Linstead, *et al.*,[13] proposed (on the basis of the configurations of products isolated from catalytic hydrogenation under conditions similar to those used in our work) that the aromatic nucleus is adsorbed flatwise on the surface of the catalyst and that the orientation of adsorption of the nucleus is affected by steric hindrance between the catalyst and the substrate. Smith, *et al.*,[14] however (on the basis of kinetic studies), proposed that the aromatic nucleus is adsorbed edgewise on the catalyst in such a manner that substituents on the ring would protrude outward from the catalyst, if at all possible.

Our results seem entirely unexplainable in terms of Smith's model. If the olefinic double bond were adsorbed edgewise (as seems unlikely due to its relatively hindered position which results from its facing in the direction of the naphthalene ring), steric factors should be approximately equal for all olefins used and the rate of hydrogenation of I should not be exceptional. If the naphthalene nucleus were adsorbed edgewise (especially with the cycloalkenyl group protruding outward from the catalyst), a close fit of the olefinic bond to the catalyst would appear highly improbable.

Flatwise adsorption should most readily occur if the entire molecule were essentially coplanar. Then hydrogen could add either to the olefinic double bond or the naphthalene nucleus and might add to both simultaneously (as was observed). Any hindrance to the attainment of complete coplanarity of the naphthalene nucleus and the cycloalkenyl double bond might result in a decreased chemical reactivity toward hydrogenation.

We believe that the low reactivity of I in both the Diels–Alder reaction[15] and catalytic hydrogenation is the result of such steric hindrance to the attainment of complete coplanarity in I (but not in II–IV) during the complex-forming phases of the reactions[16] due to the fact that collision between hydrogen atoms attached to carbons 2 and 8′ of I will occur and seriously hinder free rotation around the bond between carbons 1 and 1′. The contraction of the cyclopentenyl ring in II as compared to the cyclohexenyl ring in I could be sufficient to allow rotation around the 1,1′-bond with little or no interference of hydrogen atoms and, hence, to allow coplanarity of the cyclopentenyl double bond with the naphthalene ring.[17] The ready addition of hydrogen to V (as observed by Cook and Lawrence) might also be explainable on the basis that the two hydrogen atoms in the 4′-position do not interfere appreciably with the hydrogen in the 2-position inasmuch as the former extend above and below the plane of the aromatic ring and not in the plane of this ring. No hindrance to free rotation and coplanarity should be possible in the *β*-substituted naphthalenes (III and IV).

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[13] R. P. Linstead, W. E. Doering, S. B. Davis, P. Levine and R. R. Whetstone, THIS JOURNAL, **64**, 1985 (1942).

[14] See footnote (11), references for (1945).

[15] For a discussion of the stereorelationship involved in the Diels-Alder reaction see the article by M. C. Kloetzel in R. Adams, "Organic Reactions," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1948, Chapter I.

[16] That the analogy between these two reactions is, however, not complete is apparent from comparison of the divergent effects of increased methylation of the aromatic substrate on relative chemical reactivity. Thus, the rate of catalytic hydrogenation was found to decrease in general in the series benzene, toluene, ... , hexamethylbenzene, H. A. Smith and E. F. H. Pennekamp, THIS JOURNAL, **67**, 279 (1945); whereas, the rate of the Diels-Alder reaction was found to increase in general (and with preferential addition of maleic anhydride to the alkylated ring) in the series methylnaphthalene, ... , 1,2,3,4-tetramethylnaphthalene, M. C. Kloetzel, *et al.*, *ibid.*, **72**, 273, 1991 (1950).

[17] W. E. Bachmann and N. C. Deno, *ibid.*, **71**, 3062 (1949), have suggested that the ultraviolet absorption spectra of I and II may indicate a lesser tendency toward coplanarity in the former compound. Further spectral investigations on I-IV are underway in our laboratory.

BLOOMINGTON, IND. RECEIVED APRIL 19, 1951

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Effect of the Sulfonyl Group on the Nucleophilic Displacement of Halogen in *α*-Halo Sulfones and Related Substances[1]

BY F. G. BORDWELL AND GLENN D. COOPER

The inertness of *α*-halo sulfones and related compounds toward nucleophilic displacements of the halogen, which is apparent from accounts in the literature, is further demonstrated with chloromethyl phenyl sulfone. It is suggested that this retardation is due to a steric blocking of the attacking reagent by the sulfonyl group. This postulate is supported by the observation that 1-(*p*-toluenesulfonyl)-3-chloro-1-propene, $C_7H_7SO_2CH{=}CHCH_2Cl$, in which the steric effect of the sulfonyl group is largely eliminated, reacts with potassium iodide in acetone at a rate about fourteen times that of allyl chloride (thousands of times that of chloromethyl phenyl sulfone).

The effect of the sulfonyl group, $-SO_2-$, on the reactions of other functional groups in organic molecules is usually roughly comparable in direction and magnitude to that of carbonyl, cyano, and other electron attracting groups. This is reflected in the ability of the sulfonyl group to enhance the acidity of *α*-hydrogens, its meta orienting effect in aromatic substitution, the facile decarboxylation of *α*-sulfonylcarboxylic acids, etc. The sulfonyl group differs markedly, however, in its effect on the rate of replacement of an *α*-halogen atom. Whereas phenacyl chloride, $C_6H_5COCH_2Cl$, and chloroacetonitrile, $N{\equiv}CCH_2Cl$ react with potassium iodide in acetone at rates approximately 100,000 and 3,000 times that of *n*-butyl chloride,[2] and undergo reactions with other nucleophilic agents (amines, alkoxides, thiourea, etc.) with especial ease, the inertness of *α*-halo sulfones, sulfonamides, and sulfonates has been

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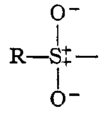
[1] This investigation was supported by the Office of Naval Research under Contract No. N7onr-45007.

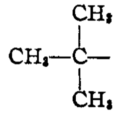
[2] J. B. Conant and W. R. Kirner, THIS JOURNAL, **46**, 232 (1924).

observed and commented on several times in the literature. Bromomethyl phenyl sulfone, $C_6H_5SO_2CH_2Br$, is unreactive toward piperidine and benzyldimethylamine.[3] Bromomethyl *p*-tolyl sulfone is unreactive toward tetrahydroquinoline, dimethylamine, potassium cyanide and sodium acetate; sodium ethoxide or sodium mercaptides in alcohol slowly reduce it to methyl *p*-tolyl sulfone.[4] Chloromethanesulfonanilide, $ClCH_2SO_2NHC_6H_5$, fails to react with sodium phenoxide, and chloromethanesulfonamide, $ClCH_2SO_2NH_2$, on treating with aniline at 100° for 14 days released only 23% of its halogen.[5] Sodium chloromethanesulfonate, $ClCH_2SO_3Na$, released only 46% of its halogen after treatment with concd. ammonia at 160° for six days (22% in three days).[6] Similar results were obtained in the present investigation with chloromethyl phenyl sulfone, $C_6H_5SO_2CH_2Cl$. No reaction was observed on refluxing with piperidine in benzene for three days. Excess morpholine at 140° and thiourea in cyclohexanol at 160° gave only tarry products. Heating with piperidine at 180° in a sealed tube gave largely intractable material from which 19% of reduction product, methyl phenyl sulfone, was isolated. No reaction was observed with potassium iodide in acetone in 12 hours at 56° or after ten weeks at 0°. Judging from the latter experiment, the rate with potassium iodide can be no more than one-fortieth that of *n*-butyl chloride,[2] and is probably much less.

If the enhanced reactivity toward nucleophilic displacement of the halogen in $RCOCH_2X$, $N\equiv CCH_2X$, $ROCOCH_2X$, etc., is correctly accounted for by preliminary addition of the reagent to the unsaturated grouping,[7] or by no-bond resonance in the transition state,[8] the failure of the sulfonyl group to increase the reactivity of an α-halogen can be rationalized by its inability to function in a similar manner due to structural differences.[7] The marked *retarding* effect of the sulfonyl group, however, remains unexplained. The sulfonyl group shows a formal similarity to the neopentyl group,



$$R-\overset{O^-}{\underset{O^-}{S^{++}}}-$$



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-$$

and it seemed possible that it, like the neopentyl group,[9] might exert a steric blocking effect. From an examination of models, however, one would expect only a small steric effect for the sulfonyl group, unless it is assumed that the partial negative charge on the oxygen atoms would greatly extend their effective radius in blocking an incoming nucleophilic reagent.

In order to test the steric *versus* the electronic nature of its retarding effect, the sulfonyl group was separated from the chloromethyl group by interspersing a vinyl group, following the idea used by Bartlett and Rosen for the neopentyl case.[9] The desired compound, 1-*p*-toluenesulfonyl-3-chloro-1-propene (I), $C_7H_7SO_2CH{=}CHCH_2Cl$, was prepared from the corresponding alcohol, which is readily obtainable by the intriguing reaction between sodium *p*-toluenesulfinate and epichlorohydrin recently described by Culvenor, Davies and Savige.[10] For comparison of chloride activity 1-cyano-3-chloro-1-propene (II), $N\equiv C-CH{=}CH-CH_2Cl$, was prepared by dehydration of 3-cyano-1-chloro-2-propanol.

The second order rate constant for the reaction of I with potassium iodide in acetone at 0° was found to be $k = 1.10$ liters mole^{-1} hr.$^{-1}$, compared with $k = 1.41$ for II, and $k = 0.082$ for allyl chloride[11] (1-benzenesulfonyl-3-chloro-1-propene reacted at approximately the same rate as I, but the rate constant shows a downward drift). From these data it appears that I is many thousands of times as reactive toward potassium iodide in acetone as is chloromethyl phenyl sulfone, whereas the reactivity of II is comparable to that of chloroacetonitrile[12] (Table I).

TABLE I

RELATIVE REACTIVITIES TOWARD POTASSIUM IODIDE IN ACETONE

$CH_3CH_2CH_2CH_2Cl$	1[a]
$C_7H_7SO_2CH_2Cl$	<0.02
$CH_2{=}CH-CH_2Cl$	80[a]
$C_7H_7SO_2CH{=}CHCH_2Cl$	1100
$N\equiv C-CH{=}CHCH_2Cl$	1400
$N\equiv C-CH_2Cl$	3000[a]

[a] See ref. 2.

Thus the sulfonyl and cyano groups exert large effects of an opposite nature on the rate of displacement of the halogen atom by nucleophilic reagents when they are attached directly to a $-CH_2Cl$ group, but exert comparable effects when separated from the group by $-CH{=}CH-$. These results are consistent with the postulate of a strong steric effect for the sulfonyl group.[13]

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(3) T. Thomson and T. S. Stevens, *J. Chem. Soc.*, 69 (1932).

(4) W. M. Ziegler and R. Connor, THIS JOURNAL, **62**, 2596 (1940).

(5) T. B. Johnson and I. B. Douglass, *ibid.*, **63**, 1571 (1941).

(6) F. Raschig and W. Prahl, *Ann.*, **448**, 307 (1926).

(7) J. W. Baker, *Trans. Faraday Soc.*, **37**, 632 (1941).

(8) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, pp. 436–440.

(9) The steric nature of the neopentyl effect appears to be well established; see I. Dostrovsky, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 173 (1946); P. D. Bartlett and L. J. Rosen, THIS JOURNAL, **64**, 543 (1942).

(10) C. C. J. Culvenor, W. Davies and W. E. Savige, *J. Chem. Soc.*, 2198 (1949).

(11) As would be expected, both I and II react much more slowly with alcoholic silver nitrate (S_N1 mechanism) than does allyl chloride.

(12) No definite decision concerning the geometric configuration of I and II can be made on the basis of the preparative method. L. F. Hatch, *et al.*, THIS JOURNAL, **72**, 5643 (1950), and previous papers, have measured the rates of reaction of a number of geometrically isomeric allylic chlorides with potassium iodide and have found that the isomers do not differ by magnitudes greater than ten. A difference of this order would not affect the conclusions drawn from the present work.

(13) This conclusion is based on the assumption that electronic effects are transmitted without major alteration by a vinyl group. The fact that the sulfonyl group, when substituted for a γ-hydrogen, increases the activity of the chlorine in allyl chloride toward displacement by iodide ion suggests that the electronic effect of the sulfonyl group in $C_6H_5SO_2CH_2Cl$ is activating in such reactions but that this effect is over-shadowed by the steric effect. The chlorine atom resembles the sulfonyl group in deactivating methyl chloride (compare CH_2Cl_2) and activating allyl chloride (L. F. Hatch, L. B. Gordon and J. J. Russ, *ibid.*, **70**, 1093 (1948), have shown that the 1,3-dichloropropenes are 2.9 and 8.6 times allyl chloride in activity toward potassium iodide). This seems to provide evidence for the steric effect of a chlorine atom postulated by E. R. Alexander ("Principles of Ionic Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 89). Similarly, the deactivation of methyl chloride by a methyl

In contrast to the behavior described above, several compounds with halogen alpha to a sulfonyl group are known from which the halogen is readily released as halide ion. Thus chloromethanesulfonamide and chloromethanesulfonanilide are easily cleaved by aqueous alkali[5]; *o*-(chloromethylsulfonyl)-benzoic acid readily releases chloride ion to form salts of *o*-carboxybenzenesulfinic acid in alkaline solutions,[14] and α-bromoethyl ethyl sulfone reacts rapidly at 100° with 2 *N* potassium hydroxide to give 85% of *cis*-2-butene, potassium bromide and potassium sulfite.[15] The rapid and quantitative release of halide ions in these reactions is believed to be made possible in each instance by an *intramolecular* attack of a nucleophilic agent on the halogen carbon. The mechanisms of these reactions will be discussed in forthcoming papers from this Laboratory.

Experimental

Phenyl Chloromethyl Sulfone.—Phenyl chloromethyl sulfone has been prepared by the reaction of sodium benzene sulfinate with sodium dichloroacetate or with methylene chloride,[16] and by oxidation of phenyl chloromethyl sulfide with monoperphthalic acid in ether.[17] A more convenient route is oxidation of phenyl chloromethyl sulfide (readily obtained by chlorination of phenyl methyl sulfide with sulfuryl chloride[14]) with commercial 40% peracetic acid, which yields phenyl chloromethyl sulfone almost quantitatively. Five grams of anhydrous sodium acetate was added to 80 g. (0.43 mole) of 40% peracetic acid. The solution was cooled in an ice-bath, and 15.7 g. (0.1 mole) of phenyl chloromethyl sulfide was added dropwise, with vigorous stirring, over a period of 30 minutes. The mixture was stirred for 15 minutes after the addition was completed. The sulfone was precipitated by the addition of 100 ml. of water; weight 18.1 g. (95%), m.p. 49–52°. Recrystallization from ethanol-water yielded 17.0 g. (90%) of phenyl chloromethyl sulfone, m.p. 52–53°; literature[16] m.p. 52–53°.

Reaction of Phenyl Chloromethyl Sulfone with Nucleophilic Reagents. Piperidine in Benzene.—One gram (0.0053 mole) of phenyl chloromethyl sulfone was refluxed for 72 hours with 1.27 g. (0.015 mole) of piperidine in 20 ml. of benzene. No precipitate was formed; 90% of the starting material was recovered.

Piperidine.—Three grams of phenyl chloromethyl sulfone was heated with 25 ml. of piperidine in a sealed tube at 180° for seven hours. The precipitate of piperidine hydrochloride (1.6 g., 85%) was filtered off and the dark brown filtrate was evaporated at 2 mm. pressure. The dark brown tarry residue was distilled in a short-path still at 0.5 mm., yielding 0.70 g. of a low melting yellow solid. Crystallization from water yielded 0.45 g. (18%) of phenyl methyl sulfone, m.p. 87–88°; literature[18] m.p. 88°. A mixture with an authentic sample of phenyl methyl sulfone melted at 87–88°.

Potassium Iodide in Acetone.—One gram (0.0053 mole) of phenyl chloromethyl sulfone was refluxed for 12 hours with 200 ml. of 0.03 *M* potassium iodide in acetone. No precipitate was formed and the sulfone was recovered almost quantitatively. In an experiment carried out for 10 weeks at 0° no change in iodide concentration was observed.

Reaction of Allylic Chlorides with Potassium Iodide in Acetone at 0°. Reagents.—Acetone and potassium iodide were purified according to the directions of Conant and Kirner[2]. Allyl chloride was Eastman Kodak Company white label product and was purified by distillation through a short column packed with glass helices; a fraction boiling at 44.8–45.2° was used. 1-(Benzenesulfonyl)-3-chloro-1-propene was prepared by the method of Culvenor, Davies and Savige[10] and purified by repeated crystallization from pentane. The pure product melted at 58.0–58.5°, literature[10] m.p. 58.5°. 1-(*p*-Toluenesulfonyl)-3-chloro-1-propene was prepared and purified in the same manner, m.p. 57.2–58.3°, literature[10] m.p. 58°. γ-Chloro-β-hydroxybutyronitrile was prepared from epichlorohydrin and sodium cyanide according to the procedure of Culvenor, Davies and Haley.[19] Dehydration with phosphorus pentoxide yielded 30% of 1-cyano-3-chloro-1-propene, b.p. 68° (12 mm.); literature[20] b.p. 73–73.5° (15 mm.).

Procedure.—The allylic chloride was weighed into a glass-stoppered flask and the flask immersed in a mixture of water and shaved ice in a dewar flask. Fifty milliliters of a solution of potassium iodide in acetone (cooled to 0° and standardized against 0.00300 *M* potassium iodate solution just before use) was transferred to the flask and a 5-ml. sample immediately withdrawn and titrated with 0.00300 *M* potassium iodate solution. Samples were withdrawn and titrated at appropriate intervals. No iodine was liberated in any of the reactions. The results are summarized in Table II.

Table II

Rates of Reaction of Allylic Chlorides with Potassium Iodide in Acetone at 0°[a]

Chloride	Chloride (molar)	KI (molar)	k (l. mole^{-1} hr.$^{-1}$)
$C_6H_5SO_2CH{=}CHCH_2Cl$	0.1052	0.0310	1.30 ± 0.07[b]
$C_7H_7SO_2CH{=}CHCH_2Cl$	.1155	.0308	1.10 ± .02
$N{\equiv}C{-}CH{=}CHCH_2Cl$	.1824	.0365	1.41 ± .06
$CH_2{=}CH{-}CH_2Cl$	.2156	.0368	0.082 ± .002[c]

[a] Reactions followed to 50–75% completion. [b] Rate constant drifts downward 15% during 45% reaction. [c] Followed to 13% completion. J. B. Conant, W. R. Kirner and R. E. Hussey (This Journal, **47**, 498 (1925)) obtained k_{25} = 0.66; L. F. Hatch, L. B. Gordon and J. J. Russ (*ibid.*, **70**, 1093 (1948)) obtained k_{20} = 0.60; the values reported by Conant and Hatch are for $0.4343k$.

Evanston, Illinois Received May 17, 1951

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group (compare CH_3CH_2Cl) and the activation of allyl chloride by methyl has been interpreted as support for a steric effect for the methyl group (I. D. Webb and W. G. Young, This Journal., **73**, 777 (1951)).

[14] Unpublished results from this Laboratory.

[15] L. Ramberg and B. Bäckland, *Arkiv. Kemi. Mineral. Geol.*, **13A**, No. 27 (1940); *C. A.*, **34**, 4725 (1940).

[16] R. Otto, *J. prakt. Chem.*, [2] **40**, 527 (1889).

[17] H. Böhme, H. Fisher and R. Franck, *Ann.*, **563**, 54 (1949).

[18] R. Otto, *ibid.*, **284**, 301 (1895).

[19] C. C. J. Culvenor, W. Davies and F. G. Haley, *J. Chem. Soc.*, 3123 (1950).

[20] M. R. Lespieau, *Compt. rend.*, **130**, 1410 (1900).