trum[7] *m/e* (rel intensity) 153 (17), 96 (100, α cleavage of molecular ion followed by a McLafferty rearrangement, loss of CH_3COCH_2, metastable at 60.2), 70 (15, α cleavage followed by a retro Diels–Alder[8] reaction). Recrystallization of **7b** picrate from CH_3OH gave the analytical sample, mp 227–229° dec.

Anal. Calcd for $C_{15}H_{18}N_4O_8$: C, 47.11; H, 4.74; N, 14.65. Found: C, 47.37; H, 4.86; N, 14.62.

Acknowledgment. The authors thank Mr. John Naworal, University of Pittsburgh, for the mass spectral data, performed under Grant RR-00273 from the National Institutes of Health.

Registry No. 1, 4670-09-1; **2**, 43152-25-6; **3a**, 43152-26-7; **3b**, 43152-27-8; **4a**, 43152-28-9; **7a**, 43152-29-0; **7a HCl**, 43152-30-3; **7b**, 43152-31-4; **7b** picrate, 43152-32-5.

References and Notes

(1) (a) Part III: M. Mokotoff, *J. Heterocycl. Chem.*, in press. (b) This work was supported in part by Grant RR-05455-11 from the National Institutes of Health, Bethesda, Md. 20014.
(2) E. L. May and J. G. Murphy, *J. Org. Chem.*, **19**, 618 (1954); **20**, 1197 (1955). F. Ramirez and J. W. Sargent, *J. Amer. Chem. Soc.*, **77**, 6297 (1955). P. G. Gassman and J. H. Dygos, *Tetrahedron Lett.*, 4749 (1970).
(3) W. J. Gensler, C. D. Gatsonis, and Q. A. Ahmed, *J. Org. Chem.*, **33**, 2968 (1968); R. Furstoss, P. Teissier, and B. Waegell, *J. Chem. Soc. D*, 384 (1970).
(4) W. Theilacker and W. Schmidt, *Justus Liebigs Ann. Chem.*, **570**, 15 (1950).
(5) G. W. Anderson, J. E. Zimmerman, and F. M. Callahan, *J. Amer. Chem. Soc.*, **89**, 5012 (1967).
(6) W. F. Gannon and H. O. House, *Org. Syn.*, **40**, 14 (1960); M. Stiles and A. L. Longroy, *J. Org. Chem.*, **32**, 1095 (1967); E. Wenkert and D. P. Strike, *J. Amer. Chem. Soc.*, **86**, 2044 (1964); ref 3.
(7) The fragmentations are similar to those reported for several other azabicyclo systems: E. C. Blossy, H. Budzekiewicz, M. Ohashi, G. Fodor, and C. Djeressi, *Tetrahedron*, **20**, 585 (1964); A. M. Duffield, C. Djerassi, L. Wise, and L. A. Paquette, *J. Org. Chem.*, **31**, 1599 (1966); R. D. Guthrie and J. F. McCarthy, *J. Chem. Soc. C*, 1207 (1966); W. M. Bryant, III, A. L. Burlingame, H. O. House, C. G. Pitt, and B. A. Tefertiller, *J. Org. Chem.*, **31**, 3120 (1966).
(8) F. W. McLafferty, "Interpretation of Mass Spectra," W. A. Benjamin, New York, N. Y., 1967, p 141.

Synthesis and Acid-Catalyzed Decomposition of *o*-Nitrophenylsulfonyldiazomethane

A. Wagenaar, G. Kransen, and Jan B. F. N. Engberts*

Department of Organic Chemistry, The University, Zernikelaan, Groningen, The Netherlands

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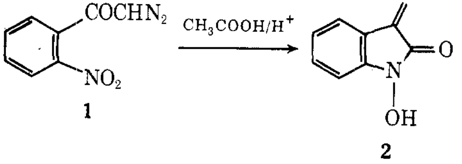
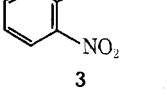
Chemical transformations involving neighboring-group interaction in ortho-substituted nitrobenzene derivatives is a subject of continuing interest.[1] The acid-catalyzed cyclization of *o*-nitrobenzoyldiazomethane (**1**) to 1-hydroxyisatin (**2**) is an intriguing example.[2-4] The detailed mechanism of this unusual reaction has not been defined, although ^{14}C labeling has been employed to eliminate some of the possible reaction paths.[5] The initial stages of the reaction likely involve protonation of the diazo ketone function (on carbon) followed by intramolecular nucleophilic attack of the nitro group on the diazonium ion.



1 **2**



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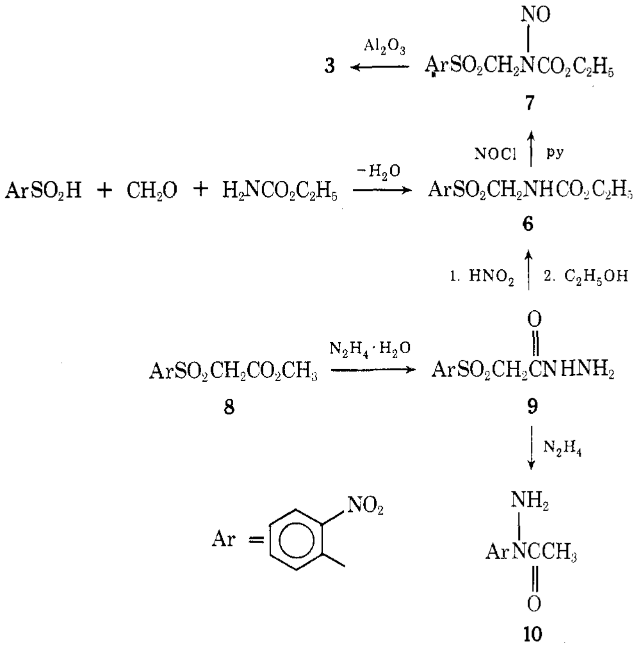
Scheme I



As part of our study of the chemistry of α-diazo sulfones,[6] we wish to describe the synthesis of *o*-nitrophenylsulfonyldiazomethane (**3**), the sulfonyl analog of **1**, and some reactions of **3** with strong acids.

The two main questions we posed in this study follow: does the nitro group participate in the acid-promoted decomposition of **3** and, if so, are the *o*-nitro substituted compounds[7] **1** and **3** significantly more labile toward acids than their *p*-nitro substituted isomers (p-$NO_2C_6H_4COCHN_2$, **4**; p-$NO_2C_6H_4SO_2CHN_2$, **5**) as a result of this participation?

Results and Discussion

Synthesis. α-Diazo sulfone **3** was prepared by the usual method[8] from the *N*-nitrosocarbamate **7** (Scheme I). Carbamate **6** was obtained by a Mannich-type condensation[9] of *o*-nitrobenzenesulfinic acid with formaldehyde and ethyl carbamate. The low yield (18%) was due to the formation of unidentified by-products and decomposition of the sulfinic acid (at 70°).[10] As an alternative route to **6**, hydrazide **9** was prepared by reaction of ester **8** with hydrazine at −10°. At higher temperatures, hydrazine-catalyzed Smiles rearrangement[11] to **10** is a competing reaction. Diazotization of **9** and Curtius rearrangement gave **6** in 40% yield. Attempts to obtain **6** by oxidation of ethyl *o*-nitrophenylthiomethylcarbamate (**11**) were unsuccessful.

Nitrosation of **6** to **7** gave no problems. The desired **3** was obtained by stirring a solution of **7** with a slurry of active, basic Al_2O_3 in a mixture of dichloromethane and ether. The usual work-up provided **3** in 30–60% yield as yellow crystals: ir ν (N═N) at 2109 cm^{-1} (CCl_4); nmr ($CDCl_3$) δ (CHN_2) 5.88 ppm;[12] uv, no discrete $n \rightarrow \pi^*$ maximum, ϵ 240 at 370 nm in 60% (v/v) dioxane–water. *Unfortunately, the crystalline* **3** *proved to be highly explosive.* Although a number of α-diazo sulfones have been prepared in this laboratory[13] (including *p*-nitrophenylsulfonyldiazomethane), explosive properties have not been encountered before. *Unless appropriate safety precautions are observed, manipulations with solid* **3** *should not be undertaken.* However, dilute solutions of **3** in inert solvents at room temperature or below can be kept for extended periods of time[14] without noticeable decomposition.

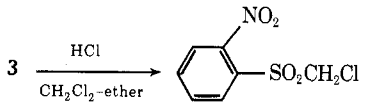
Acid-Catalyzed Reactions. Treatment of **3** with HCl in

Table I
Pseudo-First-Order Rate Constants (k_ψ) for the HCl-Catalyzed Decomposition of 1 and 3–5 at 25.1°

Compd	[HCl], mol l^{-1}	Solvent[a]	λ,[b] nm	$k_\psi \times 10^5$, sec^{-1}	Reaction mixture composition
o-$NO_2C_6H_4SO_2CHN_2$ (**3**)	0.4615	A	375	23.2	
p-$NO_2C_6H_4SO_2CHN_2$ (**5**)	0.4615	A	375	20.4	
o-$NO_2C_6H_4SO_2CHN_2$ (**3**)	1.0944	A	400	146	**12** (>90%)[c,d]
p-$NO_2C_6H_4SO_2CHN_2$ (**5**)	1.0958	A	400	160	p-$NO_2C_6H_4SO_2CH_2Cl$ (>90%)[c]
o-$NO_2C_6H_4SO_2CHN_2$ (**3**)	0.8825	B	400	102	**12** (>90%)[c]
p-$NO_2C_6H_4SO_2CHN_2$ (**5**)	0.8821	B	375	84.2	p-$NO_2C_6H_4SO_2CH_2Cl$ (>90%)[c]
o-$NO_2C_6H_4COCHN_2$ (**1**)	0.4615	A	470	95.5[f]	**2** (41%), **16** (59%)[e]
p-$NO_2C_6H_4COCHN_2$ (**4**)	0.4615	A	375	260	p-$NO_2C_6H_4COCH_2Cl$ (94%)[e] p-$NO_2C_6H_4COCH_2OH$ (6%)
o-$NO_2C_6H_4COCHN_2$ (**1**)	0.8825	B	375	~160	**2** (43%), **16** (57%)[e]
p-$NO_2C_6H_4COCHN_2$ (**4**)	0.8825	B	375	>800	

[a] A = 60% (v/v) dioxane–water, B = 40% (v/v) dioxane–water. [b] Wavelength at which the kinetic measurements were performed. [c] From uv analysis of the reaction mixture. [d] Analytically pure **12** isolated in 86% yield. [e] From nmr analysis. [f] Rate constant for the formation of **2**.

anhydrous CH_2Cl_2–ether resulted in rapid decoloration of the solution. Subsequent work-up afforded the α-chloro sulfone **12** in good yield, indicating that under these conditions apparently no participation of the nitro group had occurred. Rapid, reversible protonation[15] of **3** followed by rate-determining attack of Cl^- on the diazonium ion may account for the observed reaction.[16]



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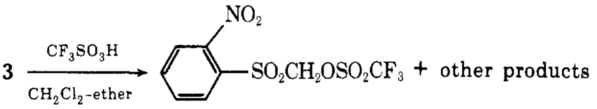
However, the reaction of **3** with CF_3SO_3H under similar conditions gave a red-colored solution from which dark-brown solid material was obtained. Washing with water followed by chromatography provided the triflate **13** in a



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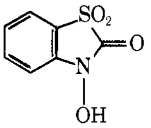
yield of only 12%.[17] Attempts to isolate other well-defined products were all unsuccessful. Only red- or brown-colored materials are formed when **3** is decomposed in glacial acetic acid (under conditions where **1** is converted into **2**)[2–5] or with $HClO_4$ in 40 and 60% (v/v) dioxane–water. We tentatively suggest that under these conditions intermolecular nucleophilic attack of acetate ions or water on the diazonium ion is completely suppressed by intramolecular attack of the nitro moiety. Accepting this hypothesis, one can envisage[1] the α-oxo sulfone **14** and o-nitrosobenzenesulfinic acid (**15**) as possible products. The former will be



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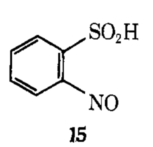

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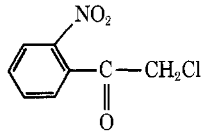
sensitive to acid-catalyzed solvolysis,[18] while the latter is expected to decompose in view of the known rapid addition of sulfinic acids to nitroso functionalities.[19] When HCl is used as the catalyst in the dioxane–water mixtures, intermolecular nucleophilic attack by Cl^- on the diazonium ion competes with the intramolecular process, leading to formation of **12** in quantities depending on the HCl concentration. Under similar conditions the α-diazo ketone **1** afforded **2**,[20] the chloromethyl ketone **16** and, at low HCl concentrations, the hydroxymethyl ketone **17**. Table I summarizes the results of some kinetic measurements on **1** and **3–5** using 40 and 60% (v/v) dioxane–water as the solvent. Although the relative rates are dependent on solvent composition and acid concentration, the data for **1** clearly reveal that in these media participation of the ortho nitro group competes favorably with intermolecular nucleophilic attack by water but does not induce enhanced rates of decomposition as compared with **4**. It should be noted, however, that the efficiency of the nitro group as an internal nucleophile may increase in solvents of low polarity.[7] The experiments with **3** were carried out at sufficiently high HCl concentrations to produce mainly **12** as the reaction product. Under these conditions almost equal reaction rates were found for **3** and **5**. At lower HCl concentrations pseudo-first-order kinetics were not satisfactorily obeyed, most likely because of subsequent conversions of the primary reaction products. The data suggest that also in these media **3** and **5** show comparable reactivities. We did not pursue kinetic studies further, however, because of the problems in handling pure **3** and the difficulties with the product analyses under these conditions.



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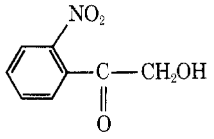

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Experimental Section

Melting points were determined on a Mettler FP 1 melting point apparatus with a Mettler FP 52 microscope attachment. Elemental analyses were carried out in the Analytical Department of this laboratory under the supervision of Mr. W. M. Hazenberg. Infrared (ir) spectra were run on a Perkin-Elmer instrument, Model 257. Nmr spectra were determined with a Varian A-60 instrument. TMS was used as an internal standard. Ultraviolet (uv) spectra were obtained on a Zeiss PMQ II spectrophotometer.

Kinetic Measurements. The rate measurements were carried out by following the decrease in absorbance at a suitable wavelength (375–400 nm for the diazo compounds, 470 nm for **2**). The formation of **2** from **1** could be monitored at 470 nm, since there is no appreciable absorption due to **1** at this wavelength. The reactions were carried out in 2.0-cm quartz cells, equipped with a magnetic stirring device, and placed in the thermostated (25.1 ± 0.04°) cell compartment of a Zeiss PMQ II spectrophotometer. Pseudo-first-order kinetics were found for at least 3 half-lives. Pseudo-first-order rate constants (k_ψ) were averaged over at least two measurements and were reproducible to within 2%. After completion of all kinetic runs the uv spectrum of the reaction product(s) was taken. Dioxane–water mixtures were usually made up by weight. Dioxane (Merck uvasol No. 2967) was chromatographed over Al_2O_3 (Merck No. 1077) in a nitrogen atmosphere. The diazo compounds **1**,[2–5] **4**[21] and **5**,[8] and N-hydroxyisatin[2] (**2**) were prepared according to known procedures.

***o*-Nitrophenylsulfonylacethydrazide (9).** A solution of 8 (44.0 g, 0.17 mol) in THF (400 ml) was added dropwise during 30 min to a stirred mixture of hydrazine hydrate (20 ml, 0.40 mol) and methanol (20 ml). The temperature was kept below −10°. During the addition a colorless precipitate separated from the yellowish-orange solution. After stirring for an additional 30 min the crystals were removed, washed well with cold water, and crystallized from water (550 ml) to give 9 (31 g, 70%): mp 179–180°; nmr (DMSO-d_6) δ 4.28 (s, 2), 2.7–5.0 (broad m, 3), 7.5–8.1 ppm (m, 4); ir (Nujol) 1165, 1340 (SO_2), 1350, 1560 (NO_2), 1660 cm^{-1} (CO); mass spectrum m/e 259 (M^+).

Anal. Calcd for $C_8H_9N_3O_5S$: C, 37.07; H, 3.50; N, 16.20; S, 12.37. Found: C, 36.84; H, 3.49; N, 16.27; S, 12.24.

***N*-Acetyl-*N*-(*o*-nitrophenyl)hydrazine (10).** A solution of 8 (1.3 g, 5 mmol) in 10 ml of THF was added dropwise to a stirred mixture of hydrazine hydrate (1 ml, 2 mmol) and methanol (1 ml). After refluxing for 30 min, the solvent was evaporated and the residue was dissolved in 100 ml of dichloromethane. After washing with water, the solution was dried over anhydrous $MgSO_4$. Removal of the solvent and chromatography of the residue over silica gel, using subsequently tetrachloromethane and dichloromethane–ether (1:1) as the eluent, gave, after crystallization from THF–petroleum ether (bp 30–60°), 10 in a yield of 62%: mp 90–91°; nmr ($CDCl_3$) δ 2.17 (d, hindered rotation, 3), 4.58 (broad s, 2, signal disappeared in the presence of D_2O), 7.30–8.15 ppm (m, 4); ir (Nujol) 1370, 1530 (NO_2), 1640 (CO), 3230, 3370 cm^{-1} (NH_2); mass spectrum m/e 195 (M^+).

Anal. Calcd for $C_8H_9N_3O_3$:C, 49.23; H, 4.65; N, 21.53. Found: C, 49.42; H, 4.70; N, 21.22.

Ethyl *O*-Nitrophenylsulfonylmethylcarbamate (6). A. From the Curtius Rearrangement. A solution of 9 (31.0 g, 0.12 mol) in a mixture of acetic acid (120 ml) and 1 *N* hydrochloric acid (210 ml) was cooled to 0° and added during 5 min to a stirred solution of $NaNO_2$ (9 g, 0.13 mol) in 18 ml of water. Stirring was continued for 5 min and some azide already crystallized from the solution. The reaction mixture was poured into ice water, and the azide was filtered off, washed with water until free from base, and dissolved in 200 ml of dichloromethane. After drying the solution with 10 g of anhydrous $MgSO_4$ for 1.5 hr, the solution was filtered directly into dry ethanol (500 ml). This mixture was kept at 55° for 2 hr while some dichloromethane was allowed to distil over. After an additional 10 hr at 40°, the solvent was removed *in vacuo* and the oily residue was taken up in 25 ml of ether. After 2 days at −15°, crude 6 separated as colorless needles (7.5 g, 26 mmol), mp 97–98°. The solvent was removed from the mother liquor and the residue was chromatographed on a silica gel column (500 g) using dichloromethane as the eluent. Ethyl *o*-nitrobenzenesulfinate emerged first in a yield of 3.65 g (14%): mp 53–54°, nmr ($CDCl_3$) δ 1.30 (t, 3), 3.77–4.57 (m, 2), 7.60–8.42 ppm (m, 4); ir (Nujol) 1345, 1550 (NO_2), 1130 cm^{-1} (SO).

Anal. Calcd for $C_8H_9O_4NS$: C, 44.64; H, 4.22; N, 6.31; S, 14.90. Found: C, 44.65; H, 4.29; N, 6.38; S, 14.76.

The second product obtained was 6 (6.4 g): total yield 13.9 g (40%); mp 97–98°; nmr ($CDCl_3$) δ 1.13 (t, 3), 4.02 (q, 4), 5.61 (d, 2), 5.75–6.30 (broad t, 1), 7.6–8.4 ppm (m, 4); ir (Nujol) 1160, 1350 (SO_2), 1350, 1560 (NO_2), 1695 (CO), 3300 cm^{-1} (NH).

Anal. Calcd for $C_{10}H_{12}N_2O_6S$: C, 41.66; H, 4.20; N, 9.72; S; 11.12. Found: C, 41.46; H, 4.14; N, 9.74; S, 11.27.

Continued development of the column furnished minor quantities of unidentified materials.

B. From the Mannich-Type Condensation. A mixture of *o*-nitrobenzenesulfinic acid (1.87 g, 10 mmol), formaline (1.2 ml, 15 mmol), and ethyl carbamate (1.3 g, 15 mmol) in water (20 ml)–formic acid (5 ml) was heated at 70° for 12 hr. The reaction mixture was poured into 300 ml of water and extracted twice with dichloromethane. The combined extracts were washed with water and then dried with anhydrous $MgSO_4$. The residue, obtained after removal of the solvent *in vacuo*, was dissolved in ether and cooled at −12° for 2 days. This afforded 0.54 g (18%) of crystalline 6, mp 98–99°. No additional 6 was obtained after further work-up of the mother liquor.

Ethyl *o*-Nitrophenylthiomethylcarbamate (11). A solution of sodium nitrite (1.56 g, 23 mmol) in 4 ml of water was added to an ice-cold solution of *o*-nitrophenylthioacethydrazide[22] (4.8 g, 21 mmol) in a mixture of acetic acid (8 ml) and 1 *N* hydrochloric acid (36 ml). After stirring for 3 min the azide was removed by filtration, washed with water, and taken up in 100 ml of dichloromethane. The solution was dried with anhydrous $MgSO_4$ and mixed with 200 ml of dry ethanol. After refluxing for 5 hr, the solvent was removed *in vacuo* and the yellow oily residue was dissolved in ether–*n*-pentane. Upon cooling at −12°, 11 was obtained as yellow needles (3.76 g, 70%): mp 84–85°; nmr ($CDCl_3$) δ 1.20 (t, 3), 4.12 (q, 2), 4.77 (d, 2), 5.2–5.6 (broad s, 1), 7.1–8.3 ppm (m, 4); ir (Nujol) 1350, 1520 (NO_2), 1725 (CO), 3480 cm^{-1} (NH).

Anal. Calcd for $C_{10}H_{12}N_2O_4S$: C, 46.87; H, 4.72; N, 10.93; S, 12.51. Found: C, 46.69; H, 4.51; N, 11.15; S, 12.59.

Oxidation of 11. Attempts to oxidize 11 to 6 produced exclusively water-soluble products: (1) with hydrogen peroxide in acetic acid at 10° and at 50°; (2) with 6% excess of *m*-chloroperbenzoic acid (MCPBA) in refluxing ether; (3) with less than 2 equiv of MCPBA in refluxing ether.

Ethyl *N*-nitroso-*N*-*o*-nitrophenylsulfonylmethylcarbamate (7) was prepared from 6 according to the procedure of Van Leusen and Strating:[8] yield 91%; mp 87° dec; nmr ($CDCl_3$) δ 1.45 (t, 3), 4.56 (q, 2), 5.62 (s, 2), 7.68–8.12 ppm (m, 4); ir (Nujol) 1180, 1190 (SO_2), 1360 (SO_2, NO_2), 1540, 1560 (NO, NO_2), 1760 cm^{-1} (CO).

Anal. Calcd for $C_{10}H_{11}N_3O_7S$: C, 37.85; H, 3.50; N, 13.25; S, 10.10. Found: C, 37.98; H, 3.52; N, 12.95; S, 10.13.

***o*-Nitrophenylsulfonyldiazomethane (3).** A solution of 7 (0.957 g, 3 mmol) in a mixture of dichloromethane (15 ml) and ether (35 ml) was stirred with 10 g of alumina (active, basic, Merck No. 1076) for 3.5 hr under nitrogen. The conversion of 7 was followed by observing the decrease of the carbonyl absorption in the ir spectrum. The solution was rapidly washed through a small column of alumina (active, neutral, Merck No. 1077,) (4 g) and collected at −30° under nitrogen. The alumina was washed twice with 25-ml portions of ether. The combined ethereal solutions were concentrated to 7 ml at −20° *in vacuo*. After the addition of *n*-pentane, yellow crystals of 3 separated from the cold solution in varying yields (30–60%): mp 25° dec; nmr ($CDCl_3$) δ 5.88 (s, 1), 7.68–8.36 ppm (m, 4); ir (neat) 2110 ($-N_2$), 1350, 1550 (NO_2), 1350, 1150 cm^{-1} (SO_2).

Anal. Calcd for $C_7H_5N_3O_4S$: S, 14.12. Found: S, 14.36.

Caution! Several times severe explosions occurred when crystalline 3 was allowed to warm to room temperature. Therefore, all manipulations with solid 3 should be carried out at the lowest temperatures possible and under nitrogen. The usual safety precautions in handling explosives should be taken at all times.

Reaction of 3 with acids. Usually, these experiments were carried out using pure 3. A nitrogen atmosphere was maintained over all reaction mixtures.

Chloromethyl *o*-Nitrophenyl Sulfone (12). A solution of 3 (0.155 g, 0.68 mmol) in 5 ml of dichloromethane was added to 25 ml of ether saturated with dry hydrogen chloride. After 15 min the yellow color of 3 had disappeared completely. Removal of the solvent *in vacuo* furnished crude 12 (0.170 g, mp 110–115°). The analytically pure sample was obtained in a yield of 61% after crystallization from dichloromethane–ether–*n*-pentane: mp 115–117°; nmr ($CDCl_3$) δ 5.10 (s, 2), 7.85–8.50 ppm (m, 4); ir (Nujol) 1350, 1530 (NO_2), 1140, 1320 cm^{-1} (SO_2).

Anal. Calcd for $C_7H_6ClNO_4S$: C, 35.69; H, 2.57; Cl, 15.08; N, 5.95; S, 13.61. Found: C, 36.01; H, 2.68; Cl, 15.52; N, 5.94; S, 13.35.

***o*-Nitrophenylsulfonylmethyl Triflate (13).** The ethereal solution of 3 obtained from 7 (0.951 g, 3 mmol) as described above was treated with a solution of trifluoromethanesulfonic acid (4.5 g, 30 mmol) in a mixture of dichloromethane (15 ml) and ether (25 ml). The solution immediately turned red and a dark brown material separated from the solution. The solution was filtered, washed rapidly with water, and dried with anhydrous $MgSO_4$. Upon evaporation of the solvent *in vacuo* a residue was obtained that was chromatographed over silica gel, affording the pure triflate 13 (0.125 g, 12% calcd on 7): mp 103–105°; nmr ($CDCl_3$) δ 5.72 (s, 2), 7.77–8.40 ppm (m, 4); ir (Nujol) 1140, 1160, 1315, 1370 cm^{-1} (SO_2).

Anal. Calcd for $C_8H_6F_3NO_7S_2$: C, 27.50; H, 1.73; N, 4.02; S, 18.33. Found: C, 27.66; H, 1.76; N, 3.86; S, 18.15.

Reaction of 3 with Acetic Acid. A. When a few crystals of 3 are dissolved in 50% aqueous acetic acid (10 ml), a yellow solution is obtained. Thermal or acid-catalyzed decay of 3 is very slow under these conditions, as evidenced by ir spectra taken at time intervals. Addition of 1 drop of concentrated perchloric acid led to rapid decomposition. Work-up gave a mixture of brown unidentified materials.

B. When 0.140 g (0.62 mmol) of 3 was covered with 0.7 ml of glacial acetic acid a very vigorous reaction took place, affording a black tar. A mixture of red-colored unidentified compounds was obtained when a larger volume of acetic acid was employed.

Registry No. 1, 4203-26-3; **3**, 49558-46-5; **4**, 4203-31-0; **5**, 1538-94-9; **6**, 49558-49-8; **7**, 49558-50-1; **8**, 49558-51-2; **9**, 49558-52-3; **10**, 49558-53-4; **11**, 49558-54-5; **12**, 49558-55-6; **13**, 49558-56-7; ethyl *o*-

nitrobenzenesulfinate, 49558-57-8; *o*-nitrophenylthioacethydrazide, 4871-40-3.

References and Notes

(1) For an extensive review see P. N. Preston and G. Tennant, *Chem. Rev.*, **72,** 627 (1972).

(2) F. Arndt, B. Eistert, and W. Partale, *Chem. Ber.*, **60,** 1364 (1927).

(3) E. Giovannini and P. Portmann, *Helv. Chim. Acta,* **31,** 1381 (1948).

(4) J. A. Moore and D. H. Ahlstrom, *J. Org. Chem.*, **26,** 5254 (1961).

(5) E. C. Taylor and D. R. Eckroth, *Tetrahedron,* **20,** 2059 (1964).

(6) J. F. J. Engbersen and J. B. F. N. Engberts, *Syn. Commun.*, **1,** 121 (1971).

(7) Ortho nitro groups can act as good internal nucleophiles; see S. Kim, S. S. Friedrich, L. J. Andrews, and R. M. Keefer, *J. Amer. Chem. Soc.*, **92,** 5452 (1970), and references cited therein.

(8) A. M. van Leusen and J. Strating, *Recl. Trav. Chim. Pays-Bas,* **84,** 151 (1965).

(9) J. B. F. N. Engberts and J. Strating, *Recl. Trav. Chim. Pays-Bas,* **84,** 942 (1965).

(10) When *o*-nitrobenzenesulfinic acid is heated in ethanol under reflux for several hours, nitrobenzene is formed together with sulfur dioxide: A. Wagenaar, unpublished results.

(11) For a review of the Smiles rearrangement, see J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, **49,** 362 (1951).

(12) For the *p*-nitro substituted isomer, this absorption is found at δ 5.33 ppm in $CDCl_3$. The exact origin of the low-field shift of the methine proton absorption in **3** is under investigation.

(13) A. M. van Leusen and J. Strating, *Quart. Rep. Sulfur Chem.*, **5,** 67 (1970).

(14) The uv absorption between 300 and 400 nm of a dilute solution of **3** in 60% (v/v) dioxane-water changed less than 2% after 3.5 hr at room temperature.

(15) Complete hydrogen-deuterium exchange of the methine proton of **3** was observed within 10 min in 60% (v/v) dioxane-deuterium oxide at 36°. Under these conditions exchange is much slower for the *p*-nitro isomer (35% exchange after 17 hr). It is not clear, however, whether in this neutral medium exchange is primarily acid catalyzed.

(16) J. B. F. N. Engberts and B. Zwanenburg, *Tetrahedron,* **24,** 1737 (1968).

(17) A series of arylsulfonylmethyl triflates has been prepared previously: K. Hovius and J. B. F. N. Engberts, *Tetrahedron Lett.*, 2477 (1972). The triflate **13** is very sensitive toward nucleophilic substitution by nonbasic nucleophiles as demonstrated by the almost instantaneous reaction with LiCl to give **12** in acetone-DMF (4:1).

(18) Owing to their instability, simple α-oxo sulfones, $R_1COSO_2R_2$ have not been isolated thus far. Only when the carbonyl group is made less prone to nucleophilic attack by appropriate substitution may α-oxo sulfones to be obtained: (a) R. J. Gaul and W. J. Fremuth, *J. Org. Chem.*, **26,** 5103 (1961); (b) A. Senning, O. N. Sorensen, and C. Jacobson, *Angew. Chem.*, **80,** 704 (1968); (c) T. Olijnsma, J. B. F. N. Engberts, and J. Strating, *Recl. Trav. Chim. Pays-Bas,* **89,** 897 (1970).

(19) T. A. J. W. Wajer, H. W. Geluk, J. B. F. N. Engberts, and T. J. de Boer, *Recl. Trav. Chim. Pays-Bas,* **89,** 696 (1970).

(20) The decomposition of **2** in 40% (v/v) dioxane-water containing 0.8825 *N* HCl was followed at 470 nm and found to be much slower than that of **1** in this medium.

(21) P. Karrer and J. Schuker, *Helv. Chim. Acta,* **28,** 820 (1945).

(22) F. L. Rose and B. R. Wilson, British Patent 782,420 (1957); *Chem. Abstr.*, **52,** 2907*i* (1958).

Remote Oxygen Participation in the Solvolysis of *endo*-4-Oxatricyclo$[5.2.1.0^{2,6}]$dec-8-yl Methanesulfonate

Pelham Wilder, Jr.,* and Carol Van Atta Drinnan[1]

Paul M. Gross Chemical Laboratory, Duke University, Durham, North Carolina 27706

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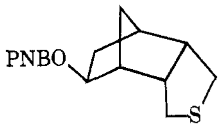
The report of significant participation by remote sulfur in the *endo*-4-thiatricyclo$[5.2.1.0^{2,6}]$decane system (1)[2] prompted the reexamination of analogous oxygenated compound 3 and its skeletal isomer 4 to determine if similar oxygen participation could be detected. In a preliminary investigation of this problem Cash found no kinetic evidence for participation in the ethanolysis of **3a-6a,** but he was severely hampered by the low purity of his starting esters.[3] It had previously been noted that addition of acidic reagents to 7 proceeded with little rearrangement to the exo-fused ring and it was proposed that intervention of an ion such as 8 prevented the expected rearrangement (see Scheme I).[4] The same ion 8 should be formed in solvolysis of 3, either concurrent with departure of the leaving group or subsequent to formation of the secondary carbonium ion.



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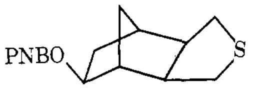

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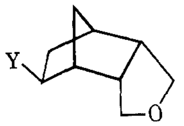
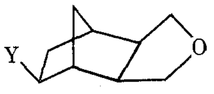
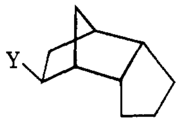


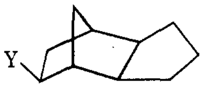
3a, Y = TsO
b, Y = MsO
c, Y = OH



4a, Y = TsO
b, Y = MsO
c, Y = OH

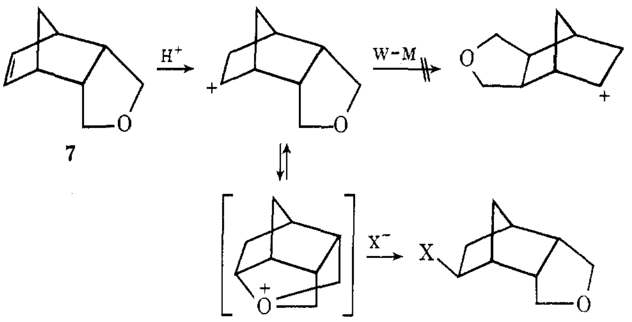


5a, Y = TsO
b, Y = MsO
c, Y = PNBO
d, Y = OH

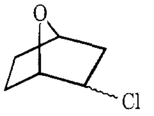


6a, Y = TsO
b, Y = PNBO

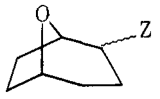
Scheme I



The phenomenon of neighboring group assistance by oxygen is well documented;[5] participation by the oxygen atom of sulfinyl,[6] carbonyl,[7] hydroxyl,[8] and ether[9] groups has been described. Ether participation has been extensively studied in the carbohydrate field,[10] but until recently investigations of such oxygen participation in conformationally rigid molecules other than carbohydrates have been lacking. Martin and Bartlett found no participation of bridge oxygen in solvolysis of 9 where the sole



9



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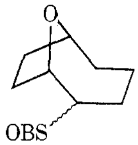
Z = I, OBs



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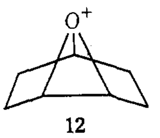

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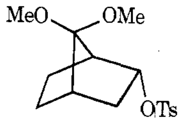
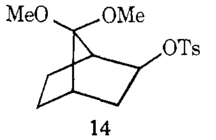


13



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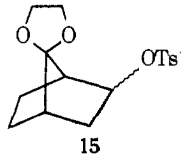

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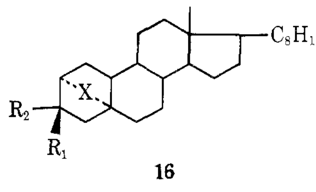

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