term $[K_{11}K_a/[H^+] + K_{12}][G]$ may be considered small and neglected. Since three values of k_{11} are available from part E, three equations may be formed in three unknowns; $[k_{11}\cdot K_{11}K_a]$, $[k_{12}K_{12}]$, and K_a. Solving these equations it is found that $K_a = 0.09$, $k_{12}K_{12} = 0.3285$ and the term $k_{11}K_{11}\cdot K_a$ is very nearly zero (*ca.* 0.0001). Therefore either k_{11} or K_{11} is negligible. The fact that the rate is independent of $[H^+]$ at higher glycol concentration indicates that K_{11} is negligible and no appreciable $Ce(OH)X_3G$ is formed. Since very little $Ce(OH)X_3G$ is formed, it is assumed that the di- and triglycolated species of the hydroxylated cerium can also be neglected. Under these assumptions, equation (4) becomes

$$-\frac{dt_{Ce}}{dt} = \frac{k_{12}K_{12}[G] + k_{22}K_{12}K_{22}[G]^2 + k_{32}K_{12}K_{22}K_{32}[G]^3}{1 + K_a/[H^+] + K_{12}[G] + K_{12}K_{22}[G]^2 + K_{12}K_{22}K_{32}[G]^3}\,T_{Ce} \quad (21)$$

which is of the same form as equation (4) except for the modified subscripts and addition of the hydrogen dependency term.

Again at low glycol concentrations ($[G] = 0.05$), the diglycolated complex concentrations may be considered negligible. Using the value of k' from Part A, and the values of K_a, $k_{12}K_{12}$, and $[H^+]$, $K_{12} = 15$ and $k_{12} = 0.0225$ sec.$^{-1}$. These values, when used to calculate values of k' are found to fit the experimental data only at the lower glycol concentration. Evaluation of equilibrium constants for the di- and triglycolated species is accomplished by trial and error. It was found unnecessary to include the cubed power of glycol to fit experimental data. Selecting two higher values of k' at higher glycol concentrations and using the equation

$$k' = \frac{k_{12}K_{12}[G] + k_{22}K_{12}K_{22}[G]^2}{1 + K_a/[H^+] + K_{12}[G] + K_{12}K_{22}[G]^2} \quad (22)$$

it was found that $K_{22} = 2.3$ and $k_{22} = 0.0117$ sec.$^{-1}$. In view of the uncertainties encountered in the experimental determination of pseudo rate constants, the values of rate constants and equilibrium constants are assigned the limits of error in Table II.

TABLE II

$K_a = 0.09 \pm 0.02$
$K_{12} = 15 \pm 1$
$K_{22} = 2.3 \pm 0.4$
$k_{12} = 0.0225 \pm 0.0010$ sec.$^{-1}$
$k_{22} = 0.0117 \pm 0.0020$ sec.$^{-1}$

AMES, IOWA RECEIVED MAY 21, 1951

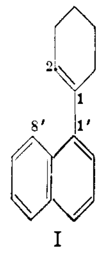
[CONTRIBUTION NO. 520 FROM THE CHEMICAL LABORATORIES, INDIANA UNIVERSITY]

Kinetics of Catalytic Hydrogenation of Naphthyl-1-cyclopentenes and Naphthyl-1-cyclohexenes[1]

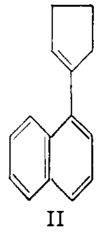
BY L. H. KLEMM AND WILLIAM HODES

Kinetic studies of catalytic hydrogenation of the four parent naphthyl-1-cyclopentenes and naphthyl-1-cyclohexenes showed that addition of hydrogen to the olefinic double bond occurs simultaneously with the slower hydrogenation of the aromatic nucleus. 1-(1′-Naphthyl)-1-cyclohexene was found to differ from the other olefins in reacting at a considerably slower rate. A theory is proposed to explain this difference of reactivity in terms of requisite coplanarity of the olefins when adsorbed on the catalyst.

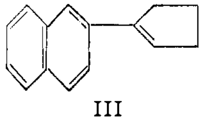
Two major instances have been recorded in the literature on the lower reactivity of 1-(1′-naphthyl)-1-cyclohexene (I) as compared to 1-(1′-naphthyl)-1-cyclopentene (II). Thus Cook and Lawrence[2] reported very great resistance to catalytic hydrogenation of I while Bachmann and Klemm[3] found that II added hydrogen readily under the same conditions. Bachmann and Kloetzel[4] successfully condensed II as well as 1-(2′-naphthyl)-1-cyclopentene (III) with maleic anhydride by fusion of the reactants on a steam-bath, but Bergmann and Bergmann[5] could not accomplish this reaction with I under the same conditions though they did find that 1-(2′-naphthyl)-1-cyclohexene (IV) reacted readily. Later Bergmann and Szmuszkowicz[6] succeeded in condensing I with maleic anhydride at a considerably higher temperature to yield an impure adduct and thereby to indicate that the inertness of I was a matter of degree rather than of type.



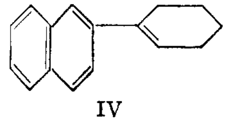
I



II

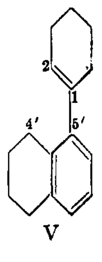


III



IV

Cook and Lawrence[2] attributed the chemical inertness of I to a "mutual saturation of the free affinities of the carbon atoms 2 and 8′, which can come within atomic distances of each other" and supported their hypothesis by showing that 1-(5′-tetralyl)-1-cyclohexene (V) behaved nor-



V

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[1] (a) Abstracted from a thesis submitted by William Hodes to the Faculty of the Graduate School of Indiana University in partial fulfillment of the requirements for the degree Master of Arts, June, 1950. A detailed description of the construction and manipulation of the apparatus used in this research may be found in the dissertation, available from the Chemistry Library, Indiana University. (b) Part of this material was presented at the Cleveland meeting of the American Chemical Society, April, 1951.

[2] J. W. Cook and C. A. Lawrence, *J. Chem. Soc.*, 1431 (1936).

[3] W. E. Bachmann and L. H. Klemm, THIS JOURNAL, **72**, 4911 (1950).

[4] W. E. Bachmann and M. C. Kloetzel, *ibid.*, **60**, 2204 (1938).

[5] F. Bergmann and E. Bergmann, *ibid.*, **62**, 1699 (1940).

[6] F. Bergmann and J. Szmuszkowicz, *ibid.*, **69**, 1367 (1947).

mally on hydrogenation. Bergmann and Weizmann[7] discounted this explanation on the basis that it should also be as readily applicable to the reactive II and suggested instead an inherent difference between the cyclohexene–cyclohexane and the cyclopentene–cyclopentane pairs. Their explanation, however, would not account for the high reactivities of both III and IV.

This paper presents the results of our first attempts to place the reactivities of compounds I–IV on a more nearly quantitative basis in an effort to help clarify the situation.

Experimental

The olefins (I–IV) were prepared according to the directions of Bachmann and Kloetzel[4] as modified by Kleene[8] for the preparation of II. The Grignard reagent from 74–83 g. of 1- or 2-bromonaphthalene was treated with cyclopentanone or cyclohexanone and the crude tertiary alcohol was dehydrated directly with formic acid to the olefin which was distilled *in vacuo*. Further purification was effected by conversion of each olefin to the picrate and crystallization of the picrate to constant melting point. The olefins were stored in this form. Immediately before use each picrate was dissociated by passing a dilute benzene solution of it through a chromatographic column (4.3 × 20 cm.) packed with activated alumina–celite (1:1). Vacuum distillation of the effluent under nitrogen or over sodium, followed by crystallization (except for the oil II) to constant melting point completed the purification. Solutions of all olefins in carbon tetrachloride or glacial acetic acid absorbed bromine. Data relative to the olefins and their picrates are given in Table I.

TABLE I

PHYSICAL CONSTANTS OF NAPHTHYLCYCLOALKENES

	Purified olefin		Olefin picrate	
Olefin	M.p., °C. Found	M.p., °C. Reported	M.p., °C. Found	M.p., °C. Reported
I	46.5–47.5	36[a] 44, 46[b] 47–47.5[c]	126.5–127	120–121.5 124.5–125.5[b] 127.5–128.4[c] 129[5]
II	Oil[d]	Oil[e,f]	75.5–76	79–80[4], 82[g]
III	85–86	85–86[4]	103–104[h]	....
IV	60–61	61–62[5]	81.5–82	78[5]

[a] R. Weiss and K. Woidich, *Monatsh.*, **46**, 453 (1925). [b] J. W. Cook, C. L. Hewett and C. A. Lawrence, *J. Chem. Soc.*, 71 (1936). [c] M. Orchin and L. Reggel, THIS JOURNAL, **69**, 505 (1947). [d] B.p. 122–123° (0.5 mm.). [e] E. Bergmann and F. Bergmann, *ibid.*, **59**, 1443 (1937), report b.p. 115° (0.04 mm.). [f] Bachmann and Klemm[3] give b.p. 122–124° (0.1 mm.). [g] See reference in footnote *e*. [h] Obtained as orange-red needles from methanol. *Anal.* Calcd. for $C_{21}H_{17}O_7N_3$: N, 9.9. Found: N, 10.1.

The catalyst, Adams platinum oxide (American Platinum Works) was taken from the same batch in each case. Unless otherwise specified the solvent was du Pont C.P. glacial acetic acid, 99.5%, used from the same bottle without further purification. The hydrogen was used (without further purification) directly from the high pressure tanks supplied by the Indiana Oxygen Company.

Kinetic studies were made with a Model CA Parr Catalytic Hydrogenation Apparatus and a mercury manometer connected to the apparatus in such a manner that by adjusting a mercury-filled leveling bulb the volume of the system could be maintained constant to within 1% and the decrease in pressure could be accurately measured. In a typical experiment 50 ml. of 99.5% acetic acid solvent, 0.0025 or 0.005 mole of olefin, and 0.075 g. (or other definite amount) of platinum oxide were shaken at 225 cycles per minute at an initial pressure of 1520 mm. and at 25 ± 1° (throughout the reaction). The logarithm of the ratio of the initial pressure, p_0, to the instantaneous pressure, p,[9] was plotted against the time, t, in minutes and the slopes (k' and k_b') of the two linear portions of the resulting curve were determined graphically. The corresponding specific reaction rates, k and k_b, were calculated from the relationships, $k = 2.303\ k'V$ and $k_b = 2.303\ k_b'V$, where V = the gaseous volume of the apparatus in ml.[10] The rate constant for the faster or principal reaction, k_a, was calculated from the equation $k_a = k - k_b$. The rate constant for the slower or side reaction was taken as k_b.

Results and Discussion

A blank run on the regular solvent alone (with no added catalyst) showed that saturation of the solvent with hydrogen was complete in less than six seconds, a negligible length of time as compared to the reaction time of hydrogen with the catalyst or the olefin. Blank runs on the solvent–catalyst combinations showed that (1) the rate of absorption of hydrogen by the catalyst was apparently directly proportional to the amount of catalyst used, (2) use of 99.5% acetic acid which had been carefully distilled from potassium permanganate or previously treated with hydrogen and the catalyst made little or no change in the rate of reaction, and (3) use of 99.9% acetic acid (Eastman Kodak Co.) instead of the regular 99.5% acetic acid not only decreased the rate of absorption of hydrogen but also eliminated a large part of the original linearity present in the absorption curve for the 99.5% acid (Fig. 1).

Results of the experiments with the olefins are shown in Table II and Fig. 1. Observations of k_a and k_b values for Runs 1–8 show that (within experimental error) the rates of the principal and side reactions are zero order in concentration of the hydrocarbon[11] and the rate constants for the principal reactions are essentially identical for compounds II, III and IV but are nearly twice as great as for compound I. Though the data are somewhat inconclusive it appears that the position of substitution on the naphthalene ring governs the k_b value which is greater in the case of β-substitution than of α-substitution. Results on compound IV

TABLE II

RATES OF HYDROGENATION OF NAPHTHYL-1-CYCLOALKENES[a]

Run	Olefin	Moles of olefin × 10³	k_a, ml./min.	k_b, ml./min.
1	I	2.5	6.4	0.53
2	I	5.0	5.1	.53
3	II	2.5	11.6	.63
4	II	5.0	11.0	.58
5	III	2.5	11.2	1.00
6	III	5.0	12.1	1.00
7	IV	2.5	12.6	1.06
8	IV	5.0	11.7	0.85
9[b]	IV	5.0	7.9	0.42
10[c]	IV	5.0	22.5	2.3
11[d]	III	2.5	6.3	0.79

[a] Unless otherwise specified the reactions were run in du Pont C.P. glacial acetic acid (99.5%) and with 0.075 g. of Adams catalyst. [b] With 0.05 g. of catalyst. [c] With 0.15 g. of catalyst. [d] In Eastman Kodak Co. white label 99.9% acetic acid.

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(7) F. Bergmann and A. Weizmann, *J. Org. Chem.*, **9**, 352 (1944).

(8) R. D. Kleene, THIS JOURNAL, **63**, 631 (1941).

(9) Observed pressures were corrected for barometric conditions but not for absorption of hydrogen by the solvent or the catalyst.

(10) For dependence of the specific reaction rate on the gaseous volume see J. F. Fuzek and H. A. Smith, THIS JOURNAL, **70**, 3743 (1948).

(11) These results are consistent with the observations of H. A. Smith, *et al.*, *ibid.*, **67**, 272, 276, 279 (1945); **71**, 81, 413, 415, 3765, 3772 (1949), on a variety of aromatic and olefinic compounds.

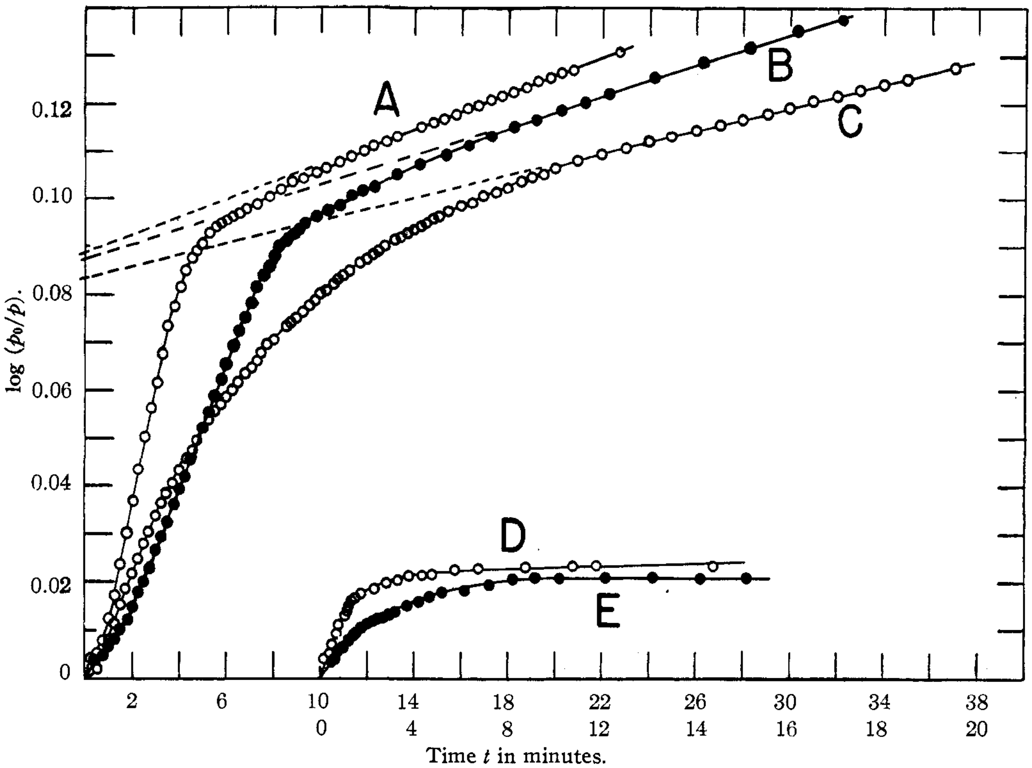

Fig. 1.—Kinetics of catalytic hydrogenation using 0.075 g. of Adams catalyst and 50 ml. of solvent: ○, 99.5% acetic acid as solvent; ●, 99.9% acetic acid as solvent. Curves A and B, for 0.0025 mole of 1-(2′-naphthyl)-1-cyclopentene; Curve C, for 0.0025 mole of 1-(1′-naphthyl)-1-cyclohexene; Curves D and E, catalyst only (no olefin present). Upper time scale refers to Curves A, B and C; lower time scale, to Curves D and E.

(Runs 8, 9 and 10) show that the rate constant k is directly proportional to the weight of catalyst used.[11] The exact nature of the variation of k_b with weight of catalyst is still questionable though k_b increases almost in direct proportion to the catalyst weight. Runs 5 and 11 represent identical conditions except for the solvent used. Here, however, just as in the case of the reaction of hydrogen with the catalyst, the 99.9% acetic acid caused a slower reaction than did the 99.5% acetic acid. The magnitude of the solvent effect was roughly the same for both the catalyst alone (ratio of k values of 2.0:1) and the catalyst–olefin combination (ratio of k_a values of 1.8:1).

On a macro-preparative run using a regular Parr hydrogenation apparatus the product obtained from II after absorption of only slightly more than one molar equivalent of hydrogen gave a negative Baeyer test (in contrast to a positive test given by II itself). None of the solutions of the products obtained in the hydrogenation studies absorbed bromine after slightly less than two moles of hydrogen per mole of olefin had been absorbed. Hence, the cycloalkenyl double bonds must have been saturated in every case.

The calculated end-points for absorption of amounts of hydrogen equimolar to those of the olefins reduced (plus amounts necessary for saturation of the catalyst and solvent) are 0.089 and 0.167 for log p_0/p using 0.0025 and 0.005 mole of olefin, respectively. Extrapolation to zero time of all of the second linear portions of the kinetics curves for the olefins gave intercepts of 0.085–0.089 and 0.164–0.169, respectively, in remarkably close agreement with the calculated values and indicating that the initial linearity in each of these curves is the result of two different reactions starting and continuing simultaneously. The principal and faster reaction involved in this initial phase is that of hydrogenation of the cycloalkenyl double bond. This is accompanied by a considerably slower net side reaction of rate constant equal to k_b. The kinetics, however, do not allow one to distinguish conclusively between the following two possibilities (or a combination of them) for the reactions extant during the initial phase:

(1) Consecutive reactions $\mathrm{A} \xrightarrow{k_a} \mathrm{B} \xrightarrow{k_b} \mathrm{C}$

or

(2) Simultaneous reactions $\mathrm{A} \xrightarrow{k_a} \mathrm{B}$

$\mathrm{A} \xrightarrow{k_c} \mathrm{D} \xrightarrow{k_d} \mathrm{C}$

where A = cycloalkenylnaphthalene, B = cycloalkylnaphthalene, C = cycloalkyltetrahydronaphthalene and/or cycloalkyldecahydronaphthalene, D = cycloalkenyltetrahydronaphthalene and/or cycloalkenyldecahydronaphthalene. Inasmuch as the transition from the initial to the second linearity heralds the disappearance of all unsaturation to bromine in the products, it is almost certain that the second linearity is to be represented exclusively by hydrogenation of the aromatic nucleus.[12]

[12] Curves for compounds II and IV are of similar shape to those shown for III. The exceptionally long transitional period found for I may indicate an appreciably different course of reaction for the intermediate stage in the hydrogenation of I, as compared to the others. Present data seem insufficient to justify kinetic treatment of this transitional stage.

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).