[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

The Addition of Dialkylamino- and Alkylaminomagnesium Halides to α-Phenylcinnamonitrile

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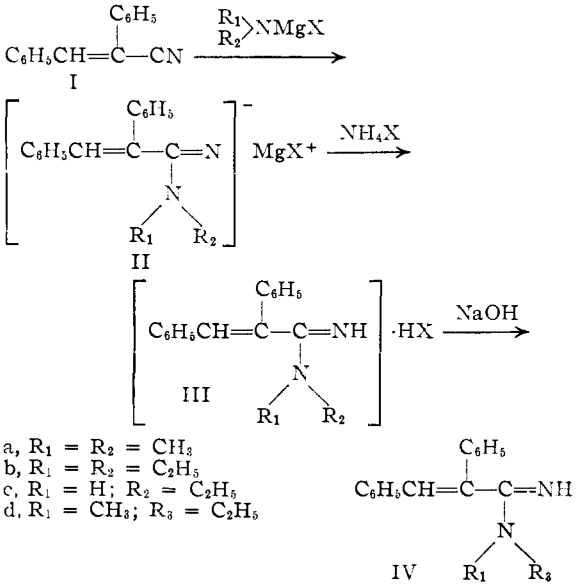
RECEIVED OCTOBER 30, 1954

Dimethylaminomagnesium iodide, diethylaminomagnesium bromide, diethylaminomagnesium iodide and ethylaminomagnesium iodide react with α-phenylcinnamonitrile and form amidines. The intermediate complex could not be alkylated further with alkyl halides to the trialkylamidines. The amidine structure was demonstrated with N,N-dimethyl-α-phenylcinnamamidine by catalytic reduction to 1-dimethylamino-2,3-diphenylpropane and pyrolysis to α-phenylcinnamonitrile.

Alkylmagnesium halides have been found to add to α-arylcinnamonitriles in a 1,4-manner and to give complexes which can be hydrolyzed to α,β-diphenyl-β-alkylpropionitriles[2,3] and alkylated with alkyl halides on the carbon atom alpha to the nitrile group.[2,4] The similarity in behavior of alkylaminomagnesium halides with many organic compounds to that of the usual Grignard reagents suggested a study of the reaction of the former with α-phenylcinnamonitrile (I).

The reaction of dimethylaminomagnesium iodide, diethylaminomagnesium bromide, diethylaminomagnesium iodide and ethylaminomagnesium iodide with α-phenylcinnamonitrile was found to proceed differently from that of the alkylmagnesium halides and to give addition in a 1,2-manner. The product in each case after decomposition of the intermediate complex II was an amidine IV. This type of addition already has been observed with simpler nitriles.[5,6]

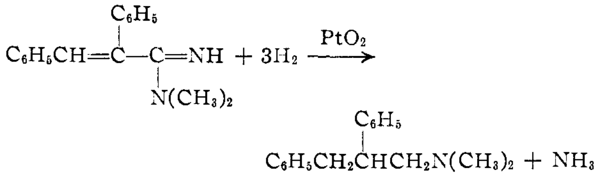


$$C_6H_5CH{=}C(C_6H_5){-}CN\ (\mathrm{I}) \xrightarrow{R_1R_2NMgX} \left[C_6H_5CH{=}C(C_6H_5){-}C(NR_1R_2){=}N\right]^- MgX^+\ (\mathrm{II}) \xrightarrow{NH_4X} \left[C_6H_5CH{=}C(C_6H_5){-}C(NR_1R_2){=}NH\right]\cdot HX\ (\mathrm{III}) \xrightarrow{NaOH} C_6H_5CH{=}C(C_6H_5){-}C(NR_1R_3){=}NH\ (\mathrm{IV})$$

a, $R_1 = R_2 = CH_3$
b, $R_1 = R_2 = C_2H_5$
c, $R_1 = H$; $R_2 = C_2H_5$
d, $R_1 = CH_3$; $R_3 = C_2H_5$

Only in the reaction with diethylaminomagnesium bromide was there any indication of 1,4-addition; two products were isolated. The isomeric compound, however, was not obtained in large enough amounts to be characterized.

The amidine structure was demonstrated conclusively using N,N-dimethyl-α-phenylcinnamamidine (IVa) as an example. Reduction catalytically using platinum oxide gave mainly 1-dimethylamino-2,3-diphenylpropane which had been prepared previously from 1,1-dimethyl-3-phenyl-1,2,3,4-tetrahydroquinolinium chloride.[7] The products (IVb, IVc) from diethylaminomagnesium iodide and from ethylaminomagnesium iodide must have similar amidine structures since their ultraviolet spectra are identical with that of the dimethylamino derivative IVa.



$$C_6H_5CH{=}C(C_6H_5){-}C(N(CH_3)_2){=}NH + 3H_2 \xrightarrow{PtO_2} C_6H_5CH_2CH(C_6H_5)CH_2N(CH_3)_2 + NH_3$$

The N,N-dimethyl (IVa), N,N-diethyl (IVb) and N,N-methylethylamidines underwent typical amidine decomposition when pyrolyzed and gave α-phenylcinnamonitrile (I). The N-ethylamidine (IVc) was stable under these conditions but could be decomposed in the same manner by using its hydroiodide.

Attempts to form the N,N,N^1-trialkylamidine by alkylating the complex from diethylaminomagnesium bromide and diethylmagnesium iodide (IIb) with ethyl bromide and ethyl iodide, respectively, did not occur even though a color change was observed in the complex. Decomposition of the solution with ammonium chloride gave a mixture of the hydrobromide and hydrochloride of the amidine IIIb for the former and the hydroiodide IIIb with the latter. Steric factors were apparently not important in preventing this alkylation since the complexes from dimethylaminomagnesium iodide and ethylaminomagnesium iodide likewise were not affected by methyl iodide. In the attempted alkylation of the ethylaminomagnesium iodide addition product IIc the reaction was further complicated by the insolubility of the complex. To overcome this difficulty methyl iodide was added in one run immediately following the addition of α-phenylcinnamonitrile (I) without any intermediate reflux period. The product under these conditions was the N,N-methylethylamidine (IVd) and resulted from the addition of methylethylaminomagnesium iodide, formed by the interaction of methyl iodide with ethylaminomagnesium iodide, to α-phenylcinnamonitrile. The formation of

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[1] Abstracted in part from the Ph.D. Thesis, August, 1953, of Robert R. Nagler, du Pont Fellow, 1951-1952.

[2] E. P. Kohler, *Am. Chem. J.*, **35**, 386 (1906).

[3] S. Wawzonek, THIS JOURNAL, **73**, 5746 (1951).

[4] S. Wawzonek, *ibid.*, **68**, 1157 (1946).

[5] R. Hullin, J. Miller and W. Short, *J. Chem. Soc.*, 394 (1948).

[6] E. Lorz and R. Baltzly, THIS JOURNAL, **70**, 1904 (1948).

[7] J. v. Braun, J. Seeman and A. Schultheise, *Ber.*, **55**, 3803 (1922).

methylethylamine in this manner actually was demonstrated and is similar to the reported formation of a tertiary amine from benzyl-*n*-butylaminomagnesium bromide and *n*-butyl bromide.[6]

The N,N-ethylmethylamidine (IVd) also was synthesized by treating N-ethyl-α-phenylcinnamamidine (IVc) with methyl iodide in ether and decomposing the hydroiodide formed with alkali. The unsymmetrical structure of this compound was indicated by its pyrolysis to α-phenylcinnamonitrile.

Experimental[8]

N,N-Diethyl-α-phenylcinnamamidine (IVb).—To a solution of diethylaminomagnesium iodide prepared by adding diethylamine (29.3 g.) to ethylmagnesium iodide (0.3 mole) in ether (350 ml.) was added solid α-phenylcinnamonitrile[9] (41 g.) in small amounts. The resulting greenish-brown mixture was refluxed for 16 hours and then treated with ammonium chloride in ice-water. The hydroiodide formed was filtered and dried; yield 51 g. (70%), m.p. 238–244° dec. After three crystallizations from water the sample melted at 258–260° dec.

Anal. Calcd. for $C_{19}H_{23}N_2I$: C, 56.16; H, 5.70. Found: C, 56.38; H, 5.51.

This solid was dissolved in hot water and treated with alkali. The amidine which was liberated, melted at 85–87°. A dry ether solution gave with anhydrous hydrogen chloride the amidine hydrochloride melting at 215–218°. Fractional crystallization from a mixture of ethanol–ethyl acetate gave two compounds in a ratio of approximately 20:1. The amidine hydrochloride IIIb present in the larger amount melted at 220–221°.

Anal. Calcd. for $C_{19}H_{23}N_2Cl$: C, 72.40; H, 7.35; N, 8.91. Found: C, 72.18; H, 7.13; N, 8.52.

The isomeric compound present in the smaller amount melted at 251–252°. A mixture of equal amounts of the two compounds melted at 201–204°.

Anal. Calcd. for $C_{19}H_{23}N_2Cl$: C, 72.40; H, 7.35. Found: C, 72.13; H, 7.29.

The amidine IVb liberated from the 220–221° hydrochloride melted at 86–87°: absorption λ_{max} 294 mμ (ε 82900) in 95% ethanol.

Anal. Calcd. for $C_{19}H_{22}N_2$: C, 81.96; H, 7.97; N, 10.07. Found: C, 81.53; H, 8.17; N, 10.43.

The amine liberated from the 251–252° melting hydrochloride melted at 63–64°. A mixture of the two products melted at 52–56°.

Anal. Calcd. for $C_{19}H_{22}N_2$: C, 81.96; H, 7.97; N, 10.09. Found: C, 81.47; H, 8.14; N, 10.29.

Studies on the Attempted Alkylation of the Grignard Complex.—The Grignard addition product prepared as above when refluxed with ethyl iodide (109.3 g.) for 36 hours and then decomposed with ammonium chloride solution gave the hydroiodide of the amidine IVb (47 g., 64%) melting at 258–260° dec. after three crystallizations from water.

The use of diethylaminomagnesium bromide and ethyl bromide in place of the corresponding iodides gave a mixture of the hydrobromide and the hydrochloride of the amidine IVb (28 g.) (60%), m.p. 221–225°. Recrystallization three times from a mixture of absolute ethanol and (100–140°) petroleum ether and once from water gave the pure hydrobromide melting at 233–235°.

Anal. Calcd. for $C_{19}H_{23}N_2Br$: C, 63.50; H, 6.46; Br, 22.24. Found: C, 63.33; H, 6.39; Br, 22.22.

N,N-Dimethyl-α-phenylcinnamamidine (IVa).—Using conditions similar to those given for the formation of N,N-diethyl-α-phenylcinnamamidine (IVb) except for using methylmagnesium iodide to prepare the dimethylaminomagnesium iodide, N,N-dimethyl-α-phenylcinnamamidine hydroiodide (IIIa) was formed (71.5 g., 92%) m.p. 276–283° dec. Several crystallizations from water gave only one compound melting at 291–292° dec.

Anal. Calcd. for $C_{17}H_{19}N_2I$: C, 53.99; H, 5.06; N, 7.41. Found: C, 53.93; H, 4.93; N, 7.66.

The free amidine was recrystallized from a mixture of water and acetone and melted at 99–100°; absorption λ_{max} 296 mμ (ε 44500) in 95% ethanol.

Anal. Calcd. for: $C_{17}H_{18}N_2$: C, 81.56; H, 6.82; N, 11.19. Found: C, 81.31; H, 7.38; N, 11.27.

The hydrochloride crystallized from a mixture of ethyl alcohol and ethyl acetate and melted at 275–276° dec.

Anal. Calcd. for $C_{17}H_{19}N_2Cl$: C, 71.19; H, 6.68; N, 9.32. Found: C, 71.17; H, 6.57; N, 9.85.

An attempted alkylation of the intermediate magnesium complex with methyl iodide for various periods of time was unsuccessful and gave the hydroiodide of the unchanged amidine.

N-Ethyl-α-phenylcinnamonitrile (IVc).—Ethylaminomagnesium iodide prepared from ethylamine (32.7 ml.) and methylmagnesium iodide (0.3 mole) in ether (350 ml.) was freed from excess amine by refluxing for 16 hours and then treated with α-phenylcinnamonitrile (41 g.). The blue-black solid which formed immediately turned into a viscous solid which stopped the stirrer upon refluxing for 16 hours. Decomposition with ammonium iodide and ice gave the hydroiodide (55 g.) melting at 183–183.5°. Recrystallization from water did not change the melting point.

Anal. Calcd. for $C_{17}H_{19}N_2I$: C, 53.99; H, 5.06; N, 7.41. Found: C, 53.95; H, 5.10; N, 7.75.

The free amidine melted at 124–125°; absorption λ_{max} 293 mμ (ε 79400).

Anal. Calcd. for $C_{17}H_{18}N_2$: C, 81.56; H, 7.25; N, 11.19. Found; C, 81.32; H, 6.99; N, 11.54.

An attempted alkylation of the above viscous complex with methyl iodide was unsuccessful and gave the hydroiodide of the amidine (IIIc).

N,N-Ethylmethyl-α-phenylcinnamamidine (IVd).—The addition of methyl iodide (85.2 g.) to the more fluid blue-black complex, obtained immediately by adding ethylaminomagnesium iodide to α-phenylcinnamonitrile, gave after refluxing for 20 hours an amber-colored viscous intermediate. Decomposition with ammonium iodide and ice gave a hydroiodide (28 g.) melting at 248–263° dec. The ether layer yielded the starting material (21 g.). Fractional crystallization of the hydroiodide from water gave a sample melting at 269–271° dec.

Anal. Calcd. for $C_{18}H_{21}N_2I$: C, 55.17; H, 5.39; N, 7.14. Found: C, 54.96; H, 5.26; N, 7.33.

N-Ethyl-α-phenylcinnamamidine (IVc) (1.25 g.) when refluxed with methyl iodide (2.5 g.) in ether (50 ml.) for 24 hours gave a solid (1.7 g.) melting at 230–260°. Two crystallizations from water gave a sample which melted at 268–269° dec. and which did not lower the melting point of the sample isolated from the Grignard reaction.

The amidine liberated with alkali after two crystallizations from (60–70°) petroleum ether melted at 65–68°.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 81.78; H, 7.63. Found: C, 80.87; H, 7.55.

Ethylaminomagnesium iodide when refluxed with methyl iodide in ether gave methylethylamine which was characterized as its hydrochloride.

Catalytic Reduction of N,N-Dimethyl-α-phenylcinnamamidine.—N,N-Dimethyl-α-phenylcinnamamidine (IVa) (5 g.) in ethanol (100 ml.) was treated with hydrogen under 45 pounds pressure in the presence of platinum oxide (0.2 g.). The resulting solution which had a strong ammonia smell gave an oil upon removal of the solvent. The oil was taken up in ether and extracted with dilute hydrochloric acid. At this point a small amount of solid (0.14 g.) separated which after two crystallizations from ethyl acetate melted at 220–223°. This solid from the elementary analysis proved to be di-(β,γ-diphenylpropyl)-amine hydrochloride.

Anal. Calcd. for $C_{30}H_{32}NCl$: C, 81.54; H, 7.25. Found: C, 81.47; H, 7.39.

The hydrochloric acid solution was neutralized with alkali and shaken with benzenesulfonyl chloride. The oil which did not react with this reagent amounted to 1.85 g. and formed a picrate in ether melting at 201–202.5° after one crystallization from ethyl acetate.

Anal. Calcd. for $C_{23}H_{24}N_4O_7$: C, 58.97; H, 5.13. Found: C, 58.64; H, 5.06.

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[8] Melting points are not corrected.

[9] S. Wawzonek and E. H. Smolin, *Org. Syntheses*, **29**, 83 (1949).

This amine had all the properties of 1-dimethylamino-2,3-diphenylpropane.[7] It formed a methiodide which was hygroscopic. The methochloride formed a chloroplatinate melting at 244–247° dec. and a gold salt melting at 167–169°. The literature[7] reports melting points of 236 and 164°, respectively, for these two compounds.

Pyrolysis of α-Phenylcinnamamidines.—All three N,N-dialkyl-α-phenylcinnamamidines (IV) (2 g.) when distilled at reduced pressure (10–20 mm.) at 180–200° gave α-phenylcinnamonitrile (1.0–1.3 g.).

N-Ethyl-α-phenylcinnamamidine (IVc) distilled practically unchanged at 250–280° under reduced pressure (30 mm.). The hydroiodide (3.5 g.) under similar conditions gave α-phenylcinnamonitrile (1.8 g.).

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Methylphenoxyacetylene and Phenoxypropadiene

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RECEIVED OCTOBER 18, 1954

Methylphenoxyacetylene and phenoxypropadiene have been prepared and characterized. The methylphenoxyacetylene was synthesized by the reaction between sodium phenoxyacetylide and methyl iodide. The phenoxypropadiene was prepared by the dehydrobromination of 2-bromo-1-phenoxy-1-propene. Both compounds appear to be stable toward acetylenic–allenic rearrangement under normal preparative and storage conditions.

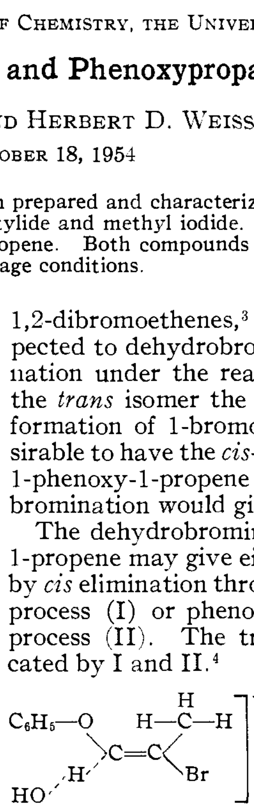
Phenoxyacetylene, ethylphenoxyacetylene and butylphenoxyacetylene have been reported in the literature,[1] but there is no reference to the preparation of either methylphenoxyacetylene or its allenic isomer phenoxypropadiene. Because of the current interest in acetylenic–allenic rearrangements, these two compounds have been prepared.

Methylphenoxyacetylene was formed by the reaction between sodium phenoxyacetylide and methyl iodide in liquid ammonia. The methyl phenoxyacetylene was characterized by its physical properties and molecular refraction (Table I) and by its infrared spectrum (Fig. 1). Its spectrum contains the characteristic —C≡C— stretching frequency at 4.44 μ and does not contain the 5.1 μ absorption characteristic of allenes.[2] The methylphenoxyacetylene apparently does not undergo acetylenic–allenic rearrangement under normal handling conditions, but does decompose quite rapidly at room temperature. Spectral evidence indicated the presence of a phenolic –OH group, probably formed by hydrolysis of the methylphenoxyacetylene. Under rigorously maintained anhydrous conditions, the compound should show a greater stability.

Phenoxypropadiene was prepared by the dehydrobromination of 2-bromo-1-phenoxy-1-propene. This bromide was formed by the reaction between potassium phenoxide and *trans*-1,2-dibromo-1-propene. In this latter reaction it is possible to form either 2-bromo-1-phenoxy-1-propene or 1-bromo-2-phenoxy-1-propene or a mixture of the two. Only one compound was formed, 2-bromo-1-phenoxy-1-propene, and its formation involved the primary bromine atom as would be expected in a reaction between an organic halide and the salt of an organic acid. The absence of the 1-bromo-2-phenoxy-1-propene was confirmed by the fact that the product could be dehydrobrominated.

trans-1,2-Dibromo-1-propene was used instead of either the *cis* isomer or a mixture of the *cis* and *trans* isomers to reduce the side reaction of dehydrobromination to 1-bromo-1-propyne. By analogy to the 1,2-dibromoethenes,[3] the *cis* isomer would be expected to dehydrobrominate readily by *trans* elimination under the reaction conditions. Even with the *trans* isomer the yield was low because of the formation of 1-bromo-1-propyne. It was also desirable to have the *cis*-(H,Br) derivative of 2-bromo-1-phenoxy-1-propene so that subsequent dehydrobromination would give phenoxypropadiene.

The dehydrobromination of 2-bromo-1-phenoxy-1-propene may give either methylphenoxyacetylene by *cis* elimination through a carbanion-intermediate process (I) or phenoxypropadiene by a concerted process (II). The transition states may be indicated by I and II.[4]



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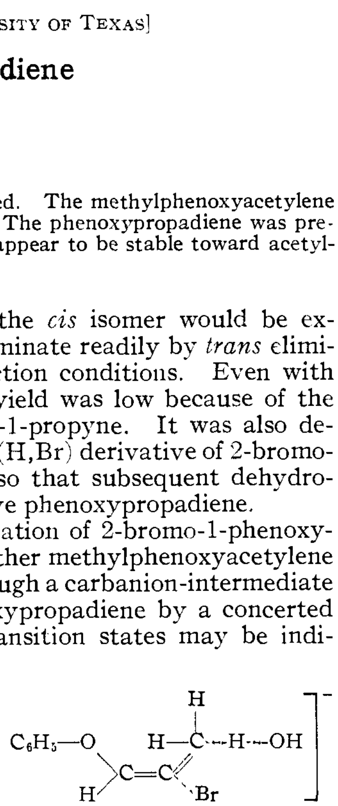

II

By analogy to the conclusions of Cristol and Norris in respect to the dehydrobromination of *cis*- and *trans*-*p*-nitro-β-bromostyrene[4d] the presence of the aryloxy group on the number 1 carbon atom should favor the dehydrohalogenation by a carbonion-intermediate process by decreasing the negative charge on this carbon atom. The rapid concerted process involving a hydrogen atom of the methyl group still should be the predominant reaction, however.

The phenoxypropadiene was characterized by its physical properties and molecular refraction (Table I) and infrared spectrum (Fig. 1). The spectrum has the 5.12 μ absorption of the allene system and does not contain an absorption characteristic of an acetylene.

Acknowledgment.—This research was supported by the United States Air Force under Contract No. AF 18(600)-430. Monitored by Hq., Air Research and Development Command, P. O. Box 1395, Baltimore 3, Md.

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(1) T. L. Jacobs, R. Cramer and F. T. Weiss, THIS JOURNAL, **62**, 1849 (1940).

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(4) (a) S. J. Cristol, THIS JOURNAL, **69**, 338 (1947); (b) S. J. Cristol, N. L. Hause and J. S. Meek, *ibid.*, **73**, 674 (1951); (c) S. J. Cristol and A. Begoon, *ibid.*, **74**, 5025 (1952); (d) S. J. Cristol and W. P. Norris, *ibid.*, **76**, 3005 (1954).