

cis-2-butene (and evaporation of solvent) was dissolved in 70 ml. of dry acetic acid, and to this was added a mixture of 27 g. of 30% hydrogen peroxide in 20 ml. of dry acetic acid. The mixture was let stand at room temperature, and after one day a white precipitate (probably the sulfoxide) was noted. After standing three more days, this precipitate disappeared, and the solution was poured on 500 g. of crushed ice, the excess peroxide was decomposed with ferrous sulfate solution, and the white product collected and dried; yield 7.5 g. (85%), m.p. 58–60°. Three recrystallizations from hot aqueous methanol (30 vol. CH₃OH:5 vol. H₂O) raised the m.p. to 59.5°. An alternate procedure for isolation of the sulfone was to extract it with chloroform. (2) To obtain the sulfone of the *p*-toluenesulfonyl chloride adduct to *trans*-2-butene, the distilled adduct (b.p. 131–132° (4 mm.)), 4.2 g. was let stand for ten days at room temperature with a mixture of 22 g. of 30% hydrogen per-

oxide and 50 ml. of dry acetic acid. Pouring the solution on ice gave 3.5 g. (75%) of crude sulfone, m.p. 51–54°. Recrystallization from methanol/water, 18 vol./13 vol., gave the analytical sample, m.p. 56°. The adduct of *p*-toluenesulfonyl chloride to *cis*-2-butene, however, failed to yield a solid sulfone under identical conditions. A possible reason for this may be that the adduct from the *cis* olefin appears to lose hydrogen chloride more readily than does the corresponding *trans* adduct.

The infrared spectra of Fig. 1 were obtained with a Baird double-beam instrument, using a sodium chloride prism and 0.1 mm. cells, with chloroform solutions, containing 23.2 mg. of the *cis* adduct and 21.1 mg. of the *trans* adduct in 0.25 cc. of the solutions. The other infrared spectra (*cf.* footnote 5) were made on the same type of spectrophotometer, using Nujol mulls.

LOS ANGELES, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NEW YORK UNIVERSITY]

Sulfonic Acid Esters of 2-Nitro-2-methyl-1-propanol¹

BY ROBERT NEILSON BOYD AND RALPH H. HANSEN²

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A number of sulfonic acid esters of 2-nitro-2-methyl-1-propanol were prepared and tested as alkylating agents with various basic reagents. Only the reaction with sodium iodide in absolute acetone proceeded to a measurable extent, and then only when the sulfonyl moiety possessed electron-attracting substituents. The inactivity of the sulfonic acid esters in this type of reaction may be due chiefly to steric effects arising from the neopentyl-like structure.

Since alkylations using halonitroalkanes have not proved consistently successful,^{3,4} it was thought advisable to investigate the use of sulfonic acid esters of nitroalkanol as alkylating agents for the introduction of the nitroalkyl group. Those esters which have the structure, RR'C(NO₂)CH₂O₃SAr, are readily available in good yield through the procedure of Riebsomer.⁵ In the present investigation, the sulfonic acid esters of 2-nitro-2-methyl-1-propanol were chosen for study for the following reasons: (1) The nitroalkanol is a tertiary nitro compound; therefore the formation of nitroalkenes, which usually are produced when esters of primary or secondary nitroalcohols are treated with bases,⁶ will be obviated. (2) The nitroalcohol is a primary alcohol; and primary sulfonic acid esters, in addition to being more readily formed, are found (*e.g.* in the sugar series) to react quantitatively in at least one displacement reaction, namely, that with sodium iodide in acetone.⁷ On the other hand, secondary sulfonates, in addition to being more difficult to prepare, react only slowly, if at all, with sodium iodide.⁷

Only those arylsulfonic acid esters of 2-nitro-2-methyl-1-propanol which have highly electron-attracting substituents on the aryl group enter to any appreciable extent into a reaction with sodium iodide in acetone, as might be expected from the ef-

fect of electron-withdrawing groups upon the carbon-oxygen bond of the ester. Similar activation has been observed in the hydrolysis (in weakly alkaline solutions) of various arylsulfonic acid esters of ethanol.⁸ Those esters possessing negative substituents such as nitro groups hydrolyzed at rates ten to twenty times the rates of the benzenesulfonic acid ester or *p*-toluenesulfonic acid ester.

Since displacements on carbon are probably inhibited by the "neopentyl" structure of the esters of the nitroalcohol, displacement may have proceeded through rupture of the sulfur-oxygen bond of the sulfonate. Although this is unusual for arylsulfonic acid esters of aliphatic alcohols, for the alkyl-oxygen bond is ordinarily the one which is cleaved by basic reagents in displacement reactions, it may be possible that under the present experimental conditions the sulfur-oxygen bond was somewhat more vulnerable to cleavage. (This type of cleavage is found for the arylsulfonic acid esters of phenols, which will introduce the ArO- group in alkylation reactions.⁹) This mechanism would account for the formation of 2-nitropropane by dealdolization of the 2-nitro-2-methyl-1-propanol obtained on hydrolysis.

Acknowledgment.—The elemental analyses were done by the Micro-Chemical Laboratory at New York University, under the supervision of Professor T. S. Ma. Analyses were carried out by Mr. J. D. McKinley, Jr., Mr. N. R. Watt and Mr. R. E. Lang.

Experimental

Preparation of the Esters.—The arylsulfonic acid esters of 2-nitro-2-methyl-1-propanol were prepared according to the method of Riebsomer⁵ or Baker.¹⁰ The yields, melting

(1) Presented at the 122nd Meeting of the American Chemical Society at Atlantic City, N. J., September 19, 1952.

(2) Based on a dissertation presented by R. H. Hansen to the Graduate School of New York University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1952.

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TABLE I
 SULFONIC ACID ESTERS OF 2-NITRO-2-METHYL-1-PROPANOL

	Acid	M.p., °C.	Yield, %	Analyses Nitrogen, %		Method of purifica- tion
				Calcd.	Found	
1	<i>p</i> -Nitrobenzenesulfonic	147.9-148.3	70	9.21	9.20	<i>k</i>
2	<i>m</i> -Nitrobenzenesulfonic	92.4-93.2	61	9.21	8.92	<i>l</i>
3	<i>m</i> -Carboxybenzenesulfonic ^c	122.4-123.1	77	6.93	6.52	<i>k</i>
4	<i>p</i> -Acetamidobenzenesulfonic	152.3-153.4 ^b	97 ^b	<i>l</i>
5	Sulfanilic ^c	120.9-122.0	100	10.22	10.07	<i>l</i>
6	<i>p</i> -Fluorobenzenesulfonic	62.2-63.7	96	5.05	4.68	<i>m</i>
					5.42	
7	<i>p</i> -Bromobenzenesulfonic	108.6-109.7	71	4.14	4.30 ^e	<i>l</i>
8	3,4-Dichlorobenzenesulfonic	92.7-93.8	64	4.27	4.46 ^f	<i>l</i>
9	2,5-Dichlorobenzenesulfonic	145.0-146.3	58	4.27	4.50 ^g	<i>k</i>
10	<i>p</i> -Toluenesulfonic	75.3-76.7 ^d	67 ^d	<i>l</i>
11	<i>o</i> -Toluenesulfonic	80.7-81.9	79	5.13	5.05	<i>l</i>
12	α -Toluenesulfonic	88.2-88.7	90	5.13	5.23	<i>m</i>
13	2,5-Dimethylbenzenesulfonic	135.1-135.7	73	4.88	4.52 ^h	<i>k</i>
14	2,4-Dimethylbenzenesulfonic	83.2-85.2	82	4.88	4.70 ⁱ	<i>n</i>
15	2-Naphthalenesulfonic	95.4-95.9	85	4.53	4.62 ^j	<i>l</i>
16	Methanesulfonic	50.3-51.2	67	7.10	7.22	<i>m</i>
17	2-Thiophenesulfonic	85.7-86.7	75	5.28	5.22	<i>m</i>

^a Both acidic groups were esterified. ^b Riebsomer (ref. 5) reported m.p. 153-154°, yield 46%. ^c Prepared by hydrolysis of ester No. 4 with 10% aq. H₂SO₄. ^d Riebsomer (ref. 5) reported m.p. 73-74°, yield 77%. ^e Calcd.: C, 35.51; H, 3.58. Found: C, 35.6; H, 3.4. ^f Calcd.: C, 36.60; H, 3.38. Found: C, 36.4; H, 3.3. ^g Calcd.: C, 36.60; H, 3.38. Found: C, 36.3; H, 3.3. ^h Calcd.: C, 50.16; H, 5.97. Found: C, 50.3; H, 6.0. ⁱ Calcd.: C, 50.16; H, 5.97. Found: C, 50.2; H, 6.0. ^j Calcd.: C, 54.36; H, 4.89. Found: C, 54.1; H, 4.5. ^k Recrystallized from 80% methanol-20% acetone. ^l Recrystallized from 95% methanol-5% water. ^m Recrystallized from 90% methanol-10% water. ⁿ The ester was purified by eluting about 90% of the crude solid with methanol followed by reprecipitation by adding an excess of water. After repeating twice, method *l* was employed. The elution procedure was necessary because the ester was contaminated with the far less soluble isomeric 2,5-dimethylbenzenesulfonate which precipitated with it.

points, analyses and methods of purification are given in Table I. The sulfonyl chlorides were the best available commercially, and they were used without further purification. The 2-nitro-2-methyl-1-propanol was obtained through the courtesy of Commercial Solvents Corporation.

Reaction with Sodium Iodide.—The method used was the same for each of the esters. In a 250-ml. flask, equipped with a condenser and a drying tube which was filled with sodium hydroxide and calcium chloride, were placed 0.01 mole of the sulfonate, 2.0 g. (0.013 mole) of anhydrous sodium iodide and about 100 g. (120 ml.) of absolute acetone. This solution was heated under reflux and, after 2 to 6 hours, shiny plates began to appear in the refluxing liquid if a reaction was taking place. At the end of 30 hours, the precipitated solid was recrystallized from a mixture of methanol and ether, and then washed thoroughly with acetone, in which it seemed to be insoluble. In the case, for example, of the 2,5-dichlorobenzenesulfonic acid ester, 3.3 g. of the ester gave 1.1 g. of a solid which gave the correct analysis for sodium 2,5-dichlorobenzenesulfonate. This amount of solid was equivalent to 45% of the ester.

The acetone solution from which the plates had formed was then treated as follows. The acetone was evaporated on a steam-bath. The solid which remained was washed with anhydrous ether to remove the 2-nitro-2-methyl-1-iodopropane, and then washed with water to remove the unreacted sodium iodide, after which it was dried. In the case of the 2,5-dichlorobenzenesulfonic acid ester, the solid that was obtained amounted to 1.4 g., and proved to be unreacted sulfonate, as was determined by mixed melting points. This amount was 43% of the ester that was originally treated with the acetone solution of sodium iodide. Apparently, therefore, 57% of the ester reacted.

Results for the other esters are listed in Table II.

2-Nitro-2-methyl-1-iodopropane.—The ether extracts containing the nitroalkyl iodide from all the sodium iodide-acetone reactions were combined and, after removal of the ether, the residue was distilled under reduced pressure. After the distillation, the product, which was black, was treated with a dilute aqueous solution of sodium thiosulfate and then washed with water; finally it was dried and redistilled. 2-Nitro-2-methyl-1-iodopropane distilled at 104° under 17 mm. pressure, with some decomposition. It was obtained as a colorless liquid (*n*_D²⁰ 1.5250) which turned yellow on standing. *Anal.* Calcd. for C₄H₉O₂N: C,

 TABLE II
 REACTIONS WITH SODIUM IODIDE

Ester, sulfonates	Yield,	
	based on salt isolated, %	based on ester recovered, %
1 <i>p</i> -Nitrobenzene	51	47
2 <i>m</i> -Nitrobenzene	40	20
3 <i>m</i> -Carbalkoxybenzene	Traces	5
4 <i>p</i> -Acetamidobenzene	Traces	0
5 <i>p</i> -Aminobenzene	Traces	0
6 <i>p</i> -Fluorobenzene	8	61 ^a
7 <i>p</i> -Bromobenzene	19	23
8 3,4-Dichlorobenzene	61	70
9 2,5-Dichlorobenzene	45	57
10 <i>p</i> -Toluene	1	4
11 <i>o</i> -Toluene	Traces	11
12 α -Toluene	1	15
13 2,5-Dimethylbenzene	0	0
14 2,4-Dimethylbenzene	0	7
15 2-Naphthalene	8	3
16 Methane	Traces	0
17 2-Thiophene	2	20

^a Large loss due to high solubility of the ester.

20.97; H, 3.52; N, 6.12. Found: C, 21.40; H, 3.28; N 5.94.

Although the iodo compound was not isolated in each individual case, the yields of isolated sodium sulfonates listed in Table II give an approximate measure of the extent of the displacement, which ranged from 40 to 60% of theoretical. Similar treatment of 2-nitro-2-methyl-1-bromopropane with sodium iodide in acetone, gave a 36% yield of isolated sodium bromide.

Attempted Alkylations.—The alkylation of various substances by approximately molar equivalents of the sulfonic acid esters was attempted according to the following procedures, the reactant, the solvent, the reaction conditions, and the esters used being given in that order: (1) Sodium salt of ethyl acetoacetate; absolute ethanol; refluxed for

20 hours; esters 1,2,5,7,8,10,12,15,17 of Table I. (2) (a) Potassium cyanide, sulfonic acid ester dissolved in hot 95% ethanol, cyanide dissolved in 60% ethanol, refluxed for 12 hours; esters 1,2,5,7,8,10,11,12,15,16,17. (b) Cuprous cyanide, anhydrous pyridine, refluxed for 40 hours, ester 10. (3) Benzylmagnesium chloride, absolute ether, refluxed for 8 hours and allowed to stand for 16 hours; esters 1,2,5,6,7,8,10,12,16,17. (4) Benzylmagnesium chloride; *n*-butyl ether; refluxed for 8 hours; ester 8. (5) 2-Aminopyridine; benzene; refluxed for 48 hours or allowed to stand for 30 days at room temperature; ester 8.

The working-up of the reaction mixtures was carried out in straightforward fashion and offered no difficulties. Small amounts of tarry residues were not further investigated.

The alkylations were uniformly unsuccessful, the yield of recovered ester being usually about 90% where there was no reaction at all. In other cases, decomposition of the sulfonates occurred. The recovery of unreacted ester and decomposition products frequently accounted for about 80% of the starting material.

In reaction (2), several variations in conditions were imposed, *e.g.*, heating of the sulfonate with solid potassium cyanide or in pyridine with cuprous cyanide, or using aqueous Carbitol rather than aqueous ethanol as the solvent, with no greater success. In fact, when the tosylate was heated with a mixture of solid potassium cyanide and sodium iodide, in the hope that the iodide might catalyze the displacement, a small amount of the idonitroalkane was apparently formed instead of the desired nitrile.

In several instances it was noticed that ammonia was given off while the esters were refluxed with potassium cyanide (especially in the cases of the high-temperature reactions using aqueous Carbitol as a solvent, but also in the cases of the *p*-bromobenzenesulfonate and the 3,4-dichlorobenzenesulfonate, where aqueous ethanol was the solvent). Since there was the possibility that a nitrile was being formed and then hydrolyzed to the potassium salt of β -nitro- β -methylbutyric acid and ammonia, an attempt was made to isolate this acid in the case of the *p*-bromo and the 3,4-dichloro esters. For example, the basic aqueous solution, which remained after removal of the alcohol and of the sulfonic acid ester and other ether-soluble non-acidic organic

materials, and which would contain any acid, was acidified with dilute hydrochloric acid; but the expected evolution of hydrogen cyanide was not observed. The solution was then extracted with ether; the ether extract was dried over magnesium sulfate; and the ether was removed under vacuum. Two substances were obtained from the green ether solution: an oil, and a white solid with a pungent odor. The two were separated by filtration. Distillation of the oil gave mainly one substance, an acidic liquid, b.p. 105°, which did not contain nitrogen, and which presumably was formic acid. The white solid was quite soluble in most organic solvents, giving an intense blue solution in each case. It was found to contain nitrogen, and after recrystallization from chloroform it melted at 74–75° to give a blue liquid that decomposed immediately. The blue color of the solutions and of the pure liquid indicated that the substance was a nitroso compound, and probably the pseudo-nitrole, $(\text{CH}_3)_2\text{C}(\text{NO}_2)\text{NO}$, which has a melting point of 76°. A mixed melting point of an authentic specimen (prepared by acidification by dilute hydrochloric acid of a solution of sodium nitrite and 2-nitropropane in dilute sodium hydroxide) with the material from the cyanide reaction showed no depression. Evidently 2-nitropropane and nitrogen oxides were formed by the decomposition of the sulfonates.

The amount of ester that was recovered in the attempted alkylation of potassium cyanide with the *p*-bromobenzenesulfonate in aqueous ethanol was 55%. The pseudo-nitrole which was obtained accounted for an additional 20% (0.01 mole of the pseudo-nitrole was obtained when 0.1 mole of the ester was used). The remaining 25% was not accounted for, but may have given additional amounts of nitrogen oxides as decomposition products, and thus would not be isolated.

Oxides of nitrogen were observed in reaction (4); in reaction (2) if Carbitol was the solvent; and in reaction (5) if nitrobenzene was used in place of benzene as the solvent. The ester of 3,4-dichlorobenzenesulfonic acid (Table I, ester 8) was selected for reactions (4) and (5) because it had given the highest yield in the reaction with sodium iodide in acetone. Appreciable amounts of toluene and bibenzyl were isolated from reactions (3) and (4).

NEW YORK, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

Reaction Rates by Distillation. V. The Effect of Changes in Structure on the Basicity of Selected Ketones, Esters, Ethers and Alcohols¹

BY ERNEST F. PRATT AND KEN MATSUDA²

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The relative basicities of sixty-one selected ketones, esters, ethers and alcohols have been quantitatively determined by measuring their ability to decrease the rate of the acid-catalyzed self-etherification of benzhydrol or the dehydration of *t*-butyl alcohol in benzene solution. The major conclusions are: (1) alcohols are much more basic than the corresponding symmetrical ethers. (2) Olefinic bonds at the α,β -position greatly increase the basicity of ketones. (3) The basicity of ethers increases as the number of α -phenyl groups decreases or as a phenyl group is shifted away from the oxygen. (4) The basicity of esters increases as the number of α -chlorine atoms decreases or as a chlorine atom is shifted away from the oxygen. (5) The basicity of para substituted acetophenones increases as the electron releasing ability of the substituent is increased in the order NO_2 , Cl, H, CH_3 , $(\text{CH}_3)_2\text{C}$ and CH_3O . A similar trend was established for the para substituted ethyl benzoates. (6) In $\text{CH}_3\text{CO}(\text{CH}_2)_n\text{COCH}_3$ and $\text{C}_2\text{H}_5\text{OCO}(\text{CH}_2)_n\text{COOC}_2\text{H}_5$, the basicity decreases rapidly as *n* decreases; when *n* is zero the basicities are far below those for the corresponding monofunctional compounds. (7) The extent to which the changes in basicity for the six groups of compounds of items (4), (5) and (6) may be quantitatively correlated with the changes in acidity of the corresponding carboxylic acids is shown graphically.

Increasing interest is being shown in the basicities of organic oxygen bases³ as well as of the even less

basic aromatic hydrocarbons.⁴ Data on the basicities of these extremely weak bases have numerous important applications, *e.g.* (1) in predicting which of two functional groups will react preferentially with a proton, carbonium ion, or other acidic particle^{5,6}; (2) in the separation of mixtures by con-

(1) For the preceding article in this series see E. F. Pratt and L. Q. Green, *THIS JOURNAL*, **75**, 275 (1953).

(2) From the Ph.D. thesis of Ken Matsuda, Sept., 1951.

(3) Recent pertinent publications not referred to more specifically elsewhere in this paper are: E. A. Braude, *J. Chem. Soc.*, 1971 (1948); M. H. Dilke, D. D. Eley and M. G. Sheppard, *Trans. Faraday Soc.*, **46**, 261 (1950); J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," Third Ed., Reinhold Publishing Corp., New York, N. Y., 1950, p. 420; S. Searles and M. Tamres, *THIS JOURNAL*, **73**, 3704 (1951); R. E. Van Dyke and H. E. Crawford, *ibid.*, **73**, 2018 (1951).

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(5) F. E. Condon, *ibid.*, **74**, 2528 (1952).

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