress, even if the mixing time were in the 10-msec range. It is to be realized that when the aqueous acid and **7c** in basic 90% DMSO are added together, it not only takes time for the pH of the microenvironment to be lowered but also for part of the DMSO around **7c** to be replaced by water molecules. However, since a relatively small increase of the water content (*very* early stage of mixing process) has already a large accelerating effect on $\tilde{k}_3$, $\tilde{k}_3$ must apparently have reached a high enough value by the time the pH of the microenvironment has somewhat dropped to allow **5c** to accumulate on thermodynamic grounds. Better stirring as well as the use of a higher acid concentration allow the microenvironment of **7c** to reach a relatively low pH value at an earlier stage of the mixing process, thus cutting down the time during which formation of **5c** *via* **6c** competes with formation of **8c**. Both factors are expected to enhance the yield of **8c**, in agreement with experimental observation.

The method described here for synthesizing *N*-methyl-*β*-aminoethyl nitroaryl ethers is likely to be applicable to compounds with activating groups other than nitro. Based on the accumulated understanding of the relation between structure and thermodynamics as well as kinetic stabilities of Meisenheimer complexes,[16] one may in fact predict that the method is likely to work for all systems in which the Meisenheimer complex is as stable as or more stable than that of the 2,4-dinitrophenyl system.

On the other hand the method appears ill suited for systems lacking the *N*-methyl or some other *N*-alkyl group for two reasons. (1) In analogy to other systems, formation of the cyclic Meisenheimer complex is expected to compete unfavorably with proton loss according to eq 6 and possibly with nucleophilic



attack by HO^- at the 3 position of the aromatic ring. (2) Even if some cyclic Meisenheimer complex is formed, acidification would not yield significant amounts of the *β*-aminoethyl aryl ether because very likely $k_2 \gg k_{-1}$.[8a]

In fact, when a basic solution of *N*-*β*-hydroxyethyl picramide, which showed a spectrum somewhat similar to the one of **7a**, was acidified, the starting material was recovered almost quantitatively.

Experimental Section

***N*-Methyl-*N*-*β*-hydroxyethyl picramide (5a)** was prepared by adding 7.14 g (95 mmol) of freshly distilled *N*-methylethanolamine in 20 ml of ethanol to a solution of 11.8 g (47.5 mmol) of picryl chloride in 200 ml of ethanol. The dark red solution was refluxed for 15 min. After cooling, crystallization of the product started immediately, yielding 94% of the product, mp 144° after two recrystallizations from ethanol. *Anal.* Calcd for $C_9H_{10}N_4O_7$: C, 37.80; H, 3.52; N, 19.60. Found: C, 37.73; H, 3.64; N, 19.70. Uv max (H_2O) 384 nm[17] (ϵ 10,700).[17]

***N*-Methyl-*N*-*β*-hydroxyethyl 2,4-dinitronaphthylamine (5b)** was prepared after the same procedure as for **5a** by starting with

(15) C. F. Bernasconi, R. H. de Rossi, and C. L. Gehriger, unpublished results.

(16) For recent reviews see (a) M. R. Crampton, *Advan. Phys. Org. Chem.*, **7**, 211 (1969); (b) M. J. Strauss, *Chem. Rev.*, **70**, 667 (1970).

(17) From spectrum a in Figure 1. Possibly in equilibrium with traces of **8a** and/or **9a** and **7a**.

2,4-dinitrochloronaphthalene. Refluxing time was 2 hr. Purification was achieved by redissolving the filtered crystals in ethanol and precipitating by adding the solution to ice-cold water, yield 96%, mp 73–73.5°. *Anal.* Calcd for $C_{13}H_{13}N_3O_5$: C, 53.70; H, 4.45; N, 14.40. Found: C, 53.75; H, 4.38; N, 14.48. Uv max [2% DMSO–98% H_2O (v/v)] 420 nm[18] (ϵ 7620).[18]

N-Methyl-N-β-hydroxyethyl 2,4-dinitroaniline (5c) was available from a previous study.[12]

Meisenheimer complexes 7a and 7b were prepared by adding a solution of 4 mmol of KOH in 10 ml of ethanol to a solution of 2 mmol of **5a** (**5b**) in 10 ml of ethanol. **7a** was precipitated with cold ether, yield 93%. Recrystallization from ethanol[19] yielded a product decomposing at 298°. *Anal.*[20] Calcd for $C_9H_9N_4O_7K$: C, 33.33; H, 2.80; M, 17.28. Found: C, 32.87; H, 2.91; N, 17.14. Pmr (DMSO-d_6) δ 2.11 (s, 3, CH_3N), 3.24 (m, 2, CH_2N), 4.13 (m, 2, CH_2O), and 8.51 ppm (s, 2, ring); uv max (H_2O) 427 nm (ϵ 22,500). **7b** after crystallization from the reaction solution was filtered and washed with ether *Anal.*[20] Calcd for $C_{13}H_{12}N_3O_5K$: C, 47.42; H, 3.65; N, 12.77. Found: C, 47.32; H, 4.56; N, 12.63. Pmr (DMSO-d_6) δ 1.90 (s, 3, CH_3N), 3.21 (m, 2, CH_2N), 4.25 (m, 2, CH_2O), 8.95 (s, 1, H_3),[21] 8.6 (m, 1, H_8),[21] and 7.3 ppm (broad m, 3, $H_{5,6,7}$);[21] uv max [2% DMSO–98% H_2O (v/v)] 497 nm (ϵ 13,000) and 338 (11,900); uv max (DMSO) 518 nm (ϵ 28,300) and 362 (17,000).

N-Methyl-β-aminoethyl picryl ether hydrochloride (8a) was prepared by rapidly adding 0.5 ml of concentrated HCl to a solution of 730 mg (2.25 mmol) of Meisenheimer complex **7a** in 70 ml of ethanol. KCl precipitated and was filtered off, and the solution was concentrated for crystallization of the product, which was obtained in 76% yield, mp 140°. Recrystallization did not increase the melting point. *Anal.* Calcd for $C_9H_{11}N_4O_7Cl$: C, 33.48; H, 3.44; N, 17.35. Found: C, 33.41; H, 3.53; N, 17.20.

N-Methyl-β-aminoethyl 2,4-dinitronaphthyl ether hydrochloride (8b) was prepared by adding a solution of 300 mg (0.91 mmol) of Meisenheimer complex **7b** in 30 ml of ethanol to 15 ml of ethanolic 0.5 *M* HCl; this latter solution was prepared from HCl gas and ethanol. After the precipitated KCl was filtered off the solution was added to 50 ml of ether, whereupon the product precipitated. For purification the filtered product was redissolved in acidic ethanol and precipitated with ether, yield 50%, mp 180–181°. *Anal.* Calcd for $C_{13}H_{14}N_3O_5Cl$: C, 47.71; H, 4.27; N, 12.84. Found: C, 47.50; H, 4.35; N, 12.71.

N-Methyl-β-aminoethyl 2,4-Dinitrophenyl Ether Hydrochloride (8c).—A 0.25-ml portion of a 14 *M* KOH solution in water was added to 834 mg (3.46 mmol) of *N*-methyl-*N*-β-hydroxyethyl 2,4-dinitroaniline (**5c**) in 2.5 ml of DMSO. The resulting emulsion was added to 10 ml of 1.2 *M* HCl in 90% DMSO. After addition of 4 ml of ethanol most of the KCl precipitated; it was filtered off and the solvent was evaporated at about 40° (0.3 mm). The residue was extracted with ether to remove DMSO and traces of **5c**. The last traces of DMSO were removed by column chromatography with alumina oxide (Baker Analyzed Grade, activity grade I, acid). The ether hydrochloride **8c** was eluted with 0.5 *M* HCl in ethanol. Precipitation with ether, redissolving in acidic ethanol, and reprecipitation with ether yielded a product with mp 182–183°. *Anal.* Calcd for $C_9H_{12}N_3O_5Cl \cdot H_2O$: C, 36.7; H, 4.75; N, 14.25. Found: C, 37.01; H, 4.45; N, 14.12.

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Registry No.—**5a**, 40711-00-0; **5b**, 40711-01-1; **5c**, 37580-86-2; **7a**, 40704-76-5; **7b**, 40704-77-6; **8a**, 40711-03-3; **8b**, 40711-04-4; **8c**, 40711-05-5; *N*-methylethanolamine, 109-83-1; picryl chloride, 88-88-0; 2,4-dinitrochloronaphthalene, 2401-85-6.

(18) From spectrum a in Figure 2. Probably in equilibrium with traces of **8b** as indicated by preliminary kinetic experiments.

(19) The crystallization was very slow. Use of trimethylbenzylammonium ion as gegenion gives better crystallization characteristics.[11]

(20) Meisenheimer complexes notoriously yield poor analyses.

(21) Assignments as for the spiro complex from 1-(2-hydroxyethoxy)-2,4-dinitronaphthalene.[22]

(22) E. J. Fendler, J. H. Fendler, W. E. Byrne, and C. E. Griffin, *J. Org. Chem.*, **33**, 4141 (1968).

Photoreduction of 1,9-Methanodecal-2-ones. Comparison of Cis and Trans Isomers

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Photoreduction of *cis*-1,9-methano-10-methyldecal-2-one (**1c**) occurs with retention of the stereochemistry at C9 to give *cis*-9,10-dimethyldecal-2-one (**3c**); however, photoreduction of the trans isomer **1t** occurs with inversion of the stereochemistry at C9 to also give **3c** as the major product. When the angular methyl group is absent, photoreduction of either isomer occurs with retention of the stereochemistry at C9. A conformational argument is offered as a possible explanation for this difference.

Irradiation (n–π^*) of bicyclo[4.1.0]heptan-2-ones in 2-propanol usually affords cyclohexanones derived from reductive opening of the C1–C7 cyclopropyl bond.[1] Recently, it has been reported that this reaction course can be altered when the bicyclo[4.1.0]-heptan-2-one moiety is part of a decalone or steroidal ketone molecule. Photoreduction of either *cis*- or *trans*-4,5-methanocholestan-3-one gave predominantly *cis*-5-methylcholestan-3-one.[2] Likewise, photoreduction of *trans*-dihydromayurone gave *cis*-8,8,9,10-tetramethyldecal-2-one as one of several products, but no *trans*-8,8,9,10-tetramethyldecal-2-one was found.[3]

From inspection of molecular models, one would *a priori* predict that both *trans*-4,5-methanocholestan-3-one and *trans*-dihydromayurone should photoreduce with retention of the trans stereochemistry. The present study reports the results from photoreduction of a series of isomeric 1,9-methanodecal-2-ones which whould help to elucidate this problem.

The isomeric cyclopropyl ketones were prepared by Simmons–Smith cyclopropylation[4] of the corresponding $\Delta^{1,9}$-octal-2-ols, followed by Jones oxidation.[5] In each case the major alcohol obtained from lithium aluminum hydride reduction of the corresponding

(1) W. G. Dauben, L. Schutte, R. E. Wolf, and E. J. Deviny, *J. Org. Chem.*, **34**, 2512 (1969).

(2) W. G. Dauben, L. Schutte, and E. J. Deviny, *ibid.*, **37**, 2047 (1972).

(3) G. W. Shaffer, *ibid.*, **37**, 3282 (1972).

(4) W. G. Dauben, P. Lang, and G. H. Berezin, *ibid.*, **31**, 3869 (1966).

(5) A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, 2548 (1953).