volumetric flask containing weighed quantities of piperonal, or Schiff base, and nitromethane. Diluted 1-ml. samples were analyzed with the spectrophotometer. The extinction coefficient of PNM at 364 mμ, the main absorption peak, was 1.65 × 10^4 over the concentration range used. It was necessary to avoid acid solutions in which the very similar spectrum of the Schiff base salt would interfere. One run (0.5 *M* $BuNH_3OAc$), followed by gravimetric analysis for piperonal + Schiff base, gave k_2 = 0.0200 l./mole-min., which checks within 10% the value of 0.0221 obtained using the spectrophotometer. Table III shows the data obtained using approximately 0.2 *M* $BuNH_3OAc$, yielding the value of k_2' given in Table II.

TABLE III

RATE OF NITROSTYRENE FORMATION

Piperonal concn., *M*	CH_3NO_2 concn., *M*	$BuNH_3OAc$ concn., *M*	Induction period, min.	k'_2, l./mole-min.
0.02044	0.2018	0.2018	14	0.0194
.01987	.2018	.2018	13	.0194
.02273	.2411	.2025	14	.0200
.02017	.2187	.1922	14	.0197
.02611	.0205	.1768	14	.0194
.01996	.0195	.1768	12	.0190
.02089	.0200	.1768	15	.0190
.04375	.2018	.2018	(19)	.0187
		Average	14	.0193

The *curve* in Fig. 3 is based on the following experiments: (a) Schiff base formation from 0.02017 *M* piperonal in 0.1922 *M* butylammonium acetate: k_1 = 0.0601 $min.^{-1}$. (b) PNM formation from 0.02218 *M* Schiff base and 0.2187 *M* nitromethane in 0.1922 *M* $BuNH_3OAc$ and 0.0215 *M* acetic acid: k_2 = 0.0191 l./mole-min. The *points* represent 0.02017 *M* piperonal, 0.2187 *M* nitromethane and 0.1922 *M* $BuNH_3OAc$.

Acknowledgment.—We are indebted to the Research Corporation for the grant which supported this work.

CHARLOTTESVILLE, VA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

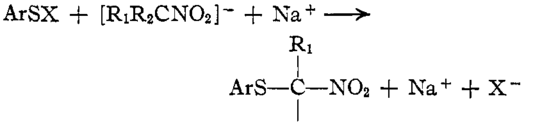
Derivatives of Sulfenic Acids. VIII. Studies of Some α-Nitro Sulfides and Sulfones

BY NORMAN KHARASCH AND JAMES LORNE CAMERON

RECEIVED JULY 23, 1952

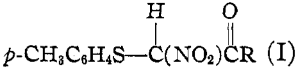
2-Chloroethyl 1-nitroethyl sulfone and 3-nitrophenyl 1-nitroethyl sulfone were obtained by oxidizing the products from the appropriate sulfenyl chlorides and the sodium salt of nitroethane. The reductions of 1-nitroethyl *p*-tolyl sulfide and of the corresponding sulfone, as well as the reaction of the latter with sodium *p*-toluenesulfinate, are also described.

In a previous paper[1] the synthesis of a series of α-nitro sulfides, by reaction of sulfenyl halides and sodium salts of nitroalkanes (equation 1, Ar = aryl; X = Cl, Br or SCN; and R_1, R_2 = alkyl or H) was reported, and evidence for the designated structures of the products was cited.



$$ArSX + [R_1R_2CNO_2]^- + Na^+ \longrightarrow ArS\text{—}\underset{R_2}{\overset{R_1}{C}}\text{—}NO_2 + Na^+ + X^- \quad (1)$$

The present paper describes further work with this novel class of sulfides and with some related α-nitro sulfones.

Besides the work of Melnikov,[2] in which certain α-nitro sulfides were mentioned as unstable intermediates, the only other reference to such substances which we have encountered is to the preparation (as intermediates, in unstated yields) of compounds as  $p\text{-}CH_3C_6H_4S\text{—}\overset{H}{C}(NO_2)\overset{O}{\overset{\|}{C}}R$ (I), R = CH_3 or C_6H_5, by reaction of the corresponding β-keto sulfides with sodium ethoxide and ethyl nitrite, followed by acidification.[3]

Investigations of the related α-nitro sulfones have also been limited. By treatment of I (R = CH_3) with hydrogen peroxide, Arndt and Rose[3] obtained a low yield of nitromethyl *p*-tolyl sulfone; and this sulfone was also obtained by Shriner and Greenlee,[4] *via* sodium *p*-toluenesulfinate and bromonitromethane. By reaction of sodium benzenesulfinate and chloronitromethane, Tröger and Nolte[5] obtained a low yield of nitromethyl phenyl sulfone, but were unable to repeat their original preparation. The synthesis of *p*-bromophenyl nitromethyl sulfone is also mentioned in their paper. Recently, Backer[6] reported products as di- and tri-(methylsulfonyl)-nitromethane. 1-Nitroethyl *p*-tolyl sulfone and 2-nitrophenyl 1-nitropropyl sulfone were reported in our earlier paper.[1]

The syntheses of two new α-nitro sulfones, by oxidation of the corresponding crude sulfides, were effected in the present study. The intermediate α-nitro sulfides involved were 2-chloroethyl 1-nitroethyl sulfide and 1-nitroethyl 3-nitrophenyl sulfide. The pure α-nitro sulfides were not isolated, since the products were oils which failed to crystallize, and which decomposed on distillation at reduced pressures. Yields of the pure sulfones were: 2-chloroethyl 1-nitroethyl sulfone, II (61%) and 1-nitroethyl 3-nitrophenyl sulfone, 57%. The corresponding crude sulfides were obtained in 85 and 91% yields, respectively. 2-Chloroethyl 1-nitroethyl sulfide and the corresponding sulfone represent the first examples of their respective groups in which the sulfur moiety stems from an aliphatic sulfenyl chloride ($ClCH_2CH_2SCl$). The latter sulfone (II) neutralized two moles of alkali, suggesting that dehydrochlorination, as well as salt formation, was involved.

The ultraviolet absorption spectra of sulfone II and of nitroethane were determined and found to be

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[1] N. Kharasch and J. L. Cameron, THIS JOURNAL, **73**, 3864 (1951).

[2] N. Melnikov, *J. Gen. Chem.* (*U.S.S.R.*), **7**, 1546 (1937); *C. A.*, **31**, 8504 (1937); *cf.* also ref. 1.

[3] F. Arndt and J. D. Rose, *J. Chem. Soc.*, **147**, 1 (1935).

[4] R. L. Shriner and S. O. Greenlee, *J. Org. Chem.*, **4**, 242 (1939).

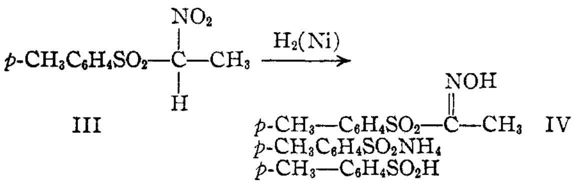
[5] J. Tröger and E. Nolte, *J. prakt. Chem.*, **101**, 136 (1920).

[6] H. J. Backer, *Rec. trav. chim.*, **68**, 827, 844 (1949); **69**, 610 (1950).

nearly identical. This confirms the presence of a nitro group in II, and suggests that its precursor was, indeed, 2-chloroethyl 1-nitroethyl sulfide.[7] The absorption spectrum of 1-nitroethyl *p*-tolyl sulfone in absolute alcohol also was determined. The curve obtained by plotting the data given in the Experimental section is distinctly different from the one recorded by Fehnel and Carmack[8] for methyl *p*-tolyl sulfone in the same solvent; and when the curve for nitroethane was added to the one for methyl *p*-tolyl sulfone, the resultant did not correspond to the curve for 1-nitroethyl *p*-tolyl sulfone. These observations suggest that interesting structural data concerning the effects of the close proximity of the sulfone and nitro functions should result from further studies of the absorption spectra of suitably selected examples, including corresponding β-nitro sulfones.

Heath and Lambert[9] found that 2-nitroethyl *p*-tolyl sulfide and the corresponding sulfone are readily hydrogenated to the related amino compounds. In our study of the reductions of the isomeric 1-nitroethyl *p*-tolyl sulfide and its sulfone, some interesting differences between the 1-nitroethyl and 2-nitroethyl isomers were encountered.

1-Nitroethyl *p*-tolyl sulfide was recovered unchanged after treatment with hydrogen (at 40 p.s.i.) with Raney nickel or Adams catalyst. Reduction of the sulfone, however, led to a small amount of the corresponding oxime (IV, 10% crude yield), ammonium *p*-toluenesulfinate (28%) and an oil, whose major component (*ca.* 50%) was *p*-toluenesulfinic acid, contaminated with some *p*-toluenesulfonic acid. The structure of IV was assigned on the basis of elementary analysis, the acidity of the product, and its necessary relation to III.

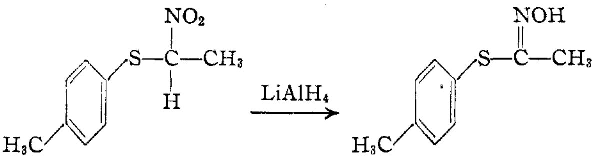


$$p\text{-}CH_3C_6H_4SO_2\text{—}\overset{NO_2}{\underset{H}{C}}\text{—}CH_3 \xrightarrow{H_2(Ni)} \begin{array}{l} p\text{-}CH_3\text{—}C_6H_4SO_2\text{—}\overset{NOH}{\overset{\|}{C}}\text{—}CH_3 \quad IV \\ p\text{-}CH_3C_6H_4SO_2NH_4 \\ p\text{-}CH_3\text{—}C_6H_4SO_2H \end{array}$$

III

The adjacency of the nitro and sulfone functions thus appears to promote the easy hydrogenolysis of the bonds between carbon and $CH_3\text{-}C_6H_4SO_2\text{-}$, as well as between the carbon atom and the nitro group.

Reduction of V with lithium aluminum hydride also led, in low yield (14–16% crude), to an oxime, VI. While the distinct odor of *p*-thiocresol was always noted when the reaction mixture was acidified, the other products of the reduction of V were not identified in the present work. However, since the oxime is not the usual product observed when the nitro group is reduced by lithium aluminum hydride,[10] an alternate synthesis of VI was effected by reaction of the sodium salt of V with benzyl chloride—as suggested by the recent work of Hass and Bender.[11]



V VI

Treatment of III with lithium aluminum hydride and acidification of the basic reaction mixture also caused scission of the C–S bond, leading to *p*-toluenesulfinic acid (*ca.* 80% crude yield).

In studies which led to our previously published synthesis of 1-nitroethyl *p*-tolyl sulfone (III) (in 71% yield, from 1-chloro-1-nitroethane and sodium *p*-toluenesulfinate)[1] we had observed that the yield of sulfone decreased markedly if excess sodium *p*-toluenesulfinate was used. From the present work, it appears that the decreased yields of III were caused by a competing reaction of the initially-formed sulfone (III) and sodium *p*-toluenesulfinate, leading to two isolable products—an acidic component (A) and a neutral product (N). Table I shows the effect of varying conditions on yields of products isolated in the reaction of sodium *p*-toluenesulfinate and 1-chloro-1-nitroethane.

TABLE I

REACTION OF SODIUM *p*-TOLUENESULFINATE WITH 0.025 MOLE OF 1-CHLORO-1-NITROETHANE

$p\text{-}CH_3C_6H_4\text{-}SO_2Na$ (dihydrate), mole	Solvent	Reflux time, hr.	Yield, % sulfone (III)	A[c]	N
0.075	Abs. ethanol	40	—[a]	21	20
.050	Abs. ethanol	40	26	15	17
.033	95% ethanol		63	—	1
.033	Abs. ethanol	40	61	—	1
.033	Abs. methanol	3	71[b]	—	—

[a] Dashes indicate that none of the particular product could be isolated. [b] As recorded in reference 1. [c] Product A proved to be di-*p*-toluenesulfonimide, $(p\text{-}CH_3C_6H_4SO_2)_2\text{-}NH$; the structure of N was not, however, established in the present work (*cf.* text). The yields tabulated are for the crude products. *Cf.* experimental.

That products A and N were formed by reaction of the initially-formed sulfone (III) and sodium *p*-toluenesulfinate was suggested by the fact that if III was itself heated with *p*-toluenesulfinate dihydrate, under conditions which simulated some of the runs in Table I, appreciable amounts of A, N and unreacted III were recovered. Some other experiments were also made to assure that the above reaction was the most probable route for formation of A and N. Thus, III remained unchanged on long reflux in ethanol alone, or in presence of sodium *p*-toluenesulfonate. The latter possibility was considered, since the sulfinate might have been

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(7) For other evidence confirming the structure of the products as α-nitro sulfides *vs.* the alternate possibility, $RS\text{—}O\text{—}\overset{\overset{O}{\uparrow}}{N}=\overset{\overset{R_1}{|}}{C}\text{—}R_2$; *cf.* ref. 1. The absorption spectrum for nitroethane, recorded in the Experimental part, compares closely to that given by Goodeve, *Trans. Faraday Soc.*, **30**, 504 (1934).

(8) E. A. Fehnel and M. Carmack, THIS JOURNAL, **72**, 1292 (1950).

(9) R. L. Heath and A. Lambert, *J. Chem. Soc.*, 1477 (1947). *Cf.* also W. E. Parham and T. L. Ramp, THIS JOURNAL, **73**, 1293 (1951) for examples of reductions of β-nitro sulfides to β-amino sulfides with lithium aluminum hydride.

(10) R. F. Nystrom and W. G. Brown, *ibid.*, **70**, 3738 (1948); W. G. Brown, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., N. Y., p. 469 (1951). *Cf.* also Parham and Ramp, ref. 9. An exhaustive literature search suggests that the above example is the first isolation of an oxime as product from the reduction of a nitro group by lithum aluminum hydride.

(11) H. B. Hass and M. L. Bender, THIS JOURNAL, **71**, 1767, 3482 (1949).

converted (by disproportionation or oxidation) to the sulfonate, which might then have reacted with III to form A and N.

The identity of A was assured by superposition of our product on the known di-*p*-toluenesulfonimide, prepared according to the method of Ziegler and co-workers,[12] *via* *p*-toluenesulfonamide and *p*-toluenesulfonyl chloride. The formation of the sulfonimide (A) from III and the sulfinate recalls the similar ease of cleavage encountered in the reduction studies of III, described above.

Compound N is a neutral, excellently-crystalline white solid, m.p. 115.5–116.5°, whose most likely molecular formula is $C_{16}H_{19}O_3NS_2$. A literature search failed to reveal a previously known compound on which this product could be superimposed, so that the structure remains to be established.

Acknowledgment.—We are indebted to Commercial Solvents Corporation for a grant in support of this work.

Experimental[13]

2-Chloroethyl 1-Nitroethyl Sulfone.—The sodium salt of nitroethane was prepared from 2.76 g. (0.12 mole) of sodium and 14.4 ml. (0.20 mole) of nitroethane (b.p. 113.5–114°) in 100 ml. of absolute alcohol. The salt was collected just prior to use, washed on the suction plate with dry ether, and added during 20 minutes to a stirred solution of 13.5 g. (0.1 mole) of 2-chloroethanesulfenyl chloride,[14] in 250 ml. of dry ether at 5°. The mixture was stirred for 90 minutes more and filtered. The filtrate was concentrated, at reduced pressure, to 100 ml., washed with 50 ml. of water and dried with anhydrous sodium sulfate. Aspiration of residual solvent from the gently heated solution left 15 g. of orange liquid (crude yield of sulfide, *ca.* 85%).

In larger runs, where 40–80 g. of the sodium salt of nitroethane was required, the preparation of the salt, and the reaction with 2-chloroethanesulfenyl chloride was carried out as previously described[1] for the similar reaction with *p*-toluenesulfenyl chloride. In these runs, the sodium salt was dried for about 12 hours prior to use in a large evacuated desiccator charged with calcium chloride. Yields of the crude 2-chloroethyl 1-nitroethyl sulfide averaged 85%.

To obtain the sulfone, a solution of 30.5 g. (0.18 mole) of crude 2-chloroethyl 1-nitroethyl sulfide, 54 ml. (0.54 mole) of 30% hydrogen peroxide and 200 ml. of glacial acetic acid was let stand for 24 hours at room temperature. The solution was concentrated to 50 ml. (by aspiration at room temperature) and the residue mixed with 50 g. of ice. White crystals of 2-chloroethyl 1-nitroethyl sulfone were collected and air-dried to constant weight (22.0 g., 61% yield), m.p. 50–51°. The analytical sample, m.p. 51.5–52.5°, was prepared by recrystallizing from chloroform-carbon tetrachloride mixtures. Qualitative tests for sulfur, nitrogen and halogen were positive.

Anal. Calcd. for $C_4H_8O_4NSCl$: C, 23.82; H, 4.00; N, 6.95. Found: C, 24.08; H, 4.05; N, 7.03.

The sulfone dissolved in 1% aqueous sodium hydroxide; but was not reprecipitated (in contrast to 1-nitroethyl 3-nitrophenyl sulfone and 1-nitroethyl *p*-tolyl sulfone) by acidification with dilute hydrochloric or nitric acid. The solution, acidified with nitric acid, tested strongly for chloride ions. Titration of the sulfone, in methanol, with 0.1113 N aqueous sodium hydroxide gave a phenolphthalein end-point when one equivalent of alkali had been added. Addition of excess base and back-titration, showed that two moles of alkali was neutralized.

Absorption Spectra.—These were obtained with a model DU Beckman quartz spectrophotometer. Absolute ethanol was the solvent in all cases. Readings were made at 5–10 mμ spacings, except in regions of absorption maxima, where readings were spaced at 1–2 mμ. For 1-nitroethyl *p*-tolyl sulfone, readings from 280–253 mμ were spaced 1 mμ apart. Concentrations were as follows: nitroethane: 9.72×10^{-3} M (320–233 mμ), diluted to 9.72×10^{-4} M at 233–220 mμ; 2-chloroethyl 1-nitroethyl sulfone: 1.171×10^{-2} M (320–250 mμ), diluted to 1.171×10^{-3} M at 240–230 mμ; 1-nitroethyl *p*-tolyl sulfone: 9.98×10^{-4} M (320–250 mμ), diluted to 9.98×10^{-5} M from 245–220 mμ. The following values of $\lambda/\log \epsilon$ define the observed maxima and minima. Nitroethane: 300/1.00, 275/1.35, 250/1.18, 220/3.21; 2-chloroethyl 1-nitroethyl sulfone: 300/1.63, 280/1.86, 254/1.59, 230/3.01; α-nitroethyl *p*-tolyl sulfone, 300/2.18, 279/2.64, 275/3.00, 272/2.93, 266/3.07, 258/3.03, 245/3.39, 240/3.79, 235/3.05, 230/3.14, 220/3.07.

1-Nitroethyl 3-Nitrophenyl Sulfone.—By the procedure described for preparation of 1-nitroethyl *p*-tolyl sulfide,[1] the reaction of 3-nitrobenzenesulfenyl chloride[15] and the sodium salt of nitroethane led to an oily product (91% crude yield) which is presumably 1-nitroethyl 3-nitrophenyl sulfide. The crude product was soluble in 10% aqueous sodium hydroxide.

The above product (3.42 g., 0.015 mole) and 20 ml. of 30% hydrogen peroxide, in 60 ml. of glacial acetic acid, was heated on the steam-bath for 90 minutes. The solution was cooled and diluted with 300 g. of ice. White crystals, 2.21 g. (57%), melting at 89.5–91°, were obtained. Recrystallization from methanol raised the melting point to 91–92°. The product was soluble in aqueous alkali and was reprecipitated without change (m.p. and mixed m.p.) by acidification.

Anal. Calcd. for $C_8H_8O_6N_2S$: C, 36.93; H, 3.10; N, 10.76. Found: C, 36.74; H, 3.16; N, 11.12.

Reduction of 1-Nitroethyl *p*-Tolyl Sulfone. (a) With Lithium Aluminum Hydride.—By the method of Nystrom and Brown,[10] 5.16 g. (0.025 mole) of 1-nitroethyl *p*-tolyl sulfone,[1] in 50 ml. of dry ether, was reduced with 1.90 g. (0.05 mole) of lithium aluminum hydride, in 100 ml. of dry ether. After stirring one hour, excess hydride was decomposed by dropwise addition of water and the mixture was added to 100 ml. of ice-water and acidified with 100 ml. of 10% sulfuric acid. The aqueous layer (solution a) was separated from the ethereal layer, and extracted with two 50-ml. portions of ether. The combined ether solutions were washed with water and dried with anhydrous sodium sulfate. Evaporation of the ether left 2.35 g. of white crystals, melting at 70–78°. The product was soluble in 5% alkali, but was not reprecipitated by acidifying the basic solution with hydrochloric acid. The melting point was not raised by recrystallization from chloroform, carbon tetrachloride or alcohol. The product was suspected to be crude *p*-toluenesulfinic acid and this was confirmed as follows: After standing in air for weeks, a sample of the product became water soluble and strongly acidic. The S-benzylthiuronium salt, which was then prepared, melted at 178.5–179.5°, and there was no depression with the known salt of *p*-toluenesulfonic acid. The original, acidified reaction mixture (solution a) was neutralized with 10% sodium hydroxide, the solution evaporated to dryness and the white crystals extracted with minimum water. Addition of 1.5 g. of S-benzylthiuronium chloride to this solution gave 1.60 g. of crude derivative, melting at 152–160°. Recrystallization from hot water gave white needles melting at 161–162°. The identical product was also obtained from authentic *p*-toluenesulfinic acid.

Anal. Calcd. for $C_{15}H_{18}O_2N_2S_2$: C, 55.89; H, 5.63. Found: C, 56.02; H, 5.83.

The total amount of crude *p*-toluenesulfinic acid (including the portion isolated as the thiuronium salt) represented an 80% conversion of the sulfone.

(b) **Hydrogen with Raney Nickel.**—1-Nitroethyl *p*-tolyl sulfone (14.0 g., 0.061 mole) in 150 ml. of ethanol was hydrogenated in a Parr apparatus with Raney nickel catalyst. After 42 hours, the pressure decreased from 41.6 p.s.i. to a constant reading of 23.7 p.s.i. (equivalent to 0.22 mole uptake of hydrogen). The catalyst was collected and the

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[12] K. Ziegler, A. Spath, W. Schumann and E. Winkelmann, *Ann.*, **551**, 80 (1942).

[13] Analyses were performed by Mr. J. Pirie of this Laboratory. Melting points recorded are not corrected.

[14] R. C. Fuson, C. C. Price and D. M. Burness, *J. Org. Chem.*, **11**, 471 (1946).

[15] The crude sulfenyl chloride was prepared by Miss R. Wood, in near quantitative yield, by chlorinolysis of 3-nitrophenyl disulfide, as suggested by N. E. Foss and co-workers, THIS JOURNAL, **60**, 2729 (1938). It was distilled, prior to use, at 3 mm. and 120–123°.

solution concentrated, at reduced pressure, to 10 ml. A precipitate was collected and the mother liquor reserved. The former was extracted with 25 ml. of water, leaving 0.4 g. of insoluble residue (R_1). The aqueous extract yielded 1.90 g. of white crystals (product 1); these melted at 180–190°, in a preheated bath, and slowly decomposed on raising the temperature to 250°. The mother liquor was concentrated *in vacuo* and the residual oil was extracted with 50 ml. of water, leaving a yellow solid. The latter was dissolved in 20 ml. of 5% sodium hydroxide and reprecipitated with 3% hydrochloric acid, giving—after adequate time for precipitation—a total of 1.35 g. of yellow solid (product 2). Evaporation of the filtrate, at room temperature, to constant weight, left 6.58 g. of a yellow oil (R_2).

On recrystallization of product 2 from mixtures of alcohol–chloroform or alcohol–carbon tetrachloride, or repeated treatment with dilute alkali and reprecipitation with acid, there was obtained a colorless crystalline solid, m.p. 119–120°. This was not soluble in 10% sodium bicarbonate, but dissolved in 1% sodium hydroxide solution. Tests for sulfur and nitrogen were positive, and the analysis agreed for oxime IV. The crude yield (1.35 g.) was 10%.

Anal. Calcd. for $C_9H_{11}O_3NS$: C, 50.69; H, 5.20. Found: C, 50.97; H, 4.94.

Extraction of residue (R_2) with 30 ml. of chloroform left 1.06 g. of white crystals, m.p. 160–162°. The extract (E_2) was reserved. Recrystallization of the solid residue from alcohol showed the material to be the same as product 1 (above). Vacuum distillation of the chloroform from E_2 left a residual oil (5.5 g., product 3). The combined weights of R_1 (0.4 g.), product 1 (2.96 g.), product 2 (1.35 g.) and product 3, represents 72% by weight of the original sulfone.

Repeated crystallization of product 1 from alcohol did not change its melting or decomposition behavior. The white crystals were readily soluble in water, insoluble in chloroform, and gave a distinct test for ammonium ion on heating with base. Tests for sulfur and nitrogen were positive and the S-benzylthiuronium derivative (m.p. 161–162°) was identical (m.p. and mixed m.p.) with the one obtained from *p*-toluenesulfinic acid, above. These observations, together with the analyses given below, and the fact that pure ammonium *p*-toluenesulfinate is reported[16] to melt at 174° suggested that product 1 was ammonium *p*-toluenesulfinate, contaminated with ammonium *p*-toluenesulfonate. The crude yield of 2.96 g. represented a 28% conversion of the sulfone to the ammonium *p*-toluenesulfinate.

Anal. Calcd. for ammonium *p*-toluenesulfinate, $C_7H_{11}O_2NS$: C, 48.55; H, 6.40. Found: C, 47.58; H, 6.66.

In other runs, it was noted that the yield of product 1 (ammonium *p*-toluenesulfinate) was variable, and that none of it could be isolated if elevated temperatures were used in the work-up. Instead, the product then obtained decomposed at 325–330° (recrystallized from dioxane) and tested positively for ammonium, sulfur and nitrogen. An S-benzylthiuronium derivative (m.p. 178.5–179°) corresponded (m.p. and mixed m.p.) to the known derivative of *p*-toluenesulfonic acid. This suggested that at elevated temperatures, in air, the ammonium *p*-toluenesulfinate was oxidized to the corresponding sulfonate, reported to melt at 325–330°.[17]

Product 3 (5.5 g., 54% of total weight of products) was an orange oil, soluble in excess water and chloroform. Distillation at 4 mm. caused decomposition at 200°. The aqueous solution was acidic and tested positively for ammonium. Treatment of the oil with S-benzylthiuronium chloride gave a typical derivative (*ca.* 5 g.) melting at 140–145°. This was judged to be a mixture of the S-benzylthiuronium salts of *p*-toluenesulfinic acid and *p*-toluenesulfonic acid. In a repetition of the reduction of sulfone III, the same products as recorded above were observed and the oil (product 3) represented 58% of the weight of sulfone. From the weights of S-benzylthiuronium salts obtained from 3 (and assuming 80% isolation of the derivative salts) it may be inferred that about 50% of component 3 was composed of the sulfinic and sulfonic acid. Residue R_1 was not further investigated.

Reduction of α-Nitroethyl *p*-Tolyl Sulfide (V) with Lithium Aluminum Hydride.—By a procedure identical with the one used for reduction of the sulfone with lithium aluminum hydride, 5 g. of V was reduced. Ether extraction of the basic reaction mixture did not yield a product; but after acidification with hydrochloric acid, ether extraction led to 0.70 g. of white solid, melting at 119–122°. The product was soluble in base, and was recovered on acidification. Recrystallization from carbon tetrachloride raised the melting point to 131–132°. Tests for nitrogen and sulfur were positive and the analysis agreed for oxime VI. The crude yield was 14%.

Anal. Calcd. for $C_9H_{11}ONS$: C, 59.64; H, 6.12. Found: C, 59.47; H, 5.92.

In another run, the reduction of 20 g. of 1-nitroethyl *p*-tolyl sulfide with 11.5 g. of hydride gave 2.95 g. of VI (*ca.* 16% yield). The distinct odor of *p*-thiocresol was also observed in the reaction mixture.

To prepare VI by an alternate route (*cf.* ref. 11), 4.90 ml. (0.042 mole) of benzyl chloride and 9.30 g. (0.042 mole) of the sodium salt of 1-nitroethyl *p*-tolyl sulfide,[1] in 150 ml. of absolute alcohol, was refluxed for 5 hours, and sodium chloride was removed. The filtrate was concentrated by aspiration, the residue extracted with 10% aqueous sodium hydroxide and the extract acidified with hydrochloric acid, leading to 2.0 g. of orange crystals, melting at 105–115°. Recrystallizations from aqueous ethanol and carbon tetrachloride, using decolorizing charcoal, gave 0.73 g. of white crystals, m.p. 130–131°. This product did not depress the m.p. of VI, obtained by reaction of lithium aluminum hydride with V.

Hydrogen with Raney Nickel or Adams Catalyst on V.—There was no hydrogen uptake when a solution of 6.70 g. of V, in methanol, with Raney nickel or Adams catalyst, was shaken for 48 hours at 40 p.s.i. of hydrogen pressure. Addition of fresh catalyst, in both runs, and continued shaking, did not give any noticeable hydrogen uptake.

Competing Reaction of III with Sodium *p*-Toluenesulfinate in Preparation of III *via* 1-Chloro-1-nitroethane and the Sulfinate.—By the procedure previously recorded,[1] III was obtained in 71% crude yield, by reaction of equimolar amounts of 1-chloro-1-nitroethane and sodium *p*-toluenesulfinate dihydrate. By following this procedure, but varying proportions of the reactants and solvents, as shown in Table I, A, N and unreacted III were isolated in the crude yields tabulated. The isolations and purifications were made by similar procedures as those given below, for reaction of III, itself, with sodium *p*-toluenesulfinate.

A mixture of sodium *p*-toluenesulfinate dihydrate (5.35 g., 0.025 mole) and 5.73 g. (0.025 mole) of III, in 100 ml. of absolute alcohol, was refluxed for 40 hours. Filtration of the hot mixture gave 1.72 g. of white crystals (R_1). Refrigeration of the mother liquor led to 3.10 g. of white solid (R_2), and a filtrate, F_1. Residues R_1 and R_2 were separately dissolved in 5-ml. portions of hot water and acidified with 10% hydrochloric acid, leading,respectively, to 1.71 g. (m.p. 150–162°) and 0.84 g. (m.p. 158–165°) of crude A. Recrystallization from absolute alcohol raised the m.p. to 169–170°. The purified product was soluble in 10% aqueous sodium bicarbonate and was reprecipitated by hydrochloric, but not by acetic acid. Product A contained nitrogen and sulfur and gave the following analysis: neut. equiv., 320, 324; C, 51.98; H, 4.71. Required for $C_{14}H_7O_4NS$ (di-*p*-toluenesulfonimide): neut. equiv., 325; C, 51.68; H, 4.65. An alternate synthesis by the method of ref. 12 gave a product which melted at 169–170° (recorded m.p.[12] 168.5°) and which did not depress the melting point of A on admixture.

Filtrate F_1 was concentrated *in vacuo* and the residual oil washed with water, then dissolved in 50 ml. of ether. The ether solution was extracted with 20 ml. of 5% sodium hydroxide and the extract acidified with 5% hydrochloric acid, giving 0.42 g. of crude III, m.p. 41–42°, and raised to 46–48° by recrystallizing from aqueous methanol. There was no depression in melting point on admixture with authentic III, melting at 47–48°. Concentration of the ether from separation of III left 0.58 g. of yellow residue, m.p. 80–90°. Repeated recrystallization of this neutral product from carbon tetrachloride gave excellent white crystals, m.p. 115.5–116.5°. The melting point of this product (N) was not depressed by admixture with similar products obtained *via* sodium *p*-toluenesulfinate and 1-chloro-1-nitroethane.

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Anal. Calcd. for $C_{16}H_{19}O_3NS_2$: C, 56.97; H, 5.68; N, 4.15; S, 19.0; mol. wt., 337. Calcd. for $C_{16}H_{19}O_4NS_2$: C, 54.36; H, 5.38; N, 3.97; S, 18.1; mol. wt., 353. Found: C, 57.16, 57.39; H, 5.52, 5.50; N, 4.07; S, 19.6; mol. wt. (cryoscopically in benzene), 344, 351.

In other experiments to establish the most likely route for formation of A and N: (1) a solution of 1.00 g. of III in 25 ml. of absolute ethanol was refluxed for 40 hours. Unreacted III, 0.85 g., m.p. 43–45°, was recovered. (2) Sodium *p*-toluenesulfonate dihydrate (0.0125 mole), prepared by exact neutralization of the acid and dried *in vacuo* for 12 hours, was refluxed for 40 hours with 2.87 g. (0.0125 mole) of III in 50 ml. of absolute alcohol. Only 2.27 g. of III was recovered.

LOS ANGELES, CALIF.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

Derivatives of Sulfenic Acids. IX. Reaction of 2,4-Dinitrobenzenesulfenyl Chloride with Some Symmetrical Alkynes

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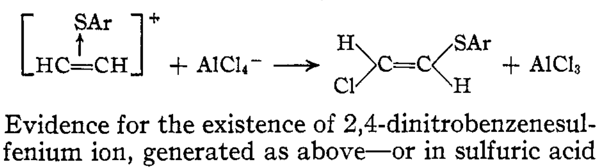
RECEIVED JULY 23, 1952

2,4-Dinitrobenzenesulfenyl chloride reacts with acetylene, 2-butyne, 3-hexyne and diphenylacetylene in accord with the equation: $RC{\equiv}CR + ArSCl \rightarrow RC(Cl){=}CR(SAr)$, Ar = 2,4-dinitrophenyl. The reaction suggests a practical method for characterizing such alkynes. Aluminum chloride catalysis was required in the case of acetylene. Addition to butynedioic acid or diethyl butynedioate could not, however, be effected.

The addition of 2-chloroethanesulfenyl chloride ($ClCH_2CH_2SCl$) to acetylene, to yield 2-chloroethyl 2-chlorovinyl sulfide,[1] appears to be the only recorded instance of reaction of a sulfenyl halide with an alkyne. The purpose of the present work was to determine whether 2,4-dinitrobenzenesulfenyl chloride (I) could participate in this type of reaction.[2]

It was found that I does react with acetylene, 2-butyne, 3-hexyne and diphenylacetylene to give sharp-melting, excellently crystalline 1:1 adducts, in yields ranging from 76–93%. The results suggest a new approach to the characterization of symmetrical alkynes. Procedures for obtaining maximum yields of products are recorded in the Experimental section.

In contrast to the reaction of I with ethylene,[2b] as well as with the higher alkynes now reported, the reaction of I with acetylene failed in the absence of a catalyst. Formation of the 1:1 adduct was, however, facilitated by catalytic amounts of aluminum chloride. The catalyst presumably functions as shown (Ar = 2,4-dinitrophenyl):



Evidence for the existence of 2,4-dinitrobenzenesulfenium ion, generated as above—or in sulfuric acid solutions of I—will be presented in a following paper. There is as yet, however, no decisive evidence that the addition occurs in the *trans* manner shown above.

While several attempts were made to add I to butynedioic acid, or to diethyl butynedioate, the reactions could not be effected. This failure is not unexpected, since the carboxyl or carbethoxy groups strongly deactivate the acetylenic bond toward addition of electrophilic reagents.

Acknowledgment.—The final stages of this study were completed under sponsorship of the Office of Ordnance Research, United States Army.

Experimental[3]

Starting Materials.—2,4-Dinitrobenzenesulfenyl chloride (I), m.p. 95–96°, was obtained by catalytic chlorinolysis of 2,4-dinitrophenyl disulfide.[4] Commercial acetylene (Prest-O-Lite) was purified by passage through concentrated sulfuric acid. 3-Hexyne (b.p. 80.8–81.1°), from Farchan Laboratories, Cleveland, Ohio, tested negatively for peroxides, and was used without further purification. 2-Butyne,[5] diphenylacetylene,[6] butynedioic acid[7] and diethyl butynedioate[8] were prepared by recorded procedures. Other reagents and solvents were C.P. grade or were purified by standard methods.

2-Chloro-1-(2′,4′-dinitrophenylthio)-ethene.—To 35 ml. of ethylene chloride, was added 2.35 g. (0.01 mole) of I and 0.1 g. of aluminum chloride. The solution was stirred magnetically and kept under an atmosphere of purified acetylene (initial pressure, 1.70 atm.) for 5 days, in an apparatus similar to the quantitative hydrogenator described by Joshel.[9] During this time, the acetylene pressure dropped to 1.35 atm. The reaction mixture was then washed with 50 ml. of 1 *N* hydrochloric acid and extracted with 150 ml. of benzene. The extract was washed twice more with 50-ml. portions of water and dried over anhydrous calcium chloride. Solvent was removed by distillation and the residue crystallized (with the aid of charcoal) from carbon tetrachloride; orange prisms, m.p. 128–129°, 1.99 g. (76%). Excellent orange needles could also be obtained from 95% alcohol. The analytical sample was recrystallized from carbon tetrachloride to m.p. 130–130.5°.

Anal. Calcd. for $C_8H_5N_2O_4SCl$: C, 36.86; H, 1.98; S, 12.30. Found: C, 36.85; H, 1.93; S, 12.22.

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(3) Microanalyses were performed by Mr. J. Pirie of this Laboratory. Melting points are not corrected.

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