action of methylmagnesium iodide with mesitoyl chloride. The yield of this material was 4% based on the acid chloride used. The material which could not be sublimed weighed 3 g.

When phenylmagnesium bromide was added to mesitoyl chloride (in the absence of cobaltous chloride), only 2,4,6-trimethylbenzophenone was isolated. The yield was 90%, based on the acid chloride used.

Reactions of Methylmagnesium Bromide and Mesitoyl Chloride in the Presence of Cobaltous Chloride.—The procedure was similar to that previously described, except that the Grignard reagent was mixed with the catalyst in a flask cooled in an ice–salt bath, and the dropping funnel into which the mixture was siphoned was equipped with a cold-finger filled with a mixture of ice and salt. Mesitoyl chloride (0.06 mole), methylmagnesium bromide (0.15 mole) and cobaltous chloride (0.0075 mole) were used. The reaction mixture was worked up in the usual manner. The quantities of the products formed are recorded in Table IV.

A total of 1700 cc. (corrected to standard) of gas was collected. The first 500 cc. of this gas was rejected. The molecular weight of the gas contained in the second 500 cc. was 19.4, and the unsaturation amounted to 10%. The gas analyses were made by the method of Kharasch, Lewis and Reynolds.[7]

When methylmagnesium bromide was added to mesitoyl chloride in the absence of cobaltous chloride, an 87% yield of 2,4,6-methylmesityl ketone was obtained; there was only a trace of the substituted benzil.

Reaction of Methylmagnesium Iodide and Mesitoyl Chloride.—In all experiments with these reagents, the concentrations and proportions of reactants, as well as the rate of addition and the manner of working up the products, were the same as previously described. The isolation procedure was similar to that of Fuson and Corse. The results of the experiments are given in Tables I, II, III and IV.

In the experiments in which metallic halides were used, the metal halide was usually added to the Grignard reagent; the resulting mixture was added to the mesitoyl chloride dissolved in ether. In the cobaltous, copper and iron chloride experiments, the Grignard reagent turned almost black; when manganous chloride was used, the solution remained clear and colorless.

Summary

1. In the reaction between mesitoyl chloride and methylmagnesium iodide it has been shown that: (a) the order of addition of the reactants is important; (b) light and small amounts of oxygen have no effect upon the reaction; (c) the use of pure magnesium in making the Grignard reagent and aging of the reagent made from ordinary magnesium give higher yields of 2,4,6,2′,4′,6′-hexamethylbenzil; (d) traces of the halides of iron, copper, and manganese limit the reaction to the normal addition; (e) small amounts of cobaltous chloride increase the yield of the substituted benzil, as is also the case when methylmagnesium bromide is used.

2. A mechanism has been proposed to account for the products of the reaction of mesitoyl chloride with Grignard reagents.

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[CONTRIBUTION FROM THE CENTRAL RESEARCH LABORATORIES OF THE MONSANTO CHEMICAL COMPANY]

Unsaturated Esters of Glycolonitrile

BY DAVID T. MOWRY

In aqueous solution a mixture of formaldehyde and sodium cyanide reacts like glycolonitrile and sodium hydroxide.

$$\mathrm{CH_2O + NaCN + H_2O \rightleftarrows HOCH_2CN + NaOH}$$

With benzoyl chloride a typical Schotten–Baumann reaction occurs to give cyanomethyl benzoate[1] in 45% yields.

$$\mathrm{C_6H_5COCl + HOCH_2CN + NaOH \longrightarrow C_6H_5COOCH_2CN + NaCl + H_2O}$$

In extending this reaction we have found that good yields (53–73%) of cyanomethyl esters of α,β-unsaturated acids can be obtained from the corresponding acid chlorides. Acrylyl chloride, however, gives poor yields because of a side reaction leading to the formation of an ester, $C_6H_9O_3N$, the structure of which has not yet been established. Furthermore, dibasic acid chlorides, such as fumaryl chloride, give only insignificant yields of diesters by the aqueous method. These esters are satisfactorily prepared by the method of Hechenbleikner[2] in which the acid chloride is treated with glycolonitrile in anhydrous ether in the presence of a tertiary amine.

Inasmuch as it has been observed[3] that acetyl chloride gives low yields in the Schotten–Baumann reaction, it is not surprising that the method is of little value for the preparation of cyanomethyl esters of saturated aliphatic acids. A better procedure appears to be the reaction of the sodium salt of the acid with chloroacetonitrile.[4] The properties of the unsaturated esters are reported in Table I.

Experimental

Reagents.—The methacrylyl, crotonyl, cinnamoyl and α-methylcinnamoyl chlorides were prepared by the action of thionyl chloride on the acids. Acrylyl chloride was prepared in 27% yields by the action of phosphorus oxychloride on sodium acrylate[5] and in 35% yield by dehydrohalogenation[6] of β-chloropropionyl chloride over alumina at 250°. β-Chlorocrotonyl chloride was obtained from ethyl acetoacetate and phosphorus pentachloride.[7] Fu-

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(1) Aloy and Rabaut, *Bull. soc. chim.*, [4] **13**, 457 (1913).

(2) Hechenbleikner, U. S. Patents 2,266,199 (1941), 2,307,649 (1943).

(3) Menalda, *Rec. trav. chim.*, **49**, 967 (1930).

(4) Henry, *Bull. soc. chim.*, [2] **46**, 42 (1886); *Rec. trav. chim.*, **24**, 170 (1905).

(5) Moureu, *Ann. chim.*, [7] **2**, 145 (1894).

(6) Fikentsher, U. S. Patent 2,050,752 (1936).

(7) Shriner and Keyser, THIS JOURNAL, **60**, 286 (1938).

TABLE I

Cyanomethyl ester of	Method	Yield, %	B. p. °C.	B. p. Mm.	M. p., °C.	n^{25}D	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found
Acrylic acid	A	17	60	4	..	1.4331	54.05	53.75	4.54	4.87	12.62	12.57
Methacrylic acid	A	58	90–91	10	..	1.4390	57.60	57.66	5.64	5.66	11.20	11.38
Crotonic acid	A	60	103–104	17	..	1.4482	57.60	57.81	5.64	5.90	11.20	11.38
β-Chlorocrotonic acid	A	53	116	16	..	1.4797	45.15	45.37	3.78	3.87	8.98	8.64
Cinnamic acid	A	73	164–165	4	63	....	70.57	70.69	4.84	4.75	7.48	7.63
	B	75										
α-Methylcinnamic acid	A	63	162–163	3	..	1.5669	71.62	72.36	5.52	5.73	6.96	6.87
Fumaric acid	B	45	.....	..	83	....	49.50	49.68	3.11	3.02	14.43	14.38
Mesaconic acid[a]	B	43	192–193	3	..	1.4815	51.92	52.50	3.87	3.98	13.46	13.42

[a] Prepared by Dr. W. Frederick Huber.

maryl and mesaconyl chlorides were made from maleic anhydride and phthalyl chloride.[8]

Glycolonitrile.—A modification of the cyanohydrin interchange method[9] was used for the preparation of glycolonitrile.

To a concentrated aqueous solution of 1040 g. of sodium bisulfite was added 720 g. (10.0 moles) of methyl ethyl ketone with stirring and cooling by addition of ice. A solution of 520 g. of 95% sodium cyanide was then added in a similar manner. The resultant supernatant oil was separated and mixed with 871 g. of 37% formalin, to which 5 g. of sodium cyanide had been added. After this solution had been stirred at 35° for two hours, 30 g. of phthalic anhydride was added and the material distilled. The regenerated ketone and water were removed at 100 mm. The product was then rapidly distilled at 20–30 mm. (slight decomposition), b. p. 100–120°. When the distillation was about two-thirds completed, the residue became very viscous. The flame had to be removed and the flask cooled immediately to avoid violent dissociation and polymerization caused by superheating. The crude product was refractionated without decomposition over 5 g. of phthalic anhydride, giving 228 g. (40% yield) of glycolonitrile, b. p. 99–100° (17 mm.), n^{25}D 1.4090.

Cyanomethyl Acrylate (Method A).—Acrylyl chloride (233 g., 2.6 moles) was added dropwise to a briskly stirred solution of 236 cc. (2.7 moles) of 37% formalin and 154 g. (2.9 moles) of 95% sodium cyanide in 300 cc. of water at 10°.

Stirring was continued for one hour after addition was complete, while the solution was allowed to rise to room temperature. The supernatant oil was taken up in several volumes of ether, washed with dilute solutions of sodium carbonate and hydrochloric acid. Distillation over hydroquinone of the dried ether solution gave 46 g. (17%) of cyanomethyl acrylate, b. p. 42–43° (1 mm.), and 50 g. of a compound, $C_6H_9O_3N$, b. p. 82–83° (1 mm.), n^{25}D 1.4248, which did not decolorize a carbon tetrachloride solution of bromine.

Anal. Calcd. for $C_6H_9O_3N$: C, 50.36; H, 6.34; N, 9.79. Found: C, 50.74; H, 6.27; N, 9.94.

Solid acid chlorides such as cinnamoyl chloride were dissolved in dioxane to facilitate dropwise addition to the aqeuous solution.

Cyanomethyl Cinnamate (Method B).—Glycolonitrile (28.5 g., 0.5 mole) was added slowly with stirring to a solution of 86 g. of cinnamoyl chloride (0.5 mole) and 60 g. of dimethylaniline (0.5 mole) in 100 cc. of anhydrous ether at 5–10°. The solution was allowed to warm to room temperature and stirred for two hours before dilution with two volumes of ether and washing with dilute solutions of sodium carbonate and hydrochloric acid. Evaporation of the ether gave 72 g. (75%) of crude cyanomethyl cinnamate, m. p. 57–60°. Three recrystallizations from dilute ethanol gave large colorless plates, m. p. 62.7–63.0°.

Summary

The reaction of an aqueous solution of sodium cyanide and formaldehyde with benzoyl chloride has been extended to the acid chlorides of monobasic α,β-unsaturated acids. The cyanomethyl esters of acrylic, methacrylic, crotonic, β-chlorocrotonic, cinnamic, α-methylcinnamic, fumaric and mesaconic acids are reported.

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(8) Kyrides, THIS JOURNAL, **59**, 207 (1937).

(9) Kung, U. S. Patent 2,259,167 (1941).

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

The Condensation of Isobutyraldehyde with Aliphatic Ketones

BY S. G. POWELL AND FRENCH HAGEMANN[1]

It has been shown that certain straight chain aliphatic aldehydes condense with methyl ethyl ketone through the methylene group of the ketone,[2] whereas homologous methyl ketones which contain six or more carbon atoms appear to condense through the methyl group.[3] On the other hand, the condensation of α-methylbutyraldehyde, α-ethylbutyraldehyde and α-ethylcaproaldehyde with various methyl ketones has been found to take place through the methyl group.[4]

The same alkaline condensing agents which bring about the above-mentioned reactions with aliphatic aldehydes cause aromatic aldehydes to react with the methyl group of the ketone, while acids bring about condensation with the methyl-

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(1) From the Ph.D. dissertation of French Hagemann.

(2) (a) Powell, *et al.*, THIS JOURNAL, **46**, 2514 (1924); **55**, 1153 (1933); (b) Salkind, *J. Russ. Phys.-Chem. Soc.*, **37**, 484 (1905); (c) Merling and Köhler, U. S. Patent 981,668 (1901).

(3) Wickert and Freure, U. S. Patent 2,088,018 (1937), British Patent 461,662 (1937).

(4) (a) Powell and Baldwin, THIS JOURNAL, **58**, 1871 (1936); (b) Wickert and Carter, U. S. Patent 2,088,017 (1937); (c) Carbide and Carbon Chemicals Corp., French Patent 782,835 (1935); (d) Ref. (3).