[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Certain Condensations at the Terminal Methyl Group of 3-Phenylpentane-2,4-dione through Its Dipotassio Derivative Cyclizations[1]

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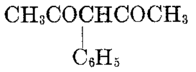
3-Phenylpentane-2,4-dione was benzylated, benzoylated, and carbonated at one of its terminal methyl groups through its dipotassio derivative, which was prepared by means of two molecular equivalents of potassium amide in liquid ammonia. The benzylation and benzoylation were best effected in the presence of pyridine, and the carbonation in ether. When the benzoylation was carried out in liquid ammonia, ether, or tetrahydrofuran, phenylacetone was obtained as by-product. This ketone evidently arose by cleavage of the original β-diketone. The benzoylation and carbonation products of the β-diketone were cyclized by means of acid to form the corresponding γ-pyrone and δ-lactone respectively. None of the possible cyclization products involving the aromatic ring was isolated.

Recently[2] acetylacetone was benzylated and benzoylated at one of its terminal methyl groups through the intermediate formation of its dipotassio derivative,[3] which was prepared by means of two molecular equivalents of potassium amide in liquid ammonia (Equation 1).

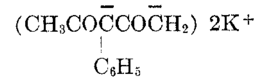
$$CH_3COCH_2COCH_3 \xrightarrow[\text{liq. NH}_3]{2KNH_2} (CH_3CO\bar{C}HCO\bar{C}H_2)2K^+ \quad (1)$$

In the present investigation a similar study was made of 3-phenylpentane-2,4-dione (I), which was converted to its dipotassio derivative II[3] in the usual manner.



$$\underset{\textstyle C_6H_5}{CH_3CO\overset{|}{C}HCOCH_3}$$

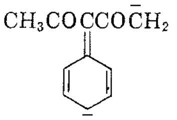
I



$$\underset{\textstyle C_6H_5}{(CH_3CO\overset{|}{\bar{C}}CO\bar{C}H_2)}\ 2K^+$$

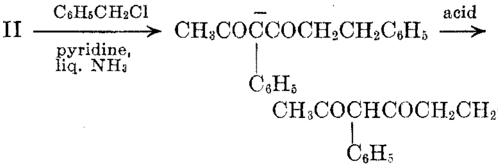
II

Like the dipotassio derivative of acetylacetone, II was obtained as a suspension in liquid ammonia. At least in this medium the latter salt was found to be less reactive than the former. This relative sluggishness of II might be due to a lower solubility in liquid ammonia and/or a lower nucleophilicity of its dicarbanion because of contributions of ring resonance structures such as II′.



II′

First, a study was made of the benzylation of II with benzyl chloride. Whereas the dipotassio salt of acetylacetone has been benzylated in 60% yield in liquid ammonia within one hour,[2] II failed to undergo appreciable benzylation under similar conditions even within two hours. However, the benzylation of the latter salt was realized under appropriate conditions, the product being the expected terminal methyl derivative III. Thus, this product was obtained in 16% yield on refluxing the reactants in ether for five hours, and in 50–62% yields on carrying out the reaction in pyridine containing a small amount of liquid ammonia (Equation 2).



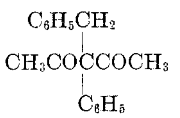
$$\text{II} \xrightarrow[\text{pyridine, liq. NH}_3]{C_6H_5CH_2Cl} \underset{\textstyle C_6H_5}{CH_3CO\overset{|}{\bar{C}}COCH_2CH_2C_6H_5} \xrightarrow{\text{acid}} \underset{\textstyle C_6H_5}{CH_3CO\overset{|}{C}HCOCH_2CH_2C_6H_5} \quad (2)$$

III

Although the 62% yield of III was obtained on stirring the reaction mixture for two hours at room temperature, almost as good a yield (52%) was realized when the cold reaction mixture was stopped after three minutes, during which time the suspension of II had dissolved.

Evidently the benzyl chloride did not first react with the pyridine to form the benzylpyridinium ion to serve as the alkylating agent, since, on first preparing the quaternary ammonium salt and then adding it to II in pyridine containing a small amount of liquid ammonia, none of the product III was isolated. In a blank experiment in which II was stirred with pyridine for two hours, I was recovered in 87% yield.

That the product was III and not the possible methinyl derivative IV was shown by the fact that it formed a copper chelate. IV, which has no readily enolizable hydrogen, could not yield the chelate. Moreover, the infrared spectrum of this chelate was similar to that of the starting β-diketone I, both giving a peak at 6.35 μ and no peaks in the region of 6.52–6.60 μ. This result is characteristic



$$\overset{\textstyle C_6H_5CH_2}{\underset{\textstyle C_6H_5}{CH_3CO\overset{|}{\underset{|}{C}}COCH_3}}$$

IV

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[1] Supported by the Office of Ordnance Research, U. S. Army.

[2] C. R. Hauser and T. M. Harris, *J. Am. Chem. Soc.*, **80**, 6360 (1958).

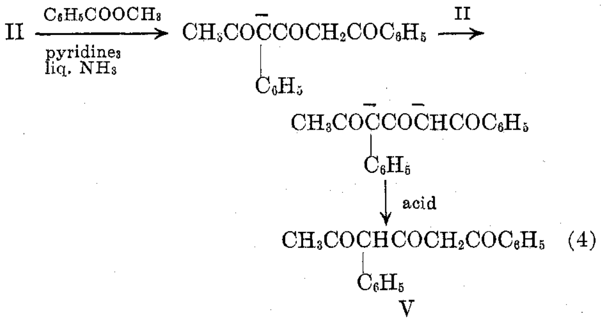
[3] For the present purpose only dicarbanion resonance forms are considered, although other resonance forms may contribute more to the structure of the molecule.

of the chelates of such β-diketones having a 3-substituent.[4]

The structure of the product was confirmed as III by an independent synthesis involving the acylation of phenylacetone with hydrocinnamic anhydride by means of boron trifluoride (Equation 3).

$$CH_3COCH_2C_6H_5 \xrightarrow[BF_3]{(C_6H_5CH_2CH_2CO)_2O} III \qquad (3)$$

Next a study was made of the benzoylation of II with methyl benzoate. Whereas the dipotassio salt of acetylacetone has been benzoylated in 60% yield in liquid ammonia (half an hour) followed by ether (one hour), II gave only a 14% yield of triketone V in liquid ammonia (five hours) and only an 11% yield in refluxing ether (five hours). However, the reaction was realized in 47% yield in pyridine containing a small amount of liquid ammonia (Equation 4).

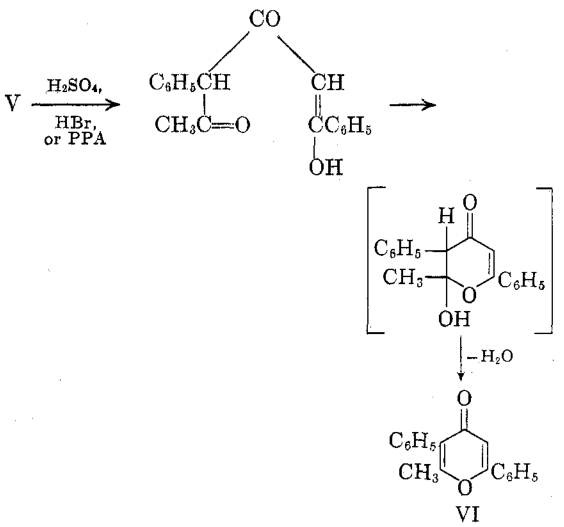


$$II \xrightarrow[\text{pyridine; liq. } NH_3]{C_6H_5COOCH_3} CH_3CO\bar{C}(C_6H_5)COCH_2COC_6H_5 \longrightarrow CH_3CO\bar{C}(C_6H_5)CO\bar{C}HCOC_6H_5 \xrightarrow{\text{acid}} CH_3COCH(C_6H_5)COCH_2COC_6H_5 \qquad (4)$$

V

In these experiments II was treated with only one half of a molecular equivalent of methyl benzoate, since half of the dicarbanion II was involved in converting the triketone to its dicarbanion (see Equation 4). Therefore the yield of V was based on the ester.[5]

The structure of the product was established as triketone V by cyclization by means of concentrated sulfuric acid, hydrobromic acid, or polyphosphoric acid (PPA) to form the γ-pyrone VI in good yields (Equation 5).

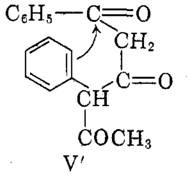


(5)

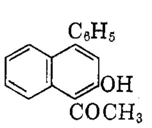
VI

The ultraviolet absorption spectrum of the cyclic product had a maximum at 270 mμ and a log ε value of 4.33, which are in close agreement with such values for certain related γ-pyrones.[6]

There was a possibility that aromatic cyclodehydration occurred as indicated in V′ to form VII, since this type of cyclization is also known to be acid catalyzed[7] especially by polyphosphoric acid.[8] However, the γ-pyrone structure of the product is supported not only by the ultraviolet spectrum mentioned above but also by the fact that it failed to give a positive enol test with ethanolic ferric chloride as should be expected if it had been a naphthol such as VII.



V′



VII

When the benzoylation of II with methyl benzoate was effected in refluxing tetrahydrofuran for five hours, the γ-pyrone VI was obtained directly in 39% yield. This accompanying cyclization under these conditions was unexpected, since the cyclization of 1,3,5-triketones have generally been considered to be catalyzed by acids but not by bases.[5] In fact certain bases have been employed to effect ring opening of γ-pyrones.[5] In the present experiment the γ-pyrone was apparently obtained first as a hemihydrate (based on analysis) which readily underwent dehydration on treatment with sulfuric acid. The possibility that the supposed hemihydrate was the intermediate cyclic hemiacetal shown in equation 5 was not supported by analysis.

It should be mentioned that, in the benzoylations of II in liquid ammonia, ether, and tetrahydrofuran described above, there was obtained phenylacetone in yields of 20–30%, 52%, and 30% respectively. This product evidently arose at least partly from the cleavage of the β-diketone I, since it was produced in 25% yield in a blank experiment, in which I was treated with two equivalents of potassium amide in liquid ammonia for five hours. By analogy with similar cleavages of β-diketones by aqueous alkali,[9] this cleavage would be considered to be initiated by the attack of the amide ion on one of the carbonyl groups of the free β-diketone, a low concentration of which would presumably be in

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(4) See R. P. Dryden and A. Winston, *J. Phys. Chem.*, **62**, 635 (1958).

(5) See R. J. Light and C. R. Hauser, *J. Org. Chem.*, in press.

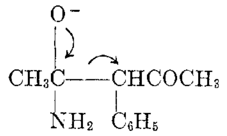
(6) See ref. 5 and P. Franzosini, G. Traverso, and M. Sanesi, *Ann. chim.* (*Rome*), **45**, 128 (1955).

(7) See C. K. Bradsher, *Chem. Revs.*, **38**, 447 (1946).

(8) See C. R. Hauser and J. G. Murray, *J. Am. Chem. Soc.*, **77**, 3858 (1955); C. K. Bradsher, L. E. Beavers, and N. Tokura, *J. Am. Chem. Soc.*, **78**, 3196 (1956).

(9) See J. Hine, *Physical Organic Chemistry*, McGraw-Hill Book Company, Inc., New York, 1956, p. 295.

equilibrium with the mono and dicarbanion. The resulting intermediate (VIII) would then decompose as indicated. Because of the presence of the phenyl group, however, it appears possible that the mono or dicarbanion might also undergo some cleavage.

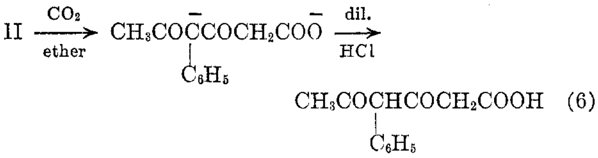


$$CH_3\overset{O^-}{\underset{NH_2}{C}}-\underset{C_6H_5}{C}HCOCH_3$$

VIII

Although the preferred agent for the benzoylation of II was methyl benzoate, benzoyl chloride was found to produce a 22% yield of triketone V on treating II in pyridine with benzoyl chloride in the ratio of two to one. No dibenzoylation product was isolated, and 64% of the original β-diketone I was recovered. In a previous study[10] of certain acylations of monosodio ketones with acid chlorides a three to one ratio of the reactants was preferred to the two to one ratio because of the tendency to form the diacylation product.

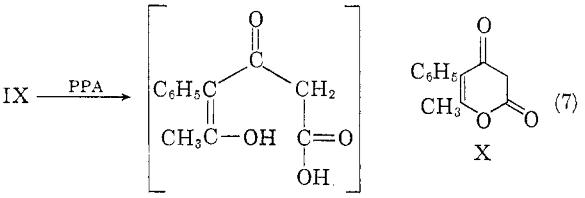
Finally II was carbonated in ether (six hours) to form the diketoacid IX in 26% yield (Equation 6).



$$II \xrightarrow[ether]{CO_2} CH_3CO\underset{C_6H_5}{\bar{C}}COCH_2CO\bar{O} \xrightarrow[HCl]{dil.} CH_3CO\underset{C_6H_5}{C}HCOCH_2COOH \quad (6)$$

IX

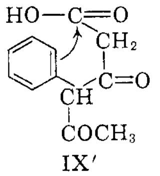
The structure of the product was established as IX by cyclization by means of polyphosphoric acid (PPA) to give the δ-lactone X in 96% yield (Equation 7).



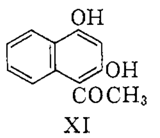
(7)

X

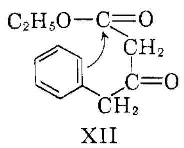
It is of interest that the diketo acid IX evidently did not undergo aromatic cyclization as indicated in IX′ to form the dihydroxynaphthalene derivative XI, a type of cyclization that also is known to be acid catalyzed. For example, β-keto ester XII has been cyclized by means of sulfuric acid to form the corresponding dihydroxynaphthalene.[11]



IX′



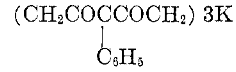
XI



XII

Evidence that the cyclic product was the lactone X and not the dihydroxynaphthalene derivative XI was provided by the fact that the product gave a negative enol test with ferric chloride, which result would be expected for a lactone such as X but not for a dihydroxynaphthalene.[11] The infrared spectrum of the product did not have a hydroxyl peak which is further evidence that its structure is lactone X rather than dihydroxynaphthalene XI.

An attempt to prepare the tripotassio salt XIII by treating I with three molecular equivalents of potassium amide in liquid ammonia was evidently unsuccessful.



$$(\bar{C}H_2CO\underset{C_6H_5}{\bar{C}}CO\bar{C}H_2)\,3K^+$$

XIII

Thus, on treating the reaction mixture with one equivalent of benzyl chloride for five hours, none of the possible dibenzylation product was isolated and only a 2% yield of the monobenzylation product III was realized. Instead there were obtained a 45% yield of stilbene based on the benzyl chloride and a 25% yield of phenylacetone based on the β-diketone I, 20% of I being recovered. The purple color associated with the formation of stilbene through the self-condensation of benzyl chloride by amide ion was observed.[12] It is possible that the self-condensation of the benzyl chloride was effected by tripotassio salt XIII but it seems more likely that this reaction was brought about by the extra equivalent of amide ion over the two equivalents involved in the formation of II.

EXPERIMENTAL[13]

Preparation of dipotassio derivative II. 3-Phenylpentane-2,4-dione[14] was synthesized from phenylacetone and acetic anhydride by the boron trifluoride method.

To a stirred solution of 0.2 mole of potassium amide in 300 ml. of commercial, anhydrous liquid ammonia was added 17.6 g. (0.1 mole) of solid β-diketone I in small portions. The resulting white suspension was stirred for 15–30 min. after which the formation of 0.1 mole of the dipotassio derivative II was assumed to be complete.

Benzylation of dipotassio derivative II. A. *In ether.* To a stirred suspension containing 0.0284 mole of the dipotassio derivative II in 300 ml. of liquid ammonia was added 3.566 g. (0.0284 mole) of benzyl chloride. The liquid ammonia was

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[10] B. O. Linn and C. R. Hauser, *J. Am. Chem. Soc.*, **78**, 6066 (1956).

[11] G. Soliman and R. W. West, *J. Chem. Soc.*, 54 (1944).

[12] C. R. Hauser, W. R. Brasen, P. S. Skell, S. W. Kantor, and A. E. Brodhag, *J. Am. Chem. Soc.*, **78**, 1653 (1956).

[13] Melting points (uncorrected) were taken on a Fisher-Johns melting point apparatus. Infrared spectra were produced with a Perkin-Elmer Model 21 Spectrophotometer by the potassium bromide method. Ultraviolet spectra were taken on a Warren Spectracord. Elemental analyses were by Galbraith Microchemical Laboratories, Knoxville, Tenn.

[14] See C. R. Hauser, F. W. Swamer, and J. T. Adams, *Org. Reactions*, **Vol. VIII**, John Wiley and Sons, Inc., New York, N. Y., 1954, p. 133.

evaporated (steam bath) as an equal volume of dry ether was added. The resulting ethereal suspension was stirred for 6 hr., and then cooled. The reaction mixture was shaken with dilute hydrochloric acid, and the two layers were separated. After washing with water, the ethereal layer was dried over Drierite, and the solvent removed. The residual oil was heated *in vacuo* until low boiling material (containing some benzyl chloride and β-diketone I) was removed, and the residue was dissolved in ether. The ethereal solution was shaken with excess saturated aqueous copper acetate solution, and the resulting copper chelate was collected on a funnel. After recrystallization from ethanol there was obtained 13 g. (16%) of gray-green platelets of the copper chelate of 1,4-diphenylhexane-3,5-dione, m.p. 190–192°.

Anal. Calcd. for $C_{36}H_{34}O_4Cu$: C, 72.76; H, 5.78; Cu, 10.70. Found: C, 72.92; H, 5.57; Cu, 10.73.

Its infrared spectrum showed the following peaks: 3.3, 6.3, 3.18, 7.0, 7.2, 7.45, 7.55, 7.75, 9.35, 9.9, 9.13, 13.0, 13.2, 14.25 μ.

B. *In pyridine and liquid ammonia.* A 0.05-mole suspension of II was prepared in 100 ml. of liquid ammonia. When most of the liquid ammonia had evaporated 6.33 g. (0.05 mole) of benzyl chloride was added to the stirred suspension followed immediately by the addition of 50 ml. of dry pyridine. The dipotassio salt dissolved within 1–2 min. giving a very light red colored solution. The reaction mixture was heated gently on the steam bath until it reached room temperature and stirring was continued at this temperature for 2 hr. It was then neutralized by addition to a mixture of concd. hydrochloric acid and crushed ice to precipitate the product which was dissolved in ether. The ethereal solution was washed with a saturated solution of sodium bicarbonate, dried over anhydrous magnesium sulfate, and the solvent removed. The residual oil was distilled *in vacuo* to give 1,4-diphenylhexane-3,5-dione, collected at 136–138°, 0.25 mm., which was dissolved in ether. The ethereal solution was shaken with a saturated aqueous solution of copper acetate to precipitate 8.64 g. (62%) of the copper chelate of III, m.p. 188–190°. A mixed melting-point determination with an authentic sample of the copper chelate of III (prepared above) showed no depression. Some (1.7 g.) of the starting diketone was recovered (collected at 60–63°, 0.25 mm.), m.p. 54–57°. A mixed melting-point determination with an authentic sample of 3-phenylpentane-2,4-dione showed no depression.

The reaction was repeated, first adding the pyridine to the dipotassio derivative in a small quantity of liquid ammonia. Some of the dipotassio derivative dissolved giving a light green colored solution, the rest of the derivative remaining in suspension. On addition of the benzyl chloride all the dipotassio derivative dissolved within 1–2 min. giving a light red colored solution which was brought to room temperature and stirred for 2 hr. The product was worked up as in the previous reaction to give 3.8 g. (51%) of the copper chelate of III, m.p. 183–185° and to recover 0.8 g. (18%) of the starting diketone, m.p. 54–56°.

The above reaction was repeated except that it was neutralized 3 min. after the benzyl chloride had been added to the suspension of the dipotassio derivative in pyridine. The product was worked up as before to give 3.45 g. (52%) of diketone III collected mostly at 155–158°, 3.0 mm. The copper chelate melted at 190–192° (ethanol). Some (0.65 g.; 15%) of the starting diketone, m.p. 53–57° was recovered.

In a blank experiment 0.05 mole of II (suspension) in pyridine containing a small quantity of liquid ammonia was stirred at room temperature for 2 hr. The reaction mixture was then neutralized by addition to a mixture of concd. hydrochloric acid and ice to precipitate 3.8 g. (87%) of the starting diketone, m.p. 52–54°. A mixed melting-point determination with an authentic sample of 3-phenylpentane-2,4-dione showed no depression.

An unsuccessful attempt was made to benzylate II with benzylpyridinium chloride, prepared by heating an equimolecular mixture of benzyl chloride and pyridine to 100° for 5 min. Solid benzylpyridinium chloride (0.025 mole) was added to a 0.025 mole suspension of II in 50 ml. of pyridine containing a small amount of liquid ammonia. An immediate blood red color appeared in the reaction mixture. After stirring for 3 min. the reaction mixture was neutralized with acid to give 2 g. (45%) of the starting diketone, m.p. 54–56°.

An attempt to benzylate II in liquid ammonia was unsuccessful. After 2 hr. none of the benzylated product was isolated and a considerable amount of starting material was recovered.

Independent synthesis of β-diketone III. A mixture of 13.4 g. (0.1 mole) of phenylpropane-2-one, 56.5 g. (0.2 mole) of hydrocinnamic anhydride, and 5.15 g. (0.03 mole) of *p*-toluenesulfonic acid was saturated at 0–10° with boron trifluoride according to the method of Hauser and Manyik.[15] The product was heated *in vacuo* until low boiling material was removed. The residue was dissolved in ether and the ethereal solution was shaken with a saturated aqueous copper acetate solution to precipitate 6.7 g. (23%) of the copper chelate of 1,4-diphenyl-3,5-dione, m.p. 188–190°. A mixed melting point determination with the copper chelate of III (obtained in a previous reaction described above) showed no depression. The infrared spectra of the copper chelates of both products were identical.

The copper chelate of III was decomposed with 10% sulfuric acid, and the free diketone was dissolved in ether. The ethereal solution was washed with water, dried over anhydrous magnesium sulfate, the solvent removed, and the residual oil distilled *in vacuo*. 1,4-Diphenylhexane-3,5-dione was collected at 127° at 0.1 mm. and redistilled at 147–148° at 0.3 mm., $n_D^{26} = 1.5769$.

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.2; H, 6.81. Found: C, 80.96; H, 6.82.

The compound gave a cherry-red enol test with alcoholic ferric chloride.

Benzoylation of II *to form triketone* V. A. *In liquid ammonia.* To a stirred suspension of 0.1 mole of II in 300 ml. of liquid ammonia was added 6.8 g. (0.05 mole) of methyl benzoate in an equal volume of ether, and stirring was continued for 5 hr. The reaction mixture was then neutralized with an excess of ammonium chloride and the liquid ammonia was replaced with an equal volume of ether. Water was added to dissolve the salts present and the resulting aqueous and ethereal layers were separated. The ethereal layer was washed with water, dried over anhydrous magnesium sulfate, and the solvent removed. The residual oil was distilled *in vacuo* to give 1.3 g. of phenylacetone, n_D^{29} 1.5165, and 7.3 g. of oil, collected at 52–58°, 0.6 mm. The oil was dissolved in ether and the ethereal solution was shaken with a saturated aqueous solution of copper acetate to precipitate 4 g. (18%) of the copper chelate of the starting diketone II, identified by its infrared spectrum. The residue in the distilling flask was washed with a small quantity of ethanol and recrystallized from the same solvent to give 2 g. (14%) of yellow crystals of 1,4-diphenylhexane-1,3,5-trione, m.p. 80–82°.

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 77.11; H, 5.75. Found: C, 76.97; H, 5.58.

The compound gave a green enol test with alcoholic ferric chloride.

Its infrared spectrum showed the peaks: 6.24, 6.35–6.5 (broad), 6.7, 6.85, 7.0, 7.25, 7.8, 8.4, 8.65, 9.1, 9.2, 9.3, 9.7, 9.8, 10.1, 10.6, 11.0, 12.3, 12.9, 13.25, 13.45, 14.15, 14.5, 14.95 μ.

B. *In ether.* The experiment was repeated in ether, the procedure being essentially the same as in the previous reaction except that the liquid ammonia was replaced by an equal volume of dry ether and the reaction mixture was stirred at reflux for 5 hr. It was then cooled and neutralized with dilute hydrochloric acid. On distillation of the product *in vacuo*, 7.6 g. of phenylacetone was collected at 61°, 0.95 mm.

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

($n_D^{26.5}$ 1.5142; 6.7 g.) and 51°, 0.6 mm. ($n_D^{26.5}$ 1.5145; 0.9 g.), identified by infrared spectra. The residue in the distilling flask was dissolved in ether and the ethereal solution was shaken with a saturated aqueous solution of copper acetate to precipitate 4.8 g. of copper chelate which after washing with boiling ethanol had a melting point of 200–240°. The copper chelate was decomposed with 15% sulfuric acid to give, after recrystallization from ethanol, 1.0 g. of 1,4-diphenylhexane-1,3,5-trione, m.p. 79–83° which did not depress the melting point of an authentic sample of the triketone (obtained in the previous reaction). A second crop of 0.5 g. of the triketone (total yield, 18%) was obtained from the filtrate.

C. *In tetrahydrofuran.* To a stirred solution of 0.9 mole of II in 400 ml. of liquid ammonia was added 6.12 g. (0.045 mole) of methyl benzoate. The liquid ammonia was replaced by an equal volume of tetrahydrofuran and the resulting suspension was boiled under reflux for 5 hr. About 300 ml. of water was added to the cooled reaction mixture which was then acidified with dilute sulfuric acid and extracted several times with ether. The combined ethereal extracts were washed with water and dried over Drierite and the solvent removed. On distillation of the residual oil *in vacuo,* 2.25 g. of oil was obtained at 36°, 0.26 mm., n_D^{25} 1.5154, which was identified by its infrared spectrum as phenylacetone. The residue in the distilling flask was washed with ether and collected on a funnel to give 4.82 g. solid, m.p. 121–126°, which on recrystallization twice from *n*-hexane (using Norit once) and finally from ethanol gave colorless prisms of 2,5-diphenyl-6-methyl-γ-pyrone (hydrated), m.p. 120–122°.

Anal. Calcd. for $C_{18}H_{14}O_2 \cdot {}^1/_2H_2O$: C, 79.66; H, 5.57. Found: C, 79.86; H, 5.77.

The compound did not give an enol test with an ethanolic solution of ferric chloride. A concd. sulfuric acid solution of the compound exhibited a bright blue fluorescence in ultraviolet light. The ultraviolet spectrum of the compound had a maximum at 270 mμ and a log ε value 4.295.

A sample of the compound was dissolved in concd. sulfuric acid, kept at 0° for 10 min. and poured onto ice water to give 2,5-diphenyl-6-methyl-γ-pyrone. It was recrystallized several times from ethanol from which it was obtained in white needles, m.p. 147–148°.

Anal. Calcd. for $C_{18}H_{14}O_2$: C, 82.41; H, 5.38. Found: C, 82.26; H, 5.31.

The ultraviolet spectrum of the pyrone had a maximum at 270 mμ and a log ε value of 4.327. It did not give a positive enol test with alcoholic ferric chloride.

D. *In pyridine and liquid ammonia.* A 0.05-mole suspension of II was prepared in 100 ml. of liquid ammonia. When most of the liquid ammonia had evaporated, 3.4 g. (0.025 mole) of methyl benzoate was added followed immediately by the addition of 50 ml. of dry pyridine. Some of II appeared to dissolve but most of it remained in suspension. The reaction mixture was stirred at room temperature for 2 hr. and then neutralized by pouring onto a mixture of excess of concd. hydrochloric acid and crushed ice to precipitate the product which was dissolved in ether. The ethereal solution was washed with a saturated solution of sodium bicarbonate, dried over anhydrous magnesium sulfate, and the solvent removed. The residual oil was distilled *in vacuo* to give 5.8 g. (66%) of the starting diketone collected mostly at 67–68°, 0.3 mm., m.p. 45–51°. Mixed melting point determination with 3-phenylpentane-2,4-dione gave m.p. 45–54°. The distillation was stopped at 70° and the residue was recrystallized from ethanol to give 2.65 g. of yellow crystals of 1,4-diphenylhexane-1,3,5-trione, m.p. 76–80°, a sample of which did not depress the melting point of an authentic sample of the compound. A second crop, 0.6 g. of the triketone (total yield, 47%) was obtained from the ethanolic filtrate.

In another experiment 0.05 mole of II was prepared in liquid ammonia. The liquid ammonia was evaporated completely (steam bath), sweeping out the last traces of it with ether. Pyridine (50 ml.) was added to II in a small amount of ether, followed immediately by the addition of 3.51 g. (0.025 mole) of benzoyl chloride. Most of the dipotassio derivative appeared to dissolve in the pyridine, and the solution assumed a deep red color. The reaction mixture was stirred for 2 hr., then neutralized by acidification and worked up as in the previous reaction to give 5.66 g. (64%) of starting diketone collected at 60–70° at 0.22 mm., m.p. 48–53°, and 2.8 g. of copper chelate of triketone V, obtained on shaking an ethereal solution of the residue (from the distillation of the product) with a saturated aqueous solution of copper acetate. The free triketone, m.p. 81–85°, was obtained on decomposition of the copper chelate with 15% sulfuric acid. A mixed melting point determination with 1,4-diphenylhexane-1,3,5-trione showed no depression. A further 0.7 g. of the copper chelate was obtained from an intermediate fraction collected at 69–70° at 0.22 mm.

Formation of 2,5-diphenyl-6-methyl-γ-pyrone. A sample of 0.25 g. of the triketone was dissolved in 5 ml. of cold concd. sulfuric acid and cooled to 0°–10° for 10 min. and then poured on to ice water to precipitate 0.2 g. (85%) of the pyrone V, m.p. 143–144°. A mixed melting point determination with an authentic sample of the pyrone obtained above showed no depression.

Samples of the triketone were also cyclized to the pyrone, in good yields, by refluxing for 2 hr. in 45% hydrobromic acid and by heating (steam bath) in polyphosphoric acid for 1.5 hr.

Carbonation of II. A 0.0284 mole suspension of II was prepared in 300 ml. of liquid ammonia. The liquid ammonia was evaporated rapidly (steam bath) as an equal volume of dry ether was added. The resulting slurry of II was poured on to a large excess of pulverized Dry Ice. The mixture was agitated at intervals and more Dry Ice was added as needed. After 6 hr. the ether slurry was extracted twice with water and the aqueous extracts combined. The aqueous solution was cooled in an ice bath, acidified, and the resulting precipitate was collected and redissolved in aqueous sodium bicarbonate solution. After washing with ether, the cooled bicarbonate solution was acidified and the resulting precipitate was collected on a funnel, washed with water, and dried to give 1.6 g. (26%) of 4-phenyl-3,5-dioxohexanoic acid which recrystallized from hexane in white prisms, m.p. 110–112°. It gave a cherry-red enol test with ethanolic ferric chloride.

Anal. Calcd. for $C_{12}H_{12}O_4$: C, 65.45; H, 5.49. Found: C, 65.41, H, 5.67.

Its infrared spectrum showed the following peaks: 3.3 (broad), 5.8, 6.2 (broad), 6.7, 7.15, 7.55, 8.55, 9.35, 9.95, 10.2, 10.8 (broad), 13.15 μ.

Formation of lactone. A 0.5-g. sample of the β-keto acid was dissolved in 5 ml. of polyphosphoric acid and heated on a steam bath for 1.5 hr. The solution was then poured onto crushed ice and the resulting precipitate was collected, washed with water, and dried, yielding 0.44 g. (96%) crude 4-hydroxy-6-methyl-5-phenyl-α-pyrone which was recrystallized from ethanol (Norit) to give 0.35 g. of the pure lactone, m.p. 227–229°. It did not give a positive enol test with alcoholic ferric chloride.

Anal. Calcd. for $C_{12}H_{10}O_3$: C, 71.27; H, 4.99. Found: C, 71.15; H, 4.96.

Its infrared spectrum showed the peaks: 3.4, 3.9, (broad), 6.0, 6.2, 6.5, (broad), 6.7, 7.95, 7.7, 7.8, 8.0, 8.5, 9.25, 9.35, 9.65, 9.9, 10.3, 10.8, 11.1, 12.05, 12.3, 13.0, 14.2 μ.

A sample of the β-keto acid was heated at 135° for 5 min. during which time carbon dioxide was evolved. The residue was recrystallized from petroleum ether (Dry Ice cooling) to give white crystals, m.p. 53–55°. A mixed melting point determination with 3-phenylpentane-2,4-dione showed no depression.

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