anhydrous sodium acetate (15 g), acetic acid (100 ml), and water (40 ml) was electrolyzed for 17 hr. The current was held at 0.50 amp (0.045 amp/cm², 0.32 faraday) by an applied voltage of 5.0 to 24.7 v. The temperature was held at 20 to 28°. The neutral product mixture (1.65 g) was a very viscous, orange liquid. For runs in anhydrous solution the acid (8.0 g), potassium acetate (20 g), acetic acid (80 ml), and acetic anhydride (40 ml) were used. The neutral product amounted to 4.8 g. A reaction in the absence of acetate was run with 3,3-diphenylacrylic acid (11.2 g, 0.05 mole), potassium hydroxide (1.3 g, 0.02 mole), methanol (110 ml), and water (15 ml). An applied voltage of 10 to 21 v was needed to maintain a current of 0.50 amp (0.045 amp/cm², 0.10 faraday) for 5.4 hr. The temperature increased from 30 to 56°. The neutral product amounted to 6.6 g. An electrolysis was also run with both diphenylacetylene (0.66 g) and 3,3-diphenylacrylic acid (9.0 g) under conditions otherwise identical with those of the run in acetic acid plus water, and 2.6 g of neutral product was obtained. Quantitative gas chromatographic analysis showed that only 12% of the diphenylacetylene remained in the product mixture. 2,2-Diphenylvinyl acetate (5.0 g) was electrolyzed under the same conditions.

Product distributions from typical expriments are summarized in Table I. These data were obtained in the same way as those in Table II. 1,1-Diphenylpropene and benzophenone were isolated by gas chromatography and identified by their infrared spectra. The benzophenone carbonyl band was detected in the infrared spectra of some of the mixtures. Benzil was isolated by gas chromatography and by the same hydrolysis procedure as in the case of diphenylacetylene, but it could not be detected in the infrared spectra of the mixtures. The benzil precursor obtained from diphenylacetylene was evident in the infrared spectra of the product mixtures obtained from 3,3-diphenylacrylic acid in acetic acid, but not in those from methanol. Benzoin acetate was isolated by gas chromatography and its identity was confirmed by its infrared spectrum. It was also detected in the infrared spectra of some of the mixtures. Both diphenylacetaldehyde and 2,2-diphenylvinylacetate were isolated by gas chromatography and identified by infrared spectra.

4-Phenylcoumarin was isolated by crystallization and by gas chromatography its identity being confirmed by comparison of its melting point (90–91°) and its infrared spectrum with those of an authentic sample.[13] Furthermore its mass spectrum agreed with the published spectrum.[20] The 4-phenylcoumarin value in Table II is a composite value for 4-phenylcoumarin and a compound which was also obtained when pure 4-phenylcoumarin was subjected to the same electrolysis conditions. This derivative has a band in the carbonyl region at 1775 and a band at 1210 cm^{-1}. These bands are consistent with an aryl acetate[5] structure. This 4-phenylcoumarin derivative was not detected when the electrolysis was carried out in methanol. No diphenylacetylene derivatives were obtained from 4-phenylcoumarin.

In addition to the products listed in Table I there were the following. Methyl 3,3-diphenylacrylate (3%) was found among the products of the run in methanol. 1,1-Diphenylethylene (<3%) was obtained from some runs. Stilbene may have been a product in methanol and 1,2-diphenylpropene may also have been a product in anhydrous acetic acid, but in each case the peak corresponding to these compounds was too small for conclusive identification by gas chromatography. There were some other unidentified minor products.

Registry No.—3,3-Diphenylacrylic acid, 606-84-8; diphenylacetylene, 501-65-5; α,α'-stilbenediol diacetate, 6316-81-0; benzoin, 119-53-9; benzil, 134-81-6.

Acknowledgment.—Valuable discussions with Dr. R. D. Offenhauer and the technical assistance of Mr. C. R. Manzoni are gratefully acknowledged.

(20) U. K. Pandit and I. P. Dirk, *Tetrahedron Letters*, 891 (1963).

Effects of Solvents on the Reactions of Trichloromethanesulfinyl Radicals

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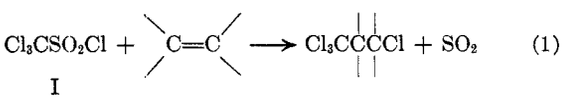
The relative rate of free-radical addition with respect to the rate of allylic halogenation of cyclohexene by trichloromethanesulfonyl chloride (Cl_3CSO_2Cl) suggests that trichloromethanesulfinyl radicals ($Cl_3CSO_2\cdot$) are complexed by alkenes. A reaction of the complexed radical with another molecule of the alkene is responsible for the addition of the trichloromethyl moiety to the alkene. Effective complexing of the trichloromethanesulfinyl radical by chlorobenzene, *t*-butylbenzene, and pyridine was also found. Competitive chlorinations of cyclohexane and toluene in the presence of pyridine show that only noncomplexed trichloromethanesulfinyl radicals are involved in hydrogen-abstraction reactions.

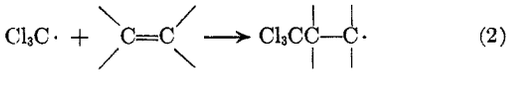
The free-radical reactions of trichloromethanesulfonyl chloride (I) with alkenes yield sulfur dioxide and addition products the same as those obtained from the free-radical addition of carbon tetrachloride to alkenes.[1] The formation of such addition products has led to the suggestion that the mechanism for this



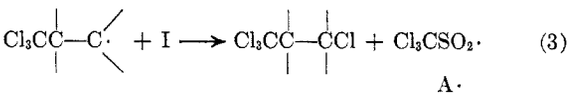
$$Cl_3CSO_2Cl + \text{>C=C<} \longrightarrow Cl_3CC\text{-}C\text{-}Cl + SO_2 \qquad (1)$$

I

reaction involves addition to the alkene of a trichloromethyl radical which is produced in the decomposition of the trichloromethanesulfinyl radical (A·) formed in the chain sequence shown in eq 2–4.[2] Free-radical



$$Cl_3C\cdot + \text{>C=C<} \longrightarrow Cl_3CC\text{-}C\cdot \qquad (2)$$

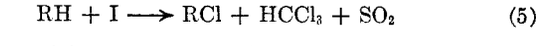


$$Cl_3CC\text{-}C\cdot + I \longrightarrow Cl_3CC\text{-}CCl + Cl_3CSO_2\cdot \qquad (3)$$

A·

$$A\cdot \longrightarrow Cl_3C\cdot + SO_2 \qquad (4)$$

reactions of Cl_3CSO_2Cl with alkanes yield halogenated alkanes, chloroform, and sulfur dioxide.[3] Investigations of this reaction showed that $Cl_3C\cdot$ was not the hydrogen-abstracting radical in the chain sequence



$$RH + I \longrightarrow RCl + HCCl_3 + SO_2 \qquad (5)$$

since competition reactions of various alkanes toward chlorination by I showed that I involved a more reactive hydrogen-abstracting radical than $Cl_3C\cdot$,[3b,c] the hydrogen atom abstracting species involved in halogenations of alkanes with $BrCCl_3$.[4] A chain sequence

(1) E. C. Ladd and L. Y. Kiley, U. S. Patent 2,606,213 (1952).

(2) H. Goldwhite, M. S. Gibson, and C. Harris, *Tetrahedron*, **30**, 1613 (1964).

(3) (a) E. S. Huyser, *J. Am. Chem. Soc.*, **82**, 5246 (1960); (b) E. S. Huyser and B. Giddings, *J. Org. Chem.*, **27**, 3391 (1962); (c) E. S. Huyser H. Schimke, and R. L. Burham, *ibid.*, **28**, 2141 (1963).

(4) E. C. Kooyman and G. C. Vegter, *Tetrahedron*, **4**, 382 (1958); E. S. Huyser, *J. Am. Chem. Soc.*, **82**, 391 (1960); G. A. Russell, C. DeBoer, and K. M. Desmond, *ibid.*, **85**, 365 (1963).

in which the trichloromethanesulfinyl radical was the hydrogen abstractor yielding trichloromethanesulfinic acid (II) which decomposed to $HCCl_3$ and SO_2 was suggested for these reactions.[3b,c] The present investi-

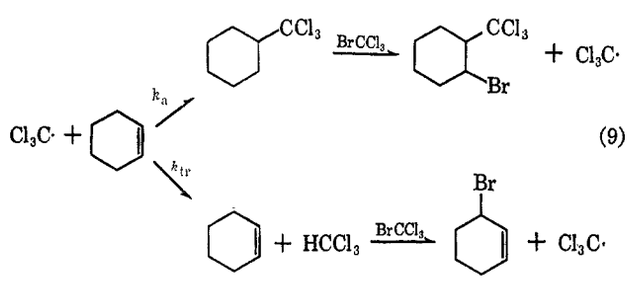
$$R\cdot + I \longrightarrow RCl + Cl_3CSO_2\cdot \quad (6)$$

$$Cl_3CSO_2\cdot + RH \longrightarrow \underset{II}{Cl_3CSO_2H} + R\cdot \quad (7)$$

$$II \longrightarrow HCCl_3 + SO_2 \quad (8)$$

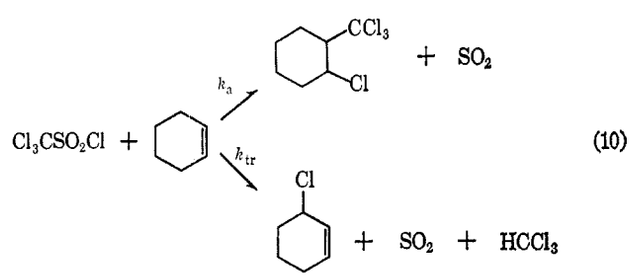
gation was directed toward finding a plausible explanation for the anomalous behavior of the chain-carrying trichloromethanesulfinyl radical in these two free-radical reactions of Cl_3CSO_2Cl.

Reactions of both $BrCCl_3$ and Cl_3CSO_2Cl with cyclohexene yield a mixture of products that result from addition of a radical to the unsaturated linkage and allylic hydrogen atom abstraction by the chain-carrying radical. In the reactions of $BrCCl_3$, which almost certainly involve the $Cl_3C\cdot$ as both the adding and allylic hydrogen-abstracting radical, the relative reactivity ratio of addition with respect to hydrogen ab-



(9)

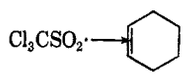
straction (k_a/k_{tr}) is 1.18 at 80°.[5] The ratio of the rate of formation of the addition product relative to that of hydrogen abstraction leading to the halogenated alkene for the reaction of Cl_3CSO_2Cl with cyclohexene, on the other hand, was found to be 1.8 at 80°. Not only does this result indicate that a chain-carrying species other than $Cl_3C\cdot$ is involved in the reac-



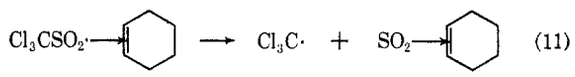
(10)

tion with Cl_3CSO_2Cl but, quite interestingly, it also appears that hydrogen abstraction does not proceed so readily as addition in the reaction of cyclohexene with Cl_3CSO_2Cl as with $BrCCl_3$. Earlier comparisons of $BrCCl_3$ and Cl_3CSO_2Cl as halogenating agents of alkanes[3b,c] indicated that Cl_3CSO_2Cl involves a more effective hydrogen-abstraction reaction than $BrCCl_3$ and, on this basis, the k_a/k_{tr} ratio for Cl_3CSO_2Cl might have been predicted to be less than that observed for the $BrCCl_3$ reaction.

One way of explaining these observations is in terms of a complexing of $Cl_3CSO_2\cdot$ with the π-electron system of the alkene in such a way that it is rendered either less reactive as a hydrogen abstractor than a non-complexed $Cl_3CSO_2\cdot$ or quite reactive as species that can add a $Cl_3C\cdot$ to the double bond of the alkene (or possibly both). Such complexing would be similar to

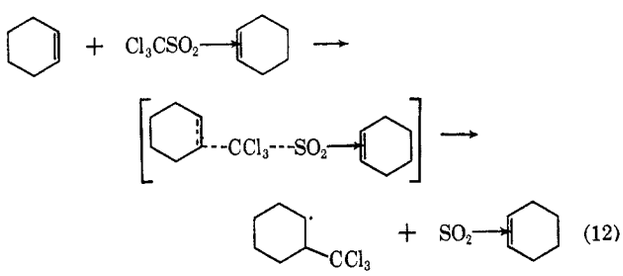


that of alkoxyl radicals reported by Walling and Wagner.[6] The alkene–$Cl_3CSO_2\cdot$ complex might be expected to decompose to the alkene–sulfur dioxide complex and $Cl_3C\cdot$, a reaction which would explain



(11)

the availability of $Cl_3C\cdot$ as the adding species in the reactions of Cl_3CSO_2Cl with alkenes. However, if this were the case, the k_a/k_{tr} ratios for $BrCCl_3$ and Cl_3CSO_2Cl would be the same. Therefore, it seems more reasonable that the complexed radical itself is involved in the reaction that adds the trichloromethyl moiety to another molecule of alkene as shown in eq 12.



(12)

The transition state for this reaction would involve attack of the alkene linkage by the trichloromethyl group of the complexed radical with simultaneous breaking of the carbon–sulfur bond and formation of an alkene–sulfur dioxide complex. The ability of the alkene to complex with sulfur dioxide produced in the reaction as well as with $Cl_3CSO_2\cdot$ may play a significant role in causing the addition of the trichloromethyl moiety to an unsaturated linkage by lowering the activation energy requirement for this reaction. Indeed, it might be suggested that there is no complexing of $Cl_3CSO_2\cdot$ in the ground state and the action of the π-electron system of the alkene is operative only in the transition state of the addition reaction. This possibility seems unlikely, however, in view of the previously observed high reactivity of $Cl_3CSO_2\cdot$ as a hydrogen abstractor. More likely retardation of the hydrogen abstraction reaction is also responsible, at least in part, for the k_a/k_{tr} ratio observed in the reaction of Cl_3CSO_2Cl with cyclohexene. The manner in which the complexed $Cl_3CSO_2\cdot$ may participate in the hydrogen atom abstraction reaction is discussed in a later part of this article.

The presence of compounds that are able to complex SO_2 more effectively than alkenes[7] might be expected to increase the k_a/k_{tr} ratios for the reaction of cyclohexene with $Cl_3CSO_2\cdot$ by either more effective complexing of $Cl_3CSO_2\cdot$ in the ground state, lowering the rate of hydrogen abstraction, or more effective complexing of the addition reaction transition state, or both. The k_a/k_{tr} ratios found for cyclohexene in

(5) E. S. Huyser, *J. Org. Chem.*, **26**, 3261 (1961).

(6) C. Walling and P. Wagner, *J. Am. Chem. Soc.*, **85**, 2333 (1963); **86**, 3368 (1964).

(7) L. J. Andrews and R. M. Keefer, *ibid.*, **73**, 4169 (1951).

chlorobenzene, *t*-butylbenzene, and pyridine were indeed higher than those found in the absence of solvent (Table I). The effect of these solvents on the k_a/k_{tr} ratios parallels their predicted ability to complex sulfur dioxide. The electron-releasing alkyl group on *t*-butylbenzene renders its aromatic ring more effective in complexing sulfur dioxide than the electron-withdrawing halogen does the aromatic ring of chlorobenzene.[7] Pyridine, a very good complexing agent of sulfur dioxide,[8] shows a very marked effect on the k_a/k_{tr} ratios. On the other hand, tetrachloroethylene, which has four strongly electron-withdrawing halogens and should show little tendency to complex with sulfur dioxide, has essentially no effect even at high concentrations of the k_a/k_{tr} ratios.

TABLE I

EFFECT OF SOLVENT OF REACTIONS OF $Cl_3CSO_2\cdot$ WITH CYCLOHEXENE AT 80°

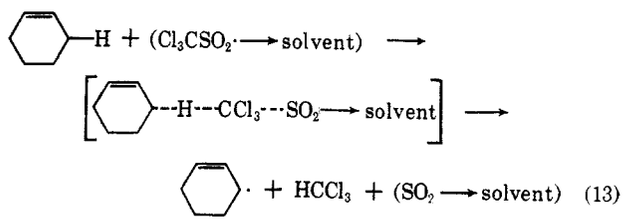
(Mole ratio of cyclohexene/Cl_3CSO_2Cl = 5.3)

Solvent	Concn, mole %	k_a/k_{tr}	Av dev	No. of runs
None	...	1.8	0.2	5
Chlorobenzene	33	2.0	0.05	2
Chlorobenzene	53.0	2.2	0.1	4
Chlorobenzene	73	2.8	0.1	5
Chlorobenzene	80	3.3	0.1	2
t-Butylbenzene	23	2.2	0.1	3
t-Butylbenzene	43	2.5	0.03	3
t-Butylbenzene	74	3.6	0.03	2
t-Butylbenzene	86	4.1	0.4	2
Perchloroethylene	57	2.0	0.2	3
Perchloroethylene	68	2.0	0.1	3
Perchloroethylene	84	2.0	0.3	4
Pyridine	23	4.5	0.8	2
Pyridine	63	11	1	2
Pyridine	87	12	1	2

The data shown in Table I indicate that very likely only complexed $Cl_3CSO_2\cdot$ is involved in the reaction of Cl_3CSO_2Cl with cyclohexene. This suggestion comes from the observation that tetrachloroethylene had little effect on the k_a/k_{tr} ratios even at very high concentrations. If the equilibrium concentration of noncomplexed $Cl_3CSO_2\cdot$ in the presence of alkene were appreciable, at high tetrachloroethylene concentrations, and hence low alkene concentrations, the amount of noncomplexed $Cl_3CSO_2\cdot$ would be appreciably larger than in the absence of this solvent. As quite likely the rate of hydrogen abstraction by a noncomplex $Cl_3CSO_2\cdot$ is faster than by a complexed $Cl_3CSO_2\cdot$ and quite possibly the addition of the trichloromethyl moiety is slower in the absence of a complexing agent, the k_a/k_{tr} ratios would have been lower in reactions carried out in high concentrations of tetrachloroethylene. In solvents that are more effective than the alkene in complexing the radical, some are complexed by the solvent and some are complexed by the alkene. Increasing the concentration of such a solvent increases the fraction of $Cl_3CSO_2\cdot$ complexed by the better complexing agent and, hence, the k_a/k_t ratio increases. The apparent leveling off of the k_a/k_{tr} ratios in higher pyridine concentrations may be indicative of predominant complexing of $Cl_3CSO_2\cdot$ by this reagent to the exclusion of any significant complexing by the alkene.

(8) J. A. Moede and C. Curran, *J. Am. Chem. Soc.*, **71**, 852 (1949).

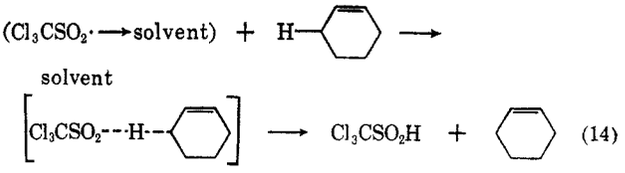
Because of its effectiveness in complexing $Cl_3CSO_2\cdot$ in the reaction with cyclohexene, pyridine was the solvent chosen to study the behavior of the complexed radical in the hydrogen-abstraction reaction. The observed effect of the complexing solvents on the k_a/k_{tr} ratios could be explained in terms of a hydrogen-abstraction reaction by the complexed radical similar to that proposed for the addition reaction. Previous work has shown that cyclohexane is more reactive than



(13)

toluene toward chlorination by Cl_3CSO_2Cl ($k_{cyclohexane}/k_{toluene}$ = 1.86 at 80°).[9] This observation was attributed to the behavior of $Cl_3CSO_2\cdot$ as a hydrogen-abstracting radical. On the other hand, cyclohexane is less reactive than toluene toward hydrogen abstraction by $Cl_3C\cdot$, a less reactive hydrogen abstractor ($k_{cyclohexane}/k_{toluene}$ = 0.25 at 80°). In order to account for the observed effect of the complexing solvents on the k_a/k_{tr} ratios in terms of a complexed radical participating in the hydrogen abstraction in the manner suggested above, the complexed radical should have a lower reactivity than a noncomplexed radical. This would cause the reactivity ratio of cyclohexane with respect to toluene to be lower in the presence of a good complexing solvent such as pyridine. However, we found the reactivity ratio to be essentially uneffected by the presence of 70 mole % pyridine ($k_{cyclohexane}/k_{toluene}$ = 2.0 ± 0.4 for eight runs at 80°). Consequently, we must conclude that the retardation of the hydrogen-abstraction reaction does not involve reaction of the complexed radical in the manner shown in eq 13.

There is a plausible explanation for the observation that a noncomplexed $Cl_3CSO_2\cdot$ is involved in hydrogen abstraction in these reactions and, yet, when compared with the rate of addition, the hydrogen abstraction is slow. Essentially complete decomposition of the ground-state complex may be necessary for hydrogen abstraction to occur. Since hydrogen abstraction involves the same portion of the radical, namely the SO_2 moiety, that is responsible for complexing of the radical, it seems quite reasonable that the complexing agent would have to be removed from the vicinity of this part of the radical for the hydrogen abstraction to occur. The energy required to attain the transition



(14)

state of the hydrogen abstraction would therefore include the energy necessary to decompose the ground-state-complexed radical and thereby lower the rate of the hydrogen-abstraction reaction. Although the

(9) R. P. Pinnell, E. S. Huyser, and J. Kleinberg, *J. Org. Chem.*, **30**, 38 (1965).

complexing agent may possibly solvate the transition state of the hydrogen-abstraction reaction to some degree, the extent of the effect it would have in this capacity would by no means be so great as that encountered in the addition reaction which does not require the removal of the complexing agent in the transition state from its location on the radical in the ground state.

Experimental Section

Materials.—Trichloromethanesulfonyl chloride (Eastman Kodak) was twice sublimed before using. Cyclohexene (Matheson Coleman and Bell) was refluxed for 12 hr over sodium and a freshly distilled center cut was used for each determination. Chlorobenzene (Fisher Certified Reagent), *t*-butylbenzene (Aldrich Chemicals), and tetrachloroethylene, toluene, and cyclohexane (Matheson Coleman and Bell) were redistilled before using. Pyridine (Fisher Certified Reagent) was distilled from barium oxide. Benzoyl peroxide (Matheson Coleman and Bell) was recrystallized from a mixture of chloroform and methanol, mp 105°.

Determination of k_a/k_{tr} Ratios for Cyclohexene.—A solution consisting of Cl_3CSO_2Cl (3.268 g, 14.9 mmoles) in cyclohexene (6.534 g, 79.5 mmoles) was prepared. Portions of this solution were sealed in tubes with about 0.01 mole % peroxide and were heated at 80° for about 1–1.5 hr in a constant-temperature oil bath. The amount of Cl_3SCO_2Cl that had reacted during this period was determined by infrared analysis using the characteristic absorption at 1191 cm^{-1} owing to the symmetrical sulfur–oxygen stretching mode of Cl_3CSO_2Cl. The amount of $HCCl_3$ produced in the reaction was determined by gas chromatographic analysis of a weighed portion of the mixture along with a weighed amount of methylene chloride which served as an internal standard.[10] The k_a/k_{tr} ratio was determined from the following equation using the quantities Cl_3CSO_2Cl that had reacted and the

$$\frac{k_a}{k_{tr}} = \frac{Cl_3CSO_2Cl \text{ used} - HCCl_3 \text{ produced}}{HCCl_3 \text{ produced}}$$

amount of $HCCl_3$ produced. For determination of the k_a/k_{tr} ratio in the various solvents, a portion of a freshly prepared solution of Cl_3CSO_2Cl in cyclohexene was diluted with the solvent. The amount of Cl_3CSO_2Cl present in the solution, determined by infrared analysis, corresponded to the calculated amount. A calibration curve for Cl_3CSO_2Cl for each of the solvents used was made and was linear in the region of the Cl_3CSO_2Cl determinations. Portions of the solutions containing the solvent, cyclohexene, and Cl_3CSO_2Cl were sealed in tubes along with 0.01 mole % benzoyl peroxide and heated at 80° for about 1–1.5 hr. Chloroform and Cl_3CSO_2Cl present in the reaction mixtures were determined in the manner outlined above and the k_a/k_{tr} ratio calculated from these amounts.

In contrast to the other solvents, pyridine appeared to react slowly with Cl_3CSO_2Cl. The rate of this reaction was very much slower than that of the reaction of Cl_3CSO_2Cl with cyclohexene in pyridine. A small correction (about 10%) in the amount of Cl_3CSO_2Cl consumed in the reaction with cyclohexene was made. The extent of this correction was determined from the amount of Cl_3CSO_2Cl that reacted in pyridine under the same experimental conditions.

Competitive Chlorination of Cyclohexane and Toluene in Pyridine.—Mixtures were prepared consisting of accurately weighed amounts of toluene, cyclohexane, chlorobenzene, and sufficient Cl_3CSO_2Cl to react with 35–40% of the total hydrocarbon content present. The initial cyclohexane/toluene ratios were 2:1, 1:1, and 1:2 for these determinations. Portions of these mixtures were diluted with sufficient pyridine to make the resulting reaction mixtures 70 mole % in pyridine. The reaction mixtures were sealed in Pyrex tubes along with about 0.01 mole % benzoyl peroxide and heated at 80° for about 8 hr. The amounts of chloroform produced and toluene remaining were determined by gas chromatographic analyses of the resulting reaction mixtures. The difference in the amount of chloroform produced and toluene consumed was taken as the amount of cyclohexane that had reacted. Cyclohexane was not determined directly owing to the observation that the cyclohexyl chloride produced in the reaction underwent considerable dehydrohalogenation as evidenced by the formation of cyclohexene. The relative reactivity ratios were determined from the initial and final amounts of cyclohexane and toluene using the following equation where the subscripts i and f refer to the initial and final amounts of the reagents, respectively.

$$\frac{k_{cyclohexane}}{k_{toluene}} = \frac{\log [cyclohexane]_i/[cyclohexane]_f}{\log [toluene]_i/[toluene]_f}$$

Registry No.—Trichloromethanesulfonyl chloride, 2547-61-7; chlorobenzene, 108-90-7; *t*-butylbenzene, 98-06-6; tetrachloroethylene, 127-18-4; pyridine, 110-86-1; perchloroethylene, 127-18-4.

Acknowledgment.—We wish to thank the National Science Foundation for support of a portion of this work.

(10) The chromatographic analyses were performed at 60° on a 5-ft × 0.25 in. Teflon column packed with 24% SF-96 on Chromasorb W (nonacid washed). The injection port of the chromatograph (Aerograph A-90 P) was fitted with a Pyrex insert and not heated. Under these conditions, mixtures containing Cl_3CSO_2Cl did not give a Cl_4C peak. We were unable to detect any formation of Cl_4C in any of our reactions of Cl_3CSO_2Cl with cyclohexene in contrast to results reported by Goldwhite, *et al.*[2] Chromatograms of the reaction mixtures on other columns, particularly metal columns with polar substrates, or using a chromatograph with a heated, metal injection port, showed the presence of Cl_4C.