product, and a low yield using Mayer's method of reduction.[3]

Application of the method of "Organic Syntheses"[6] for the reduction of xanthrone to xanthydrol gave reasonably pure 10-thiaxanthenol in almost quantitative yield when thiaxanthone was used in place of xanthone. It was found to be more convenient to add sodium to a mixture of mercury and thiaxanthone suspended in alcohol rather than to add the thiaxanthone to sodium amalgam and alcohol.

A mixture of 375 g. of mercury, 13.8 g. (0.065 mole) of thiaxanthone and 80 cc. of 95% alcohol was placed in a pressure bottle. Small pieces of sodium (4.6 g., 0.2 mole) were added during a period of 15 minutes while the mixture was being shaken. The temperature of the mixture rose during addition of the sodium, and a dark purple color developed which gradually disappeared as all of the thiaxanthone went into solution. After the mixture had been shaken mechanically for an additional fifteen minutes, the alcohol layer was decanted. The mercury amalgam was washed with two 15-cc. portions of hot alcohol and the combined alcoholic solutions were filtered and poured into one liter of water. A white, finely crystalline precipitate was collected and air-dried. A yield of 13.4 g. was obtained (96.5%). The crystalline material melted at 103–104°, and was pure enough for subsequent reactions; a sample recrystallized from high boiling ligroin melted at 104–105°. 10-Thiaxanthenol is susceptible to air oxidation in light and should therefore be stored in a sealed brown bottle.

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[6] Holleman, "Organic Syntheses," Coll., Vol. I, p. 544, 1947.

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The Reaction of Dimethylcadmium with Cyclobutanecarboxylic Acid Chloride

BY REX PINSON, JR., AND S. L. FRIESS

In connection with a study of the reaction of acetylcyclanes with perbenzoic acid, it was necessary to prepare a supply of cyclobutylmethyl ketone (I). The compound has been prepared previously by the action of dimethylzinc[1] on cyclobutanecarboxylic acid chloride (II), but the undesirable properties of the zinc reagent made preferable the newer reaction of dimethylcadmium (III) with the acid chloride for the preparative step.

In a recent survey[2] of this reaction, it has been noted that, with respect to relative reactivity toward R_2Cd, the entire $-COCl$ function is generally more reactive in a process of normal ketone formation than is its carbonyl moiety toward addition of the organometallic compound. As a result, little or no addition to the carbonyl (leading to carbinol formation) will occur unless it is unusually activated by some adjacent function. Furthermore, in acid chlorides possessing unusually high carbonyl activity, it has been observed[3] that carrying out the addition of the acid chloride to a solution of the organocadmium compound at a lower temperature than that of the refluxing solvent improves the yield of ketone.

In the present study, it has been found that a carbonyl group adjacent to a cyclobutane ring is highly reactive toward addition of cadmium reagent, and also reactive in certain other addition processes.[4] As a result of this reactivity, the customary procedures for the reaction, which employ a large excess[5] of cadmium reagent and dropwise addition of the acid chloride to an ethereal solution of dialkylcadmium held at the reflux temperature, furnish a product from II that is exclusively tertiary carbinol. This is presumably formed by a combination of normal reaction and carbonyl addition.

However, variation of conditions in the reaction of II with III has shown that the reaction may be stopped at the ketone stage, provided that (1) the addition of acid chloride is made to a well-stirred solution of the organometallic agent held at −70°; (2) the molar ratio of III to II is reduced to about 0.7; and (3) after stirring at −70° for one hour following completion of the addition of II, the reaction mixture is decomposed with water while still cold. Under these conditions, a yield of 66% (based on acid chloride) of I was realized.

A detailed description of the method using these optimum conditions, including a brief outline of the procedure for working up a reaction mixture containing a steam-volatile ketone, is given in the experimental section.

Experimental[6]

Various batches of the cyclobutanecarboxylic acid required for the reaction were prepared by the procedures of Heisig and Stodola,[7] Walborsky,[8] and Cason.[9] The acid chloride II was prepared from the acid by use of thionyl chloride, in a yield of 85%. Preparation of the dimethylcadmium reagent in absolute ether was carried out essentially according to the improved procedure of Cason.[2]

Optimum Reaction Conditions.—In a 1-l. three-necked flask fitted with stirrer, dropping funnel, and reflux condenser was prepared an ethereal solution of methylmagnesium iodide from 17.0 g. (0.71 mole) of magnesium turnings, 119 g. (0.84 mole) of methyl iodide, and a total of 375 ml. of absolute ether. The Grignard solution was cooled to 0° and 64 g. (0.35 mole) of anhydrous cadmium chloride (pulverized) added to it in small portions, with constant stirring, over a period of 45 minutes. The ice-bath was then removed and the solution stirred for one hour at room temperature, after which a Michler ketone test for residual Grignard reagent proved negative.

The dimethylcadmium solution was then cooled to ap-

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[1] (a) Perkin and Sinclair, *J. Chem. Soc.*, **61**, 47 (1892); (b) Zelinsky and Gutt, *Ber.*, **41**, 243 (1908).

[2] Cason, *Chem. Revs.*, **40**, 15 (1947).

[3] Ref. 2, p. 20.

[4] Friess and Pinson, unpublished work; the addition step in the reaction of I with perbenzoic acid is extremely rapid, as compared to the reaction rates of acetylcyclanes of larger ring size. Activation has been shown to be a function of the cyclic substituent, and not of the methyl group.

[5] In an excellent application of the reaction in the steroid series, using several times the theoretical amount of cadmium reagent, yields of methyl ketones as high as 95% were obtained; Julian, THIS JOURNAL, **67**, 1369 (1945).

[6] Melting points are corrected.

[7] Heisig and Stodola, "Organic Syntheses," Vol. 23, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 16.

[8] Walborsky, THIS JOURNAL, **71**, 2941 (1949).

[9] Cason, *J. Org. Chem.*, **14**, 1086 (1949).

proximately −70° in a Dry Ice-acetone-bath, resulting in a considerable increase in viscosity and the separation of a white solid. To this well-stirred suspension was added over a period of thirty minutes a total of 60 g. (0.50 mole) of II in 100 ml. of absolute ether, the process being accompanied by separation of a dense white sludge. After all the acid chloride had been added, the mixture was stirred for one hour at −70°. The cooling bath was then removed, and 150 ml. of water added dropwise to the cold solution, with stirring, over a period of an hour. During this decomposition step, the temperature gradually rose to the reflux point of the solvent.

The ether was then distilled off, and the residue steam distilled until about 250 ml. of distillate had been collected. The organic layer was then separated with the aid of a little ether, and the aqueous layer extracted with the ether previously distilled from the reaction mixture. The combined ether phases were dried over anhydrous sodium sulfate, the ether evaporated on the steam-bath, and the residue distilled through a short Vigreux column; yield of ketone I, 32.3 g. (66%); b. p. 134–136°, n^{28}_{D} 1.4283; semicarbazone, colorless plates from diluted ethanol, m. p. 148–149° (lit. value,[1a] 148–149°).

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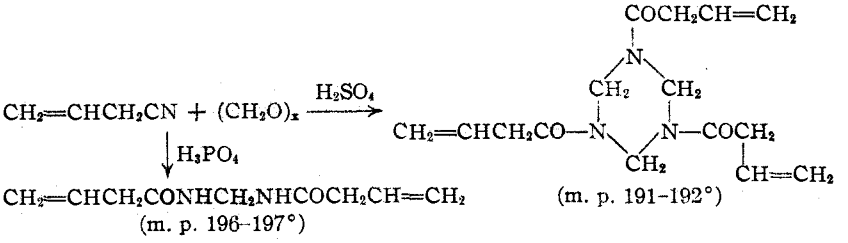
The Acid-Catalyzed Reaction of Formaldehyde with Allyl Cyanide

BY CHARLES C. PRICE AND I. V. KRISHNAMURTI[1]

A study of the reaction of formaldehyde with allyl cyanide, intended to parallel that with allyl chloride,[2] revealed that the acid-catalyzed reaction led almost exclusively to the condensation of formaldehyde with the cyanide group rather than the carbon–carbon double bond, as is reported for methallyl cyanide using 50% sulfuric acid.[3] The reaction is therefore a new example of the condensation of the nitrile group with formaldehyde recently described by Gradsten and Pollock[4] as leading to triacylhexahydrotriazines.



Both the *tris*-vinylacetyltriazine and the methylene-*bis*-vinylacetamide were hydrogenated to the corresponding butyryl derivatives and hydrolyzed to produce butyric acid.

Experimental[5]

Preparation of Allyl Cyanide.—A mixture of 680 cc. (10 moles) of allyl alcohol, 845 g. (10.5 moles) of cuprous cyanide and 1000 cc. of concentrated hydrochloric acid was charged into a 5-l., three-necked flask fitted with a mercury-sealed stirrer and a 90-cm. bulb condenser. The mixture was vigorously stirred. Within half an hour reaction set in and allyl chloride started refluxing vigorously. When necessary the flask was cooled in a bath of ice-water and stirring discontinued temporarily. In 15 minutes the reaction was over. A dark colored liquid was produced, presumably a complex between allyl cyanide and cuprous chloride. The condenser was set downward for distillation. The flask was heated by a Glas-col heating mantle. Most of the distillate came over between 90 and 92°. When the temperature reached 95° distillation could be stopped without affecting the yield. The distillate was transferred to a 2-l. separatory funnel and the upper organic layer was separated. It was dried over anhydrous potassium carbonate and redistilled to yield 500–510 g. (75%) of the allyl cyanide boiling between 116–121°, n^{20}_{D} 1.4060, d^{20}_{4} 0.8318.

Reaction of Allyl Cyanide and Paraformaldehyde in the Presence of Concentrated Sulfuric Acid as Catalyst.—A mixture of 68 g. (1 mole) of allyl cyanide and 31 g. (1 mole) of paraformaldehyde and 0.5 g. of concentrated sulfuric acid was charged into a 300-cc., two-necked flask fitted with mercury-sealed stirrer and condenser. The mixture was stirred vigorously and refluxed for one hour. Most of the paraformaldehyde sublimed into the condenser. After 1 g. of sodium acetate was added to the clear yellow liquid left in the flask, the liquid was distilled at 20 mm. to remove the unreacted allyl cyanide (50 g.). The residue was dissolved in the minimum of boiling alcohol. Cooling the alcoholic solution yielded about 5 g. of a white crystalline solid. After two recrystallizations from hot water, it melted at 191–192°. It proved to be identical with the compound prepared from allyl cyanide and trioxane with sulfuric acid as catalyst following the method of Gradsten and Pollock[3] for the preparation of triacylhexahydrotriazines, in this case, tris-vinylacetylhexahydro-*s*-triazine. It readily dissolved in boiling water, hot alcohol and chloroform. It decolorized aqueous permanganate and 5% bromine in carbon tetrachloride. It dissolved readily in strong hydrochloric acid.

Anal. Calcd. for $(C_6H_7ON)_3$: N, 14.62; mol. wt., 291. Found: N, 14.44; mol. wt. (ebullioscopic method in chloroform), 287.

Quantitative Hydrogenation of Tris-vinylacetylhexahydro-*s*-triazine.—The hexahydro-*s*-triazine was subjected to quantitative catalytic hydrogenation in the presence of 10% palladium-on-charcoal. A 0.4580-g. sample of the substance dissolved in about 25 cc. of 95% ethanol absorbed 104 cc. of hydrogen under standard conditions of temperature and pressure. This corresponds to 0.98 mole of hydrogen for every C_6H_7ON or 2.94 moles of hydrogen for $(C_6H_7ON)_3$.

Hydrolysis of Tris-butyrylhexahydro-*s*-triazine.—The tris-butyrylhexahydro-*s*-triazine was prepared by reducing the corresponding vinylacetyl compound with hydrogen at an initial pressure of 60 lb. in the presence of 10% palladium-on-charcoal as catalyst.

Ten grams of the tris-butyrylhexahydro-*s*-triazine was refluxed with 30 cc. of 20% sodium hydroxide for four hours by which time ammonia ceased to be evolved. The cooled solution was acidified to congo red with 50% sulfuric acid and extracted with 100 cc. of ether. The dried extract was distilled to remove the solvent. Distillation of the residue gave 6 g. of butyric acid, b. p. 161–162°, n^{20}_{D} 1.3982.

Reaction of Allyl Cyanide and Paraformaldehyde in 85% Phosphoric Acid Medium.—A mixture of 68 g. of allyl cyanide, 31 g. of paraformaldehyde and 10 cc. of 85% phosphoric acid was charged into a three-necked flask, provided with a mercury-sealed stirrer and a condenser. The mixture was stirred on a water-bath at 60°. The paraformaldehyde dissolved slowly and a clear solution was formed in half an hour. After 30 more minutes, the

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[1] Abstracted from a portion of the Ph.D. dissertation submitted to the Graduate School by I. V. Krishnamurti.

[2] Price and Krishnamurti, THIS JOURNAL, **72**, 5335 (1950).

[3] Arundale, U. S. Patent 2,384,268 [*C. A.*, **40**, 613 (1946)].

[4] Gradsten and Pollock, THIS JOURNAL, **70**, 3079 (1948).

[5] Analyses by Micro-Tech Laboratories, Skokie, Ill.