using substantially the procedure described for IVa. The product was obtained in 55% yield as a very viscous oil which distilled at 190–192° (1 mm.).

Anal. Calcd. for $C_{15}H_{12}Cl_4O$: C, 51.46; H, 3.46. Found: C, 51.58; H, 3.42.

Acetate of trichloromethyl-2-benzyl-4-chlorophenylcarbinol. A mixture of 2 g. of the above carbinol (IVb), 4 ml. of freshly distilled boron trifluoride etherate, and 25 ml. of glacial acetic acid was heated under reflux for 10 hr. The mixture was cooled to room temperature and poured into an ice-water mixture. A reddish yellow gum separated and was dissolved in ether. The ether solution was washed with water, a dilute sodium bicarbonate solution, and again with water. The solution was then dried and concentrated. The residue was crystallized from ethanol; yield 1.7 g. (77%), m.p. 115–116°. Several recrystallizations from ethanol raised the melting point to 116–117°.[21]

Anal. Calcd. for $C_{17}H_{14}Cl_4O_2$: C, 52.07; H, 3.60. Found: C, 52.05; H, 3.82.

Trichloromethyl-2-(3'-chlorobenzyl)phenylcarbinol (IVc). This compound was prepared by allowing the Grignard reagent of 2-bromo-3'-chlorodiphenyl-methane to react with chloral using essentially the procedure described for IVa. The product was obtained in 42% yield as a very viscous oil which distilled at 185–190° (0.1 mm.).

Acetate of trichloromethyl-2-(3'-chlorobenzyl)phenylcarbinol. This compound was prepared substantially as was the acetate of IVa using trifluoroacetic acid. Recrystallization from ethanol gave a 58% yield of white crystals; m.p. 114–115°.

Anal. Calcd. for $C_{17}H_{14}Cl_4O_2$: C, 52.07; H, 3.60. Found: C, 52.12; H, 3.56.

Trichloromethyl-2-(3'-chlorobenzyl)-4-chlorophenylcarbinol (IVd). This compound was prepared by allowing the Grignard reagent of 2-bromo-5,3'-dichlorodiphenylmethane to react with chloral using substantially the procedure described for IVa. The product was obtained in 48% yield as a very viscous oil which distilled at 185–188° (0.2 mm.).

Acetate of trichloromethyl-2-(3'-chlorobenzyl)-4-chlorophenylcarbinol. This compound was prepared substantially as was the acetate of IVa using trifluoroacetic acid. Recrystallization from ethanol gave a 53% yield of white crystals; m.p. 92–93°.

Anal. Calcd. for $C_{15}H_{13}Cl_5O_2$: C, 47.87; H, 3.07. Found: C, 47.76; H, 3.12.

BLACKSBURG, VA.

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(21) The same product was obtained in 72% yield using the trifluoroacetic acid method.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

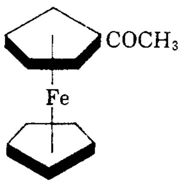
Benzoylations of Both Methyl Ketone Groups of Bisacetylferrocene with Methyl Benzoate and Alkali Amides to Form the Bis-β-diketone. Certain Derivatives[1]

CHARLES R. HAUSER AND CHARLES E. CAIN

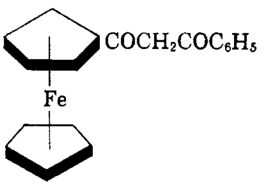
Received January 29, 1958

The benzoylations of both of the methyl ketone groups of bisacetylferrocene were effected with excess methyl benzoate and alkali amide to form the bis-β-diketone. An attempt to benzoylate only one of the methyl ketone groups was unsuccessful. The bis-β-diketone was converted to the bispyrazole, and to a copper chelate which evidently contained one molecule of the bis-β-diketone for each copper atom. Infrared data are presented for these and certain related compounds.

It has recently been shown[2] that the methyl ketone group of acetylferrocene (I) can be benzoylated with methyl benzoate by means of potassium amide to form the corresponding β-diketone (II).

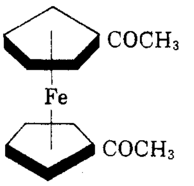


I

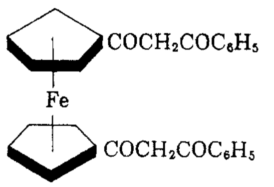


II

It has now been found that both of the methyl ketone groups of bisacetylferrocene[3] (III) can similarly be benzoylated to give the bis-β-diketone IV.[3a] For convenience these compounds are represented in the *cis*-configuration.[4]



III



IV

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(1) Supported by the National Science Foundation.

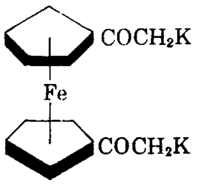
(2) Charles R. Hauser and Jacque K. Lindsay, *J. Org. Chem.*, **22**, 482 (1957).

(3) We are indebted to Linde Air Products Company, Tonawanda, N. Y., (Dr. R. L. Pruett), for a sample of this compound.

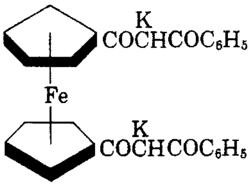
(3a) That the product was not the isomeric triacyl derivative, which might have resulted from dibenzoylation at one of the methyl ketone groups, was indicated by the absence of an infrared band at about 5.7-5.8 for the methyl ketone group which would then still be present in the molecule. Moreover, the triacyl derivative could hardly produce the bispyrazole VII and the internal copper chelate IX. Actually dibenzoylation at one of the methyl ketone groups should not be expected, since the equilibrium of similar acylations of ordinary methyl ketones with methyl benzoate is generally on the side of the anion of the β-diketone which is the monobenzoylation product (see ref. 5).

(4) Recently, D. A. Semenow and J. D. Roberts [*J. Am. Chem. Soc.*, **79**, 2741 (1957)] have presented dipole moment evidence that at least bis-*p*-chlorophenylferrocene has the *cis* configuration.

This two-fold Claisen type condensation was effected by first converting the bisacetylferrocene (III) to its dipotassio derivative IIIa by means of potassium amide in liquid ammonia and then adding methyl benzoate in ether. Almost immediately the reaction mixture became red which is the color of the bis-β-diketone and of its potassio derivative IVa, the formation of which is called for by theory.[5]



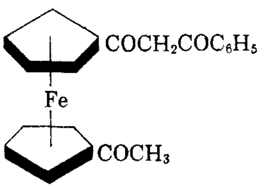
IIIa



IVa

The best yield (62%) of the bis-β-diketone IV was obtained employing four equivalents each of potassium amide and methyl benzoate to one of the bisacetylferrocene (III). Under these conditions the conversion of the bis-β-diketone IV to its dipotassio derivative IVa may be considered to be effected by the two extra equivalents of the potassium amide over the two involved in the formation of the dipotassio derivative of bisacetylferrocene IIIa. Essentially the same yield (60%) was obtained with sodium amide under the similar conditions. The proportions of reactants employed with bisacetylferrocene (III) correspond to the use of two equivalents each of the alkali amide and ester to one of a monomethyl ketone, which have been recommended when the yield is to be based on the ketone.[5]

Although this two-fold condensation might be expected to involve the intermediate formation of the mono-β-diketone V or its potassio derivative, none of this intermediate was found under the above conditions or even when the dipotassio derivative of bisacetylferrocene IIIa was treated with only one equivalent of methyl benzoate. Under the latter conditions a 20% yield of the bis-β-diketone IV was obtained, and 67% of the bisacetylferrocene (III) was recovered.

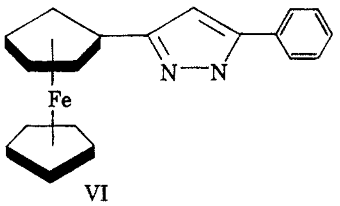


V

Moreover, when the monopotassio derivative of bisacetylferrocene was prepared by means of one equivalent of potassium amide in liquid ammonia and an equivalent of methyl benzoate then added (refluxed 5 hours in ether), none of the mono-β-diketone V was found, and 95% of the bisacetylferrocene was recovered (an infrared spectrum indicated no β-diketone present). Neither was the mono-β-diketone V isolated when bisacetylferrocene was stirred at room temperature with excess sodium methoxide and methyl benzoate in ether for 10 hours. There was obtained a black oily material, an infrared spectrum of which indicated no β-diketone present.

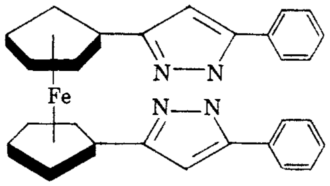
It should be mentioned that both this difficulty of preparing the mono-β-diketone by this method and the ease with which the bis-β-diketone IV was obtained were not anticipated. Apparently the second benzoyl group was introduced into the molecule much more readily than the first. The alternative possibility that the two groups were introduced simultaneously seems unlikely. The theory behind these interesting observations is being further investigated.

Derivatives and infrared data. (*A*) *Pyrazoles.* The cyclization of mono-β-diketone II with hydrazine to form the pyrazole VI has been described previously.[2]



VI

The two-fold cyclization of bis-β-diketone IV with two molecules of hydrazine to form the bis-pyrazole VII has now been effected in 82% yield employing a large excess of hydrazine. No attempt was made to prepare the mono-pyrazole of bis-β-diketone IV.



VII

In Table I are summarized some principal infrared bands of pyrazoles VI and VII and also those of the ordinary pyrazoles VIII and IX. Pyrazole VIII is well known, and its infrared spectrum has been reported previously,[6,7] but pyrazole IX appears to be new.[8]

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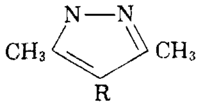
[5] See C. R. Hauser, F. W. Swamer, and J. T. Adams, *Org. Reactions*, **VIII**, 59 (1954).

[6] C. S. Rondestvedt and P. K. Chang, *J. Am. Chem. Soc.*, **77**, 6532 (1955).

[7] P. Mirone and M. Vampiri, *Atti accad. nazl. Lincei, Rend., Classe sci. fis., mat. e nat.*, 12, 583 (1952); *Chem. Abstr.*, **46**, 9423 (1952).

[8] Pyrazole IX was prepared in the usual manner from 3-phenylacetylacetone by R. J. Light in this laboratory. It was obtained in 91% yield, m.p. 128.5–129.5°. *Anal.* Calcd.: C, 76.71; H, 7.02; N, 16.27. Found: C, 76.91; H, 6.89; N, 16.20.



VIII, R = H
IX, R = C_6H_5

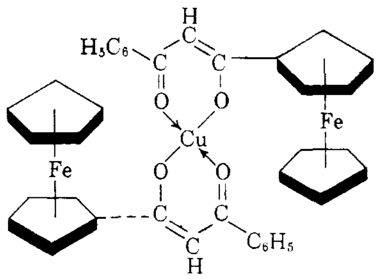
TABLE I

SPECTRA OF PYRAZOLE BANDS (μ)

Formula VIII	Formula IX	Formula VI	Formula VII
6.26	6.22	6.22	6.24
6.43	6.44	6.45	6.45
6.74	6.84	6.85	6.85
		9.02	
		9.98	

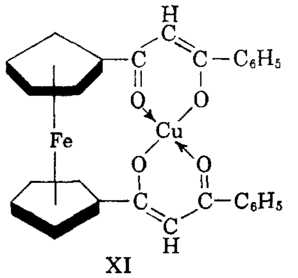
It can be seen from Table I that each of the pyrazoles listed has infrared bands at 6.28 μ, 6.44 μ, and 6.7 μ. The first two bands have been assigned[6,7] to the carbon-nitrogen double bond and to the carbon-carbon double bond respectively. The last band has apparently not been assigned but it has been considered characteristic of the pyrazole ring.[6,7] Only one of the pyrazoles listed in Table I exhibits bands at about 9 and 10 μ which are known to be characteristic of ferrocene derivatives having an unsubstituted ring.[9]

(*B*) *Copper chelates.* The reaction of mono-β-diketone II with copper acetate to form chelate X has been described previously.[2] Such chelates are known to consist of two mono-β-diketone molecules to one copper atom.[10]



X

The corresponding reaction of bis-β-diketone IV with copper acetate has now been effected to form a copper chelate which, on the basis of its molecular weight, may be represented by structure XI. Treatment of the chelate with dilute phosphoric acid regenerated bis-β-diketone IV.



XI

This conversion of bis-β-diketone IV to monomeric chelate XI is to be contrasted with that of bis-β-diketone XII to a polymeric chelate which was recently reported in a patent.[11]

XII

It should be pointed out that the *cis* relationship of the two β-diketone groups in chelate XI does not necessarily furnish evidence for the *cis* configuration of the bis-β-diketone (structure IV) since, because of the presumably low energy barrier to rotation around the iron, the bis-β-diketone might have been converted to the *cis*-chelate under the conditions employed.[9]

Such a chelate as XI involving only one bis-β-diketone molecule per copper atom might not be exactly analogous with the ordinary chelates such as X since, if the usual planar-square geometry of the copper chelate is maintained,[12] certain of the bond angles would probably have to be distorted. Actually, this distortion may be indicated by a comparison of the infrared spectrum of chelate XI with that of chelate X as discussed below.

In Table II are summarized the principal infrared bands that have been found for mono-β-diketone II and bis-β-diketone IV and their copper chelates. Also, in this table are included for comparison the bands for dibenzoylmethane which have been studied.[13]

It can be seen from Table II that in general the β-diketones and copper chelates exhibit similar infrared spectra. It is to be noted that, with the exception of chelate XI, none of the compounds listed in this table show a band at 5.7–5.9 μ which is characteristic of the free ketone carbonyl group.[14] This indicates that the β-diketones exist largely in the enol form and the copper chelates in the analogous metal enolate form.

However, certain differences are evident between the spectra of the ferrocene β-diketones and their copper chelates. In the cases of dibenzoylmethane and the two ferrocene β-diketones (II and IV) the carbonyl group band has undergone a considerable shift and reappeared in the 6.1–6.5 μ region.[13,14] With the two ferrocene β-diketones the band seems to be split into two components, one about 6.2 μ and the other about 6.35 μ.

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[9] See P. L. Pauson, *Quart. Revs.* (*London*), **9**, 391 (1955).

[10] See J. Lecomte, *Discuss. Faraday Soc.*, **9**, 125 (1950).

[11] J. P. Wilkins and E. L. Wittbecker, U. S. Patent **2,659,711**, Nov. 17, 1953.

[12] See A. E. Martell and M. Calvin, *Chemistry of the Metal Chelate Compounds*, Prentice-Hall Inc., Englewood Cliffs, N. J., 1952, p. 263.

[13] See R. S. Rasmussen, D. D. Tunnicliff, and R. R. Brattain, *J. Am. Chem. Soc.*, **71**, 1068 (1949).

[14] See L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, New York, N. Y., 1954, p. 123.

TABLE II

INFRARED SPECTRA OF BIS-β-DIKETONES AND COPPER CHELATES (μ)

Dibenzoylmethane	Mono-β-diketone II	Mono-copper chelate X	*Bis*-β-diketone IV	*Bis*-copper chelate XI
				5.82
6.1–6.5	6.22, 6.35	6.28, 6.5[a]	6.24, 6.38	6.27, 6.5[a]
6.75	6.73	6.71	6.72	6.71
—	—	6.88	—	6.88
7.14	7.07	7.12, 7.18	7.26	7.09, 7.17
—	7.25	7.26	7.40	7.25, 7.41
7.79	7.72	7.65	7.66	7.67
8.155	8.12	8.10	8.11	8.11
8.435	8.45	8.48	8.42	8.45
9.035	8.97	—	8.94	—
—	9.02[b]	9.03[b]	—	—
—	—	9.21	—	9.22
9.36	9.32	—	9.31	9.37[c]
9.72	9.69	9.60	9.60	9.64
9.98	9.80	9.78	9.80	9.77
—	9.97[b]	9.98[b]	—	—
10.24	—	—	—	—
10.765	10.74	10.55	10.71	10.54
—	12.14	12.11	—	12.05

[a] Broad. [b] Peak assigned to ferrocene substituted on one ring. [c] Weak.

In the case of the ferrocene copper chelates (X and XI) the carbonyl group band also appears to be split into two bands, but they are about 6.3μ (a sharp band) and about 6.5 μ (a broad band). Recent work on the infrared spectra of metal chelates of certain other β-diketones has ascribed this split band which was observed by Lecomte[10] in 1950 to the conjugated enol structure of such chelates. In particular, the 6.3 μ band has been ascribed to the chelated carbonyl bond, and the 6.5 μ band to the carbon-carbon double bond.[15] There is also a characteristic band at 12.15 μ which has been assigned to a carbon-carbon double bond with one hydrogen attached; such is the case with the double bond resulting from the formation of the enolic metal chelate X or XI.

It is of interest that, in the infrared spectrum of bis-β-diketone copper chelate XI, there reappeared a band in the 5.7–5.9 μ region in which ordinary ketone carbonyls usually absorb. This weak peak at 5.82 μ was in addition to the uniformly observed shifted β-diketone carbonyl band and was not evident in the spectrum of any other of the compounds compared. That this band was not due to some impurity is indicated by the lack of such a band in the spectrum of the bis-β-diketone from which the chelate was prepared and by the lack of this band in the spectrum of the bis-β-diketone recovered from the phosphoric acid hydrolysis of the chelate. This band in the region for an unconjugated simple ketone may arise from some incomplete bonding (because of steric strain) in the chelation of the metal with four oxygens.

EXPERIMENTAL[16]

Bis-β-diketone IV from bisacetylferrocene. To a stirred solution of 0.2 mole of potassium amide[17] in 250 ml. of liquid ammonia was added in small portions 13.6 g. (0.05 mole) of solid bisacetylferrocene III to produce a yellow-brown suspension. After stirring for 20 min., a solution of 27.2 g. (0.2 mole) of methyl benzoate in 100 ml. of dry ether was added dropwise. The color of the suspension changed almost immediately to a dull red. The liquid ammonia was evaporated (steam bath) as 250 ml. of dry ether was added, and the resulting suspension (still red) was stirred at room temperature for 4 hr. The mixture was then filtered rapidly, and the red solid washed with dry ether until the washings were colorless. This solid (presumably the potassium salt of the bis-β-diketone) was added with stirring to about 400 ml. of *N* hydrochloric acid. The resulting red suspension was collected in a funnel and washed with water and then ether. The crude red powder, which was insoluble in ether and water and only slightly soluble in acetone, melted at 198–201°. It was recrystallized from acetone to give 15 g. (62%) of bis-β-diketone IV (purple needles) m.p. 213.5–214°. An analytical sample was prepared through the copper chelate (see below).

Anal. Calcd. for $C_{28}H_{22}O_4Fe$: C, 70.31; H, 4.64; Fe, 11.68. Found: C, 70.22; H, 4.40; Fe, 11.50.

There was recovered from the ether washings 2.8 g. (20%) of bisacetylferrocene III. Taking this into account, the conversion yield of the bis-β-diketone IV was 78%.

The experiment was repeated employing sodium amide instead of potassium amide and stirring the ether suspension of the reaction mixture for 12 hr. There was obtained 14 g. (60%) of bis-β-diketone IV, m.p. 213–214°. Since 3.5 g. (26%) of bisacetylferrocene was recovered, the conversion yield of IV was 81%. In this experiment, a sample of the solid obtained before acidification was heated in a melting point tube. Since it did not melt at 300°, it was presumably the disodium salt of the bis-β-diketone and sodium methoxide. After acidification, the crude red solid melted at 201–

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(15) D. P. Dryden and A. Winston, paper at Southeastern Regional Meeting, ACS, Nov. 15, 1957.

(16) Analyses are by Galbraith Laboratories, Knoxville, Tenn.

(17) R. S. Yost and C. R. Hauser, *J. Am. Chem. Soc.*, 69, 2325 (1947).

203°, and at 212.5–213.5° after recrystallization from acetone.

When the reaction was carried out with 0.1 mole each of potassium amide and methyl benzoate and 0.05 mole of bisacetylferrocene (III) (ether suspension stirred for 6 hr.), there was obtained 11 g. (46%) of bis-β-diketone IV, m.p. 213–214°. Since 6 g. (45%) of the bisacetylferrocene (III) was recovered the conversion yield was 84%.

When the reaction was carried out with 0.05 mole of potassium amide and 0.025 mole each of bisacetylferrocene (III) and methyl benzoate (ether suspension stirred for 8 hr.), there was obtained 1.8 g. (20%, 40% based on the ester) of bis-β-diketone IV, m.p. 212.5–214°. Since 4.5 g. (67%) of *bis*-acetylferrocene (III) was recovered, the conversion yield of IV based on III was 61%.

Cyclization of bis-β-diketone IV with hydrazine to form bis-pyrazole VII. To a solution of 5 g. (0.01 mole) of bis-β-diketone IV in 1.5 l. of absolute ethanol was added 20 g. (0.6 mole) of 95% hydrazine in 20 ml. of absolute ethanol. The resulting deep red solution was refluxed for 1 hr., during which time the color changed to a deep orange. After cooling to room temperature and standing overnight in a refrigerator, the reaction mixture was filtered (cold) to yield 3.1 g. of bispyrazole VII (orange crystalline solid), m.p. >300° dec. Reduction of the volume of the filtrate under vacuum gave an additional 0.9 g. of an orange powder, m.p. >300° dec.; total yield 4.0 g. (82%). This compound failed to dissolve appreciably (as would be indicated by color) in various refluxing solvents including benzene, acetone, hexane, ethanol, chloroform, and dioxane. However, unrecrystallized samples from both fractions gave satisfactory analytical values.

Anal. Calcd. for $C_{28}H_{22}N_4Fe$: C, 71.49; H, 4.71; N, 11.91; Fe, 11.90. Found for orange crystals: C, 71.43; H, 4.90; N, 11.88; Fe, 11.73. Found for orange powder: C, 71.37; H, 4.88; N, 11.79; Fe, 12.14.

Formation of the copper-chelate XI of bis-β-diketone IV. To a solution of 1 g. of the bis-β-diketone IV in 500 ml. of refluxing acetone was added 20 ml. of a saturated solution (large excess) of warm, aqueous copper acetate. After refluxing for 15 min., the reaction mixture was cooled and filtered. The solid was washed with water and dried. After washing with petroleum ether and recrystallizing from benzene there was obtained 1 g. (88%) of a yellow powder, m.p. >300°.

Anal. Calcd. for $C_{28}H_{20}O_4FeCu$: C, 62.08; H, 4.09. Found: C, 62.29; H, 3.99. Mol. wt. determinations[18]: Calcd. for $C_{28}H_{20}O_4FeCu$: 541.9. Found: 529, 514, 509, 521. Limit of error, ±10%.

A portion of the chelate was reconverted to the original bis-β-diketone by stirring overnight in 20% phosphoric acid. It was identified by infrared spectrum and melting point.

Durham, N. C.

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(18) Mol. wt. determination by Laboratory of Microchemistry, Dr. Carl Tiedcke, Teaneck, N. J.

[Contribution from the Department of Chemistry, Duke University]

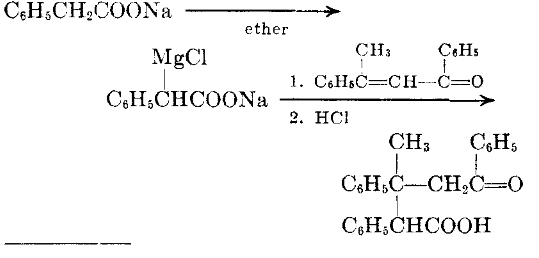
Conjugate Addition of Phenylacetic Acid and Derivatives with α,β-Unsaturated Carbonyl Compounds by Means of Sodium Amide

CHARLES R. HAUSER and MARVIN T. TETENBAUM[1]

Received October 24, 1957

Disodio phenylacetic acid prepared by means of two equivalents of sodium amide in liquid ammonia underwent conjugate addition with benzalacetophenone and ethyl cinnamate to give excellent yields of products. Addition of cold acid to the reaction mixture from the α,β-unsaturated ester produced the corresponding di-acid instead of the intermediate mono-acid-ester. Similarly the disodium salt of phenylacetamide gave with ethyl cinnamate under these conditions the mono-acid-amide. However the monosodium salt of ethyl phenylacetate formed with this α,β-unsaturated ester the corresponding diester.

Ivanoff and co-workers[2] have effected the conjugate additions of phenylacetic acid to dypnone and phorone by means of isopropylmagnesium chloride. This Grignard reagent was employed to convert the sodium salt of phenylacetic acid to its magnesium chloride derivative which was condensed with the α,β-unsaturated ketones. The reaction may be illustrated with dypnone (Equation 1).



$$C_6H_5CH_2COONa \xrightarrow[\text{ether}]{(CH_3)_2CHMgCl} C_6H_5\overset{MgCl}{CH}COONa \xrightarrow[2.\ HCl]{1.\ C_6H_5\overset{CH_3}{C}{=}CH{-}\overset{C_6H_5}{C}{=}O} C_6H_5\overset{CH_3}{\underset{C_6H_5CHCOOH}{C}}{-}CH_2\overset{C_6H_5}{C}{=}O \quad (1)$$

Although the yield was not given in this reaction, a 75% yield was reported for the corresponding reaction with phorone.[2]

In the present investigation the conjugate additions of phenylacetic acid and certain of its derivatives to benzalacetophenone and ethyl cinnamate were effected by means of sodium amide in liquid ammonia. Two molecular equivalents of this reagent were employed to convert the phenylacetic acid to its disodium derivative which was then condensed with the α,β-unsaturated carbonyl compound. The reaction with benzalacetophenone produced ketone-acid I in excellent yield (Equation 2).

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[1] American Cyanamid Company Fellow, 1956–1957.

[2] D. Ivanoff, M. Mihova, and T. Christova, *Bull. soc. chim. France*, [4], **51**, 1321 (1932).