TABLE III

PHYSICAL PROPERTIES OF INTERMEDIATES

Substituent	Benzoic acid M.p., °C.[a]	Methyl benzoate B.p. °C.	Methyl benzoate B.p. Mm.	Methyl benzoate n^{20}_D	Ethyl benzoate B.p. °C.	Ethyl benzoate B.p. Mm.	Ethyl benzoate n^{20}_D
o-Fluoro	128				85.5	8	1.4920
m-Fluoro	124.5				84	9.2	1.4848
p-Fluoro	183.5				87.5	11	1.4860
o-Chloro	141	99	8.5				
m-Chloro	154.5	106	13				
p-Chloro	240.5	112.5	8		65	1	1.5239
o-Bromo	150				135	15	1.5436
m-Bromo	154				131	17	1.5428
p-Bromo	255				129	15	1.5460
o-Iodo	163	103.5	1	1.6052			
m-Iodo	187				114	2.1	1.5830
p-Iodo	268				126.5	4	1.5877

[a] Melting point range 0.5–1.0°.

posed with saturated ammonium chloride solution and cracked ice. The ether layer and ether extracts were combined, dried with anhydrous potassium carbonate and the ether removed on a steam-cone. The product was carefully distilled at low pressures (usually 2–5 mm.) through a small fractionating column fitted with a glass spiral core. Yields of approximately 70–75% were realized. The physical properties and analyses are summarized in Table I.

Halophenyldimethylcarbinyl Chlorides.—A weighed 30-ml. round bottom flask equipped with a ground joint through which fitted an assembly containing an inlet and outlet tube was used. In this flask was placed a carefully weighed 5-g. sample of the carbinol, the flask and contents were placed in an ice-bath and dry hydrogen chloride was passed into the flask until the weight became constant. The lower layer of water saturated with hydrogen chloride was removed with the aid of a capillary, the product was treated with calcium chloride and dissolved hydrogen chloride removed by subjecting the product to evacuation. The product was used directly for the rate measurements without further treatment.

Rate Measurements.—The solvent was made up by mixing 90 parts by volume of acetone with 10 parts by volume of water. It was then adjusted with minor amounts of water or acetone until phenyldimethylcarbinyl chloride yielded a rate constant identical (±2%) with that obtained in the earlier study.[9]

Temperatures were controlled to ±0.02° by means of constant temperature baths. The solvent, 100 ml., was placed in long necked 125-ml. flask, brought to bath temperature, and approximately 1 ml. of the halophenyldimethylcarbinyl chloride was added and mixed rapidly with the solvent by vigorous agitation. After 10 minutes a 5-ml. "zero time" sample was removed, placed in 100 ml. of 0° acetone and titrated immediately with 0.0305 *N* sodium hydroxide solution, using methyl red as indicator. At appropriate intervals of time, six to seven additional 5-ml. aliquots were removed and titrated. To obtain the "infinity" titer, 5-ml. aliquots were removed, added to 100 ml. of 50% aqueous acetone, permitted to stand at room temperature for 24 to 48 hr. and titrated as before. The rate constants were calculated by the usual first-order expression, $k_1 = (2.303/t) \log (a - x_0)/(a - x)$.

The results of a typical determination are summarized in Table IV.

TABLE IV

RATE DATA FOR THE SOLVOLYSIS OF *m*-CHLOROPHENYLDIMETHYLCARBINYL CHLORIDE IN 90% ACETONE AT 25.0°

Time, min.	x, ml.	$a - x$, ml.	$k_1 \times 10^3$, hr.$^{-1}$
0	0.072	9.713	
90	.175	9.610	7.09
400	.510	9.275	6.92
1175	1.315	8.470	6.99
1495	1.610	8.175	6.92
1710	1.810	7.975	6.92
2635	2.625	7.160	6.95
3110	3.025	6.760	6.99
∞	9.785		
		Average	6.97[a]

[a] In a duplicate run, the rate was determined to be 7.02×10^{-3} hr.$^{-1}$.

The energies of activation and log *A* terms were calculated by a least squares treatment of the rate data at several temperatures. The values of the enthalpy and entropy of activation were obtained by an independent least squares analysis of the rate constants utilizing the procedure described by Cagle and Eyring.[16]

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[16] F. W. Cagle and H. Eyring, THIS JOURNAL, **73**, 5628 (1951).

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Rates of Solvolysis of the Nitro- and the Methoxyphenyldimethylcarbinyl Chlorides[1-3]

BY Y. OKAMOTO AND HERBERT C. BROWN

RECEIVED AUGUST 29, 1956

o-, *m*- and *p*-methoxyphenyl and *m*- and *p*-nitrophenyldimethylcarbinyl chlorides were solvolyzed in aqueous acetone and the rate data extrapolated to give the rate constants in 90 vol. % acetone at 25°. The *m*-methoxy derivative reacts at a rate 0.6 that of the parent compound but the *para* derivative at a rate of 3360 that of the unsubstituted derivative. The enormous rate increase is a measure of the powerful resonance contribution of the *p*-methoxy group. On the other hand, *m*- and *p*-nitro groups reduce the rate over the parent phenyl derivative by factors of 1150 and 3900, respectively. The ratio of the rate constants for *p*-methoxy and *p*-nitrophenyldimethylcarbinyl chlorides is 10^7, indicating the high sensitivity of this electrophilic reaction to the electronic contributions by the substituents.

In an earlier publication it was proposed that a set of substituent constants, σ^+, could be developed which would permit the quantitative treatment of aromatic substitution.[4] In the first paper of this group it was pointed out that the rates of solvolysis of the phenyl- and tolyldimethylcarbinyl chlorides obeyed the empirical relationship, $\log p_f = 1.310 \log (p_f/m_f)$, which describes the substitution behavior of toluene.[5] This suggested that the rates of solvolysis of the aryldimethylcarbinyl chlorides might provide a convenient experimental route to the desired substituent constants.

In examining this possibility, a study was made

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[1] Directive Effects in Aromatic Substitution. XIII.

[2] Supported by the Petroleum Research Fund of the American Chemical Society.

[3] Based upon a thesis submitted by Y. Okamoto, in 1956, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[4] C. W. McGary, Jr., Y. Okamoto and H. C. Brown, THIS JOURNAL, **77**, 3037 (1955).

[5] H. C. Brown, J. D. Brady, M. Grayson and W. H. Bonner, *ibid.*, **79**, 1897 (1957).

of the rates of solvolysis of the monoalkyl- (Me, Et, *i*-Pr, *t*-Bu)[5] and the monohalo (F, Cl, Br, I) phenyldimethylcarbinyl chlorides,[6] along with related naphthyl derivatives.[7] A preliminary application of the data for the development of a set of σ^+-constants was highly promising.

However, the total range of electronic effects covered by the alkyl and halo substituents is relatively narrow. In order to provide a more rigorous test of the utility of these constants, it appeared desirable to extend the study to include substituents which lie near the extremes in their electronic behavior. Accordingly, we undertook to synthesize the nitro- and methoxyphenylcarbinyl chlorides and to determine their rates of solvolysis in 90% acetone.

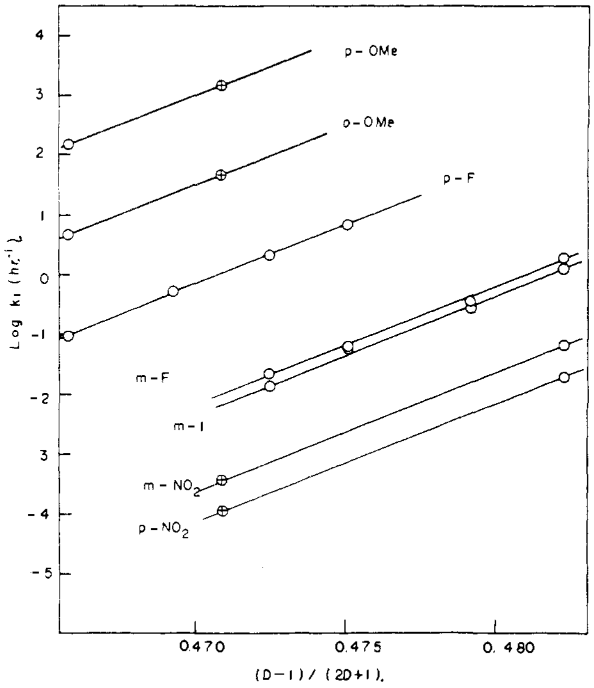

Fig. 1.—Variation of solvolysis rates as a function of the dielectric constant of the medium at 25°: O, experimental points; ⊕, calculated points.

With these results available, it became possible to derive a set of σ^+-constants for all of the substituents studied and to examine rigorously their utility in correlating the available data on aromatic substitution and other electrophilic reactions.

Results

The isomeric methoxybenzoic acids were esterified and treated with methylmagnesium iodide. In the case of the *meta* derivative, the carbinol was readily isolated in pure form and converted to the tertiary chloride in the usual manner.

However, the *o*- and *p*-methoxy isomers proved to be so unstable that the pure carbinols could not be isolated—instead mixtures of carbinol and olefin were obtained. Accordingly, the products were converted to the olefins and these were used for the preparation of the tertiary chlorides.

m- and *p*-nitrocumene were treated with N-bromosuccinimide to form the two tertiary bromides. These were dehydrohalogenated into the two isomeric olefins, *m*- and *p*-nitro-α-methylstyrene. Hydrogen chloride was added to these olefins to form the desired tertiary chlorides.

Difficulties were encountered in attempting to determine the solvolyses rates in 90% acetone by the procedures previously applied.[5-7] The nitrophenyldimethylcarbinyl chlorides underwent solvolysis in this solvent at a rate far too slow for measurement. Contrariwise, the solvolysis rates of the corresponding *o*- and *p*-methoxy derivatives were far too fast for measurement.

We decided to study the solvolyses in acetone solvents of aqueous content controlled to give solvolysis rates in a range practical for measurement. The rates were then extrapolated to 90% aqueous acetone by utilizing the equation[8,9]

$$\ln k = \ln k_0 - \frac{1}{kT} \times \frac{D-1}{2D+1}\left(\frac{\mu_A^2}{r_A^3} + \frac{\mu_B^2}{r_B^3} - \frac{\mu_{\ddagger}^2}{r_{\ddagger}^3}\right) + \frac{\Sigma\Phi}{kT}$$

To test the applicability of this treatment to the present system, the rates of solvolysis of *p*-fluoro-, *m*-fluoro- and *m*-iodophenyldimethylcarbinyl chlorides were determined in aqueous acetone of varying water content. A plot of the logarithms of these rate constants *versus* the quantity $(D - 1)/(2D + 1)$[8] gives a reasonably good linear relationship for each compound (Fig. 1). Moreover, the slopes of the lines are quite similar.

Accordingly, the rates of solvolysis of *m*- and *p*-nitrophenylcarbinyl chloride were measured in 60% wt. % aqueous acetone and the value extrapolated to 90% vol. % acetone by utilizing the average slopes for the halogen derivatives (Fig. 1).

Unfortunately, the rates of solvolysis of the *o*- and *p*-methoxyphenylcarbinyl chlorides proved to be too fast to measure at 25° even in 94.8 wt. % aqueous acetone. Therefore for these compounds the rates were measured at low temperatures (−45.8 to −23.7°) for *p*-methoxy- and extrapolated to 25° (Fig. 2). These extrapolated 25° values were extrapolated further from 94.8 wt. % to 90 vol. % aqueous acetone (Fig. 1).

The rate constants are summarized in Table I.

In Table II are listed the derived data together with the observed and calculated rate constants at 25° and 90 vol. % acetone.

It should be noted that the ratio in rate constants between the *p*-methoxy- and the *p*-nitrophenyldimethylcarbinyl chlorides in 90% acetone is over 10,000,000, indicating the high sensitivity of this electrophilic reaction to the electronic influences of the substituents and emphasizing the difficulties experienced in the present study in measuring the rate constants under conditions which would permit their direct comparison.

Discussion

In the *meta* position the methoxy group reduces the rate, as compared to the parent compound, by a factor of 0.6. This is in accord with the electron-

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[6] H. C. Brown, Y. Okamoto and G. Ham, THIS JOURNAL, **79**, 1906 (1957).

[7] Y. Okamoto and H. C. Brown, *ibid.*, **79**, 1903 (1957).

[8] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp. 419 ff.

[9] A similar extrapolation has been utilized for the solvolysis of *p*-methoxybenzyl tosylate; J. K. Kochi and G. S. Hammond, THIS JOURNAL, **75**, 3445 (1953).

TABLE I

RATE DATA FOR THE SOLVOLYSIS OF SUBSTITUTED PHENYLDIMETHYLCARBINYL CHLORIDES IN AQUEOUS ACETONE

Substituent	Solvent, % acetone[a]	Temp., °C.	Rate constant $k_1 \times 10^5$ (sec.$^{-1}$)
m-Iodo	60	25.0	1.27
	70	25.0	0.288
	80	25.0	.0580
	85	25.0	.0195
m-Fluoro	60	25.0	1.86
	70	25.0	0.370
	80	25.0	.0641
	85	25.0	.0224
p-Fluoro	80	25.0	6.89
	85	25.0	2.18
	90	25.0	0.533
	94.8	25.0	0.0947
m-Nitro	60	25.0	1.84
	60	35.0	5.64
	60	45.0	17.9
p-Nitro	60	25.0	0.539
	60	40.0	2.74
	60	55.0	17.5
o-Methoxy	94.8	−24.3	0.792
	94.8	−13.4	2.89
	94.8	0.0	13.0
	94.8	25.0	134[c]
m-Methoxy	90[b]	0.0	0.336
	90[b]	25.0	7.55
	90[b]	35.0	24.5
p-Methoxy	94.8	−45.8	4.61
	94.8	−36.8	13.1
	94.8	−23.7	63.3
	94.8	25.0	4220[c]

[a] Wt. % except where otherwise indicated. [b] Vol. %. [c] Calculated from values at lower temperatures.

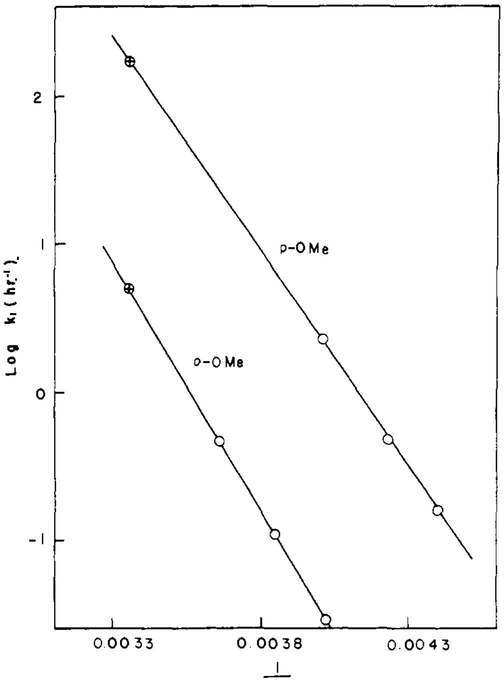


Fig. 2.—Activation energy data for the solvolysis of 2-chloro-2-(*o*- and *p*-methoxyphenyl)-propane: ○, experimental points; ⊕, calculated points at 25°.

TABLE II

DERIVED DATA FOR THE SOLVOLYSIS OF THE NITRO- AND METHOXYPHENYLDIMETHYLCARBINYL CHLORIDES

Substituent	Solvent, wt. % acetone	*E*act	log *A*	$\Delta H^\ddagger$	$\Delta S^\ddagger$	Rate constant $k_1 \times 10^5$ (sec.$^{-1}$), 90 vol. % acetone, 25°	Rate ratio, 25°
Hydrogen	90[a]					12.4	1.00
m-Nitro	60	21.5	11.1	21.0	−10.0	0.0108	0.000871
p-Nitro	60	22.5	11.2	21.9	− 9.3	0.00319	0.000257
o-Methoxy	94.8	15.5	8.53	15.0	−21.2	1300	105
m-Methoxy	90[a]	20.4	10.9	19.9	−11.1	7.56	0.610
p-Methoxy	94.8	13.4	8.52	12.9	−21.1	41700	3360

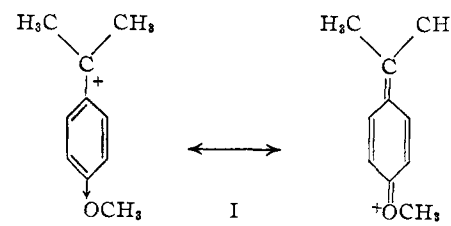
[a] Vol. %.

withdrawing inductive effect of the methoxy group.[10]

In the *para* position, instead of a similar rate decrease, there is observed an enormous rate increase. *p*-Methoxyphenyldimethylcarbinyl chloride undergoes solvolysis at a rate that is 5500 times greater than that of the *meta* isomer. This increase in rate is attributed to resonance stabilization of the carbonium ion I.

From the free energies of ionization of these compounds it can be estimated that resonance stabilization due to the *p*-methoxy group must amount to 5.1 kcal./mole.

A similar explanation serves to account for the enhanced rate of the *p*-fluoro derivative.[6] However, in the case of the fluoro derivatives the ratio $k_{p\text{-F}}/k_{m\text{-F}}$ is only 85, so that the resonance stabilization by the *p*-fluoro substituent can be no larger than 2.6 kcal./mole. Since both fluorine and oxygen are first row elements with presumably similar abilities to form double bonds, the greater capacity of oxygen (and presumably nitrogen) to form double bonds must be attributed to its lower nuclear charge and consequently greater ability to accommodate the formal charge (I).



I

The enhancement in rate for the *o*-methoxy group is smaller than for the *para* derivative. This is reasonable in terms of an increased electron-withdrawing inductive effect and a decreased electron-

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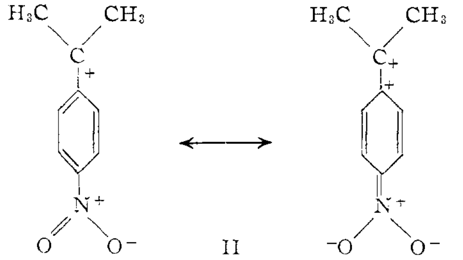
[10] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953.

supplying resonance effect, the latter arising from a partial steric inhibition of resonance.[6]

The marked decrease in rate observed for the nitro derivatives is in accord with the powerful electron-withdrawing effect of nitro substituents.[10] The slightly greater effect of the more distant *para* substituent must be attributed to a small resonance contribution which increases the electron deficiency in the incipient carbonium ion II.[11]


II

We are now in position to examine whether these data can be used to derive a set of substituent constants which will provide a quantitative treatment of aromatic substitution[12] and other electrophilic reactions.

Experimental Part

m-Methoxyphenyldimethylcarbinol.—m-Methoxybenzoic acid, m.p. 105–106°, was converted into the ethyl ester, b.p. 94–97° (2 mm.), $n^{20}D$ 1.5154, and treated with methylmagnesium iodide. Following distillation, b.p. 112–114° (2 mm.), and recrystallization from light petroleum ether, the carbinol, m.p. 34–35°, was obtained in 78% yield.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.57; H, 8.62.

o- and m-Methoxy-α-methylstyrene.—Attempts were made to prepare the o- and p-methoxycarbinols by the same procedures utilized above for the *meta* isomer. However, in spite of the greatest precautions, the carbinols underwent partial dehydration upon distillation at 2 mm. Consequently, the olefins were isolated and utilized for the preparation of the tertiary chlorides.

o-Methoxybenzoic acid, m.p. 97–98°, was converted into the ethyl ester, b.p. 120–122° (4 mm.), $n^{20}D$ 1.5213. After treatment with the methyl Grignard, a 53% yield of o-methoxy-α-methylstyrene, b.p. 56.5–57° (2 mm.), $n^{20}D$ 1.5340, was obtained. In view of the discrepancy with the literature constants,[13] an analysis was made.

Anal. Calcd. for $C_{10}H_{12}O$: C, 81.15; H, 8.17. Found: C, 81.33; H, 8.50.

In the same way, a 45% yield of p-methoxy-α-methylstyrene, b.p. 99.5–101° (4.5 mm.), m.p. 33.0–33.8°, was obtained *via* p-methoxybenzoic acid, m.p. 183–184.5°, and the ethyl ester, b.p. 151–151.8° (7 mm.), $n^{20}D$ 1.5251.

Anal. Calcd. for $C_{10}H_{12}O$: C, 81.15; H, 8.17. Found: C, 81.65; H, 7.91.

o-, m- and p-Methoxyphenyldimethylcarbinyl Chlorides.—The chlorides were formed from the above products in methylene chloride solution by treatment with hydrogen chloride at −10 to −20° by essentially the procedure described previously.[6] Since the tertiary chlorides formed are highly unstable, they were used directly for the rate measurements, following removal of the solvent at low pressures, without further purification.

p-Nitro-α-methylstyrene.—p-Nitrocumene, b.p. 111–114° (2 mm.), $n^{20}D$ 1.5365, was treated with N-bromosuccinimide and benzoyl peroxide in carbon tetrachloride solution. The product, upon distillation, lost hydrogen bromide, and p-nitro-α-methylstyrene, b.p. 121–130° (3 mm.), was obtained in 88% yield. After recrystallization from absolute ethanol, the product exhibited m.p. 51–52.5°.[14]

m-Nitro-α-methylstyrene.—p-Nitrocumene was converted into m-nitrocumene,[15] b.p. 95–100° (4 mm.), $n^{20}D$ 1.5310. It was converted into m-nitro-α-methylstyrene by identical procedures as those used for the *para* isomer. The product, b.p. 98–99° (3 mm.), $n^{20}D$ 1.5703, was obtained in 60% yield.

Anal. Calcd. for $C_9H_9O_2N$: C, 66.24; H, 5.56; N, 8.58. Found: C, 65.97; H, 5.51; N, 8.75.

m- and p-Nitrophenyldimethylcarbinyl Chlorides.—An attempt was made to add hydrogen chloride by the procedures utilized above for the methoxy derivatives. However, no reaction was observed. The addition was successful in the presence of anhydrous ferric chloride as a catalyst.

Halophenyldimethylcarbinyl Chlorides.—These products were samples prepared previously.[6]

Kinetic Measurements.—The procedures were similar to those previously described.[5,6] Because of the rapidity of the solvolysis reactions in the case of o- and p-methoxyphenyldimethylcarbinyl chlorides, the hydrogen chloride formed in the reaction was determined by titration with a standard solution of sodium ethoxide in absolute ethanol (0.036 M) at −20 to −10°.

The precision realized by this procedure is indicated by the typical rate data in Table III.

Table III

Rate Data for the Solvolysis of o-Methoxyphenyldimethylcarbinyl Chloride in 94.8 Wt. % Aqueous Acetone at −13.4°

Time, min.	x, ml.	$a - x$, ml.	k_1, hr.$^{-1}$
0	0.230	1.880	
20	.302	1.816	0.103
42	.370	1.748	.105
60	.431	1.687	.108
72	.461	1.657	.106
80	.485	1.633	.106
103	.532	1.586	.099
120	.581	1.537	.107
140	.630	1.488	.100
160	.682	1.436	.101
∞	2.118		
			Average 0.104 ± 0.003

The original rate measurements[5-7] were carried out in 90 vol. % aqueous acetone as a convenient solvent, easily prepared in large amounts. In obtaining rate data in other solvents, we required dielectric constant data for water-acetone mixtures. Since the data are given for mixtures expressed in terms of wt. %,[16] it proved convenient to determine these rate constants in solvents prepared on a wt. % basis.

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[11] A similar interpretation is used to account for the greater strength of p-nitrobenzoic acid as compared to the *meta* isomer; G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 353.

[12] H. C. Brown and Y. Okamoto, This Journal, **79**, 1913 (1957).

[13] E. Bergmann and A. Weizmann, *Trans. Faraday Soc.*, **32**, 1318 (1936), report b.p. 56–60° (1 mm.) and $n^{20}D$ 1.5296 for the *ortho* isomer, b.p. 114° (20 mm.) for the *para*.

[14] G. Brubacker and E. Suter, *Helv. Chim. Acta*, **33**, 256 (1950), report m.p. 54–55°.

[15] M. C. Carpenter, W. M. Foster and T. F. Wood, *J. Org. Chem.*, **16**, 586 (1951), report b.p. 92° (3.5 mm.), $n^{20}D$ 1.5301.

[16] G. Åkerlöf, This Journal, **54**, 4125 (1932).