The increase in yield with lowered temperature is shown in Table III. The catalyst concentration was 1.5 g./mole of acetyl chloride.

TABLE III

Addition temp., °C.	Catalyst	Yield of 2-hexanone, %	Addition temp., °C.	Catalyst	Yield of 2-hexanone, %
34	Cu_2Cl_2	12	34	$CoCl_2$	4
15	Cu_2Cl_2	25	15	$CoCl_2$	13
5	Cu_2Cl_2	37	15	$FeCl_3$	47
−30	Cu_2Cl_2	41	−65	$FeCl_3$	72
−65	Cu_2Cl_2	48	−65	None	31

TABLE IV

RCOCl/RMgX (moles/mole)	Addition temp., °C.	Catalyst, g./mole RCOCl	Yield[a] of 2-hexanone, %
1/1	5	1.5 Cu_2Cl_2	37
3/1	5	1.5 Cu_2Cl_2	39
1/1	15	1.5 $FeCl_3$	47
3/1	15	1.5 $FeCl_3$	50
3/1	−65	1.5 $FeCl_3$	72
3/1	−65	None	31
3/1	−65	10.0 $FeCl_3$	68

[a] The small variance in yield between comparable reactions is presumably the reproducibility of a single reaction.

The effect of varying ratio of reactants is shown in Table IV.

The fact that the reaction proceeds instantaneously was shown in three reactions using $FeCl_3$ at −65° (Table V).

TABLE V

Period of RMgX addition, hr.	Additional stirring time at −65°	Heating period at 100°	Yield of 2-hexanone, %
5	12 (hr.)	3 (days)	72
5	12 (hr.)	0	66
5	5 (min.)	0	71

The time of addition is apparently limited only by the efficiency of heat transfer during this very exothermic reaction.

Preparation of Hexamethylacetone.—To a solution of 241 g. (2 moles) of trimethylacetyl chloride in 2 l. of ethyl ether was added 2 g. of ferric chloride, and the reactants were heated to reflux. During 2 hours, 2 moles of *t*-butylmagnesium chloride (approximately 3 *M*) was added. The reactants were stirred at reflux temperature for an additional hour and the mixture was then decomposed by the addition of a water–ice mixture. The layers were separated and the product was fractionated through column II to give 477 g., 1.68 moles, of hexamethylacetone, b.p. 152°, $n^{20}D$ 1.4192. The yield is 84%. The identification of this product has been described.[1]

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

Derivatives of Sulfenic Acids. XI. Reactions of Sulfenyl Halides with the *cis*- and *trans*-2-Butenes

BY NORMAN KHARASCH AND ANTON J. HAVLIK[1]

RECEIVED MARCH 20, 1953

2,4-Dinitrobenzenesulfenyl chloride, bromide and thiocyanate, 2-nitrobenzenesulfenyl chloride, *p*-toluenesulfenyl chloride and 2,4-dichlorobenzenesulfenyl chloride react with the *cis*- and *trans*-2-butenes to give excellent yields of the corresponding 1:1 adducts. On the basis of melting points, oxidations to different sulfones, refractive indices and infrared spectra, it is concluded that the products are diastereomeric racemates. The probable mode of formation of the adducts is briefly discussed.

While the reaction of sulfenyl halides with olefins is now well known,[2] the only example involving a *cis–trans* olefin pair is the characterization of the isomeric 2-phenyl-2-butenes, reported by Cram.[3] In undertaking our work on this aspect of sulfenyl halide chemistry, it therefore seemed desirable to investigate, initially, the reactions of several sulfenyl halides with the simplest *cis–trans* olefin pair. Table I summarizes the results with six selected sulfenyl halides. The additions of the halides to the 2-butenes were carried out at room temperature, in dry ethylene chloride solutions, in a gas-addition apparatus similar to the one described by Joshel.[4]

The six adducts from 2,4-dinitrobenzenesulfenyl chloride, bromide and thiocyanate and the 2-butenes were excellent solid derivatives. The melting points of the corresponding adduct pairs differed between themselves, and mixtures of the isomeric adducts showed decided melting point depressions. The adducts from 2-nitrobenzenesulfenyl chloride, 2,4-dichlorobenzenesulfenyl chloride and *p*-toluenesulfenyl chloride, however, were liquids. Since the four adducts resulting from 2-nitrobenzenesulfenyl chloride and 2,4-dichlorobenzenesulfenyl chloride were readily converted to corresponding pairs of sulfones, the isolations of the pure 1:1 adducts were not effected in these cases. For the 1:1 adducts from the 2-butenes and *p*-toluenesulfenyl chloride, however, isolations of the pure liquids were carried out, since conversion to a solid sulfone could be effected only for the adduct from the *trans*-2-butene. The adduct of *p*-toluenesulfenyl chloride and *cis*-2-butene did not yield a solid sulfone, even though identical conditions were used to carry out the oxidation as were used in the formation and isolation of the sulfone from the isomeric *trans* adduct. While this difference implied that the *p*-toluenesulfenyl chloride adducts were not identical, the variation in indices of refraction of the pure adducts, as well as the results of the infrared spectrograms (Fig. 1) definitely confirmed the implied difference.[5]

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[1] Atomic Energy Commission Predoctoral Fellow, University of Southern California, 1951–1953.

[2] N. Kharasch and C. M. Buess, THIS JOURNAL, **71**, 2724 (1949). and references cited therein. *Cf.* also *ibid.*, **74**, 3422 (1952).

[3] D. J. Cram, *ibid.*, **71**, 3884 (1949).

[4] L. M. Joshel, *Ind. Eng. Chem., Anal. Ed.*, **15**, 590 (1943).

[5] Infrared spectrograms in the 2 to 16μ region were also obtained for all the other 1:1 adducts or corresponding sulfones of Table I. While the differences between the *cis* and *trans* adducts of *p*-toluenesulfenyl chloride (Fig. 1) are more marked than those from any other pair of the products, the results in every case support the conclusion that the products stemming from *cis*-2-butene are different from the corresponding products resulting from *trans*-2-butene. The remaining spectra, together with those of the sulfenyl halides and several groups of related products stemming from the latter, will be described in a later paper.

TABLE I

PRODUCTS FROM THE REACTIONS OF SULFENYL HALIDES WITH THE *cis*- AND *trans*-2-BUTENES

Sulfenyl halide	1:1 Adduct from *cis*-2-Butene	1:1 Adduct from *trans*-2-Butene	Sulfone from *cis*-Adduct	Sulfone from *trans*-Adduct	Analyses,[a] % Carbon Calcd.	Analyses,[a] % Carbon Found	Analyses,[a] % Hydrogen Calcd.	Analyses,[a] % Hydrogen Found	Compound
2,4-Dinitrobenzenesul-	128–129°[b]	76.5–77.5°[c]	...[d]	...[d]	41.31	41.51	3.81	3.96	*cis*-Adduct
fenyl chloride	(90%)	(89%)			41.31	41.52	3.81	3.93	*trans*-Adduct
2,4-Dinitrobenzenesul-	136.5–137°	91.5–92°	...[d]	...[d]	35.83	35.84	3.31	3.50	*cis*-Adduct
fenyl bromide	(92%)	(85%)			35.83	35.90	3.31	3.41	*trans*-Adduct
2,4-Dinitrobenzenesul-	71.5–72.5°	75.5–76.5°[e]	...[d]	...[d]	42.16	42.16	3.54	3.68	*cis*-Adduct
fenyl thiocyanate	(90%)	(57%)			42.16	42.17	3.54	3.73	*trans*-Adduct
2-Nitrobenzenesulfenyl	......[f]	......[f]	59–59.5°	133–134°	43.24	43.19	4.36	4.32	*cis*-Sulfone
chloride			(85%)	(83%)	43.24	43.34	4.36	4.15	*trans*-Sulfone
2,4-Dichlorobenzenesul-	......[f]	......[f]	59°	57.5°	39.82	39.86	3.68	3.68	*cis*-Sulfone
fenyl chloride			(99%)	(95%)	39.82	39.84	3.68	3.58	*trans*-Sulfone
p-Toluenesulfenyl	B.p. 122–123°	B.p. 131–132°	....[g]	56°	61.52	61.48	7.04	7.10	*cis*-Adduct
chloride	(3 mm.)	(4 mm.)			61.52	61.20	7.04	6.90	*trans*-Adduct
	(79% pure)	(74% pure)			53.54	53.72	6.13	6.19	*trans*-Sulfone
	n^{26}D 1.5498	n^{26}D 1.5530							

[a] We are indebted to Dr. Adalbert Elek and Mr. J. V. Pirie for carrying out the microanalyses. [b] This product was previously reported from reaction of the sulfenyl chloride and a 2-butene of unspecified geometry.[2] Numerical values in degrees are for the melting points (uncor.), unless indicated for the boiling points (b.p.). Yields of adducts are for the crude dry products, generally melting within a few degrees of the melting points recorded for the analytical samples. The greatest deviation was in the case of the adduct of 2,4-dinitrobenzenesulfenyl bromide to *cis*-2-butene (crude m.p 127–134°). The yields for the *p*-tolyl derivatives are for the distilled adducts. [c] This melting value is for the product as obtained in two original experiments; but on standing for extended periods, the lower melting product yielded one which melted at 83–84°. The tabulated melting point therefore appears to be for the metastable form. *Cf.* also Experimental. [d] The sulfones were not prepared in these instances, since the 1:1 adducts were excellent solids. [e] The total crude product was not recovered in this case, since the reaction of addition was extremely slow. For qualitative rates of the additions, compare the text. [f] The 1:1 adducts were liquids in these cases, obtained in near quantitative yields. They were oxidized directly to the sulfones as illustrated in the Experimental part. Yields of the sulfones are for the crude, dry products. [g] The sulfone from the *cis* adduct could not be obtained as a solid product under conditions identical to those which easily led to the sulfone from the corresponding adduct to *trans*-2-butene.

The pairs of adducts from the *cis*- and *trans*-2-butenes are undoubtedly diastereomeric racemates, whose formation would be predicted on the basis of ionic, *trans* addition, *via* a cyclic sulfonium ion, as

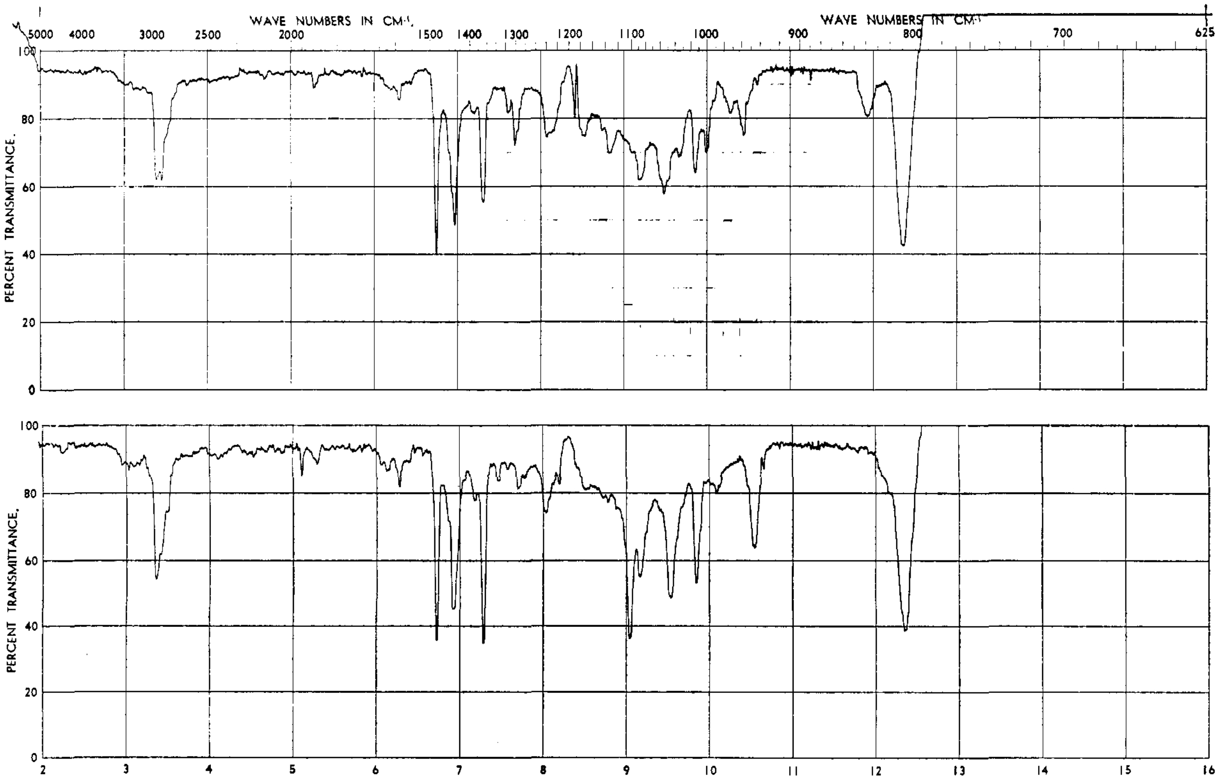

Fig. 1.—Infrared absorption spectra of the adducts of *p*-toluenesulfenyl chloride to *cis*-2-butene (above), and to *trans*-2-2-butene (below), in chloroform solutions.

already suggested in earlier work.[2,3,6] The results of the present study also suggest a general method for characterizing other *cis-trans* olefin pairs by solid derivative formation. We would consider 2,4-dinitrobenzenesulfenyl chloride as the most suitable first-choice reagent for this purpose—since this sulfenyl chloride is readily prepared and stored; and there is already considerable information about its reactions with olefins.

Some other points may also be mentioned. (1) As could have been anticipated from the nature of the substituent groups in the benzene rings, the qualitative rates of additions of *p*-toluenesulfenyl chloride and 2,4-dichlorobenzenesulfenyl chloride with the 2-butenes were decidedly faster than the corresponding reactions with 2,4-dinitrobenzenesulfenyl chloride and bromide; but, in turn, the reactions of the last two compounds were more rapid than were those of the 2-butenes with 2,4-dinitrobenzenesulfenyl thiocyanate. (2) In the reaction of 2,4-dinitrobenzenesulfenyl bromide with *trans*-2-butene, a definite initial pressure of the 2-butene (at least 1.5 atm.) was necessary before the reaction took place at an observable rate. To ensure a successful reaction between the sulfenyl bromide and *cis*-2-butene, a higher initial pressure of the olefin (1.9 atm.) also was used, so that it cannot be stated from the present data whether the reaction would have proceeded at a lower pressure of *cis*-2-butene. The effect with *trans*-2-butene and the sulfenyl bromide was, however, quite distinct, suggesting the need for further study of this point. (3) The improved synthesis of 2,4-dinitrobenzenesulfenyl thiocyanate, which is described in the Experimental part, depended on the earlier observation made in this Laboratory[7] that the preparation, *via* the reaction $ArSCl + SCN^- \rightarrow ArSSCN + Cl^-$, is markedly facilitated by the presence of water.

Acknowledgment.—We are indebted to Philip Sadtler of Samuel P. Sadtler and Son, Inc., and to Chester M. Hauck of the Rexall Drug Co. for assistance in obtaining the infrared spectra.

Experimental

Starting Materials.—The pure *cis*- and *trans*-2-butenes were obtained from the Phillips Petroleum Company. 2,4-Dinitrobenzenesulfenyl chloride,[8] the corresponding bromide,[9] 2-nitrobenzenesulfenyl chloride[10] and *p*-toluenesulfenyl chloride[11] were obtained by recorded procedures. To obtain the latter satisfactorily, special care was required to exclude moisture and light. This was done by encasing the reaction flask in aluminum foil, using dry, distilled solvent (ethylene chloride), and drying the chlorine by passage through sulfuric acid. 2,4-Dichlorobenzenesulfenyl chloride, a new compound (b.p. 94–96° (4 mm.)) was kindly supplied by Dr. M. B. Sparke, and will be described in detail in paper XII of this series.

The improved synthesis of 2,4-dinitrobenzenesulfenyl thiocyanate[12] follows: 2,4-dinitrobenzenesulfenyl chloride (23.0 g., 0.1 mole), 200 ml. of technical-grade methylene chloride, 40 g. of potassium thiocyanate and 2.5 ml. of water were shaken in a closed flask for about 20 min. (compared to 20 hr.[12]). The supernatant liquid was decanted, and the residue was washed with two 25-ml. portions of methylene chloride. The washings and solution containing the product were combined and evaporated (water pump, *ca.* 40°), and the residual yellow solid was dissolved in 60 ml. of hot methylene chloride and diluted with 500 ml. of Skellysolve F. Refrigeration of the opaque mixture gave 22.0 g. of a yellow product (87.5%), m.p. 80.5–82.5°. This was suitable for all synthetic purposes, but the melting point could be raised to 84° by repeated crystallizations.

Preparation of the Products of Table I.—The preparation of the adduct of 2,4-dinitrobenzenesulfenyl chloride to *trans*-2-butene is illustrative. Into a 250-ml. hydrogenation flask, attached to a gas-addition apparatus similar to the one described by Joshel,[4] but larger in size, was placed 6.0 g. (0.026 mole) of the sulfenyl chloride and 100 ml. dry ethylene chloride. The flask was fitted with a copper-encased magnetic stirring bar, the air in the system was evacuated (water pump), and *trans*-2-butene was added to an initial pressure of 1.4 atm. More 2-butene was added as necessary, and when 1400 ml. had been absorbed (about one hour), a negative starch–iodide test for the sulfenyl chloride was obtained. The solvent from the reaction mixture was aspirated at the water pump, while heating on the steam-bath, and the crude, dry product (7.4 g.) was dissolved in 12 ml. of hot chloroform. Addition of 15 ml. of Skellysolve F precipitated a yellow powder (6.6 g., 89%), m.p. 73–76°. Repetition of this treatment raised the m.p. to 77–78°. Admixture of this adduct and the 1-butene adduct (m.p. 74–75.5°) showed a sharp depression (58–75°). The analytical sample was prepared by four recrystallizations of the 73–76° melting product from an 80–20 mixture (by volume) of absolute alcohol–Skellysolve F. The same adduct (m.p. 74–76°, crude) was obtained in 75% yield by using glacial acetic acid as the solvent for the reaction. On keeping the analytical sample of the *trans*-2-butene adduct for several months, it was noted that the melting point rose from 76.5–77.5° to 83–84°. A similar behavior was not observed with any other of the products of Table I.

The other 1:1 adducts of Table I were obtained by similar procedures, as above. A few additional points are noted in footnotes to Table I, and below (Ar = 2,4-dinitrophenyl). (a) The initial pressure required to prepare the adduct of ArSBr to *trans*-2-butene was at least 1.5 atm. With an initial pressure of 1.9 atm., reaction was complete in less than one hour. The adduct of ArSBr to *cis*-2-butene was also obtained by using an initial pressure of 1.9 atm. (b) In the reaction of ArSSCN with *cis*-2-butene, addition was incomplete after 24 hours—under conditions where the corresponding reaction with ArSBr was complete in less than one hour. Titration ($2ArSSCN + 2I^- \rightarrow ArSSAr + I_2 + 2SCN^-$) showed *ca.* 3% unreacted ArSSCN. In another run, a negative test for ArSSCN was obtained after 48 hr. The crude product (m.p. 68–73°) was purified by diluting a hot solution of the adduct in ethylene chloride with Skellysolve F, causing crystallization of the product. A mixture of this adduct (m.p. 71–72.5°) and ArSSCN (m.p. 80.5–82.5°) melted at 48–79°. (c) Addition of ArSSCN to *trans*-2-butene, at an initial pressure of 2 atm. of 2-butene was extremely slow, and was incomplete even after five days. To avoid using large amounts of the expensive *trans*-2-butene, and because the reaction mixture had a tendency to precipitate solid material, the reaction was carried out with shaking, on a Parr hydrogenation apparatus, the 2-butene being introduced directly from its original container into a small manifold on which a pressure gage was mounted. In contrast to these slow reactions, the additions of *p*-toluenesulfenyl chloride and 2,4-dichlorobenzenesulfenyl chloride occurred as rapidly as the 2-butenes could be added to the solutions of the sulfenyl chlorides.

The oxidation of the adducts of Table I are illustrated by the following examples. (1) The oil (8 g.) obtained from the reaction of 6.0 g. of 2-nitrobenzenesulfenyl chloride with

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(6) For evidence which favors an ionic mechanism for the reaction, based on a kinetic investigation of the reaction of 2,4-dinitrobenzenesulfenyl chloride with styrene, a succeeding paper in this series (N. Kharasch and W. L. Orr) may be consulted. *Cf.* also abstracts of papers presented at the meeting of the American Chemical Society, Los Angeles, California, March 15–19, 1953.

(7) N. Kharasch and O. F. Markles, unpublished work.

(8) N. Kharasch, G. I. Gleason and C. M. Buess, THIS JOURNAL, **71**, 1796 (1949).

(9) N. Kharasch, C. M. Buess and S. I. Strashun, *ibid.*, **74**, 3422 (1952).

(10) M. Hubacher, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 220.

(11) H. Lecher and co-workers, *Ber.*, **58**, 409 (1925).

(12) Compare N. Kharasch, H. L. Wehrmeister and H. Tigerman, THIS JOURNAL, **69**, 1612 (1947).

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. CH_3OH:5 vol. H_2O) 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*-toluenesulfenyl 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 peroxide 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*-toluenesulfenyl 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-propanol[1]

BY ROBERT NEILSON BOYD AND RALPH H. HANSEN[2]

RECEIVED JULY 1, 1952

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 nitroalkanols as alkylating agents for the introduction of the nitroalkyl group. Those esters which have the structure, $RR'C(NO_2)CH_2O_3SAr$, 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 effect 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 Riebsomer[5] or Baker.[10] The yields, melting

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[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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[10] P. J. Baker, Jr., U. S. Patent 2,395,386 (Feb. 26, 1946).