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 After 17 hr, 98% of the **17** peak had disappeared and had been replaced by a new peak.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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The Chlorination of Ethylbenzene in Acetic Acid

RICHARD J. DOLINSKI AND ROBERT M. NOWAK

The Dow Chemical Company, Midland, Michigan 48640

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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.

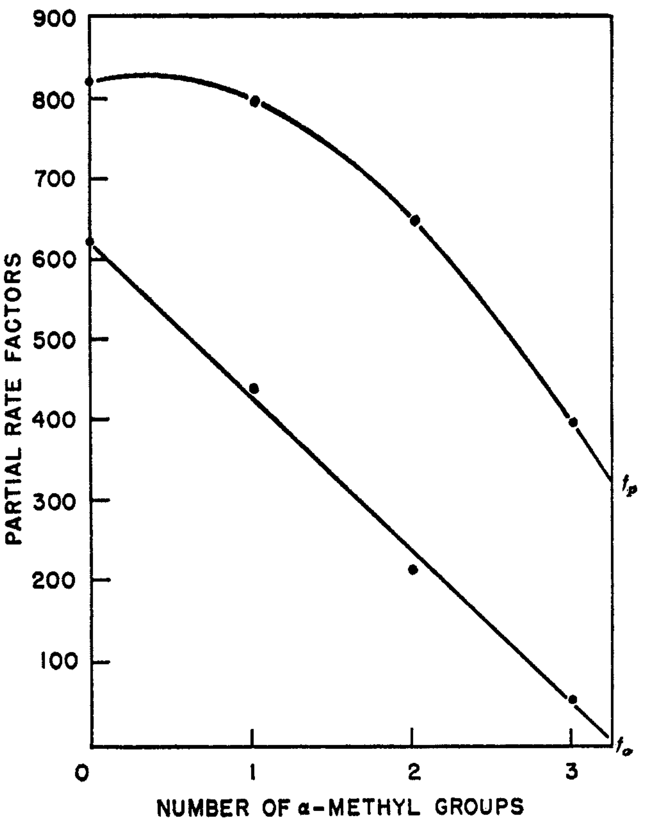

Figure 1.—Partial rate factors *vs.* number of α-methyl substituents for molecular chlorination of substituted toluenes in acetic acid.

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(toluene)/k_2(benzene) = 340, the relative rate of k_2(ethylbenzene)/k_2(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.

(4) L. M. Stock and H. C. Brown, "Advances in Physical Organic Chemistry," V. Gold, Ed., Academic Press Inc., London, 1963, p 35.

(5) H. C. Brown and L. M. Stock, *J. Am. Chem. Soc.*, **79**, 5175 (1957).

(6) H. C. Brown and A. H. Neyens, *ibid.*, **84**, 1655 (1962).

(7) P. B. D. de la Mare and P. W. Robertson, *J. Chem. Soc.*, 279 (1943).

TABLE I

SECOND-ORDER RATE CONSTANTS FOR THE REACTION OF CHLORINE WITH ETHYLBENZENE IN ACETIC ACID

T, °C	Ethylbenzene	Cl_2	Rate constant $k_2 \times 10^4$, l. mole^{-1} sec^{-1}
25	0.0976	0.0982	4.33
25	0.0997	0.0674	4.38
35	0.1188	0.0812	8.97
35	0.0982	0.1021	8.92

[a] Concentrations in mole liter^{-1}; mean $k_2^{25°} = 4.35 \times 10^{-4}$ l. mole^{-1} sec^{-1}; mean $k_2^{35°} = 8.94 \times 10^{-4}$ l. mole^{-1} sec^{-1}.

TABLE II

ISOMER DISTRIBUTION FOR THE CHLORINATION OF TOLUENE IN ACETIC ACID AT 25°

Compound	Product, mole % Observed	Reported[a]
o-Chlorotoluene	59.6	59.8
m-Chlorotoluene	0.50	0.48
p-Chlorotoluene	39.9	39.7

[a] See ref 5.

TABLE III

ISOMER DISTRIBUTIONS AND PARTIAL RATE FACTORS FOR THE CHLORINATION OF ETHYLBENZENE IN ACETIC ACID

Isomer distribution	Mole, %	Source	Partial rate factor f_o	f_m	f_p	Selectivity factor,[a] S_f
o-Chloroethylbenzene	52.3	Isomer distribution and k_2(ethylbenzene)/k_2(benzene)	441	4.47	796	2.2504
m-Chloroethylbenzene	0.53					
p-Chloroethylbenzene	47.2	Selectivity relationship	439	4.8	796	2.2430

[a] The selectivity factor, S_f, is defined as log (f_p/f_m) by H. C. Brown and C. R. Smoot, *J. Am. Chem. Soc.*, **78**, 6255 (1956).

283. A value of 290 was obtained earlier by de la Mare and Robertson.[7]

The products of the chlorination were examined by vapor phase chromatography (vpc) and by infrared spectrophotometry. The *ortho-* and *meta-* + *para*-chloro isomers were readily separated on the chromatogram but, despite the use of various column packings, lengths, and temperatures, resolution of the *meta* from the *para* isomer was not achieved. However, the amount of the *meta*-chloro compound was determined by infrared following a previously reported method.[2]

To ensure that the data on ethylbenzene was directly comparable with the literature values for toluene, the chlorination of toluene was repeated and the isomer distribution was compared with the reported results. Excellent agreement was obtained as shown in Table II.

From the isomer distributions for the chlorination of I and the relative rates of reactivity of I and benzene, the partial rate factors for each position were determined. Likewise, partial rate factors were also computed using the selectivity relationship.[4,5] Table III summarizes these results.

The agreement of the partial rate factors (f) obtained in this study with the estimated values of Stock and Brown[4] ($f_o = 450, f_p = 840$) is quite good. The determination of f_m has not been made previously. From these data, the value of ρ from the Hammett equation was calculated to be -9.9 for the chlorination reaction compared with the estimated[4] value of -10.0.

It is interesting to compare the positional partial rate factors of a series of monosubstituted benzenes in Figure 1. The decrease in f_o is most probably steric and is a linear function of the number of methyl groups. This effect is duplicated almost exactly in the nitration of these compounds in acetic anhydride.[8] In the chlorination reaction there is essentially no difference in reactivity at the *para* position as one goes from methyl to ethyl. Only upon further substitution does a substantial Baker–Nathan order become evident. This is in sharp contrast to the nitration data where f_p follows the inductive order and ethyl is significantly more activating than methyl.

Using the values of k_2 at 25 and 35°, the activation parameters for the chlorination of I were determined. These results, given in Table IV, are in good agreement with those reported for similar chlorinations of aromatic hydrocarbons.[7,9]

Experimental Section

Materials.—Ethylbenzene (99.6%) was obtained from the Dow Chemical Co. and chlorine was obtained from the Matheson Co. (99.5%). The acetic acid, used as a solvent in the kinetic determination, was obtained from Fisher Scientific Co. (99.7%). The purity of the *o*-, *m*-, and *p*-chloroethylbenzenes used as infrared standards was established by vpc.

TABLE IV

ACTIVATION PARAMETERS FOR THE CHLORINATION OF ETHYLBENZENE IN ACETIC ACID

$E^{\ddagger a}$	13.1 kcal mole^{-1}
$\Delta H^{\ddagger}_{298}$	12.5 kcal mole^{-1}
$\Delta F^{\ddagger}_{298}$	19.8 kcal mole^{-1}
$\Delta S^{\ddagger}_{298}$	-24.4 eu

[a] Arrhenius activation energy (S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960): $k_2^{25°} = 4.35 \times 10^{-4}$ l. mole^{-1} sec^{-1}; $k_2^{35°} = 8.94 \times 10^{-4}$ l. mole^{-1} sec^{-1}.

Kinetic Determinations.—Rate measurements were performed in black volumetric flasks immersed in a constant-temperature medium maintained at 25.0 or 35.0 ± 0.1°. Known concentrations of chlorine and ethylbenzene in acetic acid were brought together in the flask and an aliquot was withdrawn to establish the concentrations at time zero. The reaction was followed by periodically withdrawing samples and determining unreacted chlorine by iodometric titration. A blank run in the absence of ethylbenzene established that the reaction of chlorine with acetic acid in the dark and loss of chlorine by evaporation were negligible. Second-order rate constants, determined from 5 to 8 points per runs, are given in Table I. Analysis of the reaction mixture revealed a maximum of 1% of side-chain chlorine compounds and was therefore neglected.

Isomer Distribution Determination.—The reaction product was treated with a saturated sodium acid carbonate solution to neutralize the acids in the mixture. The organic phase was separated, washed with a saturated sodium chloride solution, and dried over anhydrous sodium sulfate. This material was subjected to vpc analysis at 150° on a 14 ft × $^1/_8$ in. column packed with 5% E-4000 polyglycol (The Dow Chemical Co.) on firebrick. Resolution of the *ortho* and *meta* + *para* peaks was

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(8) R. O. C. Norman and R. Taylor, "Electrophilic Substitution in Benzenoid Compounds," Elsevier Publishing Co., Amsterdam, 1965, p 15.

(9) L. M. Stock and A. Himoe, *J. Am. Chem. Soc.*, **83**, 1937 (1961).

accomplished in this way. The mole percentages of these materials were determined from the corrected areas of the peaks. The *meta* isomer could not be resolved despite the use of various conditions and column packings. Analysis for the *meta* isomer was carried out by a previously reported[2] standard base-line technique on a Beckman IR-9 infrared spectrophotometer at 12.90 μ. The mean of several trials was subtracted from the *meta* + *para* value obtained by vpc to give the isomer distributions. A summary of several runs is given in Table V.

TABLE V

PRODUCT ISOMER DISTRIBUTIONS IN THE CHLORINATION OF ETHYLBENZENE IN ACETIC ACID

Run	*ortho*	*meta*	*para*
1	52.1	0.53	47.4
2	53.5	0.48	46.0
3	51.2	0.58	48.3
Mean	52.3	0.53	47.2

A similar procedure was used on the products from the chlorination of toluene in acetic acid at 25°. The results, shown in Table II, are in agreement with reported values.[5] The infrared analysis for *m*-chlorotoluene was made at 12.96 μ.

Registry No.—I, 100-41-4; acetic acid, 64-19-7; *o*-chloroethylbenzene, 89-96-3; *m*-chloroethylbenzene, 620-16-6; *p*-chloroethylbenzene, 622-98-0.

Regeneration of Carbonyl Compounds from Oximes Using Iron Pentacarbonyl and Boron Trifluoride

HOWARD ALPER AND JOHN T. EDWARD

Department of Chemistry, McGill University, Montreal 2, Canada

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The parent carbonyl compound may be regenerated from an oxime by treatment of the latter in aqueous solution with sodium bisulphite,[1] levulinic or pyruvic acids,[2] or formaldehyde and concentrated hydrochloric acid.[3] However, there may be instances when it is desirable to effect this transformation under anhydrous conditions. We have found that treatment of an oxime with an equimolar quantity of iron pentacarbonyl and a catalytic amount of boron trifluoride in refluxing butyl ether results in the formation of the carbonyl compound in 55–81% yield. The examples listed in Table I indicate that the reaction is applicable to the oximes of aldehydes and ketones of widely differing character; the limitations, if any, of the reaction are not yet apparent.

The mechanism of the reaction, and hence the function of the boron trifluoride, are not yet known. Reactive of santonin oxime ($C_{15}H_{19}NO_3$) with iron pentacarbonyl alone gave a complex $C_{15}H_{19}NO_3 \cdot Fe(CO)_3$;[4] the other oximes failed to react. No reaction took place when the oximes were treated with a catalytic amount of boron trifluoride in butyl ether. No carbonyl compound was regenerated by treatment of fluorenone phenylhydrazone or of N-2,6-trichloro-*p*-benzoquinoneimine with iron pentacarbonyl and boron trifluoride. Hence it seems likely that the oxygen atom of the regenerated carbonyl group comes from the oxygen atom of the oxime.

TABLE I

YIELDS OF CARBONYL COMPOUNDS FROM OXIMES

Parent carbonyl compd	Reflux time, hr	Isolation procedure	Yield, %
Cyclohexanone	20	. . .	81
4-Methyl-4-trichloromethyl-cyclohexadien-1-one	10	b	72
Fluorenone	16	a	69
Cholest-4-en-3-one[a]	16	d	67
Santonin	18	c	67
O-Methylpodocarpinal	17	c	55

[a] Oxime mp 152–152.5, prepared according to C. W. Shoppee, G. Kreiger, and R. N. Mirrington, *J. Chem. Soc.*, 1050 (1962).

Experimental Section

A mixture of the oxime (2–35 mmoles) and iron pentacarbonyl (1.1 mole/mole of oxime) in dry butyl ether (50–100 ml) containing boron trifluoride etherate (about 5% w/w of oxime) was refluxed with stirring under nitrogen. The solution was cooled and filtered and the solvent removed at 30 mm (except when the volatile cyclohexanone was formed; this was isolated as the 2,4-dinitrophenylhydrazone by treating the filtrate with 2,4-dinitrophenylhydrazine in the usual manner). The residue of crude carbonyl compound was purified by trituration with petroleum ether (bp 30–60°), hexane, or methylene chloride (procedures a, b, or c, respectively) or by chromatography on Florisil using acetone as eluent (procedure d). The purity of the products recorded in Table I was indicated by melting points agreeing with values in the literature and by the absence of more than one spot on thin layer chromatograms.

Registry No.—Boron trifluoride, 7637-07-2.

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(2) E. B. Hershberg, *ibid.*, **13**, 542 (1948).

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(4) H. Alper and J. T. Edward, unpublished results.

The Preparation of Esters of 4-Alkyl-2,4-pentadienoic Acids by the Phosphonate Modification of the Wittig Reaction

RICHARD J. SUNDBERG, PETER A. BUKOWICK,
AND FRANK O. HOLCOMBE

Department of Chemistry, Cobb Chemical Laboratory, University of Virginia, Charlottesville, Virginia

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This note describes conditions for the rapid and convenient preparation of the ethyl esters of several 4-alkyl-2,4-pentadienoic acids from 2-alkylacroleins (**1**) and triethyl phosphonoacetate (**2**). Subsequent saponification of the esters gives the corresponding carboxylic acids and this route has been found to be useful for the preparation of several 4-alkyl-2,4-pentadienoic acids (**5**).