50° for 50 min (W-6). Their activity ratings on the W scale were obtained from comparisons with the known ratings of the W-1 and W-6 catalysts as described by Augustine.[5] In this way Hubbell and Rys'[2] catalyst preparation procedure yielded the ">W-2" catalyst, the procedure of Izumi, *et al.*,[1] yielded the ">W-1" catalyst, and one was prepared for this study, with the lowest hydrogenation activity, as the "W-0" catalyst.

Modification of Raney Nickel Catalyst. In each case the modification reaction was carried out by adding 1 l. of a 2% aqueous solution of optically active (2*R*, 3*R*)-tartaric acid (initial pH adjusted to 4.9 by addition of NaOH) to the washed catalyst and refluxing for 1 hr.

Hydrogenation of Methyl Acetoacetate. All reactions were carried out in stirred autoclaves at 60°, 90 atm H_2, and catalyst concentrations of 0.05 g of untreated Ni–Al alloy per milliliter of reactant.

Low-Conversion Calibration Curve. Samples taken during the low-conversion part of the reaction were extremely difficult to separate into their optically active alcohol product and nonoptically active ketone reactant. In addition, large volumes were required to get sufficient alcohol to fill the polarimeter cell. The use of a calibration curve allowed the determination of the optical activity of the pure alcohol product by measurement of the optical activity of the ketone–alcohol mixture.

A methyl 3-hydroxybutyrate of known optical activity was diluted with varying amounts of methyl acetoacetate (to give between 100 and 5% alcohol solutions) and the optical activities of the mixtures were measured. The same procedure was done with two other methyl 3-hydroxybutyrates of different optical activities and it was found that for the entire concentration range one curve of percentage decrease in optical activity from the pure alcohol *vs.* concentration would suffice. This curve was then used to determine the optical activity for the samples taken during the reaction.

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Registry No.—Methyl acetoacetate, 105-45-3; methyl 3-hydroxybutyrate, 1487-49-6.

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Friedel–Crafts Chemistry. IX.[1] Aluminum Chloride and Antimony Pentafluoride Catalyzed Desulfonylative Alkylation of Aromatics with Isopropyl, *tert*-Butyl, and Benzylsulfonyl Halides and Related Sulfones

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In the study of the Friedel–Crafts reactions of *tert*-alkylcarbonyl halides, such as pivaloyl chloride, it was observed that they readily decarbonylate, thus can also act as alkylating agents.[3] Consequently, alkylsulfonyl halides also may desulfonylate and alkylate aromatics, although these systems so far were reported to act exclusively as sulfonylating agents in Friedel–Crafts reactions.[4] In fact, however, desulfonylation of alkylsulfonyl chlorides is known to take place under various conditions.[5]

tert-Butylsulfonyl chloride, for example, can easily undergo homolytic decomposition to yield *tert*-butyl radical chlorine atom, and sulfur dioxide.[6] The attempted Friedel–Crafts cyclization of ω-arylalkylsulfonyl chlorides was reported to give only unidentified decomposition products.[7]

We considered it of interest to undertake a study of the Friedel–Crafts reactions of sulfonyl halides potentially capable of undergoing desulfonylation and thus give alkylated product. As the formation of *tert*-butyl cation and protonated benzylsulfinic acid has been reported in the protolysis of *tert*-butyl benzyl sulfone in "magic acid,"[8] we also extended our investigation to related Friedel–Crafts reactions of sulfones potentially capable of alkyl–sulfur cleavage. We would like to report now the observation of the novel Friedel–Crafts desulfonylative alkylation of aromatics, namely benzene and toluene, with several sulfonyl chlorides and sulfones.

Results and Discussion

Isopropyl, *tert*-butyl-, benzyl-, and *p*-methylbenzylsulfonyl chloride gave ready alkylation of aromatics in the presence of aluminum chloride–nitromethane catalyst at 25°. The reaction with *p*-nitrobenzylsulfonyl chloride needed to be carried out at 60° using aluminum chloride, not complexed with nitromethane, in excess of aromatic hydrocarbon as solvent.

$$\mathrm{ArH} + \mathrm{RSO_2Cl} \xrightarrow{\mathrm{AlCl_3}} \mathrm{ArR} + \mathrm{SO_2} + \mathrm{HCl}$$

Isopropyl *p*-tolyl sulfone, *tert*-butyl *p*-tolyl sulfone, and benzyl *p*-tolyl sulfone similarly gave alkylation in excess aromatic as solvent in the presence of aluminum chloride.

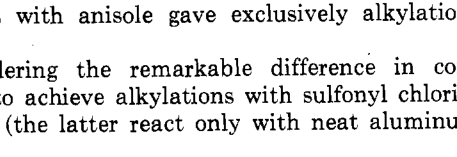
$$\mathrm{ArH} + \mathrm{RSO_2}\text{-}p\text{-}\mathrm{Tol} \xrightarrow{\mathrm{AlCl_3}} \mathrm{ArR} + p\text{-}\mathrm{TolSO_2H}$$

tert-Butyl benzyl sulfone did not alkylate in the presence of aluminum chloride at 80°, but reacted with antimony pentafluoride in 1,1,2-trichloro-1,2,2-trifluoroethane solution (Freon 113) to give *tert*-butylbenzene and -toluene from benzene and toluene, respectively. Generally, the alkylation with sulfones necessitates more severe conditions than that with sulfonyl chlorides.

Methyl- and ethylsulfonyl chlorides and sulfones did not give alkylation products, indicating that the desulfonylative cleavage has no driving force in these primary systems.

The results of desulfonylative alkylations are summarized in Table I.

We have also determined whether in the studied desulfonylative alkylations competing sulfonylation also takes place. In the case of the reaction of benzene with benzylsulfonyl chloride and *tert*-butylsulfonyl chloride only alkylation products were obtained. Isopropylsulfonyl chloride gave 94.3% alkylation products and 5.7% isopropyl phenyl sulfone, the competing sulfonylation product. All reactions with anisole gave exclusively alkylation products.



I II

Considering the remarkable difference in conditions needed to achieve alkylations with sulfonyl chlorides and sulfones (the latter react only with neat aluminum chlo-

Table I

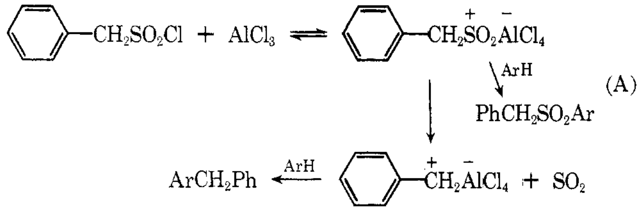
Alkylation of Benzene and Toluene with Alkylsulfonyl Chlorides and Sulfones (RSO_2X)

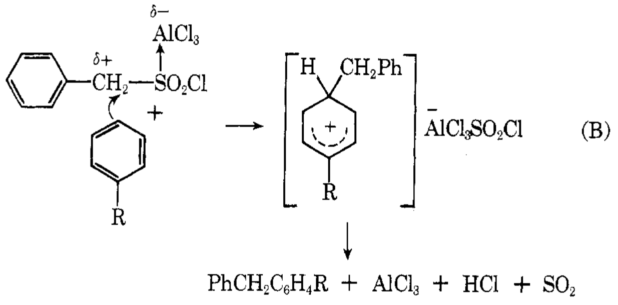
Registry no.	R	X	Solvent	Catalyst	Temp, °C	Time, hr	k_T/k_B	Isomer ratio of alkyltoluene, % o-	m-	p-
51751-71-4	*i*-Pr	*p*-Tol		$AlCl_3$[a]	60	1.0	0.5	2.2	65.1[e]	32.5[f]
10147-37-2	*i*-Pr	Cl	CH_3NO_2	$AlCl_3$	25	4.0	1.5	46.7[g]	22.6	30.7
5324-90-3	*t*-Bu	*p*-Tol		$AlCl_3$	60	1.0	0.6		33.2[h]	66.8[i]
20282-89-7	*t*-Bu	$PhCH_2$	Freon 113	SbF_5[b]	20	0.25	0.8		68.0	32.0
	t-Bu	$PhCH_2$		$AlCl_3$[c]	80	24.0				
10490-22-9	*t*-Bu	Cl	CH_3NO_2	$AlCl_3$[a]	25	0.16	16.1		8.7	91.3
51419-59-1	*p*-$CH_3C_6H_4CH_2$	Cl	CH_3NO_2	$AlCl_3$	25	1.0	30.8	30.3[j]	3.1	66.7[k]
1939-99-7	$PhCH_2$	Cl	CH_3NO_2	$AlCl_3$	25	1.0	4.2	34.4[l]	3.3	62.4[m]
	$PhCH_2$	Cl		$AlCl_3$[d]	Room	2.0		47.1		52.9
4025-75-6	*p*-$NO_2C_6H_4CH_2$	Cl		$AlCl_3$[a]	60	2.0	1.2			
	p-$NO_2C_6H_4CH_2$	Cl	CH_3NO_2	$AlCl_3$[c]	25	3.5				
3112-88-7	$PhCH_2$	Ph		$AlCl_3$[a]	60	1.0	2.5	37.5	10.1	52.4
	$PhCH_2$	Ph	CH_3NO_2	$AlCl_3$[c]	Room	48.0				

[a] Reaction conditions: 1:1 (mol/mol) benzene–toluene mixture, 10 g; solvent, 10 ml; aluminum chloride, 0.01 mol; alkylating agent, 0.005 mol. [b] Reaction conditions: 1:1 (mol/mol) benzene–toluene mixture, 10 g; 1,1,2-trichloro-1,2,2-trifluoroethane, 10 ml; antimony pentafluoride, 0.02 mol; *tert*-butyl benzyl sulfone, 0.02 mol. [c] No reaction occurred. [d] The reaction of anisole (50 ml), the chloride (0.01 mol), and aluminum chloride (0.01 mol) was carried out at room temperature for 2 hr. [e] Registry no., 535-77-3. [f] Registry no., 99-87-6. [g] Registry no., 1595-06-8. [h] Registry no., 1075-38-3. [i] Registry no., 98-51-1. [j] Registry no., 21895-17-0. [k] Registry no., 4957-14-6. [l] Registry no., 713-36-0. [m] Registry no., 620-83-7.

ride in hydrocarbon media, but not like the sulfonyl chlorides in nitromethane solution), there is little possibility for the formation of sulfones as intermediates during desulfonylative alkylations with sulfonyl chlorides.

There are two possible mechanisms for the studied Friedel–Crafts reactions with sulfonyl chlorides. The first (A) involves a stepwise formation of an alkyl cation *via* fragmentation of the corresponding sulfonyl cation, *i.e.*, SN1 type reaction involving initial ionization of the sulfonyl chloride by the catalyst. The second (B) involves displacement of the alkyl group from the polarized sulfonyl chloride–catalyst complex, *via* R–S fission, *i.e.*, SN2 type reaction. The experimental data obtained do not allow a differentiation, although there is little evidence for ionization of sulfonyl halides.[9]


(A)


(B)

Experimental Section

Melting points are not corrected. *tert*-Butylsulfonyl chloride (mp 95°, lit.[6] mp 95–95.5°), *p*-methylbenzylsulfonyl chloride[6] (mp 80–81°), *p*-nitrobenzylsulfonyl chloride (mp 93°, lit.[10] mp 89–90°), isopropyl *p*-tolyl sulfone (mp 83°, lit.[11] mp 80°), *tert*-butyl *p*-tolyl sulfone (mp 121°, lit.[12] mp 120°), and benzyl *p*-tolyl sulfone (mp 145°, lit.[13] mp 146–147°) were prepared by known methods. Other materials were commercially available. Glc analyses were carried out on Perkin-Elmer Models 226 and F-11 gas chromatographs, the former equipped with a nitrogen flame ionization detector, and using an electronic printing integrator. MBMA [*m*-bis(*m*-phenoxyphenoxy)benzene] and Apiezon L coated 150 ft × 0.01 in. open tubular stainless steel columns were used for analyses of isopropylations and *tert*-butylations, a purified Apiezon L coated column for that of benzylation, and a butanediol succinate coated column for that of *p*-nitrobenzylation, respectively. Sulfones were analyzed using Chromosorb (RAW 80/100 mesh) coated with 590 SE-30 oil (Chemical Research Services, Inc.).

General Procedure for Alkylation with Sulfonyl Chlorides. Into a mixture of benzene (10 ml) and aluminum chloride (2.66 g, 0.02 mol), benzylsulfonyl chloride (1.9 g, 0.01 mol) was slowly added at 25° with vigorous stirring under nitrogen for 2 hr. The reaction mixture was poured into 50 ml of ice–water and the aqueous layer was extracted with 50 ml of ether. The combined ether solution was washed with water, aqueous NaOH, and water, and then dried over $MgSO_4$. The evaporation of benzene and ether gave 1.21 g (72% yield) of diphenylmethane. It was analyzed by nmr and ir spectroscopy, in comparison with an authentic sample. The formation of benzyl phenyl sulfone was not observed.

The reaction of benzene (10 ml), *p*-nitrobenzylsulfonyl chloride (2.2 g, 0.01 mol), and aluminum chloride (0.03 mol) was carried out under reflux for 18 hr and gave 1.0 g (38% yield) of 4-nitrophenyl phenyl sulfone.

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Registry No.—Benzene, 71-43-2; toluene, 108-88-3; diphenylmethane, 101-81-5; nitrophenyl phenyl sulfone, 1146-39-0.

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