order of hydrocarbon reactivity: mesitylene > xylene > toluene > benzene.[9]

Deactivated benzene rings appear to be very resistent toward sulfone formation. Chlorobenzene and *p*-toluenesulfonic acid gave no sulfone product under the usual reaction conditions. No attempt was made toward finding a higher temperature at which reaction would occur.

The relative reactivities of the aromatic substrates are consistent with a mechanism involving attack on the aromatic ring by an electrophilic reagent. The attacking electrophile in this case must be weak and demands an electron rich ring. The reaction mechanism in the formation of aryl sulfones apparently involves the sulfonium cation, $ArSO_2^+$, which is very similar to the mechanism involved in the preparation of aromatic ketones in PPA *via* the acyl cation, $ArCO^+$.[10]

Field[11] has reported the synthesis of sulfonic anhydrides from the reaction of the acid with phosphorus pentoxide. Because of the similarity of conditions with the present investigation it is highly probable that the aromatic sulfonic anhydride is an intermediate in the reaction.

The sodium salt of *m*-xylenesulfonic acid was also used effectively in the synthesis of sulfones in polyphosphoric acid. This fact makes the preparation reaction of PPA very versatile and attractive from the standpoint of availability of a wider range of starting materials.

It was of some interest to see if the same or different isomers were obtained using the Friedel-Crafts synthesis of aromatic sulfones. In all the cases studied it was observed that the same sulfone isomer was isolated using the aluminum chloride method as in the synthesis with PPA.

Experimental Section

Materials.—The following chemicals were obtained commercially and used without further purification. Benzenesulfonic acid monohydrate, *p*-toluenesulfonic acid monohydrate, sodium 2,4-dimethylbenzenesulfonate, α-naphthalenesulfonic acid dihydrate, β-naphthalenesulfonic acid monohydrate, benzenesulfonyl chloride, *p*-toluenesulfonyl chloride, benzene, toluene, *m*-xylene, biphenyl, naphthalene, and chlorobenzene were all Eastman reagent grade. Mesitylene, pseudocumene, and *p*-xylene were Eastman practical grade. The polyphosphoric acid was Matheson reagent grade.

1,2,4-Trimethyl-5-benzenesulfonic acid was prepared according to the procedure of Smith and Cass.[12] Mesitylenesulfonic acid was synthesized by the direct sulfonation of mesitylene.[13] *p*-Xylenesulfonic acid dihydrate was prepared by the direct sulfonation of *p*-xylene with concentrated sulfuric acid: melting point of *p*-xylenesulfonic acid, 86° (lit.[14] mp 86°). The infrared spectra were run in carbon disulfide solution (12–15 mg/ml) on a Beckman IR-8 instrument.

Sulfone Synthesis in Polyphosphoric Acid.—Table I contains most of the pertinent data for the preparation of the various sulfones. The following procedure is presented as typical for the other preparations.

p-Tolyl-2,4-dimethylphenyl Sulfone.—A mixture of 3.8 g (0.02 mole) of *p*-toluenesulfonic acid monohydrate, 2.1 g (0.02 mole) of *m*-xylene, and 60 g of polyphosphoric acid was placed in a stoppered round-bottom flask equipped with a mechanical stirrer and heated in an oil bath. After heating at 80° and stirring for 8 hr, the hot mixture was poured into ice water. Upon cooling and stirring, the thick liquid solidified. The crude white product was filtered from solution and recrystallized from ethanol. A second recrystallization from alcohol afforded 4.0 g (77 %) of white crystals which melted at 49° (lit.[15] mp 51°). The other possible isomeric product, *p*-tolyl-2,6-dimethylphenyl sulfone, melts at 121°.[15] An infrared spectrum of the product contained two strong absorption bands at 1160 and 1320 cm^{-1} which is indicative of the sulfone group.

Desulfonation of Mesitylenesulfonic Acid in PPA.—Mesitylenesulfonic acid (5 g, 0.021 mole) was heated and stirred in 60 g of polyphosphoric acid at 80° for 8 hr. After the reaction mixture was poured into water and allowed to sit overnight, 0.2 g of brown solid was filtered from solution. Recrystallization of the solid from acetic acid gave crystals of dimesityl sulfone, mp 202° (lit.[16] mp 202°). The melting point of the product mixed with authentic sample was undepressed.

Sulfone Synthesis with Aluminum Chloride. Phenyl Mesityl Sulfone.—Aluminum chloride (2.7 g, 0.02 mole) was added to 10 ml of mesitylene and 3.5 g (0.02 mole) of benzenesulfonyl chloride was added dropwise. The reaction flask was cooled as needed. After the addition was complete, the reaction solution was refluxed for 2 hr. The mixture was then poured into water and an additional 20 ml of benzene was added. The benzene layer was extracted twice with a bicarbonate solution and then washed with water. After drying, the benzene solution was concentrated and cooled to give crystals of the product. Recrystallization of the solid product from ethanol gave needles which melted at 74°. The yield was only 1.9 g. The infrared spectrum of this product was identical with that of the sulfone isolated in the PPA synthesis using benzenesulfonic acid and mesitylene. A mixture melting point of these two compounds was undepressed.

p-Tolyl-*m*-xylyl Sulfone.—*p*-Toluenesulfonyl chloride (3.8 g, 0.02 mole), 2.7 g (0.02 mole) of aluminum chloride, and 10 ml of *m*-xylene were reacted together in the manner described above. An oil was obtained after evaporation of the organic extract. Recrystallization of the product from ethanol eventually yielded crystals which melted at 45°. Although this melting point was slightly lower than that of the product isolated from the PPA preparation, the infrared spectra of both compounds were identical.

Acknowledgment.—The author is grateful to the National Science Foundation for financial support under an academic year extension grant of the Research Participation for College Teachers program and is also grateful to Professor D. A. Shirley for his assistance.

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[9] The low yields in the case of benzene may also be due to its lower boiling temperature. At the temperature of the reaction (80°) benzene tended to vaporize from the reaction vessel. Benzene vapor tended to escape even when a sealed flask with magnetic stirrer was used.

[10] D. A. Shirley, "Organic Chemistry," Holt, Rinehart, and Winston, Inc., New York, N. Y., 1964, p 634.

[11] L. Field, *J. Am. Chem. Soc.*, **74**, 394 (1952).

[12] L. Smith and O. Cass, *ibid.*, **54**, 1617 (1932).

[13] C. Suter and A. Weston, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1946, p 162.

[14] O. Jacobsen, *Ber.*, **10**, 1009 (1877).

[15] See ref *h* in Table I.

[16] See ref *k* in Table I.

The Preparation of Spiro[3.4]oct-1-ene

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Received April 10, 1967

In the course of our work with 5-spiro-substituted cyclopentadienes, it had been noted that diene **1** dimerizes readily at room temperature, very much in contrast to its expectedly slow reaction with conventional

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[1] (a) Taken from the Ph.D. dissertation submitted by G. Whitney in partial fulfillment of the Cornell Graduate School requirements, 1966; (b) G. C. W. would like to acknowledge an NIH predoctoral fellowship for the years 1964–1966.

dieneophiles.[2] The related 5,5-dimethylcyclopentadiene (2) appears to react normally and gives mixed Diels–Alder products without complication.[3] Similar contrasting reactivities have been reported for the analogous ketal **3** and the related 5,5-dimethyl ether **4**.[4,5]


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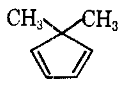

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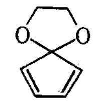

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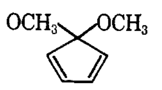

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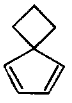
As part of an examination of the source of this unusual preference of **1** for dimerization, it seemed desirable to synthesize the still unknown diene **5** so that the kinetics of the entire series of dienes might be compared. The work described here reports the preparation of spiro[3.4]oct-1-ene (**6**) and several unsuccessful attempts to transform it into diene **5**. Of the several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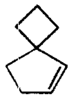
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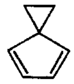
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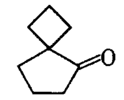

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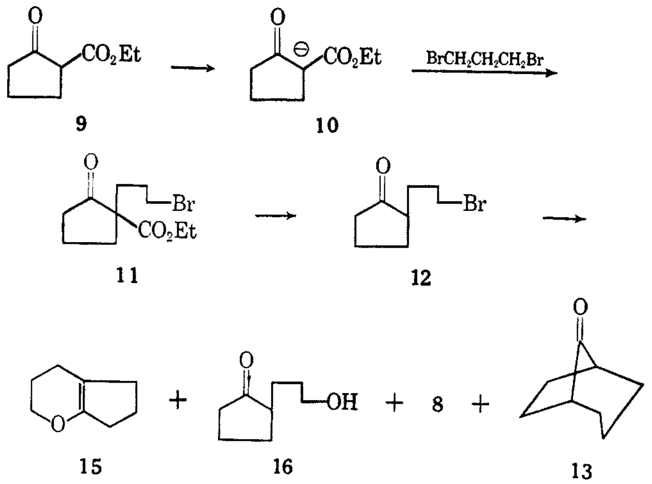
possible routes to diene **5**, the most direct would be the successive displacement by a cyclopentadienyl anion of the two terminal bromine atoms of 1,3-dibromopropane. Although by analogy to other chemical cyclizations it would be anticipated that this reaction would probably fail for **5**, the preparation of it as well as dienes **1** and **7** by this route has been reported.[6] Curiously, however, it was reported that all three dienes were stable in dilute solution and could not be isolated in the pure state. Others[2,7,8] who have prepared **1** and **7** have been able to collect pure samples by distillation. Numerous attempts at different times to prepare **5** in this manner led only to polymeric material while **1** and **7** were prepared easily under the same conditions. This route was abandoned.

Preparation of Spiro[3.4]octan-1-one (8).—The use of the previously characterized spiroketone **8** as a starting point for the preparation of **5** offered a promising alternative. The most practical preparation of **8** seemed to be that developed by Mayer,[9] who used the sequence of reactions given in Scheme I. In Mayer's description of the treatment of ketobromide **12** with potassium hydroxide only cyclized ketones **8** and **13** were reported. A small amount of alcohol **16** had been isolated from this same reaction.[10] Very recently, after the present work was completed, enol ether **15** was reported to be a significant product (22%) when potassium *t*-butoxide dissolved in benzene was employed as the base.[11] Because the best yield (60%) of **8** reported at the time this work was initiated was with potassium hydroxide and benzene, this combination was tried initially. Analysis of the distilled product by gas chromatography indicated the presence of *three* components in the ratio of 61:37:2. Several repetitions of the reaction gave similar distributions.

Scheme I



The minor component was identified as **13** by its melting point, the melting point of its 2,4-dinitrophenylhydrazone derivative, and its unique carbonyl absorption in the infrared which were all consistent with previously reported values.[9,12] The ^{1}H nmr spectrum showed a broad multiplet at τ 8.1 (ten protons) and a second multiplet at τ 7.78 (two protons).

The 37% product was identified as the desired ketone **8** by its infrared carbonyl absorption and the melting point of its 2,4-dinitrophenylhydrazone derivative.[9,10] The 60-mc ^{1}H nmr consisted of a one broad multiplet centered about τ 8 which is reasonable for the assigned structure. The α and β hydrogens of cyclopentanone absorb at τ 7.97[13] and the methylene hydrogens of cyclobutane are observed at *ca.* τ 8.[14] The major component was identified as enol ether **15** by its strong absorption at 5.95 μ, its ^{1}H nmr spectrum, and slow formation of a 2,4-dinitrophenylhydrazone derivative under strongly acidic conditions identical with that formed from **8**.

Enol ether **15** could be hydrolyzed with 5% nitric acid to the known keto alcohol **16**. An attempt to determine the purity of **16** by glpc gave only one peak identical in retention time with that of **15**. It was confirmed by infrared analysis of a small sample of eluate that the alcohol had indeed dehydrated either in the injector or on the column to reform **15**. It was ascertained by immediate infrared analysis of the products of the dehydromination reaction that **15** was a component of the original mixture and not formed during the subsequent isolation procedure.

In an attempt to improve the yield of spiroketone, **8**, several base–solvent combinations were tried. In

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(2) C. F. Wilcox, Jr., and R. R. Craig, *J. Am. Chem. Soc.*, **83**, 3866 (1961).

(3) C. F. Wilcox, Jr., and M. Mesirov, *J. Org. Chem.*, **25**, 1841 (1960).

(4) C. H. DePuy, B. W. Ponder, and J. D. Fitzpatrick, *ibid.*, **29**, 3508 (1964).

(5) P. E. Eaton and R. A. Hudson, *J. Am. Chem. Soc.*, **87**, 2769 (1965).

(6) G. Chiurdoglu and B. Tursch, *Bull. Soc. Chim. Belges*, **66**, 600 (1957).

(7) R. Y. Levina, N. H. Mezentsova, and O. V. Lebedev, *Zh. Obsch. Khim.*, **25**, 1097 (1955); R. Y. Levina and T. I. Tantsireva, *Dokl. Akad. Nauk SSSR*, **89**, 697 (1953).

(8) P. L. Pauson and B. F. Hallam, *J. Chem. Soc.*, 646 (1958).

(9) R. Mayer, G. Wenschuh, and W. Töpelmann, *Chem. Ber.*, **91**, 1616 (1958).

(10) R. R. Craig, Ph.D. Thesis, Cornell University, June 1961. Craig, in attempting to repeat Mayer's work, had obtained considerably poorer over-all yields. Although the ratio of **8** to **13** found by fractional distillation was about one, the absolute yield of **13** was about the same as the present experiments. It is possible that **8** was lost selectively during the distillation.

(11) S. J. Etheredge, *J. Org. Chem.*, **31**, 1990 (1966).

(12) A. C. Cope, J. Grisar, and I. Borowitz, *J. Am. Chem. Soc.*, **82**, 4299 (1960).

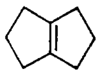
(13) L. M. Jackman, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959.

(14) N. M. R. Spectra Catalog, Varian Associates, Inc., Palo Alto, Calif., 1963.

addition to trying freshly fused potassium hydroxide (ground and suspended in benzene), aqueous potassium hydroxide and sodium methoxide in benzene were also used. The yields and proportions were not strikingly different. The best over-all yield of spiroketone (32%, isolated as 1:1 mixture with **15**) was obtained with sodium methoxide (*ca.* 2.5 equiv/equivalent of bromide) in hot benzene.

Spiro[3.4]oct-1-ene.—The impure (*ca.* 50%) spiroketone **8** was readily reduced with lithium aluminum hydride to give the known[15] corresponding alcohol **17**. Although **17** could be separated from reduced **13** and unreacted **15** by preparative glpc, it was used in subsequent steps after only partial purification by fractional distillation. Only fractions containing at least 80% of **17** were used. The major contaminant was enol ether **15**.

Because of the known tendency for **17** to rearrange under solvolytic conditions, initial dehydration attempts were with thionyl chloride in pyridine,[16] a reagent combination commonly used for dehydration of sensitive alcohols. However with **17** only ring expanded olefin **18** was obtained. Alcohol **17** was converted to its tosylate derivative and that was treated with potassium *t*-butoxide in dimethyl sulfoxide.[17] About a 10% yield (isolated) of the desired monoene **6** was obtained along with a nearly equal amount of **18**. The structure of **6** was assigned on the basis of its infrared spectrum (3.28, 6.59, and 13.68 μ) and ^{1}H nmr spectrum (τ 4.2 (2), 7.8 (2), 8.05 (complex, 8)). Because of the low yields in the tosylic acid elimination reaction, an attempt was made to pyrolyze the acetate of **17**. Only low-boiling fragmentation products were isolated; a lower pyrolysis temperature gave similar products along with much unreacted acetate.



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The best method found for preparing **6** was the pyrolysis of the xanthate of **17** which gave **6** in yields of up to 71% based on the starting alcohol. Analysis of the fractionally distilled pyrolysate by glpc indicated *ca.* 96% purity with at least two other contaminants of similar retention time. The method of preparing spirenes *via* the decomposition of the *p*-toluenesulfonylhydrazones developed by Krapcho and Donn[18] was not tried since their results suggested that in small ring systems 1,3 insertion and ring expansion would predominate. An attempt to brominate **6** with NBS gave a small amount (*ca.* 10% by weight) of an unstable liquid with an nmr spectrum compatible with the desired allylic bromide. Because of the limited sample available and its obvious impurity, the failure of attempts to convert it into diene **5** is considered inconclusive. Additional efforts in this direction are planned.

Experimental Section

2-(γ-Bromopropyl)cyclopentan-1-one (12).—Bromoketone **12** was prepared by the three-step procedure of Mayer[9] starting from the commercially available (Arapahoe) 2-carboethoxycyclopentanone (analysis by glpc indicated that 35% of our sample was actually the methyl ester). The typical over-all yield was 50%.

Spiro[3.4]octan-1-one (8).—A solution of 113 g (0.55 mole) of bromoketone **12** in 200 ml of dry benzene was added dropwise over a 7-hr period to a stirred suspension of 118 g (2.2 moles) of sodium methoxide in 550 ml of dry benzene heated to 65° under a nitrogen atmosphere. The reaction mixture was stirred for an additional 2 hr at 65°, then cooled in an ice bath, and finally poured into 500 ml of ice water. The benzene layer, after several water washes, was dried over potassium carbonate and then concentrated by distillation through a 50-cm Vigreux column. The residue was fractionally distilled through a 90- × 1-cm spinning-band column. Two fractions totaling 40.5 g were collected. The second, weighing 23 g, bp 68–69° (22 mm), contained 75% spiroketone. The combined fractions, containing 50% spiroketone **8**, corresponded to a 32% yield of **8**. Numerous other combinations of bases and reaction conditions were tried. Only the best procedure is reported here.

2,3,4,5,6,7-Hexahydrocyclopenta(*b*)pyran (15).—This enol ether could be obtained pure by preparative glpc on a 20% FFAP column (Varian Aerograph) of early distillation fractions obtained from the treatment of bromide **12** with base. It added bromine readily and reacted slowly with 2,4-dinitrophenylhydrazine in 2 *N* hydrochloric acid to give the hydrazone of the alcohol **16**. In 5% nitric acid the enol ether was about 70% hydrolyzed to give **16** after 10 min. The vinyl ether also hydrolyzed slowly on exposure to atmospheric moisture.

Anal. Calcd for $C_8H_{12}O$: C, 77.39; H, 9.74. Found: C, 76.94; H, 9.41.

Spiro[3.4]octan-1-ol (17).—Spiroketone **8** contaminated by about 50% of the vinyl ether was reduced with a suspension of lithium aluminum hydride in diethyl ether. In a typical run, 34.7 g (0.28 mole) of mixture containing 17.3 g (0.14 mole) of **8** was added dropwise over a 1.75-hr period to a stirred suspension of 10.6 g (0.28 mole) of hydride in 250 ml of ether cooled in an ice bath and under a nitrogen atmosphere. After stirring for an additional 3 hr, the excess hydride was decomposed by slow addition of 42.4 g of water. The crystalline aluminum salts were removed by filtration and washed with ether. The residue obtained by concentrating the dried ether solution was distilled through a 20-cm spiral tantalum wire column to yield **17** contaminated by vinyl ether. From glpc analysis of the several fractions, a total yield of *ca.* 80% was calculated. In subsequent steps only fractions containing at least 80% of **17** were used. It could be purified easily by preparative glpc on a 20% FFAP column at 130°. The physical properties observed for **17** agreed with those recorded in literature.[15,19]

Spiro[3.4]oct-1-ene (6). A.—Following the method of Heilmann and Glenat,[16] 0.55 g (0.004 mole) of 95% pure **17** in 1.5 ml of ether was treated with 0.55 ml of thionyl chloride and 0.85 ml of pyridine dissolved in 1.5 ml of ether for 3 hr at 0–25°. After addition of 5 ml of water and extraction of the product mixture with 10 ml of ether, approximately 0.1 g of a liquid was collected by distillation at 60–65° (30–35 mm). Analysis of the liquid by glpc on a 10% 20M Carbowax column at 75° showed it to be composed of three components in a ratio of 1:10:1. The nmr spectrum of the mixture did not show any olefinic protons and was virtually identical with the spectrum of **18** prepared in tosylate elimination reaction described next.

B.—The tosylate of alcohol **17** prepared by the method of Krapcho and Benson[15] from 3.8 g (0.29 mole) of 95% pure **17** was dissolved in 25 ml of dry dimethyl sulfoxide and the solution added over a 10-min period to a stirred suspension of potassium *t*-butoxide in 25 ml of dry dimethyl sulfoxide maintained at 20°. After stirring for an additional 30 min at 20°, 20 ml of heptane was added and the dark green solution was poured into 100 ml of ice water. After repeated extraction of the organic materials from the aqueous layer with fresh heptane, the combined heptane solutions were dried over magnesium sulfate and the heptane was removed by fractional distillation. The distillate was monitored by glpc for products other than heptane and showed none. Analysis of the residue on a 6 × 0.25 in. 10% FFAP column at 75° indicated the presence of two materials (54:46) in addition to solvent. These were isolated in *ca.* 0.3-g quantities by preparative glpc on a 20% FFAP column at 80°. The 46% sample was identified as the rearranged olefin **18** by its infrared

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(15) A. P. Krapcho and M. Benson, *J. Am. Chem. Soc.*, **84**, 1036 (1962).

(16) R. Heilmann and R. Glenat, *Bull. Soc. Chim. France*, 1586 (1955).

(17) C. H. Snyder and H. R. Soto, *J. Org. Chem.*, **29**, 742 (1964); **30**, 673 (1965).

(18) A. P. Krapcho and K. Donn, *ibid.*, **30**, 641 (1965).

(19) E. Vogel, *Chem. Ber.*, **91**, 1616 (1958).

spectrum[12] and its nmr spectrum (only a sharp multiplet at 2.16 ppm). The 54% material had the infrared and ^1H nmr spectra described in the discussion and was assigned the structure of the spiro monoene **19**.

Anal. Calcd for C_8H_{12}: C, 88.81; H, 11.18. Found: C, 89.04; H, 11.27.

C.—The acetate of alcohol **17** was prepared by addition of 4.3 g (0.042 mole) of acetic anhydride to a solution of 5 g (80% pure, 0.032 mole) of **17** in 25 ml of dry pyridine. The mixture was analyzed periodically by glpc. After 17 hr, 98% of the **17** peak had disappeared and had been replaced by a new peak. The acetate was isolated by addition of water, extraction with ether, and distillation of the dried ether solution to give 5.4 g of material boiling at 88–92° (10 mm). Pyrolysis of this material through a vertical Vycor tube packed with 10 cm of glass helices and heated to 580 ± 5° gave only products with extremely short retention times and gave no trace of material in the retention time range of authentic **19**. Repetition of the experiment at 500 ± 5° gave the same low-boiling products and 20% unreacted acetate.

D.—The xanthate of **17** was prepared by the procedure described for cyclopentanol.[20] To a stirred suspension of 8.6 g (0.21 mole) of sodium hydride (58.6% by weight in oil) in 150 ml of ether was added dropwise 26.5 g (0.17 mole) of 85% pure **17** and the reaction mixture at reflux for 3 hr. The mixture was cooled in an ice bath and 15.2 g (0.20 mole) of carbon disulfide added dropwise. The resulting mixture was heated under reflux for an additional 3 hr during which time the suspension changed from white to orange. The reaction mixture was cooled again in an ice bath and 28.4 g (0.2 mole) of freshly distilled methyl iodide added. The mixture was refluxed for a final 3 hr and then cooled in an ice bath and 100 ml of ice water was added to the mixture. After separation of the ether layer, it was washed twice with water and once with saturated aqueous sodium chloride and then dried over magnesium sulfate. The filtered ether solution was concentrated in a rotary evaporator to give 45.5 g of crude xanthate as a viscous orange oil that was pyrolyzed without further purification.

The crude xanthate was pyrolyzed by dropwise addition to biphenyl heated to reflux. The volatile products were collected in a cooled receiver and then fractionally distilled through a 10-cm Vigreux column to give 12.6 g of **19**, bp 115° (750 mm). Analysis of the product by glpc on a 10% FFAP column indicated 96% purity with two other olefinic impurities. The yield of **19** based on the actual amount of **17** used was 71%. The infrared spectrum of this sample was identical with that obtained from the tosylate elimination reaction.

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(20) H. R. Nace, *Org. Reactions*, **12**, 57 (1962).

The Chlorination of Ethylbenzene in Acetic Acid

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The Dow Chemical Company, Midland, Michigan 48640

Received March 24, 1967

In recent years the electrophilic chlorination of benzene and alkylbenzenes has been extensively investigated.[1-4] The rates of chlorination and isomer distributions of the products obtained with molecular chlorine in acetic acid solution have been determined for a number of alkylbenzenes.[5] However, it was interesting to note that the data for the chlorination of ethylbenzene (I) under these conditions has only been inferred from indirect observations. Brown and Neyens[6] have reported the *ortho/para* ratio for the chlorination of **I** in a reaction run in order to obtain the *para* isomer as a reference for a structure determination in a related problem. Also, de la Mare and Robertson[7] have measured the time required to consume 15% of the chlorine in the chlorination of benzene and several alkylbenzenes, including **I**. From these data, Stock and Brown[4] have calculated partial rate factors for the *ortho* and *para* positions. We wish to report a more detailed investigation of the reaction between chlorine and ethylbenzene in acetic acid including the direct determination of the reaction rate, the isomer distribution of the products, and the activation parameters for the reaction.

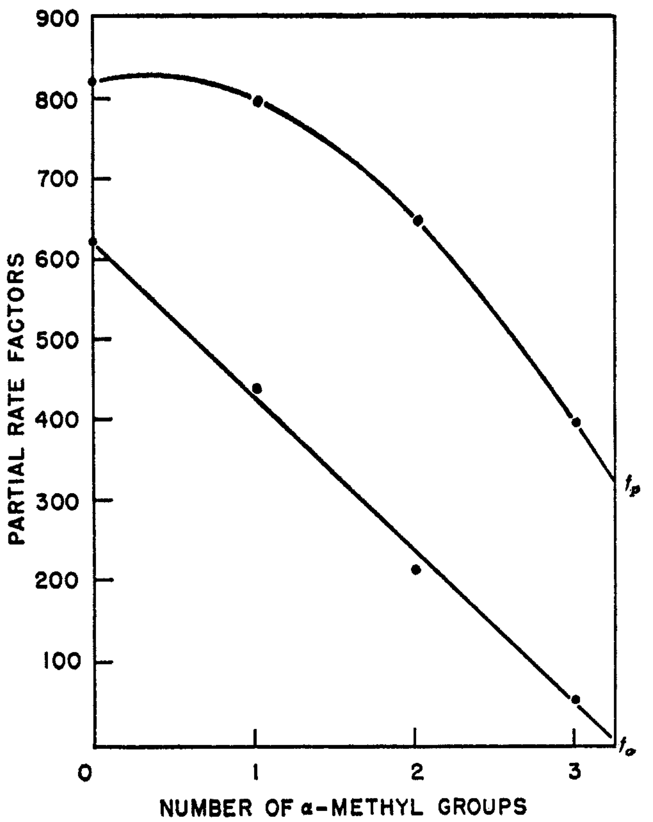

Figure 1.—Partial rate factors *vs.* number of α-methyl substituents for molecular chlorination of substituted toluenes in acetic acid.

The reaction between chlorine and **I** in acetic acid was run in a manner such that light was excluded in order to eliminate free-radical chlorination of the side chain or solvent. In a blank run it was determined that the dark reaction of chlorine with **I** and solvent was negligible. The rate of formation of the product in the reaction at 25 and 35° was determined in a manner identical with that of Brown and Stock.[5] The rate data for several runs are summarized in Table I. The second-order rate constant for the chlorination of benzene in acetic acid at 25° is reported by Brown and Stock[5] to be 15.4×10^{-7} l. mole^{-1} sec^{-1} while for toluene the value of k_2 is 5.30×10^{-4} l. mole^{-1} sec^{-1}. Thus, while the relative rate of $k_2(\text{toluene})/k_2(\text{benzene}) = 340$, the relative rate of $k_2(\text{ethylbenzene})/k_2(\text{benzene}) =$

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(1) H. P. Braendlin and E. T. McBee in "Friedel-Crafts and Related Reactions," G. A. Olah, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, Chapter XLVI.

(2) G. A. Olah, S. J. Kuhn, and B. A. Hardie, *J. Am. Chem. Soc.*, **86**, 1055 (1964).

(3) P. B. D. de la Mare and J. H. Ridd, "Aromatic Substitution," Academic Press Inc., New York, N. Y., 1959.

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