initial evolution of the oxides of nitrogen subsided. The addition was continued until the gain in weight of the solution was 30 g. The coolant was then removed and the solution allowed to warm slowly to 15° with the addition of small amounts of copper bronze from time to time. Vigorous stirring was maintained throughout. The solution was filtered and the sulfinic acid dissolved in base. After removal of unreacted copper, the solution was acidified and extracted with ether which was in turn extracted with aqueous sodium bicarbonate. The bicarbonate solution was shaken with charcoal, acidified and the product isolated with ether, 1.1 g. (22%) being obtained. The low yield here is somewhat surprising in view of the much higher yields obtained in this Laboratory from the conversion of similar anilines to the corresponding sulfinic acids. Such anilines, however, differed from 2-benzyl-4,6-dimethylaniline in having only a single *o*-substituent, while the latter is substituted in both the 2- and 6-positions. The decomposition of its diazonium salt may, therefore, occur at appreciably higher temperatures than those required for similar amines with only a single *o*-substituent.

After crystallization from aqueous acetone as above, the acid melted at 92.7–94.7° dec. and had a neutral equivalent of 263.0; calculated for 2-benzyl-4,6-dimethylbenzenesulfinic acid is 260.3.

The Reaction of Mesityl *p*-Tolyl Sulfone with *n*-Butyllithium.—A solution of 24.7 g. (0.090 mole) of mesityl *p*-tolyl sulfone in 600 ml. of ether at 0° was treated, over a period of 15 minutes, with a solution of *n*-butyllithium from 1.61 g. (0.23 g. atom) of lithium wire and 15.5 g. (0.113 mole) of *n*-butyl bromide in 135 ml. of ether. Assuming an 80% yield of the organometallic, 0.09 mole of *n*-butyllithium was added.

After stirring for 1.5 hours at 0°, the reaction mixture was allowed to warm to room temperature and stand overnight. Hydrolysis with 100 ml. of 3 *N* hydrochloric acid was followed by separation and extraction of the ether layer with two 75-ml. portions of 8% sodium hydroxide and one 75-ml. portion of water. The washings were combined and acidified to give an oil which crystallized almost immediately. Solution of this acid in methanol and treatment with charcoal followed by crystallization, after adding water, gave 18.8 g. (76% of theory) of colorless needles, m.p. 90–91° dec. The neutral equivalent of this acid was 278; calcd. for 2-(4-methylbenzyl)-4,6-dimethylbenzenesulfinic acid, 274.

2-Chloromercuri-3,4′,5-trimethyldiphenylmethane.—Using the procedure described by Whitmore, *et al.*,[23] the chloromercuri derivative was prepared from 1.00 g. (0.00368 mole) of the sodium salt of 2-(4-methylbenzyl)-4,6-dimethylbenzenesulfinic acid and 1.00 g. (0.00365 mole) of mercuric chloride. Crystallization of the product from aqueous alcohol gave fine white needles, weight 0.71 g. (44% of theory), m.p. 132–133°.

Anal. Calcd. for $C_{16}H_{17}HgCl$: Cl, 7.96. Found: Cl, 7.96.

Oxidation and Desulfonation of the Reaction Product of Mesityl *p*-Tolyl Sulfone and *n*-Butyllithium.—This process was carried out in the same manner as described above for the oxidation and desulfonation of the rearrangement product of mesityl phenyl sulfone, using a 7.0-g. (0.026 mole) sample of the sulfinic acid. The product weighed 2.34 g. (43%) and boiled at 130–131° (4 mm.), $n^{20.5}\text{D}$ 1.5613. The refractive index of 3,4′,5-trimethyldiphenylmethane (below) is 1.5611 at 21°.

Anal. Calcd. for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.52; H, 8.87.

3,4′,5-Trimethylbenzophenone was prepared from 14.1 g. (0.084 mole) of 3,5-dimethylbenzoyl chloride, 18.8 g. (0.204 mole) of toluene and 12.3 g. (0.092 mole) of aluminum chloride in the manner described above for the preparation of 3,5-dimethylbenzophenone. After vacuum distillation, the yellow solid was purified by low-temperature crystallization from methanol. The fine white crystals so obtained melted at 75.0–75.5°, 12.9 g. (68%) being obtained.

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.75; H, 7.19. Found: C, 85.84; H, 7.40.

3,4′,5-Trimethyldiphenylmethane.—The above 3,4′,5-trimethylbenzophenone was reduced by the Wolff-Kishner method as modified by Huang-Minlon[19] using sodium hydroxide, 85% hydrazine hydrate, diethylene glycol and 8.9 g. (0.040 mole) of the ketone. Vacuum distillation of the product at 110–115° (1 mm.) gave a hydrocarbon, $n^{21}\text{D}$ 1.5611.

Anal. Calcd. for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.44; H, 8.52.

Acknowledgment.—We wish gratefully to acknowledge the support of this work by these several organizations: National Science Foundation (W.J.R., Jr.), Union Carbide and Carbon Chemical Co. (W.J.R., Jr.), National Institutes of Health (O.L.N.) and Purdue Research Foundation (D.B.E.).

LAFAYETTE, INDIANA

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[23] F. C. Whitmore, F. H. Hamilton and N. Thurman, THIS JOURNAL, **45**, 1066 (1923).

[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY]

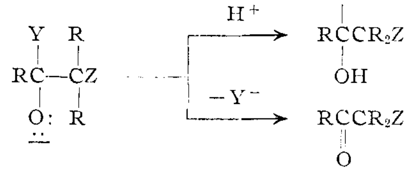
Chemistry of Enolates. II. Self-condensation of Methyl Trityl Ketone. A Novel Claisen Condensation

BY JANICE L. GREENE[1] AND HARRY D. ZOOK

RECEIVED JANUARY 25, 1958

β-Diketones have been prepared by acylation of the sodium enolate of methyl trityl ketone. Acylation by the ketone itself results in a Claisen-type condensation in which the condensate anion is converted to the β-diketone by elimination of triphenylmethide ion. An improved preparation for methyl trityl ketone and the instability of this ketone in sulfuric acid are described.

Base-induced condensations of carbonyl compounds give condensate anions which may be stabilized by either of two paths: (1) extraction of a proton from the solvent (aldol condensation) or (2) elimination of a stable anion (Claisen condensation).



(1)

(2)

The latter reaction is familiar in the condensa-

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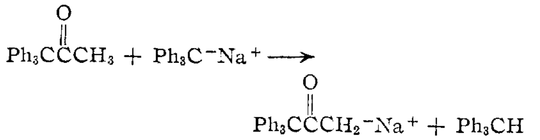
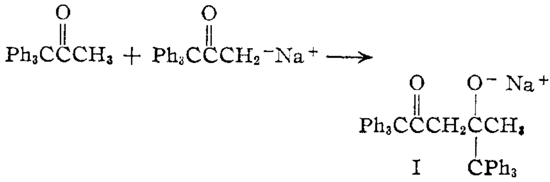
[1] This paper forms part of a Ph.D. thesis by Janice L. Greene, Allied Chemical and Dye Corporation Fellow, The Pennsylvania State University, 1954–1955.

tion of esters[2] and has been observed in acylations by esters, acyl chlorides,[3] anhydrides[3] and N,N-dialkylamides[4] where Y = OR, Cl, OCOR and NR_2, respectively. Self-condensation of aldehydes or ketones heretofore has resulted in aldols, ketols or their dehydration products; dissociation of hydride or alkyde ions from the condensed anion has been undetected.

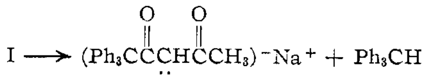
In the present study, a Claisen-type self-condensation of a ketone has been effected in which the cleaved carbanion is the relatively stable triphenylmethide ion. Methyl trityl ketone condenses with its own sodium enolate to form the β-diketone, 1,1,1-triphenyl-2,4-pentanedione. In the usual aldol condensation, a ketol would be obtained from anion I upon reaction with an acid.



$$Ph_3C\overset{\overset{\displaystyle O}{\|}}{C}CH_3 + Ph_3C^-Na^+ \longrightarrow Ph_3C\overset{\overset{\displaystyle O}{\|}}{C}CH_2{}^-Na^+ + Ph_3CH \quad (3)$$



$$Ph_3C\overset{\overset{\displaystyle O}{\|}}{C}CH_3 + Ph_3C\overset{\overset{\displaystyle O}{\|}}{C}CH_2{}^-Na^+ \longrightarrow \underset{\text{I}}{Ph_3C\overset{\overset{\displaystyle O}{\|}}{C}CH_2\overset{\overset{\displaystyle O^-\,Na^+}{|}}{\underset{\underset{\displaystyle CPh_3}{|}}{C}}CH_3} \quad (4)$$



$$\text{I} \longrightarrow (Ph_3C\overset{\overset{\displaystyle O}{\|}}{C}\underset{\cdot\cdot}{C}H\overset{\overset{\displaystyle O}{\|}}{C}CH_3)^-Na^+ + Ph_3CH \quad (5)$$

Here instead, the ketol salt dissociates to a product typical of a Claisen condensation (equation 5).

The self-condensation occurs rapidly in the fused state at 220°, much more slowly at 125°, and to no appreciable extent at these temperatures in the presence of xylene as a diluent. The results of seven experiments are summarized in Table I. No trace of the ketol could be detected by infrared analysis of the products.

TABLE I

SELF-CONDENSATION OF METHYL TRITYL KETONE

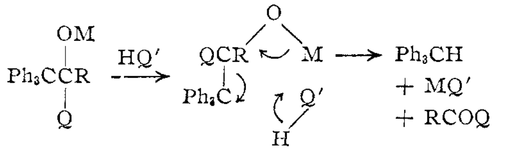
Ketone, moles × 10^3	Enolate, moles × 10^3	Temp., °C.	Time, hr.	Medium	β-Diketone, %
1.86	1.80	203–207	8	Melt	76
1.82	1.82	204–210	4	Melt	92
1.71	1.69	122–128	13	Melt	59
1.86	1.82	220–223	1	Melt	91
7.50	7.50	35	5	Ether	0[a]
3.02	3.02	76	12	Benzene	0[a]
3.02	3.02	196–202[b]	48	Xylene	0[a]

[a] Product consisted almost entirely of triphenylmethane and recovered ketone. Solvents were removed and infrared spectra determined in potassium bromide. [b] Sealed tube.

Evidence for the structure of the β-diketone was obtained from its analysis, infrared spectrum, reactivity with copper acetate and alcoholic ferric chloride, and independent synthesis from acetyl chloride and methyl trityl ketone. The best synthetic route is the self-condensation of methyl trityl ketone. Acylation of this ketone by acetyl chloride leads to complex mixtures of products unless a large excess of the enolate is employed.

An analogous β-diketone, 1,1,1,4-tetraphenyl-2,4-butanedione, $(C_6H_5)_3CCOCH_2COC_6H_5$, was prepared from the enolate of methyl trityl ketone by acylation with ethyl benzoate.

Cleavage of a trityl anion at the site of a carbonyl group is not without precedent. The formation of triphenylmethane by the action of alcoholic potassium hydroxide on trityl ketones is a customary method of structure proof.[5] Tritylphenylcarbinol is rapidly cleaved to benzaldehyde and triphenylmethane by hot alcoholic sodium hydroxide,[6] and attempts to prepare tertiary alcohols by the action of certain organometallic compounds on phenyl trityl ketone result in cleavage of the trityl group.[7] These cleavages may be aided by active-hydrogen compounds (solvent or enolizable ketonic product) according to the general scheme shown in equation 6, where (Q,Q′) =



(6)

(OEt, OEt), (H, OEt), (CH_3, CH_2COPh) and (CH_2COCPh_3, $CH(COCH_3)COCPh_3$). Reaction within a coördination complex would be expected in media of low ion-solvating power.[8] No cleavage occurs in several instances where compounds containing active hydrogen atoms are lacking.[9] Only a small amount of such compound would be required to initiate cleavage, provided that the product, RCOQ, then could act to promote further cleavage. In this work, the β-diketone would play this role and be converted to its sodium enolate.

The methyl trityl ketone required for this study was prepared from benzil by successive treatment with phenyl and methyl Grignard reagents followed by rearrangement of the resulting triphenylpropylene glycol. Treatment of this glycol with concentrated sulfuric acid according to the procedure of McKenzie and Myles[10] gave α,α-diphenylpropiophenone rather than the reported methyl trityl ketone. Because of this discrepancy, the effects of acidic reagents on the glycol and both ketones were investigated in some detail. Methyl trityl ketone is the main product when the rearrangement of the glycol is effected by iodine in acetic acid, or when a benzene solution of the glycol is treated

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(2) C. R. Hauser and B. E. Hudson, Jr., "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 266.

(3) B. E. Hudson, Jr., E. H. Dick and C. R. Hauser, THIS JOURNAL, **60**, 1960 (1938).

(4) G. W. Chelintsev and E. D. Osetrova, *Ber.*, **69**, 374 (1936); G. W. Chelintsev and B. M. Dubinin, *ibid.*, **69**, 2024 (1936); G. Gilbert, THIS JOURNAL, **77**, 4413 (1955).

(5) P. J. Montagne, *Rec. trav. chim.*, **24**, 122 (1904); S. A. Koopal, *ibid.*, **34**, 140 (1915); H. Wieland and H. Kloss, *Ann.*, **470**, 201 (1929); W. E. Bachmann and F. H. Moser, THIS JOURNAL, **54**, 1127 (1932).

(6) L. Ellison and J. Kenyon, *J. Chem. Soc.*, 779 (1954).

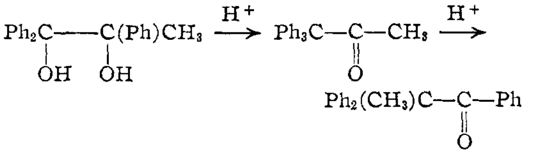
(7) E. Bergmann, *ibid.*, 412 (1936); W. A. Mosher, T. H. Fairbanks and L. J. Prucino, Abstracts of Papers, American Chemical Society, 126th Meeting, New York, N. Y., September, 1954.

(8) Compare the alkylation of enolates, A. Brandstrom, *Arkiv. Kemi*, **6**, 155 (1953); **7**, 81 (1954), as well as the several six-center-type reactions demonstrated in Grignard processes.

(9) W. A. Mosher and M. L. Huber, THIS JOURNAL, **73**, 795 (1951); **75**, 4604 (1953); R. C. Fuson and J. P. Freeman, *ibid.*, **76**, 911 (1954); R. C. Fuson and P. E. Wiegert, *ibid.*, **77**, 1138 (1955).

(10) A. McKenzie and J. Myles, *Ber.*, **65**, 209 (1932).

with phosphorus pentoxide. Methyl trityl ketone is extremely unstable in strong sulfuric acid solutions; none can be recovered after a few minutes of complete solution in 96.1% acid. The specific rate for the disappearance of the ketone is greater than 7 × 10^{-3} sec.$^{-1}$. However, only 24% of the ketone is rearranged to α,α-diphenylpropiophenone; the remainder is converted to water-soluble products, probably by sulfonation. Thus, the specific rate *for the rearrangement* at 30° in 96.1% sulfuric acid is greater than 1.5 × 10^{-3} sec.$^{-1}$ rather than the value previously reported.[11] α,α-Diphenylpropiophenone also is converted to water-soluble products by 96.1% sulfuric acid. The rates of all these reactions decrease with decreasing concentration of sulfuric acid. The concentrated acid used by McKenzie and Myles[10] must have been considerably more dilute than that now available.



$$\mathrm{Ph_2C(OH)\text{—}C(OH)(Ph)CH_3} \xrightarrow{H^+} \mathrm{Ph_3C\text{—}C(=O)\text{—}CH_3} \xrightarrow{H^+} \mathrm{Ph_2(CH_3)C\text{—}C(=O)\text{—}Ph} \quad (7)$$

Experimental

Phenylbenzoin (α-Hydroxy-α,α-diphenylacetophenone).—Benzoin[12] was prepared in 86% yield from 523 g. of benzaldehyde, and oxidized to benzil,[13] m.p. 93-94.5°, in 82% yield. To a solution of 80 g., 0.38 mole, of benzil in 1200 ml. of dry ether was added 300 ml., 0.39 mole, of an ethereal solution of phenylmagnesium bromide. After stirring in an atmosphere of nitrogen for 13 hours, the precipitated bromomagnesium salt was filtered by suction from the ethereal phase containing unreacted benzil. The salt was decomposed with dilute hydrochloric acid, and the product in ether was washed with 10% sodium carbonate solution and water. The crude ketone, m.p. 76–80°, weighed 79 g. (72%). Two crystallizations from ethanol and eight from ligroin were required to give 31 g. (28%) of phenylbenzoin,[14] m.p. 84.5–85°.

1,1,2-Triphenyl-1,2-propanediol.—Phenylbenzoin, 30.7 g., 0.11 mole, was dissolved in 200 ml. of dry thiophene-free benzene and added with stirring over a period of two hours to 250 ml., 0.8 mole, of a filtered ethereal solution of methylmagnesium iodide. After refluxing for 40 hr. in an atmosphere of nitrogen, the mixture was hydrolyzed with a saturated solution of ammonium chloride. Ether and benzene were distilled, and the residual oil was evacuated for 9 hr. at 3 mm. and crystallized in the ice-box. The product was recrystallized three times from ligroin to give 19.2 g. (59%) of glycol, m.p. 78.5–79.5°. The reported m.p. of 1,1,2-triphenyl-1,2-propanediol[15] is 76–77°. When benzene was not used as a solvent, the iodomagnesium salt of phenylbenzoin precipitated and did not react further with the Grignard reagent. Phenylbenzoin was recovered upon hydrolysis.

Methyl Trityl Ketone (1,1,1-Triphenyl-2-propanone).—A solution of 1.0 g. of 1,1,2-triphenyl-1,2-propanediol in 5 ml. of a 0.2% solution of iodine in glacial acetic acid was refluxed for five minutes and cooled to 0°. The product was recrystallized from ethanol to give needles melting at 137.5–139°. In a similar manner, 174.5 g. of the crude glycol was converted to 66 g. of the ketone, m.p. 137.5–138°. In this synthesis, the phenylbenzoin was not isolated: benzil was treated in succession with equivalent quantities of phenyl and methyl Grignard reagents. The over-all yield for the three-step process from benzil was 32%.

A 0.7-g. sample of the ketone was cleaved by refluxing for 1 hr. with 25 ml. of 95% ethanol containing 4 g. of potassium hydroxide. A white precipitate formed when the solution was poured into water. Recrystallization from ethanol gave triphenylmethane, m.p. and mixed m.p. 90.5–92°.

An oxime was prepared from 1 g. of the ketone, 1 g. of hydroxylamine hydrochloride, 5 ml. of absolute ethanol and 10 ml. of pyridine. A crystalline derivative was obtained after the solution had been refluxed for 28 hr. Recrystallization from methanol, then from ligroin and from ethanol, gave white needles, m.p. 223.4–223.6°. The infrared spectrum contained a very small carbonyl peak at 5.84 μ and a broad band at 6.10–6.15 μ characteristic of the carbon-nitrogen double bond.[16]

Anal. Calcd. for $C_{21}H_{19}NO$: C, 83.69; H, 6.35; N, 4.65. Found: C, 83.86; H, 6.02; N, 4.60.

This ketone is identical with the acetyltriphenylmethane, m.p. 137–138°, described by McKenzie and Myles[10] who were unable to obtain an oxime. The spectrum of the ketone in potassium bromide exhibited a carbonyl peak at 5.85 μ and other strong peaks at 6.24, 6.69, 6.91, 7.40, 8.65, 9.63, 13.08, 13.26, 13.37 and 14.2 μ.

Methyl trityl ketone could not be prepared from acetyl chloride and sodium triphenylmethide. Although equimolar amounts reacted at once with disappearance of the red color and formation of a white precipitate, the product consisted of triphenylmethane and an oil which gave a deep red color to alcoholic ferric chloride solution. A 2% yield of the ketone, m.p. 138–139.5°, was obtained by chromatography on an alumina column.

Rearrangements in Sulfuric Acid.—Trituration of 12.5 g. of 1,2,2-triphenyl-1,2-propanediol with 200 ml. of concentrated sulfuric acid gave a deep green solution. Upon dilution, only α,α-diphenylpropiophenone (1 g.), rather than the reported methyl trityl ketone, was isolated.[10] The ketone melted at 90–91° and had an absorption peak at 5.98 μ characteristic of phenyl-conjugated ketones.[17]

When 0.38 g. of methyl trityl ketone and 50 ml. of 96.7% sulfuric acid were mixed at 30.0°, the solution immediately became dark green. All of the ketone dissolved upon shaking for nine minutes. After 15 minutes, a 10-ml. aliquot was quenched in ice and extracted with carbon tetrachloride. The infrared spectrum of the extract was that of α,α-diphenylpropiophenone and showed the absence of methyl trityl ketone. One-tenth-gram samples of methyl trityl ketone would not dissolve completely in 25-ml. portions of 94, 92 and 87% solutions of sulfuric acid. However, rearrangement occurred at these concentrations. The solid ketone was filtered from the 87% solution after 31.5 hours. The filtrate was quenched in ice and extracted with carbon tetrachloride to give a solution containing methyl trityl ketone and α,α-diphenylpropiophenone in the ratio of about 2:1.

The rate of disappearance of α,α-diphenylpropiophenone in a 0.00751 *M* solution in 96.1% sulfuric acid at 30.0° was measured by analyzing 25-ml. aliquots as described above. After 64 min., only 48.5% of the ketone remained, and all had been converted to water-soluble compounds after 53 hr. The half-life of the reaction was independent of concentration. The specific rate was 3.5 × 10^{-6} sec.$^{-1}$, a value which compares favorably with the rate of disappearance of this ketone (3.8 × 10^{-6} sec.$^{-1}$) when initially formed by rearrangement of methyl trityl ketone. In the latter experiment at the same temperature and concentration of sulfuric acid, methyl trityl ketone completely disappeared after 11 min. Extrapolation of this plot to zero time gave a maximum concentration of 1.76 × 10^{-3} *M* for α,α-diphenylpropiophenone. This represents only 24% of the original methyl trityl ketone. Consequently, 76% of this ketone disappeared by a rapid reaction which did not involve rearrangement to α,α-diphenylpropiophenone. On this basis, the specific rate originally reported for this ketone[11] may be divided into a specific rate for rearrangement to α,α-diphenylpropiophenone (1.5 × 10^{-3} sec.$^{-1}$) and a specific rate for other reactions leading to its disappearance (6.0 × 10^{-3} sec.$^{-1}$).

Self-condensation of Methyl Trityl Ketone.—A 1.78-g., 0.0062-mole, sample of the ketone was converted to its sodium enolate by stirring with 37 ml., 0.0056 mole, of an ethe-

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[11] H. D. Zook, W. E. Smith and J. L. Greene, THIS JOURNAL, **79**, 4436 (1957).

[12] R. Adams and C. S. Marvel, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 94.

[13] H. T. Clarke and E. E. Dreger, *ibid.*, p. 87.

[14] S. F. Acree, *Ber.*, **37**, 2758 (1904).

[15] R. Roger, *J. Chem. Soc.*, 522 (1925).

[16] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1954, p. 227.

[17] Reference 16, p. 119.

real solution of sodium triphenylmethide.[18] The reaction required ten minutes because of the slow rate of solution and simultaneous precipitation of the light tan sodium derivative. When the red color had disappeared, an additional 1.48 g., 0.0052 mole, of ketone was added. Ether was distilled, and the temperature was increased to 200° over a period of 4 hr. The mixture was then held at this temperature for 9 hr. During this time, 0.49 g. of triphenylmethane, m.p. 91.5–92.5°, sublimed onto the cooler part of the flask. The remaining liquid solidified when cooled. Only a part of this solid dissolved when shaken vigorously with 50 ml. of ether and 75 ml. of 1:1 hydrochloric acid at 0°. The insoluble material was washed with two 5-ml. portions of ether in which it partially dissolved. The remainder, 0.57 g., melted at 175–182° and gave a deep red color to alcoholic ferric chloride solution. Recrystallization from 75 ml. of 95% ethanol, after treatment with activated charcoal, gave 0.40 g. of white crystalline 1,1,1-triphenyl-2,4-pentanedione, m.p. 182–183°.

Anal. Calcd. for $C_{23}H_{20}O_2$: C, 84.11; H, 6.14. Found: C, 84.39; H, 6.25.

An additional 4.08 g. of solid product was obtained from the combined ethereal layers. A 1.1-g. aliquot of this solid dissolved completely in 10 ml. of carbon tetrachloride. The solution was chromatographed on a 2 × 36-cm. column of Mallinckrodt analytical-grade silica gel. Development and elution with 900 ml. of carbon tetrachloride gave 0.71 g. of triphenylmethane, m.p. 91–92°. Continued elution with 1100 ml. of benzene gave recovered methyl trityl ketone, 0.13 g. (15%), m.p. 138.5–139°, followed by the β-diketone, 0.24 g., m.p. 181–184°. The total yield of β-diketone was 0.0090 mole (79%). The triphenylmethane isolated (103%) corresponded to that expected from the 0.0056 mole of sodium triphenylmethide and the 0.0090 mole of ketone condensed.

The infrared spectrum of the β-diketone in potassium bromide exhibited the extremely strong, broad peak at 6.1–6.5 μ with maximum absorption at 6.25 μ characteristic of several β-diketones.[19] The broad, general absorption at 3.7 μ due to hydrogen-bonded hydroxyl groups was extremely weak. Additional evidence for the structure of the diketone was obtained by its synthesis from acetyl chloride and methyl trityl ketone (below). The diketone could not be cleaved by refluxing for 104 hr. with 12% alcoholic potassium hydroxide.

Several condensations were conducted in which the solvent, temperature and time of heating were varied. For these studies, a weighed sample of methyl trityl ketone was dissolved in 10 ml. of dry ether. The sodium enolate did not precipitate when an equivalent amount of 0.13 *N* sodium triphenylmethide solution was put in. An additional weighed amount of ketone was added, ether was distilled, and the melt was heated for a specific time at the desired temperature. The products were dissolved in 15 ml. of benzene and hydrolyzed by an equal volume of 1:1 hydrochloric acid. Aqueous layers were extracted with two 10-ml. portions of benzene. The combined benzene layer was dried with 1 g. of Drierite and made up to 50.0 ml. The solutions contained only β-diketone, triphenylmethane and methyl trityl ketone. These compounds were determined quantitatively by infrared analysis. A major peak, at which the solvent and other two compounds had little or no absorption, was chosen for each substance. These wave lengths were 5.83, 12.2 and 12.5 μ for methyl trityl ketone, triphenylmethane and the β-diketone, respectively. Beer's law was obeyed for each compound over the range of concentration used for analysis. Spectra were measured in a 0.52-mm. cell in a Perkin–Elmer model 21 spectrophotometer equipped with sodium chloride optics. The data for these condensations are summarized in Table I.

Acylation of Methyl Trityl Ketone by Ethyl Benzoate. A solution of 1.07 g., 0.0037 mole, of the ketone in 20 ml. of dry thiophene-free benzene was converted to its enolate by a slight excess of 0.13 *M* sodium triphenylmethide.[18] The solution was refluxed for 80 hr. with 5.6 g., 0.0037 mole, of ethyl benzoate. When cool, the orange liquid and fluffy white precipitate were treated with 25 ml. of 1:1 ice and hydrochloric acid. The organic layer was washed, dried with Drierite and evaporated on the steam-bath to a yellow oil. Treatment of this oil with methanolic cupric acetate gave a green copper salt, 0.3 g. (20%),[20] m.p. 281–281.5°, after washing with ether and benzene.

Anal. Calcd. for $C_{56}H_{42}O_4Cu$: C, 79.89; H, 4.99. Found: C, 80.08; H, 5.17.

A sample of the copper salt was decomposed with concentrated hydrochloric acid, and an ether extract evaporated to give white crystals of 1,1,1,4-tetraphenyl-2,4-butanedione, m.p. 140–140.5°. The diketone gave a deep red color to alcoholic ferric chloride solution. The infrared spectrum in potassium bromide exhibited broad absorption at 3.7 μ due to hydrogen-bonded hydroxyl groups and an extremely broad peak at 6.1–6.5 μ characteristic of several β-diketones.[19]

Anal. Calcd. for $C_{28}H_{22}O_2$: C, 86.15; H, 5.64. Found: C, 86.24; H, 5.81.

Acylation of Methyl Trityl Ketone by Acetyl Chloride.—Complex mixtures of enolic materials resulted when either sodium triphenylmethide or the sodium enolate of methyl trityl ketone was treated with an excess or an equivalent amount of acetyl chloride. Triphenylacetic acid, m.p. 262–263°, was isolated in one experiment. The complexity probably resulted from multi-acylation and cleavage.[21,22] As suggested by Linn and Hauser,[22] three equivalents of enolate to one of acyl chloride finally were used. The enolate was prepared from 12.5 g., 0.044 mole, of methyl trityl ketone in 200 ml. of dry ether and a slight excess of an ethereal solution of sodium triphenylmethide. The solution containing some precipitated salt was stirred for 1 hr. at room temperature with 1.1 g., 0.014 mole, of acetyl chloride, and the resulting slurry was poured onto a mixture of ice and concentrated hydrochloric acid. Solvent was removed from the washed ethereal layer to give 25.6 g. of yellow solid which gave a deep red color to alcoholic ferric chloride solution. A partial separation of the β-diketone from triphenylmethane was accomplished by extraction with 100 ml. of boiling 95% ethanol. A copper salt was prepared from the extract and an equal volume of saturated cupric acetate solution. The salt was difficult to purify. Organic contaminants were removed by extraction with 100 ml. of hot 95% ethanol and for 3 hr. with ether in a Soxhlet extractor. The salt was separated from cupric acetate by extraction into chloroform in the Soxhlet apparatus. Evaporation of the chloroform extract gave 0.59 g. of gray powder, m.p. 252–254°. An additional 0.39 g., m.p. 259–260°, after a 24-hr. extraction with ligroin, was obtained from mother liquors. The copper salt was suspended in ether, shaken with concentrated hydrochloric acid and diluted with water. Evaporation of the ether gave 1.13 g. (25% over-all) of 1,1,1-triphenyl-2,4-pentanedione, m.p. 182–183°.

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(18) H. D. Zook and W. L. Rellahan, THIS JOURNAL, **79**, 881 (1957).

(19) R. S. Rasmussen, D. D. Tunnicliff and R. R. Brattain, *ibid.*, **71**, 1068 (1949).

(20) Complete conversion of methyl trityl ketone to its enolate was shown by rapid loss of the characteristic red color of sodium triphenylmethide until an equivalent quantity had been added. During the subsequent acylation, one-half of the sodium enolate was used to convert the β-diketone to its sodium derivative. Consequently, the maximum yield of diketone expected from this ratio of reagents is 50%.

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