and washed well with ice-water. One crystallization from aqueous alcohol with Norite decolorization gave 28.9 g. (94%) of brilliant, slender white needles of the aldehyde, m. 104.0–104.5°.

Anal. Calcd. for $C_{28}H_{24}O_4$: C, 79.22; H, 5.70. Found: C, 79.09; H, 5.83.

Gallaldehyde tribenzyl ether could not be smoothly debenzylated in the presence of alcoholic acids to yield gallaldehyde, or in the presence of acetic anhydride–hydrochloric acid, to yield gallaldehyde triacetate, due to extensive decomposition.

Gallaldoxime Tribenzyl Ether.—The oxime was prepared by treating the aldehyde with hydroxylamine hydrochloride in pyridine–absolute alcohol solution,[7] and crystallizing the product from benzene and from alcohol as long, slender white needles (from alcohol), m. p. 140.0–140.5°.

Anal. Calcd. for $C_{28}H_{25}O_4N$: C, 76.52; H, 5.73. Found: C, 76.35; H, 5.97.

Gallaldehyde Tribenzyl Ether 2,4-Dinitrophenylhydrazone.—To 10 ml. of a saturated solution of 2,4-dinitrophenylhydrazine in glacial acetic acid was added 100 mg. of the aldehyde, the mixture was refluxed for fifteen minutes, and the insoluble hydrazone filtered hot. The crude product was washed on the filter with warm glacial acetic acid and with three 15-ml. portions of hot alcohol. Crystallization from a large volume of acetone gave small, brilliant scarlet needles, m. p. 214.0–214.5°.

Anal. Calcd. for $C_{34}H_{28}O_7N_4$: C, 67.54; H, 4.67. Found: C, 67.48; H, 4.87.

2',4'-Dihydroxy-3,4,5-tris-benzyloxychalcone (V).—A mixture of 5.0 g. (0.012 mole) of gallaldehyde tribenzyl ether, 1.82 g. (0.012 mole) of resacetophenone, 40 ml. of alcohol, and 10 g. of 50% potassium hydroxide solution was refluxed on the steam-bath for two hours, and then allowed to stand overnight. The deep red reaction product was poured into 150 ml. of ice water, the mixture was acidified to litmus with dilute hydrochloric acid, filtered and the precipitate was washed well with water. After three crystallizations from ligroin (Norite) and two recrystallizations from dilute alcohol, there was obtained 1.87 g. (28%) of small, light yellow needles, m. p. 160–161°.

Anal. Calcd. for $C_{36}H_{30}O_6$: C, 77.40; H, 5.41. Found: C, 77.48; H, 5.64.

Summary

The preparation of gallaldehyde tribenzyl ether involving an improved procedure for benzylation has been described. Gallaldehyde tribenzyl ether has been condensed with resacetophenone to yield the corresponding chalcone.

LOS ANGELES, CALIF. RECEIVED SEPTEMBER 28, 1942

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(7) Shriner and Fuson, "Identification of Organic Compounds," 2nd ed., John Wiley and Sons, New York, N. Y., p. 167.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Tertiary Alkyl Primary Amines, $RR'R''CNH_2$. II

BY HENRY R. HENZE, BRUCE B. ALLEN[1] AND WILLIAM B. LESLIE

Utilization of the Grignard reaction through interaction of a nitrile and an organomagnesium halide has long been a standard procedure for the preparation of ketones. Hence, the failure[2] to obtain the anticipated ketone from reaction between ethoxyacetonitrile and allylmagnesium bromide was a distinct surprise; the product was shown to be a carbinamine of structure $C_2H_5OCH_2C(CH_2CH{=}CH_2)_2NH_2$. Equally surprising was the discovery that the ketimine formed from ethoxyacetonitrile and *n*-propylmagnesium bromide was able to react with allylmagnesium bromide to yield, after hydrolysis, another carbinamine, $C_2H_5OCH_2C(CH_2CH_2CH_3)(CH_2CH{=}CH_2)NH_2$. We have continued our study of this reaction to ascertain whether it is limited to utilization of alkoxynitriles.

In the present investigation it is clear that allylmagnesium bromide is able to react not only with alkoxyalkyl cyanides, but also with alkyl cyanides, with aralkyl cyanides, and with alkenyl cyanides to yield the corresponding carbinamines, $RR'R''CNH_2$. Likewise, allylmagnesium bromide has been caused to react with the addition product formed from interaction of *n*-butoxyacetonitrile and *n*-butylmagnesium bromide to produce another carbinamine.

Experimental

Preparation of Alkyl-, Alkoxyalkyl-, Aralkyl- and Alkenyldiallylcarbinamines.—The tertiary alkyl primary amines of these types were prepared from essentially those proportions of Grignard reagent and organic cyanide, and by the method previously described,[2] namely, one molar equivalent of a nitrile was caused to react with two molar equivalents of allylmagnesium bromide under anhydrous conditions, and then the resulting addition product was decomposed with ammonium chloride solution. The cyanides employed were *n*-butoxyacetonitrile,[3] *n*-butyronitrile,

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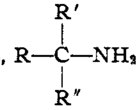
[1] Present address: Tubize-Chatillon Co., Rome, Ga.

[2] Allen and Henze, THIS JOURNAL, 61, 1790 (1939).

[3] This nitrile was obtained by the method of Gauthier [*Compt. rend.*, 143, 831 (1906)] from cuprous cyanide and *n*-butyl chloromethyl ether, the latter being formed when *n*-butanol, formaldehyde and dry hydrogen chloride were combined according to the procedure of Henry [*Bull. soc. chim.*, [2] 44, 458 (1885)]. The nitrile was purified by distillation under diminished pressure, b. p. 79° (30 mm.),

TABLE I

TERTIARY ALKYL PRIMARY AMINES, R—C—NH2



$$R\text{—}\overset{R'}{\underset{R''}{\overset{|}{\underset{|}{C}}}}\text{—}NH_2$$

	—R[a]	—R′	R″	Yield, %	B. p., °C. (cor.)	Mm.	d^{20}_4	n^{20}_D	γ^{20}	Mol. refract. Calcd.	Mol. refract. Found
1	Allyl	Allyl	Allyl	52	182.0–183.5	741	0.8445	1.4732	26.92	50.40	50.26
2	Propyl	Allyl	Allyl	30	190.0–191.0	742	.8282	1.4592	25.90	50.87	50.59
3	*n*-Butyl	Allyl	Allyl	56	205.0–206.0	742	.8288	1.4589	26.47	55.49	55.18
4	Benzyl	Allyl	Allyl	43	268.5 (dec.)	742	.9499	1.5320	32.72	65.74	65.67
5	*n*-Butoxymethyl	Allyl	Allyl	59	233.0–234.0	742	.8623	1.4542	26.38	61.75	61.98
6	*n*-Butoxymethyl	*n*-Butyl	Allyl	54	247.5–248.5	742	.8489	1.4458	26.13	66.83	67.02
7	Propyl	Propyl	Propyl		190.5–191.5	742	.7976	1.4358	25.05	51.80	51.57

	Parachor Calcd.	Parachor Found	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	M. p.,[b] °C. (cor.)	Nitrogen, %[b] Calcd.	Nitrogen, %[b] Found
1	420.8	407.9	79.42	79.38	11.33	11.37	173.5–174.5	14.73	14.69
2	431.8	417.5	78.36	78.27	12.49	12.52	149.0–149.5	14.65	14.69
3	470.8	457.2	78.97	79.26	12.65	12.40	121.5–122.0	14.14	14.08
4	526.7	506.9	83.53	83.71	9.51	9.50	139.5–140.0	12.93	12.80
5	529.8	518.6	73.04	73.33	11.75	11.86	106.5–107.0	13.05	13.15
6	579.8	568.4	73.18	73.15	12.76	13.02	79.0– 80.0	12.58	12.47
7	453.8	441.2	76.36	76.11	14.74	15.20	154.0–154.5	14.50	14.47

[a] R represents group present initially in nitrile. [b] Data for picrate of corresponding carbinamine.

n-valeronitrile, phenylacetonitrile and allyl cyanide. Addition of the cyanide was regulated so that there was a slow but regular refluxing of the solvent throughout the process. In addition to the heat effect, reaction was indicated by a progressive change in the color of the solution from the usual gray to one of olive-green; in the case of the alkoxynitrile the addition product separated as a greenish-gray oil. Completion of reaction was attempted by refluxing the mixtures over a hot-plate for three hours previous to hydrolysis. After pouring into a chilled, saturated ammonium chloride solution, the ether solution of the carbinamine (colored yellow or red) was removed, was washed with water, and dried over anhydrous sodium sulfate. In each instance, after the solvent had been removed, the carbinamine was purified by refractionation *in vacuo*.

The amines, which are of pronounced and characteristic odor (resembling that of molding wood), are all colorless oils and are readily converted into solid picrates. The latter, separating immediately when a sulfurous acid solution of the amine is treated with a saturated aqueous solution of picric acid, were found to be purified best by three crystallizations from diluted alcohol. Some of the more important physical constants and the analytical data for these amines and their picrates appear in Table I.

Preparation of Allyl-*n*-butoxymethyl-*n*-butylcarbinamine.—Twenty-eight and four-tenths grams (0.28 mole) of *n*-butoxyacetonitrile, dissolved in an equal volume of anhydrous ether, was added to the Grignard reagent produced from 6.7 g. (0.28 gram atom) of magnesium turnings, 40.8 g. (0.30 mole) of *n*-butyl bromide, and 200 cc. of anhydrous ether in the usual manner. Then to the ether suspension of the cream-colored addition product was added rapidly and with vigorous stirring an ether solution of allylmagnesium bromide which had been prepared independently from 27 g. (1.11 gram atoms) of magnesium turnings, 44.8 g. (0.37 mole) of allyl bromide and 280 cc. of dry ether. During the three-hour period following completion of this addition, throughout which the mixture was stirred and warmed over a hot-plate, there was noted a gradual change of the cream colored solid to an insoluble greenish-gray oil. Hydrolysis of the latter yielded the crude amine which was purified by repeated rectification under diminished pressure.

Preparation of Tri-*n*-propylcarbinamine.—(A) The solution of 4.8 g. (0.032 mole) of triallylcarbinamine in 25 cc. of acetone was shaken for thirty-six minutes in the presence of 0.5 g. of the Adams catalyst and hydrogen under atmospheric pressure and at room temperature. From the decrease in hydrogen pressure occurring during this period, it was noted that 0.095 mole of hydrogen had been utilized. The crude amine was purified by distillation *in vacuo*; b. p. 47–48° (5 mm.); d^{20}_4 0.7967; n^{20}_D 1.4353; *MR* calcd. 51.80; *MR* found 51.43.

(B) Eight grams of diallyl-*n*-propylcarbinamine was hydrogenated in an equal volume of ethanol, using 0.2 g. of the Adams catalyst and a hydrogen pressure of 1.3 atmospheres at 27°. Reduction was rapid and 92% of the theoretical quantity of hydrogen was taken up. The product distilled at 80–81° (15 mm.) and 190.5–191.5° (742 mm.); d^{20}_4 0.7976; n^{20}_D 1.4358; *MR* calcd. 51.80; *MR* found 51.57.

Summary

1. Further investigation of the abnormal reaction previously observed between allylmagnesium bromide and alkoxynitriles has yielded data proving that this reaction is not limited to utilization of alkoxynitriles. By means of this reaction it has been found possible to synthesize tertiary alkyl primary amines from cyanides of the alkyl, aralkyl, alkenyl and alkoxyalkyl types.

2. Again, allylmagnesium bromide has been

caused to react with the addition product resulting from interaction of another Grignard reagent with a nitrile.

AUSTIN, TEXAS RECEIVED OCTOBER 13, 1942

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Structural Effects of Unsaturation and Hyperconjugation in Aldehydes, Nitriles and Chlorides as Shown by their Dipole Moments in the Vapor State

BY EVERETT C. HURDIS AND CHARLES P. SMYTH

Formaldehyde has hitherto been the only first member of an important homologous series, the dipole moment of which has not been determined. In spite of the difficulties created by its ease of polymerization, it has, therefore, seemed desirable to investigate it and higher members of its series in order to study the effects of induction and resonance in the series. The part played by unsaturation in such effects was then studied by measuring crotonaldehyde and the investigation was extended to the unsaturated nitriles. Because of the similarity of chloride to nitrile, isocrotyl chloride was measured. The results of measurements upon diketene vapor carried out in connection with the question of its structure are included because of its relation to the aldehydes.

The dielectric constants of the vapors were measured with the apparatus and technique previously described.[1-4] The measurements were made by the "extrapolation method," in which the effects of deviations from the gas laws were eliminated by measurement over a wide range of pressure, or by the "two-point method," in which the dielectric constant was measured at two pressures only. The absolute accuracy of the method has been shown by previously published checks[4] of values established by other work. It is close to the relative accuracy evident in the data in Table I.

Preparation and Purification of Materials

Formaldehyde.—Monomeric liquid formaldehyde was prepared by the method of Spence and Wild[5] in an all-glass generator connected to the gas apparatus.

Acetaldehyde.—Material from the General Chemical Company was purified by fractional distillation under vacuum in an all glass trap system connected to the gas apparatus.

Propionaldehyde.—Material from the Paragon Testing Laboratories was dried over calcium chloride and fractionally distilled in an atmosphere of nitrogen, b. p. 47.6° (748 mm.).

***n*-Butyraldehyde.**—Material from the Paragon Testing Laboratories was fractionally distilled in an atmosphere of nitrogen, b. p. 74.4° (741 mm.).

Crotonaldehyde.—Material from the Paragon Testing Laboratories was fractionally distilled in an atmosphere of nitrogen, b. p. 101.0° (743 mm.),

Diketene.—Material which had been purified by distillation and re-crystallization was very kindly given us by Dr. F. O. Rice of Catholic University.

Propionitrile.—Two hundred grams of material from the Eastman Kodak Company was dried over calcium chloride and fractionally distilled, b. p. 96.9° (747 mm.).

Acrylonitrile.—Two hundred grams of material from the American Cyanamid Company was dried over calcium chloride and fractionally distilled, b. p. 77.3° (750 mm.); n^{22}_D 1.3907; density at 22°, 0.8076.

***trans*-Crotononitrile.**—Crotonaldoxime was prepared from crotonaldehyde by the method of Schindler.[6] Dehydration of the oxime according to Dollfus[7] resulted in 37 g. of material boiling between 114 and 124°. This sample was fractionally distilled in a column of fourteen theoretical plates and the main fraction (18 g.) with boiling range 120.1 to 120.9° (762 mm.) was used for the measurements. Density at 22° was 0.8183, n^{22}_D 1.4214, MR^{22}_D 20.79. Heim[8] gives b. p. 122.0° (755 mm.), MR^{15}_D 20.75, MR^{30}_D 20.81. (The *cis* form boils at 107.5°.)

Iso-crotyl Chloride.—Two hundred grams of material from the Eastman Kodak Company was fractionally distilled in a column of 14 theoretical plates; b. p. 66.9° (757 mm.); density at 25°, 0.9144; n^{25}_D 1.4198.

Experimental Results

The results of individual runs are given in Table I for the polarization, P, for all the substances. Where the use of the two-point method of measurement increased the error in individual P values, several runs were made at each temperature and the average of the P values, P_{av}, was used instead of a single value to calculate the moment, μ, listed in the last column. The molar

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[1] McAlpine and Smyth, THIS JOURNAL, **55**, 453 (1933).

[2] deBruyne and Smyth, *ibid.*, **57**, 1203 (1935).

[3] Wiswall and Smyth, *J. Chem. Phys.*, **9**, 352 (1941).

[4] Hurdis and Smyth, THIS JOURNAL, **64**, 2829 (1942).

[5] Spence and Wild, *J. Chem. Soc.*, 338 (1935).

[6] Schindler, *Sitzber. Akad. Wiss. Wien Math.-naturw.Klasse*, **100**, II-B, 361 (1891).

[7] Dollfus, *Ber.*, **25**, 1920 (1892).

[8] Heim, *Bull. soc. chim. belg.*, **42**, 461 (1933).