benzoylacetone and 0.430 mol of $NaNH_2$ in NH_3 (l). This procedure is analogous to that described for chloro β-diketone **1**.

Anal. Calcd for $C_{17}H_{15}ClO_2$: C, 71.20; H, 5.22; Cl, 12.36. Found: C, 71.11; H, 5.33; Cl, 12.26.

The absorption spectra for **8** contained the following: ir 3106, 2950, 1618, 1055, 756, and 694 cm^{-1}; nmr δ 2.40–3.21 (m, 4 H, $-CH_2CH_2-$), 6.0 (s, 1 H, C_2 H_{enol}), and 6.9–7.8 (m, 9 H, Ar-H).

The pyrazole of **8** was prepared in the standard manner and was recrystallized from methanol, mp 99–101°.

Anal. Calcd for $C_{17}H_{15}ClN_2$: C, 72.17; H, 5.34; Cl, 12.53; N, 9.95. Found: C, 72.43; H, 5.45; Cl, 12.76; N, 9.86.

Registry No.—**2**, 24118-62-5; **5**, 24118-63-6; **6**, 24118-64-7; **7**, 24118-65-8; **8**, 24118-66-9; pyrazole of **7**, 24110-98-3; pyrazole of **8**, 24118-71-6.

Coupling of Carbanions. Formation of Succinic Acid Derivatives

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Alkali metal diphenylmethides have previously been shown to react with certain polyhalides by a displacement on halogen to give the dehalogenation product from the halide and a benzhydryl halide.[1] While the halogenated compound has been isolated from the reaction with carbon tetrachloride,[2] under the usual reaction conditions (addition of halide to anion) it reacts further with the anion to give tetraphenylethane (Scheme I).

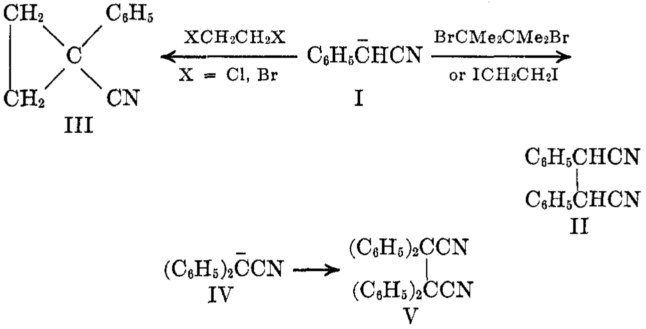
SCHEME I

$$(C_6H_5)_2CH_2 \xrightarrow{KNH_2} (C_6H_5)_2\bar{C}H \xrightarrow{X\text{-}C\text{-}C\text{-}X} (C_6H_5)_2CHX \xrightarrow{(C_6H_5)_2\bar{C}H} (C_6H_5)_2CHCH(C_6H_5)_2$$

Several such reactions to give halogen compounds from carbanions have been reported.[3] We now report the synthetic utility of this reaction in the coupling of anions from nitriles and esters to give succinic acid derivatives.

Phenylacetonitrile and Diphenylacetonitrile.—Potassio- and sodiophenylacetonitrile (I), prepared from the nitrile and potassium or sodium amide, was previously shown to undergo generally twofold alkylation with alkyl halides.[4] Thus reaction with ethylene chloride gives equal amounts of 1-phenylcyclopropanecarbonitrile (III) and phenylacetonitrile. It was previously shown that ethylene iodide and ethylene bromide react with potassium diphenylmethide by displacement on halogen to give the dimeric product (tetraphenylethane), while ethylene chloride undergoes twofold alkylation to give 1,1,4,4-tetraphenylbutane.[1] In agreement with this, ethylene iodide reacts with I to give the dimer, 2,3-diphenylsuccinonitrile (II), but ethylene bromide *does not* effect dimerization, and, like ethylene chloride, undergoes twofold alkylation (see Scheme II). In none of the cases studied did 2,3-dibromo-2,3-dimethylbutane, a ditertiary halide, undergo alkylation.

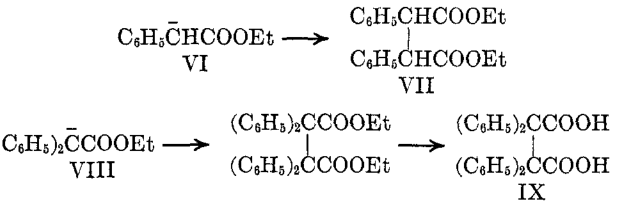
SCHEME II



The yields of II in the dimerization reactions were difficult to reproduce, apparently because this nitrile can undergo dehydrocyanation with potassium amide or other anion.[5] Such a dehydrocyanation is not possible with dimer V, which was obtained from potassiodiphenylacetonitrile (IV) in 85% yield even when the direct addition procedure was employed.

Ethyl Phenylacetate and Ethyl Diphenylacetate.—The potassium derivatives of these esters were readily prepared from the esters and ammoniacal potassium amide. The product from the latter ester, diethyl tetraphenylsuccinate, was not obtained crystalline and was identified by hydrolysis to the acid (see Scheme III). The yields of these reactions are summarized in Table I.

SCHEME III



$$\underset{\text{VI}}{C_6H_5\bar{C}HCOOEt} \longrightarrow \underset{\text{VII}}{\begin{array}{c}C_6H_5CHCOOEt\\|\\C_6H_5CHCOOEt\end{array}}$$

$$\underset{\text{VIII}}{(C_6H_5)_2\bar{C}COOEt} \longrightarrow \begin{array}{c}(C_6H_5)_2CCOOEt\\|\\(C_6H_5)_2CCOOEt\end{array} \longrightarrow \underset{\text{IX}}{\begin{array}{c}(C_6H_5)_2CCOOH\\|\\(C_6H_5)_2CCOOH\end{array}}$$

TABLE I

DIMERIZATION OF ANIONS OF ESTERS AND NITRILES

Anion (mol)	Halide (mol)	Product (yield, %)
I (0.05)	$BrCMe_2CMe_2Br$ (0.025)	II (16, *meso;* 37, *dl*) CN^- (22)
I (0.05)	$BrCMe_2CMe_2Br$ (0.025)[a]	II (6, *meso;* 63, *dl*)
I (0.1)	$BrCH_2CH_2Br$ (0.05)	Phenylacetonitrile (92) III (91)
I (0.05)	ICH_2CH_2I (0.025)	II (33)
I (0.1)	Cl_3CCCl_3 (0.05)	II (5, *meso;* 45, *dl*)
IV (0.05)	$BrCMe_2CMe_2Br$ (0.025)	V (85)
VI (0.08)	$BrCMe_2CMe_2Br$ (0.04)	VII (36)
VI (0.1)	Cl_3CCCl_3 (0.05)	VII (54, *meso;* 24, *dl*)
VIII (0.05)	$BrCMe_2CMe_2Br$ (0.025)	IX (54)

[a] The inverse addition procedure was employed.

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[4] C. R. Hauser and W. R. Brasen, *J. Amer. Chem. Soc.*, **78**, 494 (1956).

[5] For related dehydrocyanations, see C. R. Hauser and W. R. Brasen, *ibid.*, **78**, 82 (1956).

Experimental Section

Formation and Coupling of Carbanions.—The anions were prepared by addition of an ethereal solution of the ester or nitrile to 1 equiv of potassium amide in 120–200 ml of liquid ammonia and stirring for 20 min. An ethereal solution of the halide (0.5 molar equiv) was added, the ammonia was allowed to evaporate, and the residue was stirred with water and ether or chloroform and filtered. Individual work-ups follow.

2,3-Diphenylsuccinonitrile (II).—The solid on the funnel was recrystallized from acetic acid to give tan needles of the *meso* nitrile, mp 238° (lit.[6] mp 239–240°). The chloroform solution was diluted with ethanol and chilled, giving the *dl* nitrile, mp 164° (lit.[6] mp 164°). The aqueous solution gave a positive Prussian Blue test for cyanide, which was quantitatively determined.[7]

Tetraphenylsuccinonitrile (V).—The chloroform solution was evaporated, and the residue was recrystallized from chloroform–ethanol to give tetraphenylsuccinonitrile, mp 215°, undepressed by an authentic sample.[8]

Diethyl 2,3-Diphenylsuccinate (VII).—The solid on the funnel was recrystallized from aqueous methanol to give the *meso* ester, mp 140–141° (lit.[9] mp 140–141°). The ethereal solution was evaporated, and the residue was recrystallized from aqueous methanol to give the *dl* ester, mp 79–80° (lit.[9] mp 82–82.5°).

Tetraphenylsuccinic Acid.—Evaporation of the ethereal solution gave an oily solid which several recrystallizations failed to purify. The material was hydrolyzed overnight in refluxing ethanol with 5.7 g (0.1 mol) of potassium hydroxide. The ethanol was evaporated, and the residue was stirred with water and methylene chloride. The aqueous solution was acidified, and the tetraphenylsuccinic acid was recrystallized from methylene chloride–ethanol to give white crystals, mp 271° dec (lit.[10] mp 260–262°).

Reaction of I with Ethylene Bromide.—Evaporation of the ethereal solution gave 21.5 g of a yellow-brown oil, shown by nmr to be a mixture of phenylacetonitrile and 1-phenylcyclopropanecarbonitrile. The mixture was not separated by distillation through a 6 in. helix-packed column, but was satisfactorily separated by gas chromatography (1-m column, 20% methyl silicone SE-30). The nmr spectrum of a sample of pure III, collected from the gas chromatograph, was identical with the published spectrum.[11] The relative yields of the two nitriles (Table I) were estimated from the ratio of the peak areas.

Registry No.—*meso*-II, 15146-07-3; *dl*-II, 19657-49-9; III, 935-44-4; V, 3122-21-2; *meso*-VII, 13638-89-6; *dl*-VII, 24097-93-6; IX, 24097-49-2.

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The *A* Value of Hydroxyl Determined by the Nuclear Magnetic Resonance Peak Area Method at −83°

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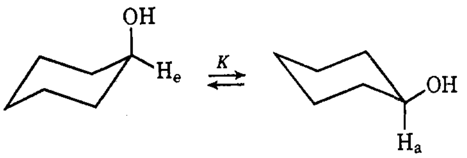
A myriad of reports have appeared concerning the measurement of the *A* value of hydroxyl (eq 1 and 2) employing a large variety of techniques.[2–4] The observed *A* values are solvent dependent but deviate seriously from one technique to another in the same solvent.[2] This paper concerns the measurement of the *A* value of hydroxyl in cyclohexanol-2,2,6,6-d_4 at −83° utilizing variable-temperature nuclear magnetic resonance (nmr) spectroscopy, a technique of proven accuracy.[3]



(1)

$$\text{A value} = -\Delta G^\circ = (RT \ln K)/1000 \qquad (2)$$

Examination of the nmr spectrum (60 MHz) of cyclohexanol-2,2,6,6-d_4 at −83° in a number of solvents revealed two resonances corresponding to the equatorial HCO proton (H_e, eq 1) at approximately δ 3.85 and to the axial HCO proton (H_a, eq 1) at approximately δ 3.28 (Figure 1). These peak assignments are consistent with those in model compounds[5] and were confirmed by deuteration of the hydroxyl group and investigation of the HCO resonance under conditions of slow, intermediate, and fast rates of exchange on the nmr time scale.

Integration by planimeter and electronic integrator of the peak areas of axial and equatorial HCO resonances at −83° gave the equilibrium constant (*K*, eq 1) of interest and the corresponding *A* values in a variety of solvents (Table I). Since the measured equilibrium constants (*K*, eq 1) are relatively large by nmr standards, a correspondingly large radiofrequency power level was necessary to obtain reasonable reproducibility in peak areas. This introduces the possibility of differential saturation effects on the two H–C–O resonances, but these effects are included in the error limit set on *K* (eq 1, Table I).

Table I
A Value of Hydroxyl as a Function of Concentration and Solvent at −83°

Group	Solvent	Concn, mol/l.	*K*	*A* value, kcal/mol
-OH	CS_2	3.0	17.0 ± 1.0	1.08 ± 0.06
		2.0	12.9 ± 0.7	0.97 ± 0.05
		1.0	11.6 ± 0.8	0.93 ± 0.05
		0.5	11.3 ± 0.8	0.92 ± 0.05
-OD	CS_2	2.0	11.6 ± 0.8	0.93 ± 0.05
-OH	Toluene	2.0	11.3 ± 0.8	0.92 ± 0.05
	Toluene	1.0	11.0 ± 0.8	0.91 ± 0.05
-OH	CD_3COCD_3	1.0	12.9 ± 0.9	0.97 ± 0.05
-OH	50% CS_2–	2.0	11.6 ± 0.6	0.93 ± 0.05
	50% α-picoline	1.0	11.5 ± 0.7	0.93 ± 0.05
	(by wt)	0.5	11.5 ± 1.8	0.92 ± 0.06
-OD	CD_3OD	1.0	16.1 ± 1.0	1.05 ± 0.06
	CD_3OD	2.0	15.8 ± 1.0	1.04 ± 0.06

[1] National Science Foundation Undergraduate Research Participant, Summer 1969.

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