[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Condensations at the Methyl Group Rather than the Methylene Group of Benzoyl- and Acetylacetone Through Intermediate Dipotassio Salts[1]

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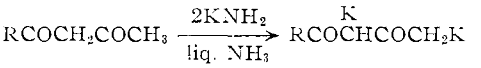
In contrast to the common reactions at the methylene group of benzoyl- and acetylacetone, several types of carbon–carbon condensations including alkylation, acylation and carbonation were realized at the methyl group of these β-diketones. These reactions were effected through intermediate dipotassio salts, which were prepared by means of two equivalents of potassium amide in liquid ammonia. Mechanisms and synthetic applications are indicated.

It is well known that β-diketones such as benzoyl- and acetylacetone can condense at the methylene group with certain reagents through the intermediate formation of the monosodio salts Ia and Ib, which can be prepared by means of sodium or sodium ethoxide. For example, these salts can be alkylated with benzyl chloride to form the 3-benzyl derivatives IIa[3] and IIb,[4] respectively.

$$\overset{Na}{RCOCHCOCH_3} \qquad \overset{C_6H_5CH_2}{RCOCHCOCH_3}$$

Ia, R = C_6H_5 IIa, R = C_6H_5
b, R = CH_3 b, R = CH_3

It has now been found that these β-diketones can enter into carbon–carbon condensations at the methyl group instead of the methylene group through the intermediate formation of the dipotassio salts IIIa and IIIb,[5,6] which can be prepared by means of two equivalents of potassium amide in liquid ammonia (eq. 1).

 (1)

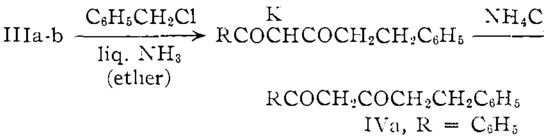
$$RCOCH_2COCH_3 \xrightarrow[\text{liq. }NH_3]{2KNH_2} \overset{K}{RCOCHCOCH_2K} \quad (1)$$

IIIa, R = C_6H_5
b, R = CH_3

Dipotassio salt IIIa readily was obtained by the direct addition of solid benzoylacetone to the alkali amide in liquid ammonia, but dipotassio salt IIIb was prepared by first converting acetylacetone to its ammonium salt or complex,[7] which was then added to the alkali amide (see Experimental).

Examples of several types of carbon–carbon condensations involving the preferential reaction of these dipotassio salts IIIa-b[5] at the 1-carbon are described below.

Alkylation.—Dipotassio salts IIIa-b were alkylated in liquid ammonia containing a little ether with molecular equivalents of benzyl chloride to form the corresponding monopotassio salts. Acidification with ammonium chloride gave the 1-benzyl derivatives IVa and IVb in yields of 77 and 60%, respectively (eq. 2).

 (2)

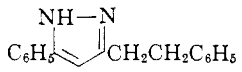
$$\text{IIIa-b} \xrightarrow[\text{liq. }NH_3\text{ (ether)}]{C_6H_5CH_2Cl} \overset{K}{RCOCHCOCH_2CH_2C_6H_5} \xrightarrow{NH_4Cl} RCOCH_2COCH_2CH_2C_6H_5 \quad (2)$$

IVa, R = C_6H_5
b, R = CH_3

The product from dipotassio salt IIIa was shown by a molecular weight determination not to be a dibenzylation derivative and by the mixed melting point method not to be the 3-benzyl derivative IIa, which was prepared from monosodio salt Ia and benzyl chloride.[3] The structure of the product was established as IVa by alkaline cleavage to form acetophenone (30%) and by an independent synthesis involving the acylation of acetophenone with methyl hydrocinnamate (eq. 3).

$$C_6H_5COCH_3 \xrightarrow[\text{ether}]{NaNH_2} C_6H_5COCH_2Na \xrightarrow{C_6H_5CH_2CH_2COOCH_3} \text{IVa} \quad (3)$$

β-Diketone IVa was cyclized with hydrazine to form the substituted pyrazole V in good yield.



V

The benzylation product from dipotassio salt IIIb may be considered to have structure IVb not only by analogy with IVa but also because its boiling point was in line with that reported for β-diketone IVb, which previously has been obtained by the acylation of acetone with ethyl hydrocinnamate by means of sodium.[8] Moreover, the color (blue) and melting point of the copper chelate were in good agreement with those previously reported for β-diketone IVb,[8] and the infrared spectrum of the chelate showed strong bands at 6.32 and 6.56 μ which is indicative of such a β-diketone unsubstituted at the methylene group.[9] On the other hand, the 3-benzyl derivative IIb, which was prepared from monosodio salt Ib, gave a dark, gray-green copper chelate having a higher melting point and showing a strong infrared band at 6.37 μ as reported to be characteristic of such 3-substituted β-diketones.[9]

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(1) Reported before the 133rd Meeting of the American Chemical Society in San Francisco, Calif., April 13–18, 1958.

(2) National Science Foundation Predoctoral Fellow, 1956–1958.

(3) E. R. Trotman, *J. Chem. Soc.*, **127**, 88 (1925).

(4) G. T. Morgan and C. J. A. Taylor, *ibid.*, **127**, 797 (1925).

(5) For the present purpose dipotassio salts IIIa-b are considered to contain 1,3-dicarbanions, although other resonance forms may contribute more to the structure of the molecules.

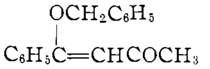
(6) Acetylacetone might possibly form the 1,5-dipotassio salt, but benzoylacetone could not produce such a salt. In this connection it should be mentioned that the dipotassio salt of acetylacetone is relatively insoluble in liquid ammonia, whereas that of benzoylacetone is readily soluble in this medium.

(7) Apparently acetylacetone is a sufficiently strong acid to precipitate as an ammonium salt from ethereal ammonia; see A. Hantzsch, *Ber.*, **40**, 3798 (1907); A. Michael and H. Hibbert, *ibid.*, **40**, 4380 (1907).

(8) G. T. Morgan and C. R. Porter, *J. Chem. Soc.*, **125**, 1269 (1924).

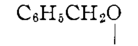
(9) R. P. Dryden and A. Winston reported at the Southeastern Regional Meeting of the American Chemical Society at Durham, N. C. Nov. 14–16, 1957, that the copper chelates of acetylacetone and similar β-diketones unsubstituted at the methylene group show infrared bands at 6.10–6.45 μ and 6.52–6.60 μ whereas the chelates of their 3-substituted derivatives exhibit only the former band.

Incidentally the benzylation products of both dipotassio salts IIIa and IIIb were shown not to be the possible O-benzyl derivatives such as IVc and IVd, since they gave positive enol tests (red) with ferric chloride and formed copper chelates with cupric acetate, reactions that are characteristic of β-diketones but not of their O-alkyl derivatives.



$$C_6H_5\overset{OCH_2C_6H_5}{\overset{|}{C}}{=}CHCOCH_3$$

IVc



$$C_6H_5COCH{=}\overset{C_6H_5CH_2O}{\overset{|}{C}}CH_3$$

IVd

As might be expected the 1-carbanion in the dicarbanion IIIa is much more nucleophilic than the 3-carbanion in Ia. Thus, the dicarbanion reacted with benzyl chloride in liquid ammonia to give a 77% yield of the 1-benzyl derivative IVa within 30 minutes, whereas the monocarbanion failed to react appreciably with the halide within 2 hours in this medium or even within 4 hours in either at room temperature.

It should be mentioned that the benzylation of dipotassio salts IIIa-b was not accompanied by appreciable self-condensation of the benzyl chloride to form stilbene, a reaction that occurs readily in the presence of the amide ion under similar conditions.[10] In fact the purple color that is associated with the formation of even a little stilbene[10] was not observed.[11] This indicates that either the equilibrium of the acid–base reaction represented by equation 1 is far on the side of the dicarbanions IIIa-b or that, if an appreciable amount of the amide ion is present at equilibrium, the dicarbanions react faster with the benzyl chloride than the amide ion.

Phenylation.—Dipotassio salt IIIb was phenylated with bromobenzene in the presence of potassium amide in liquid ammonia (benzyne intermediate)[12] to form evidently the 1-phenyl derivative VI which was isolated as its copper chelate in 13% yield.

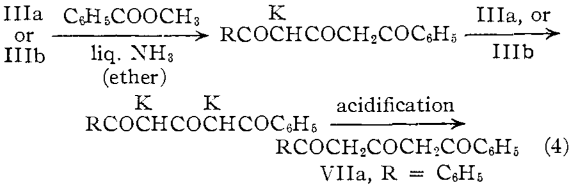
$$CH_3COCH_2COCH_2C_6H_5$$

VI

The melting point and color (blue) of the copper chelate were in agreement with those of the reported chelate of β-diketone VI, which previously has been obtained[8] by the acylation of acetone with ethyl phenylacetate by means of sodium. Moreover, the infrared spectrum of the chelate showed bands at 6.30 and 6.55 μ, which indicates the absence of a substituent at the 3-carbon,[9] in agreement with structure VI.

The copper chelate of the isomeric 3-phenyl derivative of acetylacetone, which was prepared through the boron fluoride-catalyzed acetylation of phenylacetone with acetic anhydride,[13] gave a dark green copper chelate having a different melting point and infrared spectrum. The latter spectrum showed only a single band in the region about 6.34 μ, which is characteristic of the chelates of 3-substituted acetylacetones.[9]

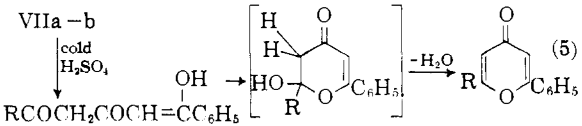
Acylation.—Dipotassio salts IIIa-b were acylated in liquid ammonia with methyl benzoate to form, on acidification, triketones VIIa and VIIb in yields of 58 and 60%, respectively (eq. 4).



$$\begin{array}{l}\begin{matrix}\text{IIIa}\\ \text{or}\\ \text{IIIb}\end{matrix} \xrightarrow[\text{liq. NH}_3\ \text{(ether)}]{C_6H_5COOCH_3} RCO\overset{K}{C}HCOCH_2COC_6H_5 \xrightarrow[\text{IIIb}]{\text{IIIa, or}} \\ RCO\overset{K}{C}HCO\overset{K}{C}HCOC_6H_5 \xrightarrow{\text{acidification}} RCOCH_2COCH_2COC_6H_5 \quad (4)\\ \qquad\qquad\qquad\qquad\text{VIIa, R} = C_6H_5\\ \qquad\qquad\qquad\qquad\quad\ \text{b, R} = CH_3\end{array}$$

In these benzoylations, the monopotassio salt that is formed in the first step presumably undergoes a relatively rapid acid–base reaction with unchanged dipotassio salts IIIa-b to give the dipotassio salts of the triketones and the monopotassio salts of benzoyl- and acetylacetone (IIa-b). The analogous mechanism has been demonstrated in the acetylations of monosodio ketones with esters to form monosodio β-diketones.[14] Accordingly two molecular equivalents of dipotassio salts IIIa-b were employed to one of the methyl benzoate, and the yields were based on the ester.[14] Although part of the triketone VIIb evidently reacted with the ammonia when the reaction mixture was neutralized with ammonium chloride in the usual manner, this side-reaction was avoided by replacing the liquid ammonia with ether before neutralization (see Experimental).

The structures of the triketones were established as VIIa-b by cyclization in cold sulfuric acid to give high yields of pyrones VIIIa and VIIIb, respectively. This cyclization presumably involves an enol form of the triketone (equation 5).



VIIIa, R = C_6H_5
VIIIb, R = CH_3

(6)

The triketones VIIa-b have previously been obtained from pyrones VIIIa-b by reversing this cyclization under basic conditions,[15,16] but the direct benzoylation of dipotassio salts IIIa-b appears more convenient. Even the present method for preparing such a symmetrical pyrone as VIIIa through the triketone might be preferable to the earlier procedures, one of which involves the base-catalyzed acylation of acetophenone with ethyl phenylpropiolate accompanied by cyclization.[17]

Carbonation.—An ethereal suspension of dipotassio salt IIIa was carbonated with excess Dry Ice to form acid IX in 58% yield (eq. 7).

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[10] See C. R. Hauser, W. R. Brasen, P. S. Skell, S. W. Kantor and A. E. Brodhag, THIS JOURNAL, **78**, 1653 (1956); C. R. Hauser and P. J. Hamrick, Jr., *ibid.*, **79**, 3142 (1957).

[11] Treatment of dibenzoylmethane with two equivalents of potassium amide in liquid ammonia, and then by a molecular equivalent of benzyl chloride produced an immediate purple color. Thus, the ionizations of both of the methylene hydrogens of this β-diketone appear impracticable.

[12] See W. W. Leake and R. Levine, Abstracts of Div. Org. Chem. of Am. Chem. Soc. Meeting at New York, N. Y., 1957, p. 37P; J. D. Roberts, D. A. Semenow, H. E. Simmons, Jr., and L. A. Carlsmith, THIS JOURNAL, **78**, 601 (1956).

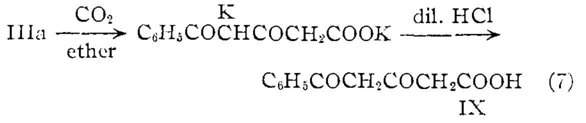
[13] C. R. Hauser and R. M. Manyik, *J. Org. Chem.*, **18**, 588 (1953).

[14] See C. R. Hauser, F. W. Swamer and J. T. Adams, "Organic Reactions," Vol. VIII, John Wiley and Sons, Inc., New York, N. Y., 1954, pp. 62–63, 114.

[15] See K. Balenovic and R. Munk, *Arkiv. Kem.*, **18**, 41 (1946); *C. A.*, **42**, 2926a (1948).

[16] See S. Ruhemann, *J. Chem. Soc.*, **93**, 1281 (1908).

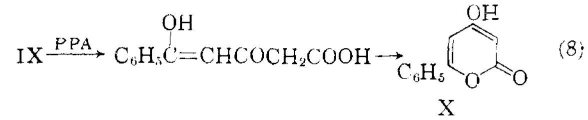
[17] See G. Soliman and I. E. El-Kholy, *ibid.*, 1755 (1954).



$$\text{IIIa} \xrightarrow[\text{ether}]{CO_2} C_6H_5CO\overset{K}{C}HCOCH_2COOK \xrightarrow{\text{dil. HCl}} \underset{\text{IX}}{C_6H_5COCH_2COCH_2COOH} \quad (7)$$

Because of the apparent insolubility of dipotassio salt IIIa in ether, this reaction occurred very slowly. It is possible that the 3-carbon also was carbonated and then decarboxylated again during the working-up process.

The structure of the product was established as IX by decarboxylation to regenerate benzoylacetone and by cyclization in polyphosphoric acid (PPA) to form lactone X (98%) (eq. 8).

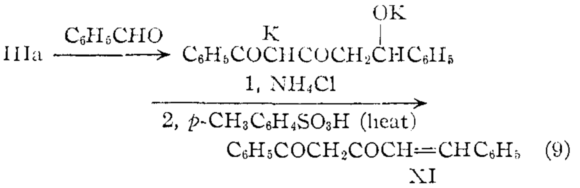


(8)

X

β-Diketone-acid IX previously has been obtained by cleavage of dehydrobenzoylacetic acid under basic conditions,[18] but the direct carbonation of the dipotassio salt IIIa appears more convenient. Even the present method for the preparation of lactone X might be regarded as preferable to earlier procedures involving acidic cleavage of dehydrobenzoylacetic acid.[19]

Condensation with Benzaldehyde.—Dipotassio salt IIIa was condensed in liquid ammonia with benzaldehyde, and the resulting addition product was dehydrated by means of toluenesulfonic acid to give cinnamoylacetophenone (XI) which was isolated as its copper chelate in an over-all yield of 28% (eq. 9).



$$\text{IIIa} \xrightarrow{C_6H_5CHO} C_6H_5CO\overset{K}{C}HCOCH_2\overset{OK}{C}HC_6H_5 \xrightarrow[\text{2, } p\text{-}CH_3C_6H_4SO_3H \text{ (heat)}]{\text{1, } NH_4Cl} \underset{\text{XI}}{C_6H_5COCH_2COCH{=}CHC_6H_5} \quad (9)$$

The structure of the product was established as XI by an independent synthesis from sodioacetophenone and cinnamyl chloride (eq. 10).[20]

$$C_6H_5COCH_3 \xrightarrow{NaNH_2} C_6H_5COCH_2Na \xrightarrow{C_6H_5CH{=}CHCOCl} \text{XI} \quad (10)$$

Experimental[21]

Dipotassio Salt IIIa.—In a 500-ml. 3-necked flask equipped with an efficient stirrer, an outlet tube, and a plug or addition funnel was placed 300 ml. of commercial, anhydrous liquid ammonia. A minimum amount of potassium was added to the stirred solution to produce a permanent blue color. To the stirred liquid was added a catalytic amount of hydrated ferric chloride followed by 7.8 g. (0.2 g. atom) of potassium in small portions. The resulting dark blue solution of potassium amide was converted to a colorless solution of potassium amide in 10–30 minutes.

To the solution of potassium amide, which was assumed to contain 0.2 mole of this reagent, was added through a powder funnel in small portions 16.2 g. (0.1 mole) of solid benzoylacetone. After stirring for 30 minutes, the resulting solution was considered to contain 0.1 mole of the dipotassio salt IIIa.

Dipotassio Salt IIIb.—To a solution of 15 g. (0.15 mole) of acetylacetone in 150 ml. of anhydrous ether was added dropwise an excess of anhydrous liquid ammonia. A vigorous reaction occurred to precipitate a voluminous white solid,[22] with subsequent cooling of the reaction mixture. The precipitate, which was evidently an ammonium salt of acetylacetone,[7] was collected rapidly on a Buchner funnel and washed with a little dry ether.

The ammonium salt of acetylacetone was added immediately to a stirred solution of 0.3 mole of potassium amide in 300 ml. of liquid ammonia. After stirring for one hour, the resulting suspension was considered to contain 0.15 mole of the dipotassio salt IIIb.

Benzylation of the Dipotassio Salt IIIa.—To a stirred solution of 0.1 mole of dipotassio salt IIIa in 300 ml. of liquid ammonia was added dropwise an ethereal solution of 12.6 g. (0.1 mole) of benzyl chloride. After stirring 0.5 hour, an excess (10 g.) of solid ammonium chloride was introduced. The liquid ammonia was evaporated (hot water-bath) as 300 ml. of ether was added from a dropping funnel. The resulting ethereal suspension was shaken with water to dissolve the inorganic salts. The two layers were separated, the water layer being discarded. The ethereal layer was dried over Drierite, and the solvent removed. The residual solid was recrystallized from 95% ethanol to give 19.3 g. (77%) of white crystals of 1,5-diphenyl-1,3-pentanedione (IVa), m.p. 50–53° and 54–55° after recrystallization from ethanol.

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39; mol. wt., 252. Found: C, 81.10; H, 6.14; mol. wt.,[23] 240, 242, 248, 250.

This product gave a red enol test with alcoholic ferric chloride and a light blue copper chelate with aqueous copper acetate.[24]

The melting point of the product IVa (m.p. 54–55°) was depressed to 32–40° on admixture with benzoylacetone (m.p. 56–58°), and to 38–45° on admixture with 3-benzylbenzoylacetone (IIa, m.p. 54–55°), which was prepared by the method of Trotman.[3]

A 2-g. sample of the product IVa was cleaved with 1 g. of potassium hydroxide in 50 ml. of 80% ethanol (steam-bath, 10 hr.) to give acetophenone which was isolated as its semicarbazone (0.4 g., 29%). This derivative was identified by the mixture melting point method.

An independent synthesis of β-diketone IVa was accomplished by treating sodioacetophenone, prepared from 0.6 mole each of sodium amide and acetophenone in ether, with 0.2 mole of methyl hydrocinnamate.[24] The product was isolated through its copper chelate[24] which was decomposed with dilute hydrochloric acid. There was obtained 25.6 g. (52%) of β-diketone IVa, m.p. 52–55°. This melting point was not depressed on admixture with a sample of the β-diketone synthesized by the benzylation of dipotassio salt IIIa.

3-Phenyl-5-β-phenethylpyrazole (V) was obtained from 2.0 g. of β-diketone IVa and an excess of ethanolic hydrazine by refluxing for 1 hr. and allowing to stand for 12 hr. The solution was poured into water, and the resulting precipitate was recrystallized from *n*-hexane to give 1.85 g. (94%) of pyrazole V (white crystals), m.p. 83–84°.

Anal. Calcd. for $C_{17}H_{16}N_2$: C, 82.22; H, 6.50; N, 11.28. Found: C, 82.20; H, 6.58; N, 11.37.

The pyrazole was converted to the picrate derivative in high yield by treating the compound with ethanolic picric acid. Recrystallization from 95% ethanol produced yellow needles, m.p. 173–175°.

Anal. Calcd. for $C_{23}H_{19}N_5O_7$: C, 57.86; H, 4.01; N, 14.67. Found: C, 57.98; H, 4.02; N, 14.56.

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[18] See K. Balenovic and D. Sunko, *Monatsh.*, **79**, 1 (1948).

[19] See F. Arndt, B. Eistert, M. Scholz and E. Aron, *Ber.*, **69B**, 2373 (1936).

[20] B. O. Linn and C. R. Hauser, THIS JOURNAL, **78**, 6066 (1956).

[21] Melting points were taken on a Fisher-Johns melting point apparatus. Infrared spectra were produced with a Perkin-Elmer Infracord by the potassium bromide pellet method. Elemental analyses were by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

[22] The direct addition of acetylacetone to liquid ammonia solutions of the alkali amide was so vigorous that the reaction was difficult to control. Even when an ethereal solution of the β-diketone was added dropwise to the liquid ammonia solution, a precipitate formed in the stem of the funnel.

[23] Molecular weight determination (Rast Method) carried out by Carl Tiedcke, 705 George Street, Teaneck, N. J.

[24] See ref. 14, p. 122–123.

Benzylation of Dipotassio Salt IIIb.—To a stirred suspension of 0.15 mole of dipotassio salt IIIb in 400 ml. of liquid ammonia was added cautiously a solution of 18.9 g. (0.15 mole) of benzyl chloride in a little ether. After stirring 0.5 hr., excess ammonium chloride (15 g.) was introduced, and the liquid ammonia replaced by ether. The resulting suspension was shaken with water, and the ethereal layer dried over Drierite. The solvent was removed, and the residue distilled *in vacuo* to give 17.9 g. (60%) of 6-phenyl-2,4-hexanedione (IVb), b.p. 133–136° at 5 mm. or 162–165° at 16 mm. (reported[8] b.p. 164–166° at 16 mm.). This product (IVb) gave a red enol test with alcoholic ferric chloride and a blue copper chelate with hot aqueous copper acetate solution.[24] The copper chelate, recrystallized from benzene, melted at 158.5–160° (reported[8] m.p. 157–159°, blue). The infrared spectrum of the chelate showed strong peaks at 6.32 and 6.56 μ.

The 3-benzyl derivative of acetylacetone (IIb), prepared by the method of Morgan and Taylor,[4] gave a dark gray-green copper chelate which, after recrystallization from a mixture of benzene and ethanol, melted at 205–207° (reported[4] m.p. 176°). The infrared spectrum of this chelate showed a strong band at 6.37 μ, and an absence of any absorption between 6.52 and 6.60 μ.[9]

Anal. Calcd. for $C_{24}H_{26}O_4Cu$: C, 65.21; H, 5.93; Cu, 14.38. Found: C, 65.07; H, 6.09; Cu, 14.37.

Phenylation of Dipotassio Salt IIIb.—To a stirred solution of 0.45 mole of potassium amide in 300 ml. of liquid ammonia was added the ammonium salt of acetylacetone prepared from 15 g. (0.15 mole) of the β-diketone as described (see dipotassio salt IIIb). After stirring 1 hr., 23.6 (0.15 mole) of bromobenzene was added dropwise. The reaction mixture was neutralized with ammonium chloride after 30 minutes. Material was obtained boiling at 100–140° at 2 mm., which was treated with aqueous copper acetate to give 3.9 g. (13%) of the light blue chelate of β-diketone VI, m.p. 221–225° and at 227–229° after recrystallization from 95% ethanol (reported m.p. for blue chelate 223-224°[8] and 235–236°[25]). The infrared spectrum of this chelate showed strong peaks at 6.30 and 6.55 μ. The isomeric 3-phenylacetylacetone[13] gave a dark green copper chelate melting at 233.5–234.5° (reported[26] m.p. 222–224°, dark green), the infrared spectrum of which showed a peak (single) at 6.34 μ.

Benzoylation of Dipotassio Salt IIIa.—To a stirred solution of 0.1 mole of dipotassio salt IIIa in 300 ml. of liquid ammonia was introduced 6.8 g. (0.05 mole) of methyl benzoate in an equal volume of ether. A precipitate began to form immediately. After one hour, excess ammonium chloride (15 g.) was added, and the liquid ammonia was evaporated as an equal volume of ether was added. The resulting slurry was washed with water to remove the suspended material. The ether solution was dried over Drierite and the solvent distilled. The residue was recrystallized twice from ethanol to give 7.6 g. (58%) of gold plates of 1,5-diphenyl-1,3,5-pentanetrione (VIIa), m.p. 107–108° (reported[15] m.p. 107–108°). This triketone gave a green-brown enol test with ethanolic ferric chloride.

A 1-g. sample of the triketone was dissolved in 10 ml. of concentrated sulfuric acid at 0°. After 10 min. at this temperature, the solution was poured into ice-water. The resulting precipitate was collected on a funnel, washed with water, and recrystallized from ethanol to give 0.88 g. (94%) of pyrone VIIIa, m.p. 138.5-141.5° (reported[15] m.p. 139–141°). This product displayed the expected solubility in both concentrated sulfuric acid and hot concentrated hydrochloric acid.[27] The picrate of this pyrone, prepared in ethanol, melted at 181–183° (reported[17] m.p. 183°).

Benzoylation of Dipotassio Salt IIIb.—To a stirred suspension of 0.2 mole of dipotassio salt IIIb in 600 ml. of liquid ammonia was added 13.6 g. (0.1 mole) of methyl benzoate in an equal volume of ether. After stirring 0.5 hr., the liquid ammonia was replaced by ether. The resulting suspension was stirred for one hour, and then poured into a slight excess of cold aqueous acetic acid. The two layers were separated, care being taken that the aqueous layer was weakly acidic. The aqueous layer was extracted with ether and the extract combined with the original ethereal layer. The ethereal solution was dried with anhydrous magnesium sulfate, and the solvent removed. The residue was taken up in 95% ethanol, and the ethanolic solution cooled to precipitate 12.25 g. (60%) of 1-phenyl-1,3,5-hexanetrione (VIIb), m.p. 101–103°. Recrystallization from 95% ethanol raised the melting point to 107–108° (reported[16] m.p. 106–107°). The triketone produce a brown enol test with ethanolic ferric chloride.

Anal. Calcd. for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 70.30; H, 6.05.

When the benzoylation was repeated and the liquid ammonia reaction mixture neutralized with ammonium chloride as described above in the benzoylation of dipotassio salt IIIa, there was obtained a 38% yield of triketone IIIb and a 16% yield apparently of 2-methyl-6-phenyl-pyridone-4, m.p. 174–176° (reported[16] m.p. 177–178°). Treatment of the latter product with ethanolic picric acid produced the picrate derivative of the pyridone (yellow needles), m.p. 191–194° (reported[16] m.p. 194–195°).

A sample of the triketone VIIb was dissolved in concentrated sulfuric acid at 0°. After 10 minutes the solution was poured into ice-water to give a good yield of pyrone VIIIb, which, after recrystallization from *n*-hexane, melted at 85.5–87° (reported[27] m.p. 87–88°).

Carbonation of Dipotassio Salt IIIa.—A solution of 0.1 mole of dipotassio salt IIIa was prepared in 300 ml. of liquid ammonia as described above, and the liquid ammonia evaporated rapidly (steam-bath) as an equal volume of dry ether was added. The resulting slurry of dipotassio salt IIIa was poured onto a large excess of pulverized Dry Ice. The mixture was agitated and more Dry Ice was added as needed. After 6 hours, the ether slurry was extracted twice with water and the aqueous extracts combined. The aqueous solution was cooled in an ice-bath and acidified. The resulting precipitate was collected on a funnel and redissolved in aqueous sodium bicarbonate solution. After washing with ether, the solution was acidified again with cold dilute hydrochloric acid to precipitate the carboxylic acid, which was collected, washed with a little water, and dried. After washing with petroleum ether (b.p. 30–60°), there was obtained 12.0 g. (58%) of 5-phenyl-3,5-dioxopentanoic acid (IX), m.p. 94–97° (reported[18] m.p. 94°). This β-diketone-acid gave a cherry-red enol test with ethanolic ferric chloride, and its infrared spectrum showed the peaks: 3.3 (broad), 5.8, 6.25, 6.4, 7.05, 7.55, 8.35, 10.25 (broad), 12.95, 13.2, 14.4 μ.

A 3.5-g. sample of the β-diketone-acid IX was dissolved in 30 g. of polyphosphoric acid (Victor Chemical) on the steam-bath. After 90 minutes, the solution was poured into 200 ml. of ice-water. The resulting precipitate was collected on a funnel and washed with water. There was obtained 3.1 g. (98%) of the lactone X, m.p. 241.5–244.5° dec. (reported[19] m.p. 245° dec.). The lactone produced no coloration with ethanolic ferric chloride. Its infrared spectrum showed the peaks: 3.3(broad), 3.9(broad), 6.2, 6.45, 7.0, 7.95, 8.15, 8.5, 12.33, 12.9, 14.45 μ.

Benzalation of Dipotassio Salt IIIa.—To a stirred solution of 0.1 mole of dipotassio salt IIIa in liquid ammonia was added 10.6 g. (0.1 mole) of benzaldehyde. After stirring for 30 minutes, the reaction mixture was poured into a solution of excess ammonium chloride (25 g.) in liquid ammonia. The ammonia was replaced with ether, and the resulting ethereal suspension was washed with water. The ethereal solution was dried over Drierite, and the solvent removed. The residual dark oil was heated with 0.1 g. of *p*-toluenesulfonic acid in an open flask in a metal-bath at 200° for 15 minutes. After cooling, the black residue was shaken with aqueous copper acetate solution,[24] forming 8.1 g. (28%) of the yellow copper chelate of cinnamoylacetophenone. The infrared spectrum of the chelate was identical with that of an authentic sample of the chelate prepared through the reaction of cinnamoyl chloride with sodioacetophenone.[20] The copper chelate was decomposed with dilute hydrochloric acid to form in high yield cinnamoylacetophenone (XIV), m.p. 110–111°. Admixture of the product with an authentic sample of cinnamoylacetophenone (m.p. 111–112°)[20] did not depress the melting point.

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