Anal. Calcd. for $C_{22}H_{20}SO_4$: C, 69.45; H, 5.30; S, 8.43. Found: C, 69.38; H, 5.35; S, 8.41.

Reduction of an 87.7-mg. (0.23-mmole) sample of the tosyl ester **15b** with zinc and acetic acid as previously described afforded a quantitative yield (49.4 mg.) of the crude ketone **9b**, m.p. 100–104°. This ketone **9b**, which melted at 108.9–109.3° after recrystallization from ether, was identified with the previously described sample by a mixed melting point determination and comparison of infrared spectra. From a comparable Neber rearrangement employing 0.0154 mole of sodium methoxide and 0.0150 mole of the oxime tosylate **3b** in a mixture of 11 ml. of methanol and 96 ml. of benzene, the yields were: 22% keto amide **15b**, 13% tosyl ester **15b**, 19% ester **14a** ($R'' = CH_3$), and 18% amide **17b**.

The Neber Rearrangement of the Oxime Tosylate 3c.—A mixture of 6.6413 g. (0.0175 mole) of the oxime tosylate **4c**, 0.0184 mole of potassium ethoxide, and 38 ml. of ethanol was stirred at 0–5° for 4.5 hr. and then subjected to the usual isolation procedure. The product that was separated after acetylation of the basic fraction was 1.4667 g. (31.4%) of the keto amide **16c**, m.p. 76–80°, identified with the previously described sample by a mixed melting point determination and by comparison of infrared spectra and retention times.[37] The neutral fraction from this reaction contained[42] the ester **14c** ($R'' = C_2H_5$) a collected sample of which was identified with an authentic sample by comparison of retention times and infrared spectra. From a comparable reaction employing 5.6925 g. (0.015 mole) of the oxime tosylate **3c**, 0.0155 mole of sodium ethoxide, and 30 ml. of ethanol with a reaction time of 15 hr. at −3 to −1°, the keto amide **16c** (22%), the ester **14c** (1%), and the amide **17a** (1%) were calculated to be present employing the previously described analytical procedure. The residue initially separated from the reaction mixture was dissolved in acetic acid and then worked up as previously described to separate 486.1 mg. (12.1%) of the acetoxy ketone **18c** as white prisms from an ether–hexane mixture, m.p. 88–89.2°. Gas chromatographic analysis[37] of the mother liquors indicated that the total yield of this material was 52%.[43] The acetoxy ketone **18c** had infrared absorption[23] at 1743 cm.$^{-1}$ (ester C═O) and 1700 cm.$^{-1}$ (conj. C═O) with an ultraviolet maximum[24] at 247 mμ mμ (ε 13,600) and a series of n.m.r. peaks[23] in the region 2.0–3.1 τ (aryl C—H) with a singlet at 3.34 τ (1H, CO(Ar) CH—OCO—) and two singlets at 7.72 and 7.89 τ (6H, aryl and acetyl CH_3).

Anal. Calcd. for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01. Found: C, 76.33; H, 6.14.

Reduction of a 134.2-mg. sample of the acetoxy ketone with zinc and acetic acid as previously described gave, after recrystallization, 35.8 mg. (34%) of the ketone **9c**, m.p. 96–97°, identified with the previously described sample by a mixed melting point determination and comparison of infrared spectra.

Reaction of 5.6925 g. (0.0150 mole) of the oxime tosylate **3c** with 0.0166 mole of sodium methoxide in 96 ml. of benzene and 11 ml. of methanol for 15.5 hr. at 5° yielded, after the usual isolation and analytical procedure, the keto amide **16c** (21%), the ester **14c** ($R'' = CH_3$) (3%), the amide **17a** (0.2%), and the tosyl ester **15c** as 1.2976 g. (22.7%) of white prisms from an ether–benzene mixture, m.p. 76–80°. Recrystallization and subsequent drying gave the pure tosyl ester, m.p. 75.7–77.7°, with infrared absorption[23] at 1703 cm.$^{-1}$ (conj. C═O), an ultraviolet maximum[24] at 248.5 mμ (ε 13,000) with a point of inflection at 228 mμ (ε 15.900) and a series of n.m.r. peaks[39] in the region 2.0–3.0 τ (aryl CH) with a singlet at 3.33 τ (1H, $CO(Ar)CHOSO_2Ar$) and two singlets at 7.65 and 7.75 τ (6H, aryl CH_3).

Anal. Calcd. for $C_{22}H_{20}SO_4$: C, 69.45; H, 5.30; S, 8.43. Found: C, 69.22; H, 5.18; S, 8.01.

Reduction of a 190.2-mg. sample of the tosyl ester **15c** with zinc and acetic acid as previously described yielded 56.2 mg. (53.4%) of the ketone **9c**, m.p. 96.2–98°, identified by a mixed melting point determination and comparison of infrared spectra.

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[42] A column packed with General Electric silicone fluid, no. xF-1150, suspended on ground firebrick was employed for this analysis.

[43] Although the gas chromatograms of the corresponding fractions from the oxime tosylates **3a** and **3b** suggested the presence of small amounts of the corresponding acetoxy ketones **18**, the amounts present in these cases were too small to permit characterization.

Exchange Reactions of Deuterated Benzene Derivatives in Alkaline Medium. II. Deactivating Substituents[1-3]

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The rates of deuterium–protium exchange have been determined for benzene-*d*, toluene-2-*d*, -3-*d*, and -4-*d*, and *tert*-butylbenzene-2-*d* and -4-*d* in a liquid ammonia solution of potassium amide at 0°. An approximate determination of the rates of the heterogeneous exchange reactions of benzene-*d*, toluene -2-*d*, -3-*d*, and -4-*d*, and potassium phenoxide-2-*d*, -3-*d*, and -4-*d* with potassium amide in refluxing isopropylamine has also been made. In general, the substituted deuteriobenzenes react more slowly than deuteriobenzene itself. As all of these substituents have negative values of σ_I, the results support the previous interpretation of exchanges on the basis of the inductive effects of the substituents, resonance effects being of little importance.

An earlier investigation of the effect of substituents on the acidity of hydrogens located on benzene rings was made as a part of a study of the benzyne mechanism[5] of nucleophilic substitution of aryl halides.[1] The electronegative substituents, —F, —CF_3, and —OCH_3, increased the acidity, the effect being greatest at the 2-, less at the 3-, and least at the 4-position. These results were interpreted on the basis of the inductive effects[6] of the substituents.

The relative acidities of the hydrogens were determined by measuring the rate of replacement of deuterium by protium in the appropriate deuterated benzene derivative in the presence of a strong base, the amide ion, and a proton-donating solvent, refluxing liquid ammonia. When activating substituents were not present, the deuterium exchanged too slowly for convenient measurement so that the overriding importance of the inductive effect was not tested with deactivating substituents. An investigation of the effects of groups expected to be deactivating is reported in the present paper.

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[1] Part I, G. E. Hall, R. Piccolini, and J. D. Roberts, *J. Am. Chem. Soc.*, **77**, 4540 (1955).

[2] M.A. thesis of E. M. L.; A. B. Honors Paper of E. L. J.

[3] This investigation was supported by a Frederick Gardner Cottrell grant from the Research Corporation. An equipment grant from the National Science Foundation made possible the purchase of the infrared spectrometer. Aid in the experimental work was provided by Miss Georgeanna Dean and Mrs. Eva G. Gans, who were supported by the Undergraduate Research Participation Program of the National Science Foundation.

[4] Joseph A. Skinner Fellow, 1960–1961.

[5] R. Huisgen, "Organometallic Chemistry," H. Zeiss, ed., Reinhold Publishing Corp., New York, N. Y., 1960, pp. 36–87.

[6] "Inductive effect" will be used in the sense which includes any field effect.

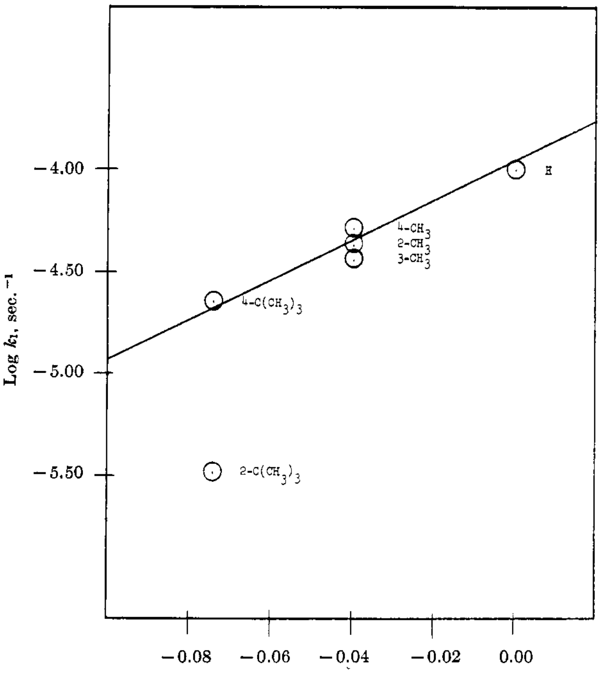

Fig. 1.—Relation between log k_1 (av.) and Taft polar substituent constant.

Conditions were sought which would allow the reactions to be carried out at higher temperatures to give increased rates; at the same time changes which would be expected to alter the mechanism of the reaction were avoided in order that the results could be compared to those of Part I. The substitution of refluxing isopropylamine for ammonia gave convenient rates with benzene-*d*, toluene-2-*d*, -3-*d*, and -4-*d*, and potassium phenoxide-2-*d*, -3-*d* and -4-*d*, although the reaction mixtures were not homogeneous. Exchange reactions in liquid ammonia at 0° in closed containers gave both convenient rates and homogeneous solutions with benzene-*d*, toluene-2-*d*, -3-*d*, and -4-*d*, and *tert*-butylbenzene-2-*d* and -4-*d*.

TABLE I

PSEUDO FIRST-ORDER RATE CONSTANTS FOR DEUTERIUM–PROTIUM EXCHANGE OF SUBSTITUTED DEUTERIOBENZENES (C_6H_4DX) WITH 0.6 *M* POTASSIUM AMIDE IN LIQUID AMMONIA (AT 0°)

X[a]	Reaction time, sec.	Mole % C_6H_4DX[b]	k, sec.$^{-1}$
H[c]	1.806×10^4	16.5	1.0×10^{-4}
	1.176×10^4	28.5	1.1×10^{-4}
	1.062×10^4	47.9	6.9×10^{-5}
	1.050×10^4	30.6	1.1×10^{-4}
	8.100×10^3	39.9	1.1×10^{-4}
			Av. 1.0×10^{-4}
2-CH_3	1.488×10^4	57.3	3.7×10^{-5}
	1.868×10^4	46.7	4.5×10^{-5}
			Av. 4.1×10^{-5}
3-CH_3	9.900×10^3	71.5	3.4×10^{-5}
	1.362×10^4	60.0	3.7×10^{-5}
			Av. 3.6×10^{-5}
4-CH_3	1.458×10^4	60.8	3.4×10^{-5}
	1.566×10^4	46.2	4.9×10^{-5}
	1.620×10^4	46.3	4.8×10^{-5}
			Av. 4.4×10^{-5}
2-$C(CH_3)_3$	3.030×10^4	90.6	3.3×10^{-6}
	1.169×10^5	68.8	3.2×10^{-6}
	1.840×10^5	57.7	3.0×10^{-6}
			Av. 3.2×10^{-6}
4-$C(CH_3)_3$	1.800×10^4	75.3	1.6×10^{-5}
	2.340×10^4	60.5	2.1×10^{-5}
	2.730×10^4	51.2	2.5×10^{-5}
			Av. 2.1×10^{-5}

[a] Initial concentrations in NH_3 solution: C_6H_5D, 0.46 *M;* $CH_3C_6H_4D$, 0.41 *M;* $(CH_3)_3CC_6H_4D$, 0.29 *M*. [b] Average value for deuterium compound remaining, obtained from three or more absorption peaks. [c] C_6H_5D was dissolved in an equal weight of pentane to avoid freezing during addition.

TABLE II

PSEUDO FIRST-ORDER RATE CONTANTS FOR HETEROGENEOUS EXCHANGE OF SUBSTITUTED DEUTERIOBENZENES (C_6H_4DX) WITH POTASSIUM AMIDE IN ISOPROPYLAMINE (AT 34°)

X[a]	Reaction time, sec.	Mole % C_6H_4DX[b]	k, sec.$^{-1}$
H	3.78×10^3	50.8	2×10^{-4}
2-O^-	1.02×10^3	49.8	7×10^{-4}
3-O^-	3.75×10^4	76.7	7×10^{-6}
4-O^-	3.60×10^4	82.9	5×10^{-6}
2-CH_3	3.72×10^3	27.1	4×10^{-4}
	1.50×10^3	82.6	1×10^{-4}
	5.40×10^3	42.0	2×10^{-4}
3-CH_3	3.66×10^3	9.5	6×10^{-4}
	1.80×10^3	69.4	2×10^{-4}
4-CH_3	7.20×10^2	89.3	2×10^{-4}
	4.20×10^3	44.5	2×10^{-4}

[a] Initial concentrations in isopropylamine solution: C_6H_5D, 0.49 *M;* $DC_6H_4O^-$, 0.41 *M;* $CH_3C_6H_4D$, 0.41 *M*. [b] Average value for deuterium compound remaining, obtained from three or more absorption peaks.

Results and Discussion

The exchange rate constants are given in Tables I and II.

The homogeneous exchanges in liquid ammonia at 0° show just the pattern that would be expected from the inductive effect, although the differences are so small that this may be in part fortuitous. The weakly electropositive methyl group causes a slight decrease in the acidity of the hydrogens attached to the ring, without significant differentiation among the three positions. With the more strongly electropositive *tert*-butyl group[7] the decrease in the acidities of the 2- and 4-hydrogens is greater and in the order 2- > 4-position. Fig. 1 shows the relation of the Taft polar substituent constants, σ_I,[7] for the groups —H, —CH_3, and —$C(CH_3)_3$ to the logarithms of the rate constants for the exchanges of the deuterium compounds. There are certainly approximations involved, such as the use of the same σ_I value for a substituent regardless of its position, but a roughly linear relation appears real, with the exception of the *tert*-butylbenzene-2-*d*, where the rate is slower than expected. Steric hindrance by the *tert*-butyl group must be an important factor here, as in many other reactions involving the position adjacent to this bulky group.[8,9] The positive slope of the line signifies a positive value for ρ_I, or that electron withdrawal speeds the reaction.

The meaning of the results in isopropylamine (Table II) is not entirely clear; and because of the difficulty

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(7) (a) R. W. Taft, Jr., *J. Am. Chem. Soc.*, **79**, 1045 (1957); (b) R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 595.

(8) G. S. Hammond and M. F. Hawthorne, chap. 3 in ref. 7b.

(9) (a) K. L. Nelson and H. C. Brown, *J. Am. Chem. Soc.*, **73**, 5605 (1951); (b) H. C. Brown and W. H. Bonner, *ibid.*, **76**, 605 (1954).

in interpreting data obtained under these heterogeneous conditions, work in this medium was abandoned without attempting to secure more than semiquantitative results. The methyl group caused little change; the negatively charged oxygen of the phenoxide ion caused a marked decrease in the rate of exchange for the 3- and 4-hydrogens. The increased rate for the 2-hydrogen, if real, seems anomalous, for the negatively charged oxygen atom should greatly decrease the acidity of the hydrogens, the decrease being in the order 2- > 3- > 4-position. In a presumably homogeneous reaction, Shatenshteĭn and Vedeneev did find that the rate of exchange of the phenoxide ion with potassium amide in liquid ammonia-d_3 was only 30% of that of benzene although their experiments did not differentiate among the hydrogens.[10]

The differences among the rates of exchange are noticeably less than those found in the previous work.[1] These smaller differences may be attributed to the weaker inductive effects of the groups studied and to the higher temperatures employed, which would decrease the discrimination among the benzenoid hydrogens.

The effect of a variety of types of substituents upon the acidities of the hydrogens at specific positions on the benzene ring has now been established by exchange reactions. The —CF_3 group has positive values for both σ_I and σ_R, —CH_3 and —$C(CH_3)_3$ (and presumably —O^-) have negative values for both, and —OCH_3 and —F have positive values for σ_I and negative values for σ_R.[7] In each case, an increase in acidity is associated with a positive σ_I (electron-withdrawing inductive effect) and a decrease with a negative σ_I (electron-furnishing inductive effect). This relation holds regardless of whether σ_R is positive or negative (electron-withdrawing or -furnishing resonance effect). The predominance of inductive over resonance effects is evident (Table III).

TABLE III

CORRELATION BETWEEN σ_I AND RATE OF EXCHANGE

X	σ_I[7]	σ_R[7]	$k_{C_6H_4DX}/k_{C_6H_5D}$, in $NH_{3(l)}$	
			at −33°[a]	at 0°
F—	+0.50	−0.44		
2-			>4×10^6	
3-			4×10^3	
4-			2×10^2	
CF_3—	+0.41	+0.14		
2-			6×10^5	
3-			1×10^4	
4-			1×10^4	
CH_3O—	+0.23	−0.50		
2-			1×10^4	
3-			1[b]	
4-			1×10^{-1}[b]	
H—			1[b]	1
CH_3—	−0.05	−0.13		
2-			[b]	4.1×10^{-1}
3-				3.6×10^{-1}
4-				4.4×10^{-1}
$(CH_3)_3C$—	−0.07	−0.12		
2-				3.2×10^{-2}
4-				2.1×10^{-1}

[a] Ref. 1. [b] Too slow for accurate measurement.

Results obtained by other investigators leads to the same conclusion. Shatenshteĭn and co-workers have determined the rates of a number of reactions where substituted benzenes were treated with potassium amide in ammonia-d_3.[10,11] They used a variety of conditions so that comparisons are often difficult, but in two cases where they examined the rates of exchange of the different benzenoid hydrogens, the rates were found to be in the order 2- > 3- > 4-position in both anisole[10] and diphenyl ether.[12] Rate studies of the formation of benzynes from substituted bromobenzenes,[13] where the rate of elimination of hydrogen bromide is taken as a simple function of the acidity of the hydrogen being eliminated,[14] again point to the predominance of the inductive effect.

Experimental

Deuterated Benzene Derivatives.—Benzene-*d*, toluene-2-*d*, -3-*d*, and -4-*d* and *tert*-butylbenzene-2-*d* and -4-*d* were prepared by a conventional procedure from the corresponding bromo compounds.[1] Phenol-2-*d*, -3-*d*, and -4-*d* were prepared by reaction of the appropriate bromo compounds with *n*-butyllithium[15] and decomposition of the lithium reagents with deuteroacetic acid. The physical constants and principal infrared absorption bands of the deuterobenzene derivatives are listed in Table IV. *o*-Bromo-*tert*-butylbenzene[9a,16–18] and *p*-bromo-*tert*-butylbenzene[19] were prepared from *tert*-butylbenzene by previously reported procedures. The physical constants of the products were in good agreement with those reported in the literature. The diazotization of 3-bromo-4-amino-*tert*-butylbenzene[9a,18,20,21] and reduction with hypophosphorous acid gave insufficient *m*-bromo-*tert*-butylbenzene with which to prepare the corresponding deuterated derivative. The other bromo compounds were obtained from commercial sources.

Exchange Reactions.—The deuterium–protium exchange reactions in refluxing isopropylamine were carried out in a 250-ml. three-necked flask equipped with stirrer, Dry Ice condenser protected with a drying tube, and a gas inlet. A solution of potassium amide in liquid ammonia was prepared by adding 1.8 g. (0.046 g.-atom) of potassium metal to 50 ml. of stirred liquid ammonia containing a small crystal of ferric nitrate nonahydrate. The Dry Ice condenser was replaced by a water condenser and the gas inlet by a dropping funnel containing 50 ml. of dry isopropylamine, which was added slowly as the ammonia evaporated. The mixture of potassium amide and isopropylamine was heated to reflux, and 3.00 g. of the substituted deuteriobenzene in 25 ml. of isopropylamine was added. The reaction mixture was stirred under reflux for the desired interval and then quenched by the addition of 4.8 g. (0.09 g. form. wt.) of ammonium chloride. The reaction mixture was diluted with 25 ml. of ether and acidified with dilute hydrochloric acid. The ethereal solution was washed with water and dried, and the reaction products were distilled twice through a semimicro fractionating column.[22] The quantities of potassium and ammonium chloride in the deuterophenol

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(10) A. I. Shatenshteĭn and A. V. Vedeneev, *Zh. Obshch. Khim.*, **28**, 2644 (1958) [*Chem. Abstr.*, **53**, 5836 (1959)].

(11) A. I. Shatenshteĭn, *Zh. Fiz. Khim.*, **25**, 1206 (1951) [*Chem. Abstr.*, **47**, 4175 (1953)]; A. I. Shatenshteĭn, *Dokl. Akad. Nauk SSSR*, **60**, 1029 (1950) [*Chem. Abstr.*, **44**, 5194 (1950)]; A. I. Shatenshteĭn, N. M. Dykhno, E. A. Izrailevich, L. N. Vasil'eva, and M. Faivush, *ibid.*, **79**, 479 (1951) [*Chem. Abstr.*, **46**, 29 (1952)]; A. I. Shatenshteĭn, L. N. Vasil'eva, N. M. Dykhno, and E. A. Izrailevich, *ibid.*, **85**, 381 (1952) [*Chem. Abstr.*, **46**, 9954 (1952)]; N. M. Dykhno and A. I. Shatenshteĭn, *Zh. Fiz. Khim.*, **28**, 11 (1954) [*Chem. Abstr.*, **48**, 10413 (1954)].

(12) A. I. Shatenshteĭn, A. N. Talanov, and Yu. I. Ranneva, *Zh. Fiz. Khim.*, **30**, 583 (1960) [*Chem. Abstr.*, **54**, 24489 (1960)].

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(14) R. Huisgen and J. Sauer, *ibid.*, **92**, 192 (1959).

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(19) C. S. Marvel, H. W. Johnston, J. W. Meier, T. W. Mastin, J. Whitson, and C. M. Himmel, *ibid.*, **66**, 914 (1944).

(20) M. S. Newman and E. K. Easterbrook, *ibid.*, **77**, 3763 (1955).

(21) C. Eaborn and R. Taylor, *J. Chem. Soc.*, 247 (1961).

(22) C. W. Gould, Jr., G. Holzman, and C. Niemann, *Anal. Chem.*, **20**, 361 (1948).

TABLE IV

PHYSICAL CONSTANTS AND CHARACTERISTIC INFRARED ABSORPTION BANDS OF SUBSTITUTED DEUTERIOBENZENES (C_6H_4DX)

X	B.p.		$n^{\circ C}_{D}$	Absorption peaks,[a] cm.$^{-1}$
	°C.	Mm.		
H	79.0–79.5	Atm.	$1.5014^{25.0}$	698 (s), 780 (s), 912 (s), 980 (w), 1070 (s), 1115 (s), 1150 (w), 1344 (w), 1444 (s), 1696 (m), 1763 (m), 1883 (w), 2270 (m), 2880 (m)
2-CH_3	108.5–109.0	Atm.	$1.4931^{24.6}$	720 (m), 728 (m), 775 (s), 862 (m), 941 (m), 1040 (s), 1122 (m), 1286 (s), 1473 (ms), 1705 (s), 2255 (m)
3-CH_3	108.5	Atm.	$1.4924^{23.8}$	650 (s), 914 (w), 1045 (m), 1078 (m), 1163 (w), 1475 (s), 2275 (m)
4-CH_3	108.0	Atm.	$1.4941^{22.8}$	708 (s), 832 (s), 860 (w), 945 (w), 1284 (m), 1666 (w), 1704 (s), 1900 (m), 2285 (m)
2-$C(CH_3)_3$	57.5	13	$1.4900^{24.0}$	637 (m), 770 (m), 872 (m), 945 (w), 1040 (m), 1098 (m), 1127 (w), 1160 (w), 1278 (w)
4-$C(CH_3)_3$	58.0	13	$1.4868^{23.4}$	850 (s), 865 (w), 1040 (w)
2-OH	66–67	10	$1.5620^{25.0}$	827 (m), 913 (m), 1037 (s), 1108 (s), 1286 (s), 1450 (m)
3-OH	66–68	10	$1.5434^{32.0}$	1031 (m), 1092 (w), 1299 (w), 1437 (m)
4-OH	65–67	11	$1.5414^{25.0}$	716 (m), 845 (s), 978 (m), 1095 (s), 1290 (m), 1322 (m), 1436 (s)

[a] Principal infrared absorption peaks which are not also present in the corresponding undeuterated C_6H_5X.

experiments were increased to 3.04 g. and 8.5 g., respectively. In the deuteriobenzene experiments, quantities of all materials were increased by one third to permit recovery of sufficient material for study.

The exchange reactions in liquid ammonia at 0° were carried out in 6-oz. Coca-Cola bottles. The dry, stoppered bottle, charged with 1.8 g. of potassium and a small crystal of ferric nitrate nonahydrate, was immersed in an acetone bath which was cooled gradually to $-70°$ by the addition of Dry Ice. Ammonia was condensed in the bottle until more than 75 ml. had been collected. The bottle was raised out of the bath and the ammonia allowed to boil off until 75 ml. remained. The bottle was again immersed in the bath and allowed to stand for 15 min. A 3-in. Pyrex test tube with a thin glass handle at the top and a 5-cm. glass rod at the bottom was charged with 3.00 g. of the deuterated compound and lowered into the reaction vessel. The bottle was removed from the bath, covered with a thin sheet of Teflon and capped. It was transferred to an ice–water bath and allowed to stand for 30 min. after which the bottle was shaken to dissolve the contents of the test tube in the liquid ammonia solution, replaced in the ice–water bath, and allowed to stand for the timed interval. The vessel was then cooled in a Dry Ice–acetone bath, uncapped, and the amide ion neutralized by the addition of 4.8 g. of ammonium chloride. The reaction mixture was treated according to the previously described procedure.[1] In the deuteriobenzene experiments, the quantities of all materials were increased by one third. Sodium-dried pentane (4 g.) was also added to the deuteriobenzene to prevent the deuteriobenzene from solidifying in the test tube.

Determination of Extent of Deuterium–Protium Exchange.—The infrared spectra of the deuteriobenzene derivatives, the nondeuterated compounds and the exchange reaction products were determined with a Beckman Model IR-4 infrared spectrophotometer. Deuteriobenzene, the deuteriotoluenes, and the deuterio-*tert*-butylbenzenes were measured neat, the deuteriophenols in carbon tetrachloride. The major absorption peaks appearing in the spectra of the deuterated compounds which were not found in the spectra of the nondeuterated substances are given in Table IV.

Measurements and determinations of the extent of deuterium–protium exchange were made according to the procedure previously described.[1]

The Condensation Products of Aldehydes and Aldol-sensitive β-Dicarbonyl Compounds[1a]

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The noncatalyzed condensation of formalin and ethyl acetoacetate to diethyl α,α′-diacetylglutarate, discovered by Rabe, has been extended to related β-dicarbonyl compounds. With formalin, the yields are good, whereas with acetaldehyde, the yields are greatly lowered, and in the case of 2,4-pentanedione, only a 1:1 condensation product forms because of steric effects. Still higher aldehydes fail to react in the absence of a catalyst. Authentic samples of two of the three possible tautomers of 3,5-diacetyl-2,6-heptanedione have been prepared and identified by chemical and physical means.

In 1904, Rabe[1b] showed that formalin and ethyl acetoacetate reacted readily in the absence of a catalyst to give a 1:2 condensation product and that this product was not the same as that obtained by Knoevenagel[2] in a base-catalyzed reaction. Furthermore, amine bases could convert Rabe's product into Knoevenagel's. From the results of work in these laboratories (below) and of Finar's,[3] it is now known that Rabe's product is diethyl α,α′-diacetylglutarate ("methylenebisacetoacetate") (I) and that Knoevenagel's product is not I as he had claimed, but rather, it is the intramolecular aldol condensation product of I, 4,6-dicarbethoxy-3-hydroxy-3-methylcyclohexanone (II), as Rabe[4] had suggested. Finar's findings are now confirmed and further substantiated with some additional chemical data and n.m.r. analyses.

First, it should be pointed out that Finar's statement concerning the noncatalyzed condensation of ethyl

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(1)(a) Communication no. 2275 from the Kodak Research Laboratories; (b) P. Rabe, *Ann.*, **332**, 1 (1904).

(2) E. Knoevenagel, *ibid.*, **281**, 25 (1894).

(3) I. L. Finar, *J. Chem. Soc.*, 674 (1961).

(4) P. Rabe and F. Elze, *Ann.*, **323**, 83 (1902).