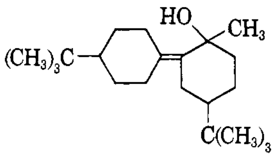
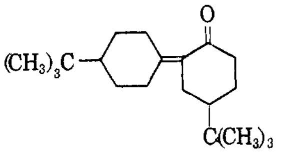
residue from this distillation was sublimed (25° at 0.1 mm.) for 48 hr. to separate the bulk of the volatile products, 4-*t*-butylcyclohexanone and the stereoisomeric 4-*t*-butyl-1-methylcyclohexanols. The residue from this sublimation was recrystallized from cyclohexane to separate a white crystalline solid melting over the range 139–190° which exhibited a single broad peak when examined by gas chromatography.[14] Since we were unsuccessful in obtaining a single pure substance from the high molecular weight material, the spectra of the mixture were examined. The mixture has infrared absorption[15] at 3580 and 3450 cm.$^{-1}$ (unassocd. and assocd. OH) with no absorption in the 6-μ region attributable to a carbonyl function. The n.m.r. spectrum[12] has a singlet at δ 0.82 (CH_3–C<) with broad, partially resolved absorption in the region 1.0–1.8 but no evidence of absorption at lower field indicative of vinyl protons. The mass spectrum[16] was particularly informative, exhibiting the highest peak at $m/e = 306$ (M^+) with high mass fragment peaks at 291 ($M - 15$), 288 ($M - 18$), 273 ($M - 15 - 18$, abundant), 249 ($M - 57$, abundant), and 231 ($M - 57 - 18$, abundant), and an intense peak at $m/e = 57$. These data are most easily accommodated by one or more of the stereoisomers of the structure **4** which would be expected to arise by an initial aldol condensation of 4-*t*-butylcyclohexanone with itself to form the ketone **5** followed by reaction with the methylmagnesium species present in solution.



4



5

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(14) A column packed with silicone gum, No. SE-30, suspended on Chromosorb W was employed.

(15) Determined as a solution in chloroform.

(16) Determined with a CEC, Model 21-103, mass spectrometer.

Some New Condensation Products in the Reaction of Diethylmagnesium with Benzonitrile

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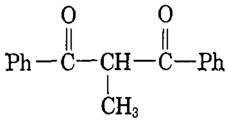
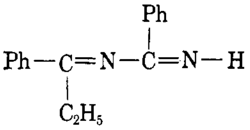
We wish to report three new condensation products from the reaction of diethylmagnesium with benzonitrile. While condensation products are well known in the reactions of alkylmagnesium compounds with nitriles, these have heretofore been observed only when either the nitrile[2] or the Grignard reagent[3] is unsaturated or when the nitrile contains active α-hydrogen atoms.[4-8] Trimerization of the nitrile to form an *s*-triazine has also been observed.[9]

From the reaction between diethylmagnesium and benzonitrile in tetrahydrofuran, when the ratio of available ethyl groups to benzonitrile was 1 or smaller, 1,3-diphenyl-2-methyl-1,3-propanedione (I) and 5-methyl-2,4,6-triphenylpyrimidine (III) were isolated. From the same reactants in ethyl ether a substance which appears to be N-(α-ethylbenzal)benzamidine (II) as well as the pyrimidine (III) were isolated. I was assumed to have formed by hydrolysis of the corresponding bisketimine salt initially formed in the reaction mixture. The origin of the bisketimine salt is reasonably represented as an aldol-type of condensation in the "nitrogen system." To our knowledge this type of reaction has been observed only once previously. Ectors[10b] has isolated 3,4,5-triphenyl-Δ^2-pyrazoline as a product in the reaction of benzylmagnesium chloride with benzonitrile. It is likely that this product is formed by attack of a salt similar to B upon another molecule of benzonitrile, followed by cyclization.



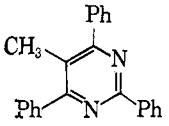
$$\mathrm{Ph{-}\overset{\substack{O\\\|}}{C}{-}\underset{\substack{|\\CH_3}}{CH}{-}\overset{\substack{O\\\|}}{C}{-}Ph}$$

I

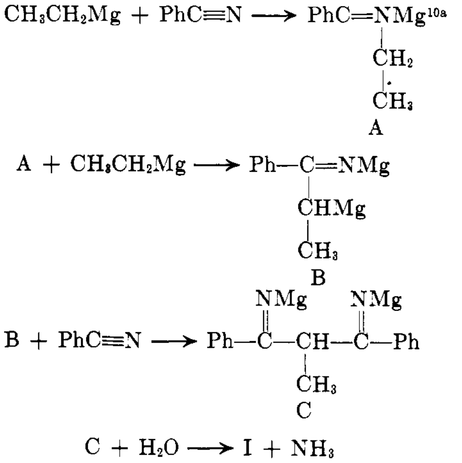


$$\mathrm{Ph{-}\underset{\substack{|\\C_2H_5}}{C}{=}N{-}\overset{\substack{Ph\\|}}{C}{=}N{-}H}$$

II



III



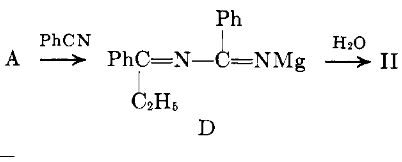
$$\mathrm{CH_3CH_2Mg + PhC{\equiv}N \longrightarrow \underset{\substack{|\\CH_2\\|\\CH_3\\A}}{PhC}{=}NMg^{10a}}$$

$$\mathrm{A + CH_3CH_2Mg \longrightarrow Ph{-}\underset{\substack{|\\CHMg\\|\\CH_3\\B}}{C}{=}NMg}$$

$$\mathrm{B + PhC{\equiv}N \longrightarrow Ph{-}\overset{\substack{NMg\\\|}}{C}{-}\underset{\substack{|\\CH_3\\C}}{CH}{-}\overset{\substack{NMg\\\|}}{C}{-}Ph}$$

$$\mathrm{C + H_2O \longrightarrow I + NH_3}$$

Formation of the benzamidine, II, is readily understood as arising from the addition of A to a second molecule of benzonitrile to give a new salt D.[11] Hydrolysis of D gives II.



$$\mathrm{A \xrightarrow{PhCN} \underset{\substack{|\\C_2H_5}}{PhC}{=}N{-}\overset{\substack{Ph\\|}}{C}{=}NMg \xrightarrow{H_2O} II}$$

D

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(1) (a) This material was abstracted from part of the doctoral dissertations of N. M. B. (1961) and A. A. S. (1965) presented to the Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements of their Ph.D. degrees. (b) To whom inquiries should be sent.

(2) H. R. Henze and L. R. Swett, *J. Am. Chem. Soc.*, **73**, 4918 (1951).

(3) H. R. Henze, G. L. Sutherland, and G. D. Edwards, *ibid.*, **73**, 4915 (1951).

(4) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall Co., Inc., New York, N. Y., 1954, pp. 774–776, 782–783.

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(6) J. Decombe, *Compt. rend.*, **234**, 2542 (1952).

(7) M. Pretot and J. Decombe, *ibid.*, **244**, 1512 (1957).

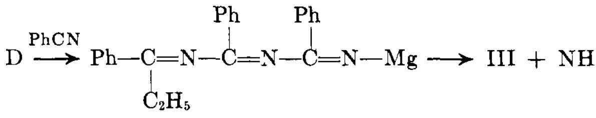
(8) F. F. Blicke and E. P. Tsao, *J. Am. Chem. Soc.*, **75**, 5587 (1953).

(9) J. D. Citron and E. I. Becker, *Can. J. Chem.*, **41**, 1260 (1963).

(10) (a) The second valence of magnesium is unspecified. (b) E. Ectors, *Bull. soc. chim. Belges.*, **33**, 146 (1924).

(11) J. J. Ritter and R. D. Anderson [*J. Org. Chem.*, **24**, 208 (1959)] assumed a similar type of condensation in the polymerization of benzonitrile with sodium.

III may be visualized as an addition of D to a third molecule of benzonitrile followed by cyclization, with the loss of ammonia.[12]



$$D \xrightarrow{PhCN} Ph-\underset{C_2H_5}{\underset{|}{C}}=N-\overset{Ph}{\overset{|}{C}}=N-\overset{Ph}{\overset{|}{C}}=N-Mg \longrightarrow III + NH_3$$

Experimental

1,3-Diphenyl-2-methyl-1,3-propanedione (I).—Diethylmagnesium (5.8 mmoles) and benzonitrile (27.0 mmoles) in 32 ml. of tetrahydrofuran were allowed to react in a closed reaction vessel for 1 week at room temperature, followed by heating on a steam bath for 40 hr. The brick red solution was decomposed in saturated ammonium chloride and extracted with ether. The ether solution was then extracted with 10% sodium bisulfite. After decomposition of the bisulfite solution, extraction with ether, and evaporation of the ether, a solid residue was obtained, which was recrystallized from 1:1 hexane–pentane to give 0.22 g. (18.3% based on benzonitrile) of colorless product melting at 81.0–82.3°. An analytical sample prepared by recrystallization from ethanol melted at 83.4–84.7° (lit.[13] m.p. 82.5–84°).

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.88, 80.86; H, 5.99, 5.73.

The infrared absorption spectrum contained a doublet at 1689 and 1667 cm.$^{-1}$. The n.m.r. spectrum contained a quartet at τ 5.74–5.76 (J = 5.9 c.p.s.) and a doublet at 8.45–8.56 (J = 5.9 c.p.s.). The aromatic proton absorption appeared as two multiplets at τ 2.15–2.38 and 2.66–2.85. The relative areas of the quartet, doublet, and two aromatic multiplets were 1:3:4:6, respectively. The melting point of I was not depressed when admixed with an authentic sample of I prepared by the alkylation of dibenzoylmethane with methyl iodide.

5-Methyl-2,4,6-triphenylpyrimidine (III).—The ether layer which remained after the extraction with sodium bisulfite in the preparation of I was concentrated to 30 ml. and, upon addition of 50 ml. of methanol, the crude solid precipitated, m.p. 167–175°. Recrystallization from ether afforded 0.98 g. (34.4% based on benzonitrile) of colorless crystals, m.p. 179.0–180.3°. An additional recrystallization from ether gave the analytical sample, m.p. 180.0–181.4° (lit.[12] m.p. 182°).

Anal. Calcd. for $C_{23}H_{18}N_2$: C, 85.68; H, 5.63; N, 8.69. Found: C, 85.85; H, 5.72; N, 8.27.

The n.m.r. spectrum contained a singlet at τ 7.70 as well as multiplets in the aromatic region at 1.68–1.76, 2.42–2.63, and 2.66–2.90. The relative areas of these peaks were 3:2:4:9, respectively. The infrared absorption spectrum contained a strong peak at 1538 cm.$^{-1}$.

A gas which was evolved when the reaction vessel above was opened was isolated on a vacuum manifold and identified as ethane by vapor phase chromatography on a Perkin-Elmer Vapor Fraktometer Model 154 using a J column. The retention time was identical with that of authentic ethane at 25°.

N-(α-Ethylbenzal)benzamidine (II). A.—To the diethylmagnesium[14,15] prepared from 14.2 g. (0.130 mole) of ethyl bromide and 1.6 g. (0.065 g.-atom) of magnesium in 200 ml. of ethyl ether, there was added 6.7 g. (0.065 mole) of benzonitrile. The solution turned yellow and a slight precipitate developed. After stirring the reaction mixture for 2 days at room temperature, 20 ml. of water was added and the mixture was filtered. The combined organic layers were evaporated to dryness. Distillation of the residue afforded 8.2 g. (0.062 mole, 95%) of propiophenone ketimine, b.p. 92–96° (7.3 mm.), $n^{22}D$ 1.5475 [lit.[16] b.p. 101.5–102.5° (13.5 mm.), $n^{22}D$ 1.5476].

B.—The above reaction was run with 0.085 mole of diethylmagnesium and 0.17 mole of benzonitrile (1 ethyl group/benzonitrile). After decomposition of the reaction mixture in water, it was extracted with ether. Upon evaporation of the ether, crystals were obtained which were white after washing with ether. The white solid weighed 3.6 g. (18%) and melted at 139–140°. An analytical sample obtained by recrystallization from aqueous methanol melted at 140.0–140.4°. The infrared spectrum showed bands at 3310 and 3470 (N–H) and at 1575–1650 cm.$^{-1}$ (C=N—Ph).

Anal. Calcd. for $C_{16}H_{16}N_2$: C, 81.32; H, 6.83; N, 11.86. Found: C, 80.89, 81.32, 80.88; H, 6.97, 7.11, 6.88; N, 11.54, 11.69, 11.62.

Attempts to prepare this compound from benzamidine and propiophenone failed. When the mother liquor from the above preparation was distilled *in vacuo*, 2.9 g. (13%) of propiophenone, b.p. 35–36° (8 mm.), $n^{25}D$ 1.6293, was isolated. The nondistillable residue was a thick, orange oil which hardened to a glass upon standing. The glass was insoluble in water, 5% sodium bicarbonate, 5% sodium hydroxide, 6 *N* NaOH, and 2 *N* HCl, but it did dissolve in concentrated hydrochloric acid.

Trituration of the "glass" with methanol dissolved the orange material leaving white crystals, m.p. 182–183°. The infrared spectrum of this material was identical with that of III.

1-(2,4-Dinitrophenyl)-3,5-diphenyl-4-methylpyrazole.—A solution of I, 0.886 g. (3.72 mmoles), in 50 ml. of ethanol was combined with a hot solution of 0.737 g. (3.68 mmoles) of 2,4-dinitrophenylhydrazine in 150 ml. of ethanol containing 10 ml. of concentrated hydrochloric acid. After cooling, 1.21 g. of yellow solid, m.p. 180–182°, was obtained by filtration. Recrystallization from 175 ml. of ethanol afforded 1.09 g. (67.0%) of yellow crystals, m.p. 183.2–185.0°. An analytical sample, prepared by recrystallization from ethanol, melted at 183.3–185.1°.

Anal. Calcd. for $C_{22}H_{16}N_4O_4$: C, 65.99; H, 4.03; N, 13.99. Found: C, 65.91; H, 3.65; N, 13.76.

Acknowledgment.—We acknowledge the generous support of part of this work by the National Science Foundation under its Grant G-14558 (A. A. S.) and by the American Cyanamid Company (N. M. B.). We also acknowledge the synthesis of 1,3-diphenyl-2-methyl-1,3-propanedione by Mr. William Greenberg.

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(12) R. M. Anker and A. H. Cook [*J. Chem. Soc.*, 323 (1941)] isolated 2-ethyl-2,4,6-triphenyl-1,2-dihydrotriazine from the reaction between ethyllithium and benzonitrile. When they heated the heterocycle at 250–300°, it was converted to III.

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(14) S. J. Stofer and E. I. Becker, *J. Org. Chem.*, **27**, 1868 (1962).

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Halogenation of Aromatic Compounds by N-Bromo- and N-Chlorosuccinimide under Ionic Conditions

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In the extensive literature involving N-halosuccinimides and related N-halo compounds, there appears to have been only one investigation of ring substitution by N-haloimides or -amides in aromatic compounds not containing highly active groups.[1] Schmid[2] found that benzene and toluene gave fair yields of their respective monobromo derivatives with N-bromosuccinimide (NBS) and aluminum chloride, but poor yields (together with polysubstituted products) following long reflux with NBS and zinc or iron(III) chlorides, or with NBS and concentrated sulfuric acid.

Our work in which *t*-butyl hypochlorite was used in aqueous sulfuric acid to attack aromatic compounds resulted in excellent yields of ring-chlorinated products,[3] but announcement of the results was anticipated

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[1] *I.e.*, aromatic compounds without hydroxy or amino groups or their derivatives.

[2] H. Schmid, *Helv. Chim. Acta*, **29**, 1144 (1946).

[3] We thank Paul J. Shlicta, Ted W. Reid, David A. Keefer, and Jerry D. Albert for extensive experimental work in developing this area, and the National Science Foundation for its support under G-2386 and under the Undergraduate Research Participation Program (G-1226).