Anal. Calcd for $C_{12}H_8N_2O_4S$: C, 52.17; H, 2.95. Found: C, 52.26; H, 2.95.

Diphenyl sulfide **8** had the following properties: infrared (KBr) 3010 (w), 1590 (m), 1520 (s), 1450 (w), 1325 (s), 1340 (m), 1310 (w), 1260 (w), 1100 (w), 1055 (w), 1040 (w), 915 (w), 880 (w), 810 (w), 790 (m), 750 (w), 735 (s), and 680 cm^{-1} (w); nmr ($CDCl_3$) δ 6.9 (m, 1 H), 7.3 (m, 2 H), 7.8 (m, 2 H), and 8.4 (m, 3 H).

2,3′-Diaminodiphenyl Sulfide (7).—Hydrogenation of sulfide **8**, prepared above (0.20 g, 0.000725 mol) in 100 ml of absolute ethanol at 40 psi over 200 mg of 10% palladium on charcoal for 6 hr, yielded an oil which was distilled at 110° (0.1 mm). The resulting clear oil, 0.102 g (65%), failed to crystallize. An analytical sample of **7** was obtained by preparative glc.

Anal. Calcd for $C_{12}H_{12}N_2S$: C, 66.63; H, 5.59. Found: C, 66.76; H, 5.70.

Aminodiphenyl sulfide **7** had the following infrared and nmr properties: infrared (thin film) 3410 (m), 3320 (m), 2980 (w), 1620 (s), 1590 (s), 1520 (m), 1480 (s), 1450 (w), 1410 (w), 1380 (w), 1330 (w), 1305 (w), 1145 (m), 1070 (w), 1020 (w), 990 (m), 940 (w–m), 855 (w–m), 835 (m), 815 (w–m), 770 (s), 750 (s), 685 cm^{-1} (m–s); nmr ($CDCl_3$) δ 3.6 (broad s, 2 H), 4.25 (s, 2 H), and 6.8 (m, 8 H).

General Procedure for Rearrangement of 2,2′-Aminonitrodiphenyl Sulfides.—Sulfides were heated in an oil bath at 195° with an excess of amine in a sealed tube. Excess solvent was removed under vacuum and the dark residue chromatographed on Florisil. Samples isolated from the column were washed with pentane and placed under vacuum for at least 8 hr.

Phenothiazine (3a).—Sulfide **2c** (0.1554 g, 0.000632 mol) in aniline gave, on elution with benzene–pentane (3:2), 0.0357 g (29%) of a white solid, mp 183° (lit.[7] mp 180°), identified as **3a** by comparison of its properties with an authentic sample. Elution with pentane–benzene (1:1) gave 0.0948 g (61%) of a yellow-orange solid, mp 86° (lit.[8] mp 85°), identified as **2c** by comparison of its properties with an authentic sample.

3-Methylphenothiazine (3b).—Sulfide **2b** (0.1596 g, 0.000614 mol) in *p*-toluidine gave, on elution with pentane–benzene (4:1), 0.0557 g (42%) of a white solid, mp 167–168° (lit.[10] mp 168°), identified as **3b** by comparison of its properties with an authentic sample. Elution with benzene gave 0.0723 g (45%) of a red solid, mp 87°, identified as **2b** by comparison of its properties with an authentic sample.

Registry No.—**1a**, 4837-33-6; **1b**, 4837-32-5; **2a**, 1144-81-6; **2b**, 27332-17-8; **2c**, 19284-81-2; **3b**, 3939-47-7; **4a**, 27332-20-3; **4b**, 27384-96-9; **5**, 27332-21-4; **6a**, 27332-22-5; **6b**, 27332-23-6; **7**, 27332-24-7; **8**, 27332-25-8; 4-*N*,*N*-dimethylamino-3′-nitrodiphenyl sulfide, 27332-26-9.

Acknowledgment.—We acknowledge support in part by a Frederick Gardner Cottrell Grant-in-Aid from the Research Corporation and helpful discussions with Dr. S. Divald.

Reduction of Aromatic Nitro Compounds with Sodium Borohydride in Dimethyl Sulfoxide or Sulfolane. Synthesis of Azo or Azoxy Derivatives

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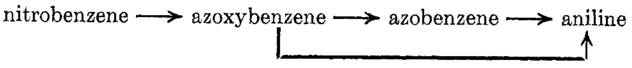
The reduction of aromatic nitro compounds with sodium borohydride in the polar aprotic solvents, DMSO and sulfolane, has been investigated. The reactions involve initial production of azoxy compounds which, in most cases, are subsequently reduced to the corresponding azo derivatives and amines. Other functional groups including cyano and amido are not reduced under the reaction conditions. Electron-withdrawing substituents facilitate both the initial production of azoxy compounds and the further reduction to azobenzenes and anilines. Electron-releasing groups slow the reductions of the azoxy compounds to the extent that these derivatives may be obtained in reasonable yields.

During a recent investigation of the reduction of aliphatic halides and tosylates with sodium borohydride in polar aprotic solvents,[2] we observed that reduction of aromatic nitro groups proceeded slowly at mild temperatures (*i.e.*, 25°) enabling benzylic halides to be selectively removed in their presence; the same results have also been obtained independently by Bell and coworkers.[3] However, at higher temperatures (*i.e.*, 85°) we have observed the ready reduction of aromatic nitro groups by borohydride in dimethyl sulfoxide or sulfolane to initially afford azoxy compounds which may be further reduced to mixtures of the corresponding azo derivatives and amines. As part of our exploratory investigations of the synthetic utility of borohydride in polar aprotic solvents,[2] we wish to report the scope of such reductions as convenient procedures for preparing azoxy and/or azobenzenes.

In order to determine the timing of production of the various observed products and thus aid in obtaining the best experimental procedures, the reduction of nitrobenzene in DMSO was monitored using gas chromatography to simultaneously measure the disappearance of nitrobenzene and appearance of azoxybenzene, azobenzene, and aniline. To conveniently accomplish this, an internal standard was added at the beginning of the reaction. Small aliquots of the reaction mixture were removed at appropriate time intervals, quenched in water, and extracted with chloroform, and the organic solution was analyzed. The results of such studies at 55 and 85° are plotted in Figure 1. Several noteworthy features of the reaction are evident from these plots. First, both cases suggest that the overall reduction occurs in three sequential steps.



This is further evidenced by the borohydride reduction of *p*,*p*′-dichloroazoxybenzene to the corresponding azo and amine derivatives (entry 24, Table I). Furthermore, the rate of formation of azoxybenzene is very much faster than is subsequent reduction at 85°; the

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[1] (a) National Science Foundation Undergraduate Research Participant, (b) Undergraduate Research Participant, 1969–present.

[2] R. O. Hutchins, D. Hoke, J. Keogh, and D. Koharski, *Tetrahedron Lett.*, 3495 (1969).

[3] H. M. Bell, C. W. Vanderslice, and A. Spehar, *J. Org. Chem.*, **34**, 3923 (1969).

TABLE I

REDUCTION OF AROMATIC NITRO COMPOUNDS WITH SODIUM BOROHYDRIDE IN DIMETHYL SULFOXIDE OR SULFOLANE

Entry	Compd	Registry no.	Solvent	T, °C	Time, hr	Yields, %[a] Amine	Azo	Azoxy	Other
1	Nitrobenzene	98-95-3	DMSO	85	1.5	22.4	74.6		
2			DMSO[b]	85	2.0	9.8	77.6		
3			Sulfolane	100	8.5	50.3	26.3	Trace	
4			Sulfolane	110	7.0	53.9	20.0	Trace	
5	*p*-Nitrotoluene	99-99-0	DMSO	85	1.5				*c*
6			Sulfolane	100	2.5	18.7	18.6	44.2	
7			Sulfolane	100	12	21.7	28.3	30.3	
8			Sulfolane	100	44	45.5	34.0		
9	*m*-Nitrotoluene	99-08-1	DMSO	85	1.5	*Ca.* 3	40.9	49.0	
10			DMSO	85	12.0	22.9	76.1		
11	*o*-Nitrotoluene	88-72-2	DMSO	85	1.5	10.5	1.4	48.3	10.5[d]
12			DMSO	85	5	14.2	5.2	53.9	
13	*p*-Nitroanisole	100-17-4	DMSO	85	1.5	*Ca.* 5	7.0	77.8	
14			DMSO	85	34	11.0	8.4	69.9	
15	*p*-Nitrophenetole	100-29-8	DMSO	85	5	*Ca.* 4	*Ca.* 3	90.0	
16	*m*-Nitroanisole	555-03-3	DMSO	85	1.5	13.3	75.9		
17	*o*-Nitroanisole	91-23-6	DMSO	85	34	63.1	22.3		
18	*o*-Nitrobiphenyl	86-00-0	DMSO	85	1.5	22.6		71.5	
19	*p*-Nitroaniline	100-01-6	DMSO	85	1.5				89.5[d]
20			DMSO	85	31				25.6[d]
21	*p*-Nitrobenzonitrile	619-72-7	DMSO	85	1.5	24.4	58.4[e]		
22	*p*-Nitrobenzamide	619-80-7	DMSO	85	1.5	*f*	50[g]		
23	*p*-Chloronitrobenzene	100-00-5	DMSO	85	1.5	38.3	41.0		
24	*p,p′*-Dichloroazoxybenzene	614-26-6	DMSO	85	1.5	32.6	56.1		
25	*o,o′*-Dinitrobiphenyl	2436-96-6	DMSO	85	1.5				79[g,h]
26	Nitrosobenzene	586-96-9	DMSO	85	1.5	12.1	78.8	Trace	
27	Phenylhydroxylamine	100-65-2	DMSO	85	1.5	7.8	82.8	Trace	

[a] Final solution 2.4 *M* in sodium borohydride, 0.4 *M* in nitro compound; yields determined by glpc analysis using standard solutions of the products (average of three to five determinations) and/or by isolation. [b] Conducted under nitrogen. [c] Orange-red highly insoluble material. [d] Starting material. [e] Mp 275° (reported[4b] mp 250°). *Anal.* Calcd for $C_{14}H_8N_4$: C, 72.40; H, 3.47. Found: C, 72.38; H, 3.76. [f] Not analyzed for. [g] Isolated yield. [h] *o,o′*-Dinitrosobiphenyl.

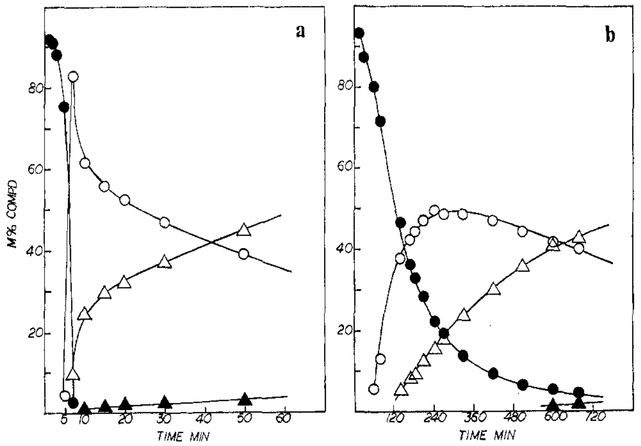

Figure 1.—Reduction of nitrobenzene with $NaBH_4$ in DMSO (concentrations determined by glpc; *N*-ethyl-*N*-methylaniline used as internal standard): nitrobenzene (●), azoxybenzene (○), azobenzene (△), aniline (▲). (a) $T = 85°$. (b) $T = 55°$.

concentration of nitrobenzene falls to zero after only 7.0 min; and the concentration of azoxybenzene attains its maximum (83%).[4] Complete reduction to azobenzene requires an additional 190 min. At 55° all the reductive steps are much slower, but the same general features are observed; as the nitrobenzene concentration decreases, the azoxybenzene concentration increases and then decreases again as azobenzene appears. Complete reduction is not obtained even after 48¹/₄ hr (concentrations 75.7% azobenzene, 3.6% aniline, 5.9% azoxybenzene). At both temperatures aniline does not appear in measurable quantities until a substantial amount of azobenzene is present, which suggests that this product may arise from the known reduction of azobenzene by borane.[5]

The mechanism for the formation of azoxybenzene probably involves initial reduction of nitrobenzene (possibly through nitrobenzene radical anion)[6,7] to nitrosobenzene and phenylhydroxylamine which are known to form the nitrosobenzene radical anion with bases in DMSO and eventually lead to azoxybenzene.[7] This is evidenced by the observations that nitrosobenzene or phenylhydroxylamine furnish similar mixtures of azobenzene and aniline as nitrobenzene upon borohydride

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(4) The sharp drop in nitrobenzene concentration which occurred between the 5- and 7-min reaction time (from 76 to 3%) suggested that the reaction was exothermic and the generated heat was not dissipated adequately enough to keep the reaction temperature at 85° until all the nitrobenzene was consumed.

(5) H. C. Brown and B. C. Subba Rao, *J. Amer. Chem. Soc.*, **82**, 681 (1960). Borane formation in DMSO or sulfolane has been reported (ref 2 and 3). The situation is complicated by the observation that treatment of azobenzene with $NaBH_4$ in DMSO at 85° for extended periods of time (*i.e.*, 24 hr) affords some hydrazobenzene which partially disproportionates under our glc conditions to a mixture of aniline and hydrazobenzene. Consequently, part of the observed aniline may arise from hydrazobenzene formation which escapes detection by glc. In addition, borane is known to reduce nitroso compounds to amines: H. Feuer and D. M. Braunstein, *J. Org. Chem.*, **34**, 2024 (1969). The origin of aniline in our reduction is therefore open to question and may arise from competition between all three of the above mentioned reductions. We are pursuing this point at present.

(6) M. G. Swanwich and W. A. Waters, *Chem. Commun.*, 63 (1970).

(7) G. A. Russell, E. J. Geels, F. J. Smentowski, K. Y. Chang, J. Reynolds, and G. Kaupp, *J. Amer. Chem. Soc.*, **89**, 3821 (1967).

reduction (compare entries 1 and 2 with 26 and 27, Table I). We are currently investigating the detailed mechanistic aspects of the reduction by esr spectroscopy and kinetic studies.

The data in Figure 1 suggested that a temperature of about 85° was adequate for preparative applications in DMSO; at higher temperatures the reduction of nitrobenzene became very vigorous and difficult to control. Preliminary experiments in sulfolane indicated that reduction occurred less readily and 100° seemed appropriate for this solvent. The experimental procedures were simple and straightforward. The nitro compound was added directly or as a solution in dimethyl sulfoxide or sulfolane to a stirred solution of sodium borohydride in the appropriate solvent maintained at the desired temperature. Progress of the reductions were followed by gas chromatography and the reaction mixtures were worked up by pouring into water and extracting into chloroform. Yields were determined in most cases by gas chromatography. Table I presents conditions and results for a variety of representative nitro compounds. The use of sulfolane appears to require longer reaction times and affords greater quantities of amines (compare entries 1–4).[8] For the preparation of azo compounds, the amines are easily removed by extraction of the chloroform solution with dilute hydrochloric acid. There appears to be no advantage to conducting the reactions under nitrogen (compare entries 1 and 2).

Several interesting features of the reductions are apparent from Table I. First, electron-withdrawing substituents enhance both the initial reduction to azoxy compounds and the further reduction to azo derivatives and amines.[9] For such cases the reactions provide relatively rapid and convenient methods for preparing azo compounds, especially since other reducible functional groups such as cyano and amido are not affected (entries 21 and 22). The corresponding azoxy compounds are also converted to the azo derivatives and amines under the reduction conditions (entry 24). Electron-releasing groups, on the other hand, retard the reactions to varying degrees dependent upon their donating ability.[9] Thus, *m*-nitrotoluene (entries 9 and 10) required 12 hr for conversion to *m*-azotoluene and *m*-toluidine; *p*-nitroanisole and *p*-nitrophenetole (entries 13–15) afforded good yields of the azoxy derivatives which were quite resistant to further reduction; *p*-nitroaniline (entries 19 and 20) was not reduced to any indentifiable product. Reduction of *p*-nitrotoluene in dimethyl sulfoxide gave an orange-red, highly insoluble solid, probably arising from base-promoted coupling of the methyl groups[10] in addition to reduction of the nitro groups. The reaction in sulfolane afforded normal reduction products (entries 6–8). The reduction of 2,2′-dinitrobiphenyl to the corresponding dinitroso derivative (entry 25) was anomalous, which probably reflects a difficulty in generating two nitroso radical anions on the same molecule (*i.e.*, a singlet dianion may be produced).

In summary, sodium borohydride in DMSO or sulfolane provides convenient systems for the preparative reduction of aromatic nitro compounds to azoxy or azo compounds especially when other reducible functions such as cyano or amido are present. The method complements the procedure of Shine and Mallory (KBH_4 in pyridine or ethanol) in that compounds bearing electron-withdrawing substituents afford azo derivatives by our procedure while that of Shine and Mallory gives good yields of the corresponding azoxy compounds. Furthermore, most rings bearing electron-releasing substituents (except NH_2) afford azoxy derivatives using $NaBH_4$ in DMSO but are inert to KBH_4 in pyridine or ethanol.

Experimental Section[11]

Materials.—The aromatic nitro compounds used in this study were commercial samples repurified by recrystallization or distillation. The products used as standards were either obtained commercially, prepared by independent methods, or isolated from the reduction reactions. In all cases, physical constants of starting materials and products agreed satisfactorily with literature values. Fisher Scientific Co. reagent dimethyl sulfoxide was either distilled from calcium hydride and stored over 4A molecular sieves or, since the commercial material contains very little water, just stored over molecular sieves. Phillips Petroleum Co. commercial sulfolane was distilled from calcium hydride and stored over 4A molecular sieves.

Reduction of Nitroaromatics. General Procedure.—A solution of sodium borohydride in dimethyl sulfoxide or sulfolane was prepared in a three-necked flask maintained at the desired temperature (Table I) and equipped with a mechanical stirrer, condenser, and drying tube. The aromatic nitro compound (0.01–0.03 mol) was then either added directly or dropwise as a solution in the appropriate solvent. The latter technique was usually followed for those nitro compounds bearing electron-withdrawing substituents since the reactions were often quite vigorous. The amounts of reagents and solvent were chosen so that the final solution was 2.4 *M* in sodium borohydride and 0.4 *M* in the nitro compound. Progress of the reactions was followed in several cases by removing small aliquots of the reaction mixture, quenching with water, extracting with a few drops of chloroform, and analyzing the chloroform solution for starting material and products by gas–liquid chromatography. After the appropriate reaction time listed in Table I, the mixtures were worked up by diluting with water and extracting into chloroform. In most cases, the chloroform solution was diluted to a constant volume and analyzed by glpc using standard solutions of the products to determine yields. In most cases (see Table I) the azo and/or azoxy compounds were isolated by washing the chloroform solution with dilute hydrochloric acid and water and drying over anhydrous magnesium sulfate followed by concentration at reduced pressure. A typical reduction procedure is given below for *m*-nitroanisole. The reaction progress data presented in Figure 1 were obtained by following the disappearance of nitrobenzene and appearance of products by gas chromatography in a similar manner as described above except that a weighed amount of *N*-methyl-*N*-ethylaniline was added as an internal standard at the beginning of the reaction. At the appropriate time intervals, 1.0-ml aliquots were removed, quenched with 5 ml of water, extracted with 0.5 ml of chloroform, and analyzed. In this manner, the concentrations of nitrobenzene, azoxybenzene, azobenzene, and aniline could be determined simultaneously using predetermined detector response factors for each compound.

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[8] The production of much larger quantities of aniline (entries 3 and 4, Table I) in sulfolane may occur because borane is essentially inert toward this solvent and thus is free to react with azobenzene. On the other hand, dimethyl sulfoxide suffers reduction by borane (ref 5) and, because of its relatively high concentration, competes very effectively with azobenzene for any borane produced.

[9] (a) H. J. Shine and E. Mallory, *J. Org. Chem.*, **27**, 2390 (1962). These authors observed that reduction of aromatic nitro compounds with potassium borohydride in ethanol or pyridine gave azoxy derivatives only if the ring substituent had a positive σ constant; otherwise, no reduction was obtained. (b) G. Otani, Y. Kikugawa, and S. Yamada, *Chem. Pharm. Bull.*, **16**, 1840 (1968). (c) The use of sodium borohydride in combination with palladium on carbon gives only the corresponding aniline from aromatic nitro derivatives with no evidence for azo or azoxy formation; see T. Neilson, H. Wood, and A. Wylie, *J. Chem. Soc.*, **371** (1962).

[10] G. A. Russell and E. G. Janzen, *J. Amer. Chem. Soc.*, **89**, 300 (1967).

[11] Gas chromatographic analyses were performed using a Hewlett-Packard Model 5250B gas chromatograph coupled to an L & N Model W recorder equipped with a Disc integrator. For all analysis, either a 6 ft × 1/8 in. 10% OV-1 on 60–80 Chromosorb W or a 1/8 in × 12 ft 10% UC-W98 on 80–100 Chromosorb W column was used. Microanalysis were performed by Midwest Microlab, Inc., Indianapolis, Ind., or by A. Bernhardt Microanalytical Laboratory, West Germany. Melting points are uncorrected.

Reduction of *m*-Nitroanisole with Sodium Borohydride in Dimethyl Sulfoxide.—To a stirred solution of sodium borohydride (3.405 g, 0.09 mol) in 25 ml of DMSO maintained at 85° was added dropwise a solution of *m*-nitroanisole (2.297 g, 0.015 mol) in 12 ml of DMSO over a 10-min period. After 1.5 hr, the solution was poured into 150 ml of water and extracted with three 25-ml portions of $CHCl_3$. The $CHCl_3$ solution was diluted to 100 ml and analyzed for yields of *m*-anisidine and *m*-azoanisole by glpc using standard solutions of the products (13.2 and 75.9% *m*-anisidine and *m*-azoanisole, respectively). The solution was washed with dilute HCl, then with water, and dried ($MgSO_4$). Removal of solvent on a rotary evaporator gave a red oil which solidified (1.96 g). A 208-mg sample was chromatographed on Florisil. Elution with 1:1 pentane-benzene afforded an orange-red solid, mp 75–76° (111.1 mg, representing a 61% yield). The ir and nmr spectra were consistent with *m*-azoanisole. One sublimation at reduced pressure gave the analytical sample.

Anal. Calcd for $C_{14}H_{14}N_2O_2$: C, 69.40; H, 5.82; N, 11.56. Found: C, 69.65; H, 5.73; N, 11.56.

***p,p'*-Azobenzamide.**—In a similar manner as above, *p,p'*-azobenzamide was obtained from *p*-nitrobenzamide in 49% yield. Three recrystallizations from DMF afforded the analytical sample, mp 360–363° (dec).

Anal. Calcd for $C_{14}H_{12}N_4O_2$: C, 62.68; H, 4.51; N, 20.88. Found: C, 62.68; H, 4.42; N, 20.86.

Registry No.—Sodium borohydride, 16940-66-2; *m*-azoanisole, 6319-23-9; *p,p'*-azobenzamide, 27332-13-4.

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Reactions of 2,2-Dinitroalkyl Tosylates with Nucleophiles

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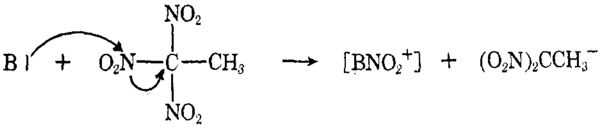
Some reactions of 2-fluoro-2,2-dinitroethyl tosylate (1) and 2,2-dinitropropyl tosylate (2) with nucleophiles were investigated. Weak bases lead to tosylate displacement, in some instances in preparatively useful yields. With strong bases side reactions such as nitrous acid elimination prevail. The reactivity of these tosylates is discussed, and some properties of 2,2-dinitroalkyl azides prepared from them are given.

The effects of β substituents on the S_N2 reactivity of alkyl halides and sulfonates have been the subject of extensive studies. No completely unequivocal rationalization of these effects in terms of steric and electronic properties of the substituents has been achieved. It seems clear, however, that β substitution generally decreases reaction rates rather strongly due to steric crowding in the transition state; if the β substituent is electron withdrawing (*e.g.*, halogen), a further smaller decrease is frequently observed.[1] A combination of these factors has been invoked, for example, to account for the observation that 1,1-di-*H*-perfluoroalkyl halides and tosylates are much less reactive toward KI in acetone or NaI in alcohols than the corresponding unsubstituted alkyl substrates.[2]

If this trend were to continue with bulkier and still more electron-withdrawing substituents such as nitro, it could result in 2-nitroalkyl sulfonates being essentially unreactive in S_N2 displacement reactions. The extent of our knowledge on this subject appeared confined to a single statement to the effect that "2,2-dinitropropyl benzenesulfonate is unreactive toward LiCl and KOAc in boiling ethanol."[3] We therefore investigated the reactions of several nucleophiles with some 2,2-dinitroalkyl tosylates which became available to us in the course of other studies with 2,2-dinitroalkanols.[4]

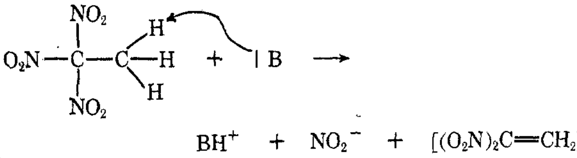
This paper deals primarily with the course of such reactions of 2-fluoro-2,2-dinitroethyl tosylate (1) and, to a lesser extent, of 2,2-dinitropropyl tosylate (2); quantitative rate data regarding their relative reactivities will be presented elsewhere. That these tosylates are, in fact, surprisingly reactive is demonstrated by the following experiment. Refluxing 1 with LiBr in acetone for 5 hr results in precipitation of *ca.* 90% of the theoretical amount of lithium tosylate, most of which deriving from a direct displacement reaction (see below), while trifluoroethyl tosylate is recovered unchanged after a reaction time of 150 hr.

Displacement reactions on 2,2-dinitroalkyl tosylates are likely to be complicated by the fact that polynitroalkanes themselves are subject to attack by nucleophiles. Thus, 1,1,1-trinitroethane undergoes two general reactions with nucleophiles under relatively mild conditions:[5] (1) attack by the nucleophile on one of the nitro groups with displacement of the 1,1-dinitroethane



$$B| + O_2N{-}C(NO_2)_2{-}CH_3 \longrightarrow [BNO_2^+] + (O_2N)_2CCH_3^- \quad (1)$$

anion, and (2) abstraction by the nucleophile of a β-hydrogen atom resulting in elimination of nitrous acid and formation of 1,1-dinitroethene as an intermediate. 1-



$$O_2N{-}C(NO_2)_2{-}CH_3 + |B \longrightarrow BH^+ + NO_2^- + [(O_2N)_2C{=}CH_2] \quad (2)$$

Halo-1,1-dinitroalkanes react similarly. When hal = Cl or Br, dinitrocarbanion formation occurs (reaction 1);[5] with hal = F, fluoronitroethene intermediates are formed (reaction 2).[6] Simple *gem*-dinitroalkanes with nonterminal dinitromethylene groups are more resistant to attack by nucleophiles. In particular, proton ab-

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(1) A. Streitweiser, Jr., *Chem. Rev.*, **56**, 691 (1956); J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1962, p 163 ff.

(2) G. V. D. Tiers, H. A. Brown, and T. S. Reid, *J. Amer. Chem. Soc.*, **75**, 5978 (1953); E. T. McBee, R. D. Battershell, and H. P. Braendlin, *ibid.*, **84**, 3157 (1962).

(3) L. W. Kissinger, T. M. Benziger, H. E. Ungnade, and R. K. Rohwer, *J. Org. Chem.*, **28**, 2491 (1963).

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(6) L. A. Kaplan, this laboratory, private communication.