

# Notes

## Oxidative Decyanation of Benzyl and Benzhydryl Cyanides. A Simplified Procedure

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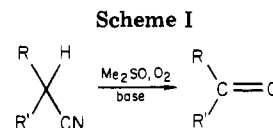
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Recent utilization of the oxidative decyanation reaction<sup>2,3</sup> prompts the updating of our initial report.<sup>4</sup> We originally encountered the reaction of interest (Scheme I) in the attempted alkylation of diphenylacetonitriles 1-3 (Table I). Whereas unsubstituted diphenylacetonitrile (1) was readily alkylated, the *p*-nitro and *p*-methoxy analogues, 2 and 3, were *not* but formed the corresponding diaryl ketones. We have now reinvestigated oxidative decyanation of the parent compound, 1, and extended our substrates to include three categories: A, diarylacetonitriles, B, arylbenzylacetonitriles, and C, other acetonitriles.

The diphenylacetonitriles (compounds 1-10, category A compounds) readily formed the corresponding ketones in excellent yields when stirred at ambient temperature in methyl sulfoxide, under air, with some K<sub>2</sub>CO<sub>3</sub> as the base. For these reactions, quenching the mixture with water and isolation were the only workup necessary. This technique is simpler but less general than the Watt procedure.<sup>2</sup> The half-life of five group A compounds were determined by NMR and showed the anticipated trend by a Hammett-type plot (see Experimental Section). The parent compound was also oxidized under two different conditions. Replacing atmospheric gases with an oxygen blanket significantly increased the reaction rate whereas a nitrogen blanket, without exhaustive deoxygenation of the solvent and a gas cover, decreased the rate. Therefore, the mechanism undoubtedly follows the carbanion formation, one-electron oxidation, loss of CN sequence proposed by Kharasch and others.<sup>5</sup> The ionic mechanism suggested earlier<sup>4</sup> is withdrawn. Rabjohn<sup>6</sup> also reports a ketone product from a cyanoacetate substrate.

Phenylbenzhydrylacetonitrile (12) required substitution of the stronger base lithium isopropylcyclohexylamide (LICA) instead of K<sub>2</sub>CO<sub>3</sub> to obtain an excellent yield of ketone. Similar observations for several other substrates of the non-A category type led to exclusive use of Me<sub>2</sub>SO/LICA in all subsequent reactions. An additional case supporting the LICA method was (*p*-chlorophenyl)(*p*-methoxybenzyl)acetonitrile which gave an insignificant amount of ketone with K<sub>2</sub>CO<sub>3</sub> at room temperature for 16 h. When this substrate and Me<sub>2</sub>SO/K<sub>2</sub>CO<sub>3</sub>



were heated at 100 °C for 72 h, the hydrolysis of nitrile to amide occurred. The presence of the strong base LICA, however, introduced a secondary complication into some reactions. The initially formed ketone frequently underwent further reaction; for example, aldol condensation, polymer formation or cleavage to acid were among the observable reactions.

The only dialkyl substrate, isobutyronitrile (24), gave a poor yield of acetone with LICA. IR analysis of the crude reaction mixture showed that strong nitrile absorbance was still present; however, there was also carbonyl and hydroxyl absorbance, indicating aldol condensation of the initially formed acetone. Substantiation for acetone formation was obtained by running the isobutyronitrile reaction under slightly reduced pressure and drawing the effluent through a solution of (2,4-dinitrophenyl)hydrazine. This removed the acetone as soon as it was formed, as the 2,4-dinitrophenylhydrazone precipitate which was no longer formed after 3 h. at room temperature, and prevented aldolization since the very small residue upon workup did not exhibit OH absorption in the IR.

In summary, category A nitriles in Me<sub>2</sub>SO/K<sub>2</sub>CO<sub>3</sub> at ambient temperature for several hours form benzophenones in excellent yields. Many category B nitriles with Me<sub>2</sub>SO/LICA also give acetophenones in high yields but also some side reactions. The conditions cited here are unsatisfactory when applied to monosubstituted nitriles or dialkyl nitriles since substantial acid (50%) and/or aldol products result. No attempt was made to maximize the oxidative decyanation process for the latter compounds. Three obvious modifications of reaction conditions would be to decrease the temperature, bubble pure oxygen into the reaction mixture, and utilize different bases. We plan no further work on this reaction.

The simplicity of the reaction conditions and the workup is the point of emphasis in this discussion. Furthermore, the necessity of rigorously excluding oxygen from carbanions, when other desired reactions are sought, is indicated.

### Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 237B instrument. Melting points were determined on a Mel Temp apparatus. All compounds give NMR and IR spectra consistent with those expected for the formula. All new compounds gave analyses (by G. I. Robertson Laboratories, Florham Park, NJ) within ±0.30% of theory. The substrate nitriles were purchased from Aldrich Chemical Co., prepared by the method of Sisidi,<sup>7</sup> or available from other work.<sup>8</sup>

**General Procedure. Me<sub>2</sub>SO/K<sub>2</sub>CO<sub>3</sub> Method.** To a solution of 1.00 g (5.1 mmol) of diphenylacetonitrile in 30 mL of dimethyl sulfoxide in a flask open to the atmosphere was added a solution of 1.00 g (7.2 mmol) of K<sub>2</sub>CO<sub>3</sub> in 1.5 mL of water. After being

(1) Taken from the Senior Honors Paper of M.J.M., Moravian College, 1980.

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Table I. Substituents and Product Data<sup>j</sup> for RR'CHCN → RC(O)R'

category	compd	R	R'	base <sup>a</sup>	mp <sup>b</sup> (found), °C	% yield
A	1	Ph	Ph	K	57-48.5	95
	2	Ph	Ph- <i>p</i> -NO <sub>2</sub>	K	138-139	100 <sup>c</sup>
	3	Ph	Ph- <i>p</i> -OCH <sub>3</sub>	K	61-61.5	90 <sup>c</sup>
	4	Ph	Ph- <i>p</i> -Cl	K	73.5-75	90
	5	Ph	Ph- <i>p</i> -Br	K	81-82.5	93
	6	Ph	Ph- <i>p</i> -CH <sub>3</sub>	K	57-58	90
	7	Ph- <i>p</i> -Cl	Ph- <i>p</i> -Cl	K	146-147	95
	8	Ph	Ph- <i>p</i> -NH <sub>2</sub>	K	121.5-123	94
	9	Ph	Ph-2-Cl,4-NH <sub>2</sub>	K	143.5-144.5	90
	10	Ph	Ph- <i>p</i> -F	K	230-233 <sup>d</sup>	90
	11	Ph	2-C <sub>5</sub> H <sub>4</sub> N	K	39.5-41	48
B	12	Ph	CH(Ph) <sub>2</sub>	L <sup>e</sup>		96
	13	Ph	CH <sub>2</sub> Ph	L	57-59	50
	14	Ph- <i>p</i> -Cl	CH <sub>2</sub> Ph- <i>p</i> -Cl	L	110-110.5	40 <sup>e</sup>
	15	Ph- <i>p</i> -Cl	CH <sub>2</sub> Ph	L		12
	16	Ph- <i>p</i> -Cl	CH <sub>2</sub> Ph- <i>p</i> -OCH <sub>3</sub>	K		<sup>f</sup>
C	17	Ph	c-C <sub>6</sub> H <sub>11</sub>	L <sup>e</sup>		97
	18	Ph	C <sub>2</sub> H <sub>5</sub>	L <sup>e</sup>		92
	19	Ph	CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	L		20 <sup>g</sup>
	20	Ph- <i>p</i> -Br	H	L		26 <sup>g</sup>
	21	Ph-2,4-Cl <sub>2</sub>	H	L		13 <sup>h</sup>
	22	Ph- <i>p</i> -F	CH <sub>3</sub>	K		44 <sup>i</sup>
	23	Ph	CH(CH <sub>3</sub> ) <sub>2</sub>	K		26 <sup>g</sup>
	24	CH <sub>3</sub>	CH <sub>3</sub>	L		60 <sup>g</sup>

<sup>a</sup> K = K<sub>2</sub>CO<sub>3</sub>; L = LICA. <sup>b</sup> Found melting points agreed satisfactorily with reported values. For other compounds the spectral data were consistent with reported and expected absorptions. <sup>c</sup> See ref 1. 2-Chloro-4-aminobenzophenone. Anal. Calcd for C<sub>13</sub>H<sub>9</sub>ClNO: C, 67.39; H, 4.32; Cl, 15.33; N, 6.05. Found: C, 67.31; H, 4.49; Cl, 15.37; N, 5.95. <sup>d</sup> Melting point of 2,4-dinitrophenylhydrazones. <sup>e</sup> Very poor yield with K<sub>2</sub>CO<sub>3</sub>. <sup>f</sup> Hydrolysis to amide; see text and Experimental Section. <sup>g</sup> Additional products formed: i.e., acid, polymer, aldol. Yield estimated by spectral absorption. <sup>h</sup> With KH as the base and *t*-BuOH as the solvent the product was the dimer 2,4-bis(2,4-dichlorophenyl)-3-amino-2-butenenitrile, mp 139.5-140.5 °C. Anal. Calcd for C<sub>16</sub>H<sub>10</sub>N<sub>2</sub>Cl<sub>4</sub>: C, 51.61; H, 2.69; N, 7.53; Cl, 38.15. Found: C, 51.74; H, 2.74; N, 7.57; Cl, 36.60. <sup>i</sup> Reaction temperature of 110 °C for 72 h; the oily product was converted to the 2,4-dinitrophenylhydrazones. <sup>j</sup> Satisfactory analytical data were reported for all new compounds listed in the table.

magnetically stirred overnight at room temperature, the mixture was added to 100 mL of ice-water. Three extractions with ether (3 × 30 mL) were combined. The extract was washed with water, dried overnight (Na<sub>2</sub>SO<sub>4</sub>), filtered, and allowed to concentrate. The residual clear oil was triturated with petroleum ether (30-60 °C) to give white crystals: 0.80 g (95%); mp 44-46 °C. After recrystallization from methanol the benzophenone melted at 47-48.5 °C (lit. mp 49 °C). The infrared spectrum matched that of an authentic sample.

**Me<sub>2</sub>SO/LICA Method.** To 50 mL of Me<sub>2</sub>SO was added 1.41 g (10 mmol) of isopropylcyclohexylamine, and then 5.5 mL of 1.8 M (9.9 mmol) butyllithium solution was slowly injected into the solution. A solution of 2.83 g (10 mmol) of phenylbenzhydrylacetonitrile in 50 mL of Me<sub>2</sub>SO was then added over 2 min. After the mixture was stirred 16 h at room temperature, the reaction workup was as above, but an acid wash to remove amine was added.

**2-(4-Chlorophenyl)-3-(4-methoxyphenyl)propanamide.** The Me<sub>2</sub>SO/K<sub>2</sub>CO<sub>3</sub> method above gave poor results; however, the reaction time and temperature were increased to 96 h and 100 °C with K<sub>2</sub>CO<sub>3</sub> as the base. The workup as above gave light yellow crystals: mp 166.5-167.5 °C; 78% yield (from methanol). The infrared spectrum did not show CN absorption but had peaks at 1680 (C=O) and at 3410 and 3530 (NH<sub>2</sub>) cm<sup>-1</sup>. Anal. Calcd for C<sub>16</sub>H<sub>16</sub>ClNO<sub>2</sub>: C, 66.32; H, 5.57; Cl, 12.23; N, 4.83. Found: C, 66.30; H, 5.72; Cl, 12.45; N, 4.79.

**Kinetic Data.** The reactions were run as in the general procedure for the preparation of benzophenone with the Me<sub>2</sub>SO/K<sub>2</sub>CO<sub>3</sub> method. At regular time intervals, a 3-mL aliquot was removed from the reaction mixture and added to 10 mL of distilled water. Extraction with portions of methylene chloride (3 × 10 mL) followed by overnight drying (Na<sub>2</sub>SO<sub>4</sub>), filtration, and concentration left a residue. This was dissolved in deuterated chloroform, and an NMR tracing, with integration, was obtained. The disappearance of the hydrogen on the α-carbon of the substrate nitrile at 5 ppm vs. time was noted. For each aliquot the ratio of aromatic hydrogens to methinyl hydrogen was plotted vs. reaction time by drawing the best straight line. In order to determine the half-life for a specific substrate, we prepared a 1:1 mixture of authentic nitrile/authentic ketone. The NMR inte-

gration ratio for the standard solution was used to read the half-life from the aliquots plot. The *t*<sub>1/2</sub> values for entries 7, 4, 5, 1, and 6 were 0.3, 1.8, 2.0, and 2.6 h, respectively.

**Registry No.** 1, 86-29-3; 1 (ketone), 119-61-9; 2, 7599-05-5; 2 (ketone), 1144-74-7; 3, 4578-79-4; 3 (ketone), 611-94-9; 4, 4578-80-7; 4 (ketone), 134-85-0; 5, 33268-46-1; 5 (ketone), 90-90-4; 6, 6974-49-8; 6 (ketone), 134-84-9; 7, 20968-04-1; 7 (ketone), 90-98-2; 8, 28694-90-8; 8 (ketone), 1137-41-3; 9, 4760-53-6; 9 (ketone), 61747-12-4; 10, 719-82-4; 10 (ketone), 345-83-5; 10 (ketone DNP hydrazone), 87184-37-0; 11, 5005-36-7; 11 (ketone), 91-02-1; 12, 5350-66-3; 12 (ketone), 1733-63-7; 13, 3333-14-0; 13 (ketone), 451-40-1; 14, 36770-81-7; 14 (ketone), 51490-05-2; 15, 5681-31-2; 15 (ketone), 1889-71-0; 16, 5422-48-0; 16 (amide), 87184-36-9; 17, 3893-23-0; 17 (ketone), 712-50-5; 18, 769-68-6; 18 (ketone), 93-55-0; 19, 5558-31-6; 19 (ketone), 582-62-7; 20, 16532-79-9; 20 (aldehyde), 1122-91-4; 21, 6306-60-1; 21 (aldehyde), 874-42-0; 22, 51965-61-8; 22 (ketone), 403-42-9; 23, 5558-29-2; 23 (ketone), 611-70-1; 24, 78-82-0; 24 (ketone), 67-64-1.

## Counteraction Effects on the Palladium-Catalyzed Allylation of Enolates<sup>1</sup>

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Our recent finding<sup>2</sup> that allylation of potassium enoxyborates, that are obtainable by the reaction of ketones with either KH or KN(SiMe<sub>3</sub>)<sub>2</sub> followed by treatment with BEt<sub>3</sub>,<sup>3</sup> can be markedly catalyzed by Pd-phosphine com-

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