Anal. Calcd. for $C_{10}H_{11}NO_3S$: C, 53.27; H, 4.92; N, 6.22; S, 14.24. Found: C, 53.47; H, 5.33; N, 6.15; S, 14.35.

Several sets of experimental conditions were tried to determine the procedure most appropriate for this compound. These are shown in Table I.

2-Mercapto-2-phenylethylamine (IIa). Anhydrous ether (1100 ml.) and 33.5 g. (0.8 mole) of lithium aluminum hydride were introduced into a 2-l. three-necked flask fitted with a sealed stirrer and a reflux condenser protected with a drying tube. The mixture was refluxed for 3 hr. Then the reflux condenser was replaced with a Soxhlet extractor containing a thimble packed with 45.2 g. (0.2 mole) of 1-phenyl-1-acetthio-2-nitroethane. The condenser of the Soxhlet extractor was also protected with a drying tube. Continuous extraction was carried out for 260 hr.; at the end of this time, 0.98 g. of the thio ester remained in the thimble. The reaction complex and unchanged lithium aluminum hydride were then hydrolyzed by the addition of 58 ml. of water introduced dropwise. Concentrated hydrochloric acid was added dropwise in the amount (66.3 ml., 0.8 mole) sufficient to form the salt with the lithium ion present but not with the alumina. Careful attention to the neutralization of the reaction mixture was found necessary, in order to extract the amphoteric mercaptoamine product with organic solvents. The mixture was filtered through an asbestos mat and the alumina precipitate was washed with several portions of ether. After evaporation of the filtrate to dryness, there remained 9.5 g. of pale yellow solid. Two recrystallizations from 95% ethanol gave 3.4 g. of white solid, m.p. 94–97°. The alumina residue above was placed in a Soxhlet extractor and extracted with ether for 50 hr. Evaporation of this extract gave an additional 14.9 g. of crude product. After one recrystallization from 95% ethanol three was obtained 9.0 g. of white solid, m.p. 95.5–97.5°; total yield 12.4 g. (41%). A sample, after further recrystallization from ethanol and vacuum sublimation, showed a m.p. of 97.5–98.5°. The mercaptan group was determined by oxidation to disulfide,[6] titrating samples iodometrically.

Anal. Calcd. for $C_8H_{11}NS$: Equiv. wt., 153.25. Found: 153, 149, 147.

Elemental quantitative analyses, as well as an infrared absorption peak at 1630 cm.$^{-1}$, indicated the presence of a small amount of bound carbon dioxide in all samples.

2-Mercapto-2-phenylethylamine hydrochloride. Dry hydrogen chloride was bubbled through an ether solution of the sublimed amine. The crude hydrochloride was collected in 98% yield by centrifugation, m.p. 160–161.5°. After two recrystallizations from isopropyl alcohol, the m.p. was 160.5–161.5°.

Anal. Calcd. for $C_8H_{12}ClNS$: C, 50.65; H, 6.38; Cl, 18.69; N, 7.38; S, 16.90. Found: C, 50.78; H, 6.15; Cl, 18.59; N, 7.25; S, 16.87.

Chlorodeoxypseudoephedrine hydrochloride.[7] This was prepared by reaction of l-ephedrine hydrochloride with thionyl chloride in chloroform, and recrystallized from ethyl alcohol, m.p. 196–197°, $[\alpha]_D^{25} + 119°$ (*C*, 1 water). Emde[7] reported a m.p. of 201°, $[\alpha]_D^{20} + 117°$.

3,4-Dimethyl-5-phenyl-2-iminothiazolidine hydrochloride (III). A mixture of 44 g. (0.2 mole) of chlorodeoxypseudoephedrine hydrochloride and 30.5 g. (0.4 mole) of thiourea in 500 ml. of absolute ethyl alcohol was heated under reflux for 88 hr. Upon cooling to room temperature, a white solid separated and was collected by filtration. This substance weighed 5.5 g., did not melt up to 300°, but started subliming at 140°. It was identified as ammonium chloride because of the ammonia odor evolved upon adding it to a cold sodium hydroxide solution and the white precipitate formed upon adding it to an acidified silver nitrate solution. The filtrate from the reaction mixture was evaporated to a gummy mass weighing 70.5 g. This was taken up in 200 ml of ice cold 5% sodium hydroxide solution and extracted five times with ether. The ether extract was dried over sodium sulfate, saturated with hydrogen chloride gas, and evaporated to dryness to obtain 46 g. of a gummy solid. Two recrystallizations from isopropyl alcohol gave 19.4 g. (40%) of white crystals melting at 245–247°. Another recrystallization from isopropyl alcohol left 12.3 g. (25%) of product, m.p. 246–247°.

Anal. Calcd. for $C_{11}H_{15}ClN_2S$: C, 54.42; H, 6.23; Cl, 14.60; N, 11.54; S, 13.21. Found: C, 54.62; H, 6.23; Cl, 14.46; N, 11.33; S, 12.99.

From a similar run involving 5.5 g. of chlorodeoxypseudoephedrine hydrochloride, 2.1 g. of thiourea, and 50 ml. of dimethyl sulfoxide, stirred at 40° for 32 hr., and then evaporated under reduced pressure at 85°, there was isolated 0.5 g. of ammonium chloride, 0.2 g. of sulfur, and 0.4 g. of cyclized product, m.p. 244–245°.

Mercaptodeoxyephedrine reineckate. 3,4-Dimethyl-5-phenyl-2-iminothiazolidine hydrochloride was hydrolyzed by refluxing for 24 hr. in 5% aqueous sodium hydroxide. The solution was neutralized, then extracted with ether. The ether solution was dried over sodium sulfate, and hydrogen chloride was passed into it. An oil separated which could not be crystallized, nor could the free base be crystallized, but treatment with a solution of reinecke salt gave a pink precipitate of the reineckate, m.p. 123–125°.

Anal. Calcd. for $C_{14}H_{22}CrN_7S_5$: C, 33.58; H, 4.43. Found: C, 33.99; H, 4.37.

COLLEGE OF PHARMACY
UNIVERSITY OF WASHINGTON
SEATTLE 5, WASH.

Alkylation Reactions in Dimethyl Sulfoxide[1]

JORDAN J. BLOOMFIELD[2]

Received April 3, 1961

In the course of other work it became necessary to prepare dimethylmalononitrile and 3,3-dimethyl-2,4-pentanedione. Although both of these compounds have been described the yields are either poor or unspecified.[3,4] We have found that in the usual solvents, *e.g.*, alcohol or benzene, the reaction of methyl iodide with 2,4-pentanedione pro-

---

[6] S. Siggia, *Quantitative Organic Analysis via Functional Groups*, J. Wiley and Sons, Inc., New York, 1949, p. 85.

[7] H. Emde, *Helv. Chim. Acta*, 12, 384 (1929).

[1] The author is grateful to Prof. C. S. Marvel for a postdoctoral appointment under a National Science Foundation Grant, G5906.

[2] Present address: Department of Chemistry, The University of Arizona, Tucson, Ariz.

(3)(a) Dimethylmalononitrile is prepared in about 30% yield by alkylation of the disilver or disodium salt of malononitrile with methyl iodide; B. C. Hesse, *Am. Chem. J.*, 18, 723 (1896). (b) Treatment of the diamide of dimethylmalonic acid with phosphorus pentoxide also affords dimethylmalononitrile, G. Errera and E. Berté, *Gazz. chim. ital.*, II, 26, 220 (1896). Both methods are general.

(4)(a) Alkylation of the sodium salt of 3-methyl-2,4-pentanedione with methyl iodide at 120–130° in a sealed tube for thirty-five hours gives 3,3-dimethyl-2,4-pentanedione, A. Combes and C. Combes, *Bull. soc. chim., France* [3], 7, 783 (1892). (b) Acylation of methyl isopropyl ketone with acetic anhydride and boron trifluoride gives 3,3-dimethyl-2,4-pentanedione in 28% yield; C. R. Hauser and J. T. Adams, *J. Am. Chem. Soc.*, 66, 345 (1944).

duces only the monomethyl derivative in low yield. When malononitrile is alkylated with an alkoxide as base the formation of imide esters is an important side reaction.[3a] This suggests the use of a nonnucleophilic base such as sodium hydride.[5] A relatively nonnucleophilic solvent capable of dissolving the intermediate salts is also desirable. The preparation of nitriles by alkylation of cyanide ion with dimethyl sulfoxide (DMSO) as solvent[6,7] and the report that the rate of alkylation of malonic esters is increased when dimethyl sulfoxide is used as a cosolvent[8,9] suggested dimethyl sulfoxide as solvent for these alkylation reactions.[11]

With the combination of dimethyl sulfoxide as solvent and sodium hydride as base the alkylation of malononitrile and of 2,4-pentanedione with methyl iodide, butyl bromide, or benzyl chloride gives the dialkylated derivatives in yields superior to those previously found.[14] Furthermore the reaction conditions are mild and reaction times are short. These conditions are best for alkylation of malononitrile, where good yields of pure or easily purified dialkyl derivatives are obtained. The reactions with secondary halides are not as satisfactory.

With 2,4-pentanedione the chief product is the 3,3-dialkyl derivative but there are varying amounts of the monoalkyl compound and other side products. The alkylation with benzyl chloride produced the unexpected product, 1,1-dibenzylacetone, probably as the result of a cleavage reaction which could have occurred during the reaction or during the work-up. Benzyl acetate was detected in the forerun and this suggests that the cleavage occurred during the reaction. A similar product may have been among the unidentified compounds detected in the butyl bromide reaction.

TABLE I

DIALKYLATION PRODUCTS OF MALONONITRILE AND 2,4-PENTANEDIONE

RX	$R_2C(CN)_2$, %	$R_2C(COCH_3)_2$, %
CH_3I	60	64
n-C_4H_9Br	75	28[a]
$C_6H_5CH_2Cl$	75	22[b]
i-C_3H_7Br	60[c]	—

[a] Determined by vapor chromatography on the reaction mixture. [b] Monobenzyl derivative, 17%, and 1,1-dibenzylacetone, 11%. [c] Based on vapor chromatographic analysis. The actually isolated, pure product, amounted to about 25%.

The ketonic products were characterized by their bis-2,4-dinitrophenylhydrazine derivatives.

EXPERIMENTAL[15]

Except for methyl iodide, the alkyl halides as well as the 2,4-pentanedione were distilled before use. Dimethyl sulfoxide, distilled at 18 mm. from calcium hydride, was stored in a tightly closed bottle. Malononitrile was distilled from phosphorus pentoxide. All the reactions were carried out under dry, oxygen-free nitrogen in a reaction apparatus which consisted of a 500-ml., three-neck flask fitted with a dropping funnel, Trubore stirrer, and condenser. The apparatus was oven-dried and assembled hot, under nitrogen. The products of the reaction were distilled through a 10-in. vacuum-jacketed, close-packed Vigreux column fitted with a total reflux head.

Dibenzylmalononitrile. Malononitrile, 16.5 g. (0.25 mole) dissolved in 45 ml. of dimethyl sulfoxide was added over 15 min. to a stirred slurry of sodium hydride, 12.0 g. (0.5 mole), in 75 ml. of dimethyl sulfoxide. The reaction mixture was stirred for another 15 min. with occasional cooling, then benzyl chloride, 63.2 g. (0.5 mole) was added over 20 min., with occasional cooling. The reaction mixture, after stirring at room temperature for 8.5 hr., was poured into 500 ml. of water and the curdy precipitate was filtered off, washed repeatedly with cold water, and air dried. This solid was crystallized from 400 ml. of hot 95% alcohol, with the aid of a charcoal treatment, and gave 39.0 g. (64.5%) of fine white needles, m.p. 131.8–132.5° (lit.[3b] m.p. 130°). Concentration of the mother liquor gave a second crop, 7 g. (11.4%) m.p. 122°.

Dibutylmalononitrile. The reaction was conducted as above using 68.5 g. (0.5 mole) of n-butyl bromide. The reaction mixture was stirred for a total of 2.5 hr. After the first 1.5 hr. 150 ml. of dry benzene was added to make the solution more fluid. A portion of the solution taken at this time was neutral to universal test paper. The reaction mixture was poured into 200 ml. of cold water and extracted once with 100 ml. of ether. The organic layer was washed with two 50-ml. portions of water and then dried over anhydrous magnesium sulfate. The solvent was removed and the residue was distilled at 18 mm. to give two fractions: (1) b.p. 118–131°, 5.8 g. (13%), n_D^{25} 1.4291 which vapor phase chromatography showed to

---

(5) In this work the sodium hydride used was a granular powder, not an oil dispersion. It was obtained from Metal Hydrides, Beverly, Mass.

(6) R. A. Smiley and C. Arnold, *J. Org. Chem.*, **25**, 257 (1960).

(7) L. Friedman and H. Schecter, *J. Org. Chem.*, **25**, 877 (1960).

(8) H. E. Zaugg, B. W. Horrom and S. Borgwardt, *J. Am. Chem. Soc.*, **82**, 2895 (1960).

(9) Since the completion of this work Cram[10] has pointed out the very great increases in the rate of proton abstraction reactions when dimethyl sulfoxide is used as a solvent or cosolvent.

(10) D. J. Cram, B. Rickborn, and G. R. Knox, *J. Am. Chem. Soc.*, **82**, 6412 (1960).

(11) Other solvents might have been chosen. For example, 2-ethoxyethyl ether and bis-2-ethoxyethyl ether have been shown greatly to increase the rate of reaction in the alkylation of the sodium enolates of butyrophenone.[12] The utility of dimethylformamide as a solvent for alkylations of enolates has been fully examined recently.[13]

(12)(a) H. D. Zook and T. J. Russo, *J. Am. Chem. Soc.*, **82**, 1258 (1960). (b) H. D. Zook and W. L. Gumby, *J. Am. Chem. Soc.*, **82**, 1386 (1960).

(13) H. E. Zaugg, D. A. Dunnigan, R. J. Michaels, L. R. Swett, T. S. Wang, A. H. Sommers, and R. W. De Net, *J. Org. Chem.*, **26**, 644 (1961).

(14) Dimethyl sulfate is not a satisfactory alkylating agent under these conditions. Substitution of dimethylformamide for dimethyl sulfoxide when dimethyl sulfate was used did permit isolation of 3-methyl-2,4-pentanedione in about 45% yield but no dimethyl derivative was found.

(15) Boiling points are uncorrected. Melting points were taken with total immersion-calibrated thermometers. Microanalyses were performed by Mr. J. Nemeth and his associates. Vapor phase chromatography was done on an Aerograph (Wilkens Instrument and Research, Inc.) using a carbowax column and a Varian recorder. Infrared spectra were determined on a Perkin-Elmer Model 21.

contain two components in the ratio of 11:12 and (2) b.p. 131–141°, 30.8 g. (69.2%), n_D^{24} 1.4310, one component by vapor phase chromatography. This fraction crystallized readily at −10 to 0° so the first fraction was crystallized four times from 10 ml. of ether at −80° and was finally distilled in a small Hickman still at 0.1 mm., bath temperature about 80°, to give an analytical sample, n_D^{24} 1.4313, n_D^{30} 1.4287.

Anal. Calcd. for $C_{11}H_{18}N_2$: C, 74.11; H, 10.17; N, 15.72. Found: C, 74.36; H, 10.20; N, 15.87.

The compound shows infrared absorption at 2940 (s), 2880 (s), 2260 (w) —C≡N, 1480 (s)—CH_2, 1385 (m)—CH_3, 1350 (w), 1275 (w), 1265 (w), 1175 (w), 1115 (w), and 1000 (m) cm.$^{-1}$ [6,17] The other component was not identified.

Dimethylmalononitrile. Reaction of 14.0 g. of malononitrile with excess methyl iodide under the conditions outlined above gave the product, 12 g. (60%), n_D^{25} 1.398, b.p. 52°/5 mm., m.p. 33.7–34.4 (lit.,[3a] m.p. 31–32°).

Anal. Calcd. for $C_5H_6N_2$: C, 63.78; H, 6.43; N, 29.8. Found: C, 64.27, H, 6.42; N, 29.8.

Diisopropylmalononitrile. Under the conditions previously described, the reaction mixture, which in the other reactions became only slightly colored, turned dark brown when the halide was added. When 0.75 mole of sodium hydride and 0.75 mole of *i*-propyl bromide were used with 0.5 mole of malononitrile, the contents of the flask set to a thick paste after one third to one half of the halide was added to the stirred slurry of hydride and malononitrile in 100 ml. of dimethyl sulfoxide. The remaining halide and an additional 50 ml. of dimethyl sulfoxide were added and the only slightly colored mass was heated for 2 hr. on the steam bath. Glacial acetic acid, 20 ml., was added in 100 ml. of petroleum ether (b.p. 60–68°) to decompose any unchanged hydride. The solution was cooled and poured into 100 ml. of water. The aqueous layer was extracted with two 150-ml. portions of ether, the combined organic solutions were washed with two 150-ml. portions of water and dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue was distilled at 18–20 mm. to give two fractions: (1) b.p. 88–95°, 1.8 g. (4.8%), two components in the ratio of 5:7 by vapor phase chromatography; (2) b.p. 95–102°, 24 g. (64%) two components in the ratio of 1:8. Redistillation of the combined fractions at atmospheric pressure gave six fractions. The first two fractions, b.p. 180–194°, contained as many as five components. The next to last fraction, b.p. 209–211°, 5.7 g. (15.2%), n_D^{24} 1.4278, had two components in ratio of 1:99. The last fraction, b.p. 211–213°, 8.9 g. (23.7%), n_D^{24} 1.4287, gave only a single peak upon vapor phase chromatography.

Anal. Calcd. for $C_9H_{14}N_2$: C, 71.95; H, 9.40; N, 18.65. Found: C, 71.73; H, 9.12; N, 19.01.

This fraction and the previous fraction had nearly identical infrared spectra with bands at 2960 (s), 2250 (w)—CN, 1465 (s)—CH_2?, 1395 (s) and 1375 (s)—$C(CH_3)_2$, 1330 (m)—CH—?, 1310 (m), 1165 (s)—$C(CH_3)_2$, 1120 (w), 1105 (w), 980 (m), 960 (m), and 890 (w) cm.$^{-1}$ [16–18]

3,3-Dimethyl-2,4-pentanedione. To a slurry of sodium hydride, 6 g. (0.25 mole) in dimethyl sulfoxide, 150 ml., was added 2,4-pentanedione, 25 g. (0.25 mole). After 30 min. methyl iodide, 40 g. (0.28 mole), was added to the cooled solution during 20 min. The temperature rose and the solution became clear. After stirring for 30 min. sodium hydride, 6 g., was added and after 15 min. (with occasional cooling) methyl iodide, 40 g., was added. The temperature rose as the methyl iodide was added and cooling was necessary. After 1 hr. a sample of the solution tested basic to universal indicator paper. Another 40 g. of methyl iodide was added and the solution was stirred for an additional 9 hr. Ether, 150 ml., was added and the solution was filtered, the salts were washed with two 75-ml. portions of ether, and the combined, pale yellow, ether solutions were washed with two 75-ml. portions of water and dried over anhydrous sodium sulfate. Distillation gave the product, b.p. 168–172°, 20.3 g. (63.5%) n_D^{23} 1.4289 (lit.[19]; $n_D^{27.8}$ 1.4262).[20]

Butyl bromide and 2,4-pentanedione. n-Butyl bromide, 83.5 g. (0.61 mole), was added during 20 min. to a stirred slurry of sodium hydride, 12 g. (0.5 mole), and 2,4-pentanedione, 25 g. (0.25 mole), in 100 ml. of dimethyl sulfoxide. The solution became viscous from the precipitated salts so 100 ml. of dry benzene was added and the solution was stirred and allowed to reflux on a steam bath for 30 min. and then cooled. Water, 100 ml., was added and after separation of layers the aqueous solution was extracted once with 100 ml. of ether. The combined organic solutions were washed with two 100-ml. portions of water, and dried over magnesium sulfate.

Distillation at 18 mm. gave a forerun, b.p. 30–108°, 2 g. (lachrymatory) and four major fractions: (1) b.p. 113–118°, 7.0 g., n_D^{26} 1.4480; (2) b.p. 119–125°, 6.4 g., n_D^{26} 1.4491; (3) b.p. 125–135°, 5.5 g., n_D^{26} 1.4498; (4) b.p. 135–150°, 15 g., n_D^{26} 1.4482. Fraction (4) in pentane was cooled to −80° and the white solid which formed was repeatedly crystallized from pentane, m.p. 11–12°. It was distilled at 20 mm., b.p. 136–142°, to give 9.3 g., n_D^{24} 1.4468. Vapor phase chromatography showed a single clean peak but analysis, even after several subsequent crystallizations and distillations, was low in both carbon and hydrogen. An analytically pure sample of 3,3-dibutyl-2,4-pentanedione was finally prepared by treatment of the compound with a saturated solution of copper(II) acetate. The mixture was filtered, the layers were separated and the organic residue was distilled in a small Hickman still under high vacuum with the bath temperature at 120°, n_D^{30} 1.4440.

Anal. Calcd. for $C_{13}H_{24}O_2$: C, 73.54; H, 11.39; Found: C, 73.63; H, 11.62.

The 2,4-dinitrophenylhydrazine derivative[21] was crystallized from ethyl acetate, m.p. 244.3–245° dec.

Anal. Calcd. for $C_{25}H_{32}N_8O_8$: C, 52.48; H, 5.64; N, 19.60. Found: C, 52.23; H, 5.23; N, 19.47.

The diketone has important infrared absorption bands at 2925 (s), 2850 (s), 1700 (s)—C=O, 1475 (s)—CH_2, 1370 (s)—CCH_3.

Vapor phase chromatography indicated that this dibutyl compound was present in about 28% yield in the combined distillates. The residue, after cooling the remaining fractions at −80°, showed five components according to vapor phase chromatography in the ratio of 1:1:1:2:1. The last component was unremoved dibutyl derivative. The major component of this residue, present in about 15% yield, was the monobutyl derivative. It was separated through its copper chelate, m.p. 183–185° (lit.,[22] m.p. 185–186°). The purified 3-butyl-2,4-pentanedione was distilled in a small Hickman still under high vacuum with the bath temperature at 100°, n_D^{30} 1.4388.

---

(16) A new band at 1705 cm.$^{-1}$, weaker than the —CN band, appeared after the sample had been stored for several months. This is undoubtedly due to partial hydrolysis. The remainder of the spectrum was virtually unchanged.

(17) Assignments are made according to L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, 2nd ed., John Wiley & Sons, Inc., New York, 1958.

(18) Analytical results on mixtures rich in this fraction are low in carbon and hydrogen and high in nitrogen. This makes it likely that the unknown component is the monoalkylated malononitrile.

(19) v. Auwers, *Ann.*, **415**, 224 (1918).

(20) A reaction on a similar scale in which the solvent was ethanol and the base was sodium methoxide gave only 17% of 3-methyl-2,4-pentanedione. When benzene was the solvent no product was obtained. *Cf.* ref. (14).

(21) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, 4th ed., John Wiley & Sons, Inc., New York, 1956, p. 219.

(22) F. G. Young, F. C. Frostick, Jr., J. J. Sanderson, and C. R. Hauser, *J. Am. Chem. Soc.*, **72**, 3635 (1950).

Anal. Calcd. for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.13; H, 10.23.

The 2,4-dinitrophenylhydrazine derivative[21] was crystallized from ethyl acetate-ethanol, m.p. 195.4–196.6°.

Anal. Calcd. for $C_{21}H_{24}N_8O_8$: C, 48.83; H, 4.68; N, 21.70. Found: C, 49.09; H, 4.78; N, 21.84.

Benzyl chloride and 2,4-pentanedione. Benzyl chloride, 63.2 g. (0.5 mole) was added during 20 min., with cooling as necessary, to a stirred slurry of sodium hydride, 12 g. (0.5 mole) and 2,4-pentanedione, 26 g. (0.25 mole) in 100 ml. of dimethyl sulfoxide. After 2.5 hr. the solution was still basic, but after an additional 1 hr. on a steam bath it was neutral. The solution was cooled and poured into 125 ml. of water. The top layer was dissolved in 500 ml. of ether and then filtered. The aqueous solution was extracted once with 100 ml. of ether and the combined organic solutions were washed with two 50-ml. portions of water. The solvent was evaporated to about 200 ml., 100 ml. of petroleum ether (b.p. 60–68°) was added, and the solution was put in a refrigerator over night. The buff solid, 14 g. (20%), was collected and after crystallization from a mixture of 100 ml. of petroleum ether and 75 ml. of benzene and then from pure petroleum ether, it had a m.p. of 113.2–113.4° (lit.,[23] m.p., 111–112°).

Anal. Calcd. for $C_{19}H_{20}O_2$: C, 81.35; H, 7.17. Found: C, 81.57; H, 7.24.

The 2,4-dinitrophenylhydrazine derivative[21] was crystallized from ethyl acetate, m.p. 252.0–253.5° dec.

Anal. Calcd. for $C_{31}H_{28}N_8O_8$: C, 58.12; H, 4.40; N, 17.50. Found: C, 58.28; H, 4.36; N, 17.00.

Cooling of the mother liquors at −80° gave another 1.8 g. (2.5%), m.p. 83–110°. The solvent was evaporated and the residue fractionated at 0.1 mm. to give six fractions: (1) b.p. 27–40°, 6.2 g., two components by vapor phase chromatography in the ratio of 1:3.4; (2) b.p. 40–78°, 1.0 g.; (3) b.p. 78–84°, 8.3 g., n_D^{24} 1.5308, vapor phase chromatography shows a small amount of the two components of the first fraction plus larger amounts of three other components; (4) b.p. 84–103°, 1.8 g., n_D^{24} 1.5363; (5) b.p. 103–125°, 6.6 g., n_D^{24} 1.5531[24] and (6) b.p. 125–140°, 0.8 g. There was a considerable quantity of a viscous orange polymeric material left in the pot.

By distillation at atmospheric pressure, infrared and vapor phase chromatography comparisons, the first fraction was determined to consist of a mixture of benzyl alcohol and benzyl acetate. No ketonic or aldehydic material was detected in this fraction. Fractions 3 and 4 were combined and treated with saturated copper(II) acetate solution to give the slate gray copper chelate of 3-benzyl-2,4-pentanedione, m.p. 203–205° (lit.,[25] m.p., 205–207°). A portion of the original fraction 3 was converted into the 2,4-dinitrophenylhydrazine derivative[21] of 3-benzyl-2,4-pentanedione which crystallized from ethyl acetate–ethyl alcohol as a bright red powder, m.p. 200.3–202.0°.

Anal. Calcd. for $C_{24}H_{22}N_8O_8$: C, 52.36; H, 4.03; N, 20.36. Found: C, 52.75; H, 4.12; N, 19.93.

The fifth fraction crystallized from pentane at −80° but melted too rapidly to allow collection. It was identified as 1,1-dibenzylacetone by its 2,4-dinitrophenylhydrazine derivative,[21] orange needles from alcohol, m.p. 124.6–125.8° (lit.,[26] m.p. 126–127°).

Anal. Calcd. for $C_{23}H_{22}N_4O_4$: C, 66.01; H, 5.30; N, 13.39. Found: C, 66.04; H, 5.46; N, 13.36, and by its infrared spectrum,[17] 1711 cm.$^{-1}$, C=O; 1456, 1370–1355 cm.$^{-1}$, —CH_3.

The other components of the reaction were not identified but it was possible to estimate yields of about 17% and 11%, respectively, for the monobenzyl-2,4-pentanedione and the dibenzylacetone from the vapor phase chromatography curves.

NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILL.

---

[23] G. T. Morgan and C. J. A. Taylor, *J. Chem. Soc.*, **127**, 797 (1925). These authors reported an over-all yield of about 12% based on alkylation of $NaCH(COCH_3)_2$ with benzyl chloride (39%) followed by alkylation of $(C_6H_5CH_2)CNa(COCH_3)_2$ with benzyl chloride (30%).

[24] J. M. Conia, *Ann. Chem.* [*Paris*], **8**, 709 (1953), gives a b.p. of 192–194°/15 mm. and n_D^{21} 1.5543 for 1,1-dibenzylacetone.

[25] C. R. Hauser and T. M. Harris, *J. Am. Chem. Soc.*, **80**, 6360 (1958).

[26] R. A. Barnes and B. D. Beitchman, *J. Am. Chem. Soc.*, **76**, 5430 (1954).

Formation of Some Organometallic Compounds in Phenyl Ether

HENRY GILMAN AND GERALD L. SCHWEBKE

Received March 13, 1961

A recent publication[1] reports that an attempt to prepare *n*-amylmagnesium bromide using phenyl ether as the solvent did not give the expected compounds, but instead there occurred a Friedel-Crafts reaction to give a coupling product. Grignard reagents have been prepared in various solvents.[2] Evans and Diepenhorst,[3] in studies of the photoluminescence of Grignard reagents, prepared the Grignard reagents of *o*-bromoanisole and of 2-bromocymene in phenyl ether, but did not give yields or experimental details. They may have used "special catalysts" as well as "heating for several hours in sealed tubes."

A difficulty which is present in the formation of organometallic compounds in the presence of aryl ethers is a tendency for metalation of the ether. Challenger and Miller[4] report that Grignard reagents in the presence of anisole and phenetole at elevated temperatures effect metalation of the ethers in the *ortho*-position in low yields. Dibenzofuran, a derivative of phenyl ether, is metalated by ethylmagnesium bromide in the 4-position.[5] The metalation of phenyl ether is effected much more readily with organolithium compounds.[6]

In the course of an investigation of the preparation of organolithium compounds in phenyl ether, it was observed that *n*-butyllithium does form, but the extent to which it forms and then metalates the solvent reduces its usefulness. Methyllithium and phenyllithium apparently did not form

---

[1] G. S. Handler, *J. Org. Chem.*, **24**, 1339 (1959).

[2] M. S. Kharasch and O. Reinmuth, *Grignard Reactions of Nonmetallic Substances*, Prentice-Hall, Inc., New York, N. Y., 1954, pp. 45–53.

[3] W. V. Evans and E. M. Diepenhorst, *J. Am. Chem. Soc.*, **48**, 715 (1926).

[4] F. Challenger and S. Miller, *J. Chem. Soc.*, 894 (1938).

[5] H. Gilman and A. Haubein, *J. Am. Chem. Soc.*, **67**, 1033 (1945).

[6] K. Oita and H. Gilman, *J. Am. Chem. Soc.*, **79**, 339 (1957). See also, H. Gilman and S. Gray, *J. Org. Chem.*, **23**, 1476 (1958).