[Contribution from the Department of Chemistry, Duke University]

Condensations of Dialkali β-Diketones with Ketones or Aldehydes to Form Hydroxy β-Diketones. Dehydration Products. Equilibrium Factors[1]

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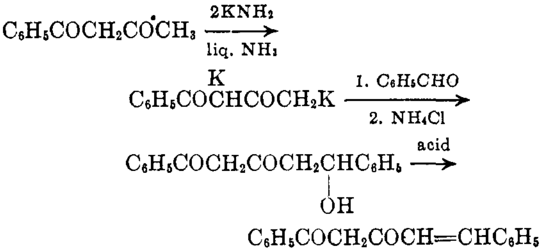
The terminal carbanion of dipotassiobenzoylacetone and dipotassioacetylacetone underwent addition reactions with the carbonyl group of certain ketones having no α-hydrogen to form the corresponding hydroxy β-diketones. While dipotassiobenzoylacetone apparently ionized the α-hydrogen of acetophenone, dilithiobenzoylacetone underwent the addition reaction with this ketone and with cyclohexanone to form the hydroxy β-diketones. Acid catalyzed dehydrations of these compounds produced corresponding unsaturated β-diketones and, in certain cases, also an isomeric product that appeared to be the dihydropyrone. Certain of the dihydropyrones were converted to the unsaturated β-diketones with ethanolic potassium hydroxide or methanolic hydrochloric acid, and each dehydration product yielded a mixture of the two isomers with cold sulfuric acid. A hydroxy β-diketone and its unsaturated β-diketone were cyclized with hydrazine to form the corresponding pyrazoles. The former pyrazole was dehydrated to give the latter. A hydroxy β-diketone underwent cleavage with potassium *t*-butoxide in *t*-butyl alcohol to regenerate the ketone and β-diketone. Equilibrium factors are considered.

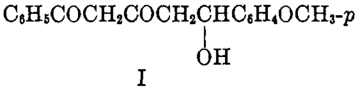
In connection with a recent study of various condensations involving the terminal methyl group of certain β-diketones,[3] dipotassiobenzoylacetone was observed to react with benzaldehyde to give, after dehydration of the crude intermediate hydroxy β-diketone, cinnamoylacetophenone in an overall yield of 28% (Equation 1).



$$C_6H_5COCH_2COCH_3 \xrightarrow[\text{liq. }NH_3]{2KNH_2} C_6H_5CO\overset{K}{C}HCOCH_2K \xrightarrow[2.\ NH_4Cl]{1.\ C_6H_5CHO} C_6H_5COCH_2COCH_2\underset{OH}{C}HC_6H_5 \xrightarrow{\text{acid}} C_6H_5COCH_2COCH{=}CHC_6H_5 \quad (1)$$

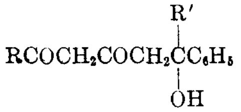
In the present investigation this novel type of condensation was studied more thoroughly. Although the intermediate hydroxy β-diketone represented in Equation 1 was obtained only as an impure oil, several other such compounds were readily isolated as crystalline solids. Thus, dipotassiobenzoylacetone, which was prepared by means of two molecular equivalents of potassium amide in liquid ammonia,was condensed with anisaldehyde, benzophenone, and *p*-chlorobenzophenone to form hydroxy β-diketones I, II, and III, respectively. Similarly dipotassioacetylacetone was condensed with benzophenone and *p*-chlorobenzophenone to give IV and V, respectively.

This aldol type of condensation may be regarded as an addition reaction of the terminal carbanion of the dipotassio β-diketone with the carbonyl group of the aldehyde or ketone as illustrated by Equation 2.



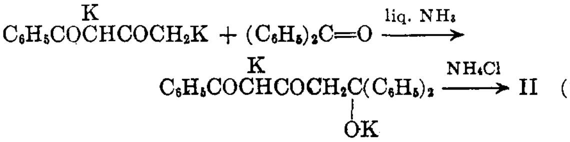
$$C_6H_5COCH_2COCH_2\underset{OH}{C}HC_6H_4OCH_3\text{-}p$$

I



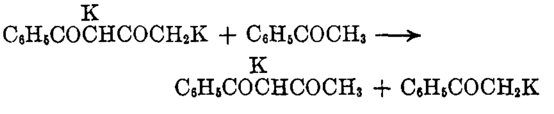
$$RCOCH_2COCH_2\overset{R'}{\underset{OH}{C}}C_6H_5$$

II. $R = C_6H_5$, $R' = C_6H_5$
III. $R = C_6H_5$, $R' = p\text{-}ClC_6H_4$
IV. $R = CH_3$, $R' = C_6H_5$
V. $R = CH_3$, $R' = p\text{-}ClC_6H_4$



$$C_6H_5CO\overset{K}{C}HCOCH_2K + (C_6H_5)_2C{=}O \xrightarrow{\text{liq. }NH_3} C_6H_5CO\overset{K}{C}HCOCH_2\underset{OK}{C}(C_6H_5)_2 \xrightarrow{NH_4Cl} \text{II} \quad (2)$$

In contrast to the ketones considered above which have no α-hydrogen, acetophenone failed to condense with dipotassiobenzoylacetone under similar conditions. Apparently potassium-hydrogen exchange occurred, since the ketone and β-diketone were largely recovered (Equation 3).



$$C_6H_5CO\overset{K}{C}HCOCH_2K + C_6H_5COCH_3 \longrightarrow C_6H_5CO\overset{K}{C}HCOCH_3 + C_6H_5COCH_2K \quad (3)$$

Since lithio ethyl acetate[4] and lithio *t*-butyl acetate[5] but not sodio ethyl acetate[6] were shown recently to condense with acetophenone, it seemed possible that dilithiobenzoylacetone might condense with this ketone instead of reacting with the α-hydrogen. This was realized. Thus, dilithiobenzoylacetone, prepared by means of two molecular equivalents of lithiumamide in liquid ammonia, was condensed with acetophenone to form hydroxy β-diketone VI (Equation 4).

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[1] Supported in part by Grant CY-4455 from the National Institutes of Health.

[2] National Science Foundation Predoctoral Fellow, 1958–1960.

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

[4] W. R. Dunnavant and C. R. Hauser, *J. Org. Chem.*, **25**, 503 (1960).

[5] C. R. Hauser and W. H. Puterbaugh, *J. Am. Chem. Soc.*, **75**, 4756 (1953).

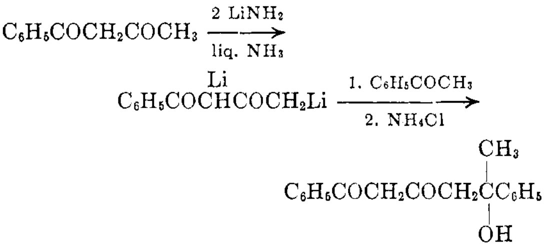
[6] C. R. Hauser and W. R. Dunnavant, *J. Org. Chem.*, **25**, 1296 (1960).

TABLE I

YIELDS AND MELTING POINTS OF HYDROXY β-DIKETONES AND MELTING POINTS OF THEIR COPPER CHELATES

Ketone or Aldehyde	β-Diketone	Base	Hydroxy β-diketone	M.P.[a]	Yield,[b] %	Copper Chelate M.P.[a]
Anisaldehyde	Benzoylacetone	KNH_2	1-Hydroxy-1-*p*-methoxyphenyl-5-phenylpentanedione-3,5 (I)	103–105[c]	49	185–187[d]
Benzophenone	Benzoylacetone	KNH_2	1-Hydroxy-1,1,5-triphenylpentanedione-3,5 (II)	115–116[c]	73	196–199[d]
p-Chlorobenzophenone	Benzoylacetone	KNH_2	1-*p*-Chlorophenyl-1,5-diphenyl-1-hydroxypentanedione-3,5 (III)	116–118[e]	69	194–196[d]
Benzophenone	Acetylacetone	KNH_2	1,1-Diphenyl-1-hydroxyhexanedione-3,5 (IV)	133–135[c]	73	178–179.5[f]
p-Chlorobenzophenone	Acetylacetone	KNH_2	1-*p*-Chlorophenyl-1-hydroxy-1-phenylhexanedione-3,5 (V)	101–102.5[g] 80–81.5[g]	52	161.5–163[e,h]
Acetophenone	Benzoylacetone	$LiNH_2$	2,6-Diphenyl-2-hydroxyhexanedione-4,6 (VI)	85–87[i]	40[j]	166–167.5[k]
Cyclohexanone	Benzoylacetone	$LiNH_2$	1-Hydroxy-1,1-pentamethylene-5-phenylpentanedione-3,5 (VII)	68–69[l]	34	207–209[d]

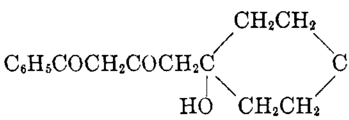
[a] Melting points given are for analytical samples. [b] The melting point for the product from which the yield was determined was usually slightly lower than that given in the Table. [c] Recrystallized from methanol. [d] Recrystallized from dioxane-water. [e] Recrystallized from 95% ethanol. [f] Recrystallized from benzene-methanol. [g] Obtained in two forms (see Experimental). [h] Both forms of V gave the same copper chelate. [i] Recrystallized from ethanol-water. [j] A 45% yield was obtained when acetophenone was condensed with the reagent formed from dipotassiobenzoylacetone and lithium chloride (see Experimental). [k] Recrystallized from methanol-water. [l] Recrystallized from petroleum ether (b.p. 30–60°).



$$C_6H_5COCH_2COCH_3 \xrightarrow[\text{liq. NH}_3]{2\ LiNH_2} C_6H_5CO\overset{Li}{C}HCOCH_2Li \xrightarrow[2.\ NH_4Cl]{1.\ C_6H_5COCH_3} C_6H_5COCH_2COCH_2\overset{CH_3}{\underset{OH}{C}}C_6H_5 \quad (4)$$

VI

Similarly, dilithiobenzoylacetone was condensed with cyclohexanone to form hydroxy β-diketone VII.

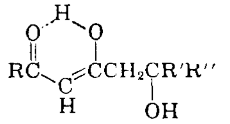


VII

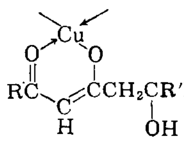
Moreover, hydroxy β-diketone VI was obtained by treating dipotassiobenzoylacetone with three molecular equivalents of lithium chloride in liquid ammonia for three hours, and then adding acetophenone. In this experiment the reactive intermediate that condensed with the ketone might have been either the dilithio β-diketone represented in Equation 4 or the potassiolithio salt, C_6H_5-$COCH(K)COCH_2Li$.

The above hydroxy β-diketones I–VII, which are apparently the first such compounds to be isolated and characterized, were obtained in yields of 34–73% (Table I). To minimize possible reversion of the condensation during neutralization, the reaction mixtures were generally poured into ammonium chloride in liquid ammonia. At least for II, however, the direct addition of ammonium chloride to the reaction mixture produced practically the same yield (69–70%) as that (73%) obtained by the inverse neutralization procedure.

The β-diketone structure of the products was indicated by red enol tests with ethanolic ferric nitrate[7] and by the formation of copper chelates. That the products were hydroxy β-diketones I–VII was supported not only by their analyses and by the analyses of their copper chelates (Table II) but also by infrared data (Table III). Thus, as should be expected for structures I–VII, an infrared band of medium intensity near 2.9 μ was observed for the free hydroxyl group.[8] Although the β-diketone portion of these compounds may exist largely in the enol form, this band cannot be ascribed to the enol hydroxyl group, as most β-diketones do not exhibit such a band because of chelation of the enol hydrogen as indicated in general formula VIII.[9] Moreover, the copper chelates IX, which would have no enol hydroxyl, still show the band near 2.9 μ for the free hydroxyl group. It can be seen from Table III that, like most ordinary β-diketones[10]



VIII



IX

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[7] See G. T. Morgan, H. D. K. Drew, and C. R. Porter, *Ber.*, **58**, 333 (1925); C. R. Hauser and J. T. Adams, *J. Am. Chem. Soc.*, **66**, 345 (1944).

[8] See L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2d. ed., Wiley, New York, 1958, p. 95.

[9] See Ref. 8, p. 104.

[10] See Ref. 8, p. 142.

TABLE II

ANALYSES[a] OF HYDROXY β-DIKETONES AND THEIR COPPER CHELATES

	β-Diketone					Copper Chelate						
	Empirical	Carbon, %		Hydrogen, %		Empirical	Carbon, %		Hydrogen, %		Copper, %	
β-Diketone	formula	Calcd.	Found	Calcd.	Found	formula	Calcd.	Found	Calcd.	Found	Calcd.	Found
I	$C_{18}H_{18}O_4$	72.46	72.66	6.08	6.04	$C_{36}H_{34}O_8Cu$	65.69	65.68	5.21	5.44	9.65	9.32
II	$C_{23}H_{20}O_3$	80.21	80.35	5.85	5.77	$C_{46}H_{38}O_6Cu$	73.67	73.35	5.10	5.41	8.47	8.07
III	$C_{23}H_{19}O_3Cl$[b]	72.92	72.69	5.06	4.92	$C_{46}H_{36}O_6Cl_2Cu$	67.44	67.51	4.43	4.63	7.75	7.60
IV	$C_{18}H_{18}O_3$	76.57	76.24	6.43	6.22	$C_{36}H_{34}O_6Cu$	69.04	69.42	5.47	5.81	10.15	9.85
V	$C_{18}H_{17}O_3Cl$[c]	68.24	68.43[d] 68.38[e]	5.41	5.28[d] 5.37[e]	$C_{36}H_{32}O_6Cl_2Cu$	62.20	61.87	4.64	4.70	9.14	9.29
VI	$C_{18}H_{18}O_3$	76.57	76.75	6.43	6.61	$C_{36}H_{34}O_6Cu$	69.04	69.25	5.47	5.73	10.15	10.30
VII	$C_{16}H_{20}O_3$	73.82	73.74	7.74	7.71	$C_{32}H_{38}O_6Cu$	66.01	66.24	6.58	6.66	10.91	11.02

[a] Ref. 21. [b] *Anal.* Calcd. for $C_{23}H_{19}O_3Cl$: Cl, 9.36. Found: 9.30. [c] *Anal.* Calcd. for $C_{18}H_{17}O_3Cl$: Cl, 11.19. Found: high melting form, 11.13; low melting form, 11.00. [d] High melting form. [e] Low melting form.

TABLE III

SOME INFRARED BANDS[a] OF HYDROXY β-DIKETONES AND THEIR COPPER CHELATES

	β-Diketone, μ			Copper Chelate, μ			
β-Diketone	Hydroxyl[b]	Carbonyl and Enol-chelate[c,d]		Hydroxyl[b]	Perturbed Carbonyls[c,e]		Double Bond[c,f]
I	2.92	6.24	6.42	2.90	6.47	7.15	6.61
II	2.90	6.24	6.43[g]	2.91	6.45	7.17	6.57
III	2.88	6.23	6.37	2.91	6.47	7.14	6.59
IV	2.91	6.19		2.91	6.38	7.17[h]	6.60
V[i]	2.92	6.18	6.32[j]	2.91	6.36	7.14[k]	6.60
VI	2.84	6.23	6.42	2.89	6.45	7.10	6.56
VII	2.90	6.23	6.42	2.90	6.46	7.17	6.56

[a] Ref. 21. [b] Medium band. [c] Strong bands. [d] Absorption bands found in the region from 5.5 μ to 6.5 μ (Ref. 10). [e] Bands that have been attributed to carbonyl absorption in the chelate ring (Ref. 13). [f] A band that has been attributed to double bond absorption in the chelate ring and that has been found to be absent in the copper chelates of β-diketones substituted at the methylene carbon (Refs. 12 and 13). [g] Broad band. [h] A shoulder on this band was present at 6.97 μ, an absorption which has been attributed to a deformation of the methyl group on the chelate ring (Ref. 13c). [i] High and low melting forms. [j] Shoulder. [k] A shoulder on this band was present at 6.96 μ. See note *h*.

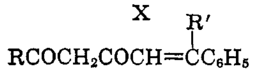
and 1,3,5-triketones,[11] the present β-diketones gave infrared bands for the enol-chelate ring in the region 6.0–6.5 μ but no band below 6.0 μ for a free carbonyl group. Also, similar to the copper chelates of β-diketones not substituted at the methylene group,[12] the present copper chelates showed a strong band in the region 6.52–6.61 μ as well as a perturbed carbonyl band below 6.5 μ and a second perturbed carbonyl band near 7.15 μ.[13]

The structures of certain of the hydroxy β-diketones were further established by dehydrations and by cyclizations with hydrazine as described below.

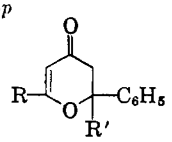
Dehydrations of hydroxy β-diketones. The acid catalyzed dehydration of the crude hydroxy β-diketone from dipotassiobenzoylacetone and benzaldehyde to form cinnamoylacetophenone reported earlier[3] was confirmed in the present investigation. Similarly the pure hydroxy β-diketones I, II, IV, and VI were dehydrated to give the unsaturated β-diketones X, XI, XII, and XIII respectively. However, II, IV, and VI also produced, under certain conditions, isomeric dehydration products which have been assigned the dihydropyrone structures XIV, XV, and XVI from their properties and reactions. The results are summarized in Table IV.

$C_6H_5COCH_2COCH{=}CHC_6H_4OCH_3\text{-}p$

X



$RCOCH_2COCH{=}\overset{R'}{\overset{|}{C}}C_6H_5$



XI. R = C_6H_5, R′ = C_6H_5
XII. R = CH_3, R′ = C_6H_5
XIII. R = C_6H_5, R′ = CH_3

XIV. R = C_6H_5, R′ = C_6H_5
XV. R = CH_3, R′ = C_6H_5
XVI. R = C_6H_5, R′ = CH_3

The β-diketone structure of the first set of dehydration products was indicated by positive enol tests[7] (greenish-brown for X, XI, and XIII; reddish-brown for XII) and by the formation of

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[11] R. J. Light and C. R. Hauser, *J. Org. Chem.*, 25, 538 (1960).

[12] R. P. Dryden and A. Winston reported [*J. Phys. Chem.*, 62, 635 (1958)] that the copper chelates of acetylacetone and similar β-diketones unsubstituted at the methylene group showed infrared bands at 6.10–6.45 μ ("A," attributed to the carbonyl group) and at 6.52–6.60 μ ("B," attributed to the C═C link). Chelates of their 3-substituted derivatives, however, exhibited only the "A" band in this region.

[13] (a) J. Lecomte, *Disc. Faraday Soc.*, 9, 125 (1950); (b) L. J. Bellamy and R. F. Branch, *J. Chem. Soc.*, 4491 (1954); (c) H. F. Holtzclaw, Jr., and J. P. Collman, *J. Am. Chem. Soc.*, 79, 3318 (1957); (d) see Ref. 8, pp. 145–146.

TABLE IV

DEHYDRATION OF HYDROXY β-DIKETONES

Hydroxy β-Diketone	Reagent	Unsaturated β-Diketone	M.P.[a]	Yield, %[b]	Dihydropyrone	M.P.[a]	Yield, %[b]
I	HCl, CH_3OH	*p*-Methoxycinnamoylacetophenone (X)	129–130.5	96	—	—	—
II	HCl, CH_3OH	β-Phenylcinnamoylacetophenone (XI)	97–98	79	—	—	—
II	H_2SO_4[c]	β-Phenylcinnamoylacetophenone (XI)	97–98	58[d]	2,3-Dihydro-2,2,6-triphenyl-4H-pyran-4-one (XIV)	147–148	15
II	H_2SO_4[e]	β-Phenylcinnamoylacetophenone (XI)	97–98	16	2,3-Dihydro-2,2,6-triphenyl-4H-pyran-4-one (XIV)	147–148	37–58
IV	HCl, CH_3OH	β-Phenylcinnamoylacetone (XII)	Oil	36[d]	—	—	—
IV	H_2SO_4[c]	β-Phenylcinnamoylacetone (XII)	Oil	11[d]	2,3-Dihydro-2,2-diphenyl-6-methyl-4H-pyran-4-one (XV)	119–120.5	21
IV	H_2SO_4[e]	β-Phenylcinnamoylacetone (XII)	Oil	—[f]	2,3-Dihydro-2,2-diphenyl-6-methyl-4H-pyran-4-one (XV)	119–120.5	48
VI	HCl, CH_3OH	β-Methylcinnamoylacetophenone (XIII)	Oil	13[d]	2,3-Dihydro-2,6-diphenyl-2-methyl-4H-pyran-4-one (XVI)	108–110[g]	66

[a] Melting points are for analytical samples. [b] The melting point for the product from which the yield was determined was usually slightly lower than that given in the table. [c] Reaction products separated by treatment with copper acetate. [d] Yield of copper chelate. [e] Reaction products separated by recrystallization. [f] Not isolated. [g] Another form, m.p. 84–86°, was first obtained, which changed to the higher melting form on recrystallization from *n*-hexane (see Experimental).

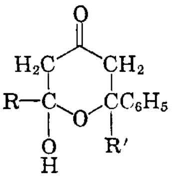
copper chelates. That these compounds were unsaturated β-diketones X–XIII was supported not only by their analyses and by the analyses of their copper chelates, but also by infrared spectra. Thus, they gave no hydroxyl band near 2.9 μ, and the carbonyl and enol-chelate absorption bands were above 6.0 μ.[10] The infrared spectra of their copper chelates showed the C=C band at 6.5–6.6 μ and the second perturbed carbonyl band at 7.1–7.2 μ, but only the copper chelate of XII showed a strong band corresponding to the first perturbed carbonyl absorption, at 6.47 μ in this case.[12,13] Possibly this carbonyl band had been shifted into the C=C absorption in the other spectra. A shoulder at 7.00 μ was present on the 7.14 μ carbonyl band in the spectrum of the copper chelate of XII. This absorption has been assigned to a deformation of the methyl group on the chelate ring,[13c] and was also found in the spectra of the copper chelates of IV and V (see notes h and k, Table III).

The structure of XI was confirmed by an independent synthesis from acetophenone and β-phenylcinnamoyl chloride (Equation 5); this is an adaptation of the method developed recently[14] for the condensation of this ketone with cinnamoyl chloride.

$$C_6H_5COCH_3 \xrightarrow{NaNH_2} C_6H_5COCH_2Na \xrightarrow{(C_6H_5)_2C=CHCOCl} \text{XI} \quad (5)$$

The dihydropyrone structure for the second set of dehydration products was indicated by their analyses and by their failure to give positive enol tests or to form copper chelates. The structures XIV–XVI were supported by their infrared spectra, which showed a band near 6.00 μ for a carbonyl group in conjugation with an aliphatic carbon-carbon double bond,[15] but no band near 2.9 μ for hydroxyl.

While the unsaturated β-diketone may be accounted for by dehydration of the keto or enol form of the hydroxy β-diketone, the formation of the dihydropyrone is not so readily explained. A possible course for the latter reaction would involve the dehydration of the hemi-acetal structure XVII, which may be in equilibrium with the keto or enol form of the hydroxy β-diketone in acid solution.



XVII

It can be seen from Table IV that the relative yields of the two types of dehydration products appeared to be dependent on the particular hydroxy β-diketone used, on the acidic reagent, and on the conditions employed. Thus, hydroxy β-dike-

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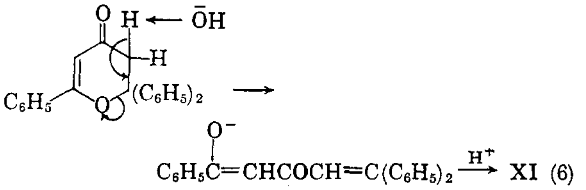
[14] B. O. Linn and C. R. Hauser, *J. Am. Chem. Soc.*, **78**, 6066 (1956).

[15] See Ref. 8, p. 136.

tones I, II, and IV gave the corresponding unsaturated β-diketone as the only isolable product with refluxing methanolic hydrochloric acid, whereas VI produced mainly the dihydropyrone with this reagent. On the other hand, II and IV afforded both of the dehydration products with cold concentrated sulfuric acid, their relative yields being dependent to some degree on the procedure of isolation.

Partial interconversion of the unsaturated β-diketone XI and the dihydropyrone XIV to one another occurred on treatment of each with cold concentrated sulfuric acid. Dihydropyrone XIV was converted to the unsaturated β-diketone XI on treatment with refluxing methanolic hydrochloric acid (86% yield) or with ethanolic potassium hydroxide at room temperature (80% yield).

Although the mechanism of the ring opening of the dihydropyrone with acid is not clear, that of dihydropyrone XIV with alcoholic alkali appeared to involve a β-elimination to give the anion of XI from which XI was recovered on subsequent acidification (Equation 6).



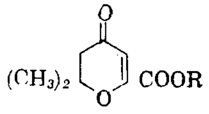
(6)

The possible conjugate addition of hydroxide ion to XIV accompanied by ring opening to form the anion of hydroxy β-diketone II as an intermediate seems unlikely, since II failed to undergo dehydration to yield XI under similar conditions. In this experiment some of II appeared to undergo cleavage by 64% of it was recovered.

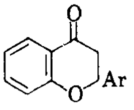
Similarly dihydropyrone XV was converted to unsaturated β-diketone XII with ethanolic potassium hydroxide. Also, these two compounds were interconverted by means of sulfuric acid.

Incidentally, these reactions of the dihydropyrones indicate the cleavage of a carbon-oxygen bond rather than a carbon-carbon bond, and provide further evidence for their structure by showing that they were not products of cyclodehydration into one of the aromatic rings.

It should be mentioned that Auwers and Dieckmann[16] postulated the dihydropyrone structure XVIII for the β-form of mesityloxide oxalic ester, the α-form being the open chain isomer. Another dihydropyrone structure is found in the flavanones XIX, which may be formed by the cyclization of o-hydroxy chalcones.[17]

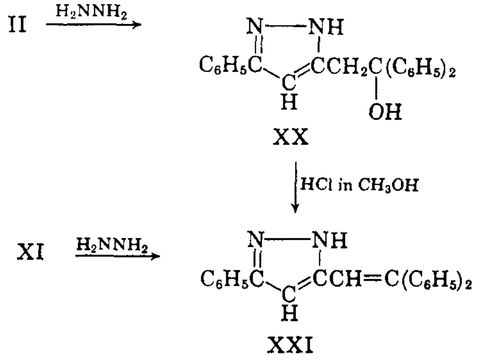


XVIII



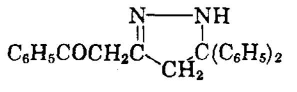
XIX

Cyclizations with hydrazine to form pyrazoles. Hydroxy β-diketone II and unsaturated β-diketone XI were cyclized with hydrazine in refluxing ethanol to form almost quantitative yields of pyrazoles XX and XXI, respectively. Dehydration of the former pyrazole produced the latter (Scheme A).



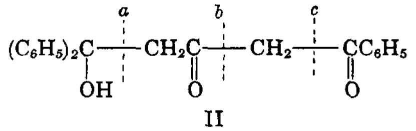
The structures of these pyrazoles were supported by analyses. Pyrazole XX gave an absorption in the infrared at 2.94 μ, indicating the hydroxyl group.[8] It also gave a broad absorption band at 3.10 μ, while pyrazole XXI gave a broad absorption at 3.25 μ. Absorption bands at 6.8 and 10.7 μ have been reported as characteristic of certain pyrazole ring systems.[18] Pyrazoles XX and XXI both gave a band of medium intensity at 6.85 μ, but no band was found near 10.7 μ.

That the product from hydrazine and unsaturated β-diketone XI was not the possible pyrazoline XXII, which might have arisen from the elimination of only one molecule of water accompanied by conjugate addition, was shown not only by its formation from the hydroxypyrazole XX (see Scheme A), but also by its analysis.



XXII

Cleavage of hydroxy β-diketone II. *Equilibrium considerations.* As II is both an aldol type of compound and a β-diketone, it might be expected to undergo alkaline cleavage at *a* or at *b* and *c*.



$(C_6H_5)_2C(OH){-}CH_2C(=O){-}CH_2{-}C(=O)C_6H_5$

II

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(16) K. v. Auwers and W. Dieckmann, *Ber.*, 56, 1527 (1923); W. Dieckmann, *Ber.*, **53**, 1772 (1920).

(17) See S. Wawzonek, *Heterocyclic Compounds*, Vol. 2, R. C. Elderfield, ed., Wiley, New York, 1951, pp. 348–9.

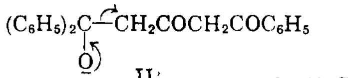
(18) C. S. Rondestvedt and P. K. Chang, *J. Am. Chem. Soc.*, **77**, 6532 (1955).

Actually this compound underwent cleavage preferentially at *a* with approximately 0.2, 1.0, or 2.0 molecular equivalents of potassium *t*-butoxide in *t*-butyl alcohol to form benzophenone and benzoylacetone (Equation 7).

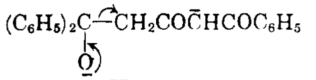
$$\text{II} \xrightarrow[(CH_3)_3COH]{KOC(CH_3)_3} (C_6H_5)_2C{=}O + CH_3COCH_2COC_6H_5 \quad (7)$$

These products were isolated in yields of 59–80% on refluxing the solutions for two hours and then distilling the solvent during one hour. A longer refluxing period (twenty-four hours) with an equivalent of the base produced appreciable amounts of the further cleavage products of the β-diketone. A blank experiment in the absence of the base failed to yield the cleavage products, and about 75% of II was recovered.

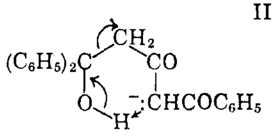
The mechanism of the reaction involves presumably the ionization of the hydroxyl hydrogen by the *t*-butoxide ion and the cleavage of the resulting anion, which may be the monoanion II′ or the dianion II″; or possibly the cyclic mechanism indicated in IIa may operate.



II′



II″



IIa

In all three mechanisms the cleavage would form the methyl carbanion, which would acquire a proton from the solvent (or other source) to regenerate the catalyst.

The cleavage of II by a catalytic amount of *t*-butoxide indicates that the ketone and β-diketone (or its monoanion) are more stable thermodynamically than the hydroxy β-diketone. The condensation of the dicarbanion of the β-diketone with the ketone is therefore suggested to occur because of the formation of the more weakly basic dianion (see Equation 2). A similar working hypothesis has recently been suggested for the condensations of sodium diphenylmethide,[19] the dianion of phenylacetic acid,[20] and the anion of ethyl and and *t*-butyl acetates[6] with the carbonyl group of ketones or aldehydes.

In line with this hypothesis, monopotassiobenzoylacetone failed to condense with benzophenone in liquid ammonia during four hours, and monolithiobenzoylacetone failed to condense with anisaldehyde during two hours. However, we cannot say that some condensation would not have been observed after a much longer time, since neither was cleavage of hydroxy β-diketone II realized with 1 or 1.2 equivalents of potassium amide in liquid ammonia during four to six hours.

EXPERIMENTAL[21]

Condensations of β-diketones with ketones or aldehydes to form hydroxy β-diketones (Tables I, II, and III). *A. Condensations of dipotassiobenzoylacetone.* Solid benzoylacetone (16.2 g., 0.1 mole) was added through a powder funnel to a stirred solution of 0.2 mole of potassium amide[3] in 300 ml. of commercial, anhydrous liquid ammonia, followed by about 50 ml. of anhydrous ether. The resulting dark green solution of dipotassiobenzoylacetone was stirred for 30 min., and 0.1 mole of the ketone (solid) or the aldehyde (in 50 ml. of ether) was then added. After stirring for 1 hr. (3 min. with the aldehyde), the reaction mixture was poured into a liquid ammonia solution of 15 g. of ammonium chloride. The liquid ammonia was evaporated on the steam bath as an equal volume of ether was added. The resulting ethereal suspension was shaken with dilute hydrochloric acid, and then washed with sodium bicarbonate solution. Finally the ethereal layer was dried over Drierite or shaken with saturated aqueous chloride and dried over sodium sulfate. The solvent was removed on the steam bath, the last bit being evaporated under vacuum. The residue was recrystallized directly or first triturated with *n*-hexane to produce the solid-hydroxy β-diketones.

When benzophenone was condensed with benzoylacetone with no ether in the reaction mixture, only an 18% yield of II was obtained. Apparently some ether was necessary to dissolve the benzophenone.

B. *Condensations of dipotassioacetylacetone.* To an ethereal solution of 20 g. (0.2 mole) of acetylacetone was carefully added liquid ammonia, and the resulting white slurry of the ammonium salt of the β-diketone[3] was added to a stirred solution of 0.4 mole of potassium amide[3] in 500 ml. of liquid ammonia, rinsing the last bit with some dry ether. The resulting white suspension of dipotassioacetylacetone was stirred for 30 min., and 36.4 g. (0.2 mole) of solid benzophenone was added. After stirring for 1 hr., the reaction mixture was poured into a solution of 25 g. of ammonium chloride in liquid ammonia, and the ammonia was replaced by ether. The resulting ethereal suspension was filtered, and the solvent was removed from the filtrate. The insoluble material was shaken with dilute hydrochloric acid to remove inorganic salts, and the crude product remaining was collected on a Büchner funnel and washed with water. This solid was combined with the residue from the ether filtrate above and was recrystallized from 95% ethanol to produce hydroxy β-diketone IV.

A suspension of 0.1 mole of dipotassioacetylacetone in 300 ml. of liquid ammonia was prepared as described above, using one half the quantities of reagents. Solid *p*-chlorobenzophenone (21.6 g., 0.1 mole) was added, and the reaction mixture was stirred for 1 hr. Neutralization and work up were the same as described for the dipotassiobenzoylacetone condensations to the point of obtaining the crude residue of hydroxy β-diketone V from the ethereal solution. Two procedures were compared for the purification of this residue. Half (13.15 g.) the crude residue was recrystallized from ligroin (b.p. 60–90°) to give 6.7 g. (42%) of V, m.p. 96–103°.

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(19) P. J. Hamrick, Jr., and C. R. Hauser, *J. Am. Chem. Soc.*, **81**, 3146 (1959).

(20) P. J. Hamrick, Jr., and C. R. Hauser, *J. Am. Chem. Soc.*, **82**, 1957 (1960).

(21) Melting points were taken on a Fisher-Johns melting point apparatus which had been calibrated with melting point standards. Infrared spectra were determined with a Perkin-Elmer Infracord by the potassium bromide pellet method unless stated otherwise. Elemental analyses were by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

The other half was treated with copper acetate as described below in procedure A to form 14.6 g. of crude copper chelate, m.p. 157–162°. The copper chelate was decomposed by shaking with ether and dilute hydrochloric acid. The ether layer was washed with aqueous sodium bicarbonate, shaken with saturated aqueous sodium chloride, and dried over sodium sulfate. The ether was removed on the steam bath to give 8.2 g. (52%) of V, m.p. 94–102°. Further purification of this product produced two forms of V, m.p. 80–81.5° and 100–102° for the analytical samples. When crystallized by cooling a ligroin or an ethanol solution of V in an ice bath, the lower melting form was produced. When crystallized from ethanol at room temperature by adding water, the higher melting form was produced. Both forms gave the same copper chelate (Table I). The infrared spectra of the two forms were the same below 12 μ, and bands above 12 μ were shifted by about 0.05 μ toward longer wave length in the lower melting form. The relative intensities of these bands were different.

C. *Condensations of dilithiobenzoylacetone.* A solution of 16.2 g. (0.1 mole) of benzoylacetone in about 50 ml. of anhydrous ether was added to a suspension of 0.2 mole of lithium amide[22] in 300 ml. of commercial, anhydrous liquid ammonia. The dark green solution was stirred for 45 min., and 0.1 mole of the ketone was then added as a solution in 50 ml. of anhydrous ether. The reaction with acetophenone, was stirred for 1 hr., and the one with cyclohexanone was stirred for 2 hr. Neutralization and work up were the same as described for the dipotassiobenzoylacetone condensations.

An alternative method for condensing benzoylacetone with acetophenone involved the addition of 12.7 g. (0.3 mole) of dried lithium chloride and 25 ml. of dry ether to a stirred solution of 0.1 mole of dipotassiobenzoylacetone in 300 ml. of liquid ammonia followed, after 3 hr. of stirring, by 12.0 g. (0.1 mole) of the ketone. The reaction mixture was stirred for 1 hr., and then worked up as described above to give a 45% yield of VI, m.p. 84–87°.

General procedures for copper chelates. In procedure A, a hot, filtered, aqueous solution of cupric acetate (20–50 ml.) was added to a methanolic solution (10–20 ml.) of the β-diketone (0.5–1.0 g.). The resulting mixture was cooled to precipitate the chelate, which was collected and recrystallized from an appropriate solvent. Oils were triturated with petroleum ether (b.p. 30–60°) or with methanol.

In procedure B, the copper acetate was added as a solution in methanol instead of water.

In procedure C, an ethereal solution of the β-diketone (sometimes containing impurities) was stirred with a saturated, aqueous solution of copper acetate, usually for several hours. The resulting chelate was removed by filtration if insoluble in ether, but obtained by evaporating the ethereal layer if soluble in this solvent.

Copper chelates of hydroxy β-diketones I–VI were prepared by procedure A, while procedure B was used for VII (Tables I, II, and III).

Dehydration of hydroxy β-diketones (Table IV). A. *With methanolic hydrochloric acid.* Solutions of 2 g. of the hydroxy β-diketones in 25 ml. of methanol and 3 ml. of concd. hydrochloric acid were refluxed for 1 hr. (14 hr. with II). The reaction mixtures from hydroxy β-diketones I and II were cooled to precipitate the products, and those from IV and VI were diluted with water and extracted with ether. The products were isolated and identified as described below.

The product from I was *p*-methoxycinnamoylacetophenone (X, 96%), m.p. 129–130.5°, which was not raised by recrystallization from benzene–ethanol.

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.31; H, 5.58.

The copper chelate of X (procedure A, using dioxane instead of methanol) was recrystallized from dioxane-water, m.p. 226–229°.

Anal. Calcd. for $C_{36}H_{30}O_6Cu$: C, 69.50; H, 4.86; Cu, 10.21. Found: C, 69.39; H, 4.87; Cu, 10.35.

The infrared spectrum of X in the carbonyl and enol-chelate region[10] showed strong bands at 6.14 μ and 6.26 μ, and a strong broad absorption from 6.55 μ to 6.70 μ. The copper chelate spectrum showed strong bands at 6.61 μ and 7.17 μ.[12,13] Only a weak band was present in the hydroxyl region at 2.9 μ in both spectra, attributable to moisture in the potassium bromide.

The product from II was β-phenylcinnamoylacetophenone (XI, 74%), m.p. 96–98°. More (5%), m.p. 95–97°, was isolated from the filtrate. This product and its copper chelate (procedure B, m.p. 219–223°) were shown by mixed melting point and infrared absorption to be identical with samples prepared by the dehydration of II with sulfuric acid (see below).

The ether extract of the product from IV was washed with aqueous sodium bicarbonate and water, and treated with aqueous copper acetate for 4 hr. (procedure C) to give the copper chelate of XII (36%), m.p. 148–162°. Recrystallization from methanol gave the chelate (19%), m.p. 161–163°, which was shown to be identical with that of XII prepared by the dehydration of IV with sulfuric acid (see below).

The ether extract of the product from VI (obtained using double quantities of reactants) was washed with aqueous bicarbonate and saturated sodium chloride solution, dried over sodium sulfate, and the solvent removed. An aliquot of the oily residue was treated with copper acetate (procedure A) to give the copper chelate of β-methylcinnamoylacetophenone (XIII, 13%), m.p. 206.6–208.5° after recrystallization from benzene–ethanol.

Anal. Calcd. for $C_{36}H_{30}O_4Cu$: C, 73.26; H, 5.12; Cu, 10.77. Found: C, 72.90; H, 5.37; Cu, 10.45.

A small sample of the copper chelate was decomposed by acid to give a trace of XIII (oil), the infrared spectrum of which (on sodium chloride plates) showed a strong broad absorption in the enolchelate region[10] from 6.2 μ to 6.65 μ. The copper chelate spectrum showed strong bands at 6.56 μ (possibly a doublet) and 7.10 μ. Only a weak band was present at 2.9 μ in the copper chelate spectrum, attributable to moisture in the potassium bromide, and no band was present in this region in the spectrum of XIII.

The remainder of the oily residue mentioned above was triturated with petroleum ether (b.p. 30–60°) to give apparently dihydropyrone XVI (66%, white crystals), m.p. 84–86°. Recrystallization from *n*-hexane produced another crystalline form, m.p. 108–110°, from which an analytical sample was prepared.

Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.99; H, 6.29.

The infrared spectrum of XVI in the carbonyl and enol-chelate region[10] showed a strong band at 6.03 μ and medium-strong bands at 6.27 μ and 6.38 μ. No band was present in the hydroxyl region at 2.9 μ. This compound produced no color with ethanolic ferric nitrate and did not form a copper chelate.

B. *With sulfuric acid.* Samples (5 g.) of the hydroxy β-diketones were dissolved with stirring in 50 ml. of cold concentrated sulfuric acid (ice bath) within about 15 min. The solutions were poured into ice water, and the resulting gummy, yellow products were worked up as described below.

The product from II was taken up in ether, and the ether solution was treated overnight with aqueous copper acetate (procedure C) to precipitate the copper chelate of XI (58%, yellowish brown), m.p. 223–27° after recrystallization from benzene–ethanol.

Anal. Calcd. for $C_{46}H_{34}O_4Cu$: C, 77.33; H, 4.80; Cu, 8.89. Found: C, 77.48; H, 4.88; Cu, 9.16.

A sample of the copper chelate was decomposed with acid to give XI (yellow needles), m.p. 97–98°, after several recrystallizations from methanol.

Anal. Calcd. for $C_{23}H_{18}O_2$: C, 84.64; H, 5.56. Found: C, 84.43; H, 5.52.

The infrared spectrum of XI in the carbonyl and enol-chelate region[10] showed strong broad absorption from 6.24 μ to 6.6. but no definite bands were present. The copper

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(22) See Ref. 4, p. 506.

chelate spectrum showed strong bands at 6.60 μ and 7.17 μ.[12,13] Only a weak band was present in the hydroxyl region at 2.9 μ in both spectra, attributable to moisture in the potassium bromide.

After filtering out the copper chelate in the work up procedure, the ether layer was separated from the aqueous copper acetate layer and washed with dilute hydrochloric acid to decompose any dissolved copper chelate. The ether solution was washed with water and dried. The solvent was removed and the residue recrystallized from methanol to give apparently dihydropyrone XIV (15%, white cubic crystals), m.p. 145–148°. A better yield of XIV was isolated when the copper acetate treatment was omitted. The gummy product obtained on pouring the sulfuric acid solution into ice water was dissolved in hot methanol, and the solution cooled slowly. The first crop of crystals consisted of XIV (37%), m.p. 141–144°, and the second crop of XI (16%), m.p. 90–98°, slightly contaminated with XIV. The yields of the two products varied in different experiments; the highest yield of XIV was 58%, m.p. 147–148° after several recrystallizations from methanol.

Anal. Calcd. for $C_{23}H_{18}O_2$: C, 84.64; H, 5.56. Found: C, 84.93; H, 5.65.

The infrared spectrum of XIV in the carbonyl and enol-chelate region[10,15] showed a strong band at 6.00 μ, and medium bands at 6.25 μ and 6.43 μ. Only a weak band was present in the hydroxyl region at 2.9 μ, attributable to moisture in the potassium bromide. No hydroxyl band was present in a spectrum made in a mineral oil mull. This compound produced no color with ethanolic ferric nitrate[7] and did not form a copper chelate.

If XIV were crystallized quickly from a very concentrated solution in methanol, it formed in white needles which partially melted at 135° and then appeared to reharden and melt at the same temperature as the cubic crystals. The infrared spectra of both crystalline forms were identical.

The product from the dehydration of IV was similarly treated with copper acetate (procedure C). The solvent was removed from the ether solution of the chelate, and the residue was triturated with petroleum ether (b.p 30–60°). The solid formed, m.p. 100–106°, was recrystallized from methanol to give the green copper chelate of XII (11%), m.p. 158–162°. Further recrystallizations raised the melting point to 161.5–163°.

Anal. Calcd. for $C_{36}H_{30}O_4Cu$: C, 73.28; H, 5.12; Cu, 10.77. Found: C, 73.11; H, 5.32; Cu, 11.02.

Decomposition of the copper chelate with acid produced XII (72%, impure oil) which failed to crystallize. The infrared spectrum of XII (on sodium chloride plates) in the carbonyl and enol-chelate region[10] showed a strong broad band from 6.14 μ to 6.39 μ. The copper chelate spectrum showed strong bands at 6.47 μ, 6.60 μ, and 7.14 μ.[12,13] Only a weak band was present at 2.9 μ in the copper chelate spectrum, attributable to moisture in the potassium bromide, and no band was present in this region in the spectrum of XII.

The methanol filtrate from which the copper chelate of XII had originally been recrystallized was diluted with water, acidified with hydrochloric acid, and extracted with ether to give apparently dihydropyrone XV (21%, white crystals), m.p. 119–121°. A better yield (48%) of XV (m.p. 118.5–119°) was obtained by evaporating the solvent from the ether solution of the dehydration product of IV (without treatment with copper acetate), and recrystallizing the residue from 95% ethanol. Further recrystallization from ethanol-water raised the melting point to 119–120.5°.

Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.69; H, 6.06.

Independent synthesis of β-phenylcinnamoylacetophenone (XI). β-Phenylcinnamic acid (m.p. 161–163°) was prepared from 1,1-diphenylethylene and oxalyl chloride by the method of Bergmann,[23] and converted to its acid chloride (b.p. 152° at 2 mm.) by means of thionyl chloride; the viscous oil partly crystallized.

To a stirred, cooled, ethereal suspension of 0.86 mole of sodioacetophenone (prepared from 0.086 mole each of sodium amide and acetophenone),[14,24] was added rapidly a solution of 6.5 g. (0.027 mole) of β-phenylcinnamoyl chloride in 50 ml. of dry ether. After 5 min. the ice bath was removed and the stirring continued for 15 min. longer. The reaction mixture was poured onto crushed ice and water to which had been added 10 ml. of concd. hydrochloric acid. The ethereal layer was separated and combined with an ether extract of the aqueous layer. The ethereal solution was worked up to give unchanged acetophenone (41%) (removed *in vacuo*) and 3.4 g. (39%) of XI (red crystals), m.p. 92–95° and at 94–98° after recrystallization from methanol. The copper chelate (procedure B) melted at 221–223°. Compound XI and its copper chelate were shown by mixed melting point and infrared spectra to be identical with samples prepared as described above.

Interconversions of unsaturated β-diketones and dihydropyrones with sulfuric acid. A 1-g. sample of unsaturated β-diketone XI was dissolved in 10 ml. of cold concd. sulfuric acid, and the solution poured into ice water (see above dehydration experiments). Recrystallization of the product from methanol gave 0.28 g. (28%) of dihydropyrone XIV (white cubic crystals), m.p. 145–148°.

A 0.5-g. sample of dihydropyrone XIV was likewise dissolved in 10 ml. of cold concd. sulfuric acid and the solution poured into ice water. Recrystallization of the product from methanol gave 0.25 g. (50%) of recovered XIV, m.p. 135–147°, and treatment of the methanolic filtrate with copper acetate yielded 0.05 g. (9%) of the copper chelate of unsaturated β-diketone XI, m.p. 220–223°.

Similarly unsaturated β-diketone XII was converted to dihydropyrone XV (29%), m.p. 119–121.5°, and this product reconverted to unsaturated β-diketone XII isolated as its copper chelate (18%), m.p. 160–162°.

Conversion of dihydropyrones to unsaturated β-diketones. A. *With methanolic hydrochloric acid.* A 0.7-g. sample of dihydropyrone XIV was refluxed 17 hr. in 15 ml. of methanol containing 1 ml. of concd. hydrochloric acid. Cooling the solution in an ice bath precipitated 0.6 g. (86%) of unsaturated β-diketone XI, m.p. 96–98°. The melting point was not depressed on mixing with an authentic sample of XI.

B. *With ethanolic potassium hydroxide.* To a solution of 0.5 g of dihydropyrone XIV in 10 ml. of hot 95% ethanol was added a solution of 1 g. of potassium hydroxide in 10 ml. of 95% ethanol, and the mixture was allowed to stand at room temperature for 2 days. Most of the ethanol was distilled, and the residue was diluted with water, acidified, and extracted with ether. The ether extract was dried and the solvent removed. Recrystallization of the residue from methanol produced 0.3 g. (60%), of unsaturated β-diketone XI, m.p. 97–98°, and 0.1 g. (20%), m.p. 94–98°. The melting point was not depressed on mixing with an authentic sample of XI. The crude copper chelate melted at 218–222°.

When a 1-g. sample of hydroxy-β-diketone II was treated with 40 ml. of 5% ethanolic potassium hydroxide under the same conditions, there was recovered 0.5 g. (50%) of II, m.p. 114.5–116.5°, and 0.15 g. (14%) of its copper chelate, m.p. 189–192°. Neither dehydrated product was detected.

A 0.5-g. sample of dihydropyrone XV was treated similarly with ethanolic potassium hydroxide. The ether extract of the reaction product was treated with copper acetate (procedure C) to give 0.3 g. (54%) of the copper chelate of unsaturated β-diketone XII, m.p. 135–145° and at 161–163° after recrystallization from methanol. This melting point was not depressed on admixture with an authentic sample of the chelate.

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(23) F. Bergmann *et al.*, *J. Am. Chem. Soc.*, 70, 1612 (1948); M. S. Kharasch, S. S. Kane, and H. C. Brown, *J. Am. Chem. Soc.*, 64, 333 (1942).

(24) See C. R. Hauser, F. W. Swamer, and J. T. Adams, *Organic Reactions*, VIII, 122–123 (1954).

When a 1-g. sample of hydroxy β-diketone IV was treated with ethanolic potassium hydroxide under the same conditions, there was recovered 0.35 g. (35%) of IV, m.p. 133–135°, and 0.1 g. (9%) of its copper chelate, m.p. 171–176°. Neither dehydrated product was detected.

Pyrazoles from β-diketones. To a solution of 1 g. of hydroxy β-diketone II in 30 ml. of hot 95% ethanol was added an excess (10 drops) of Eastman 95% hydrazine. The solution was heated on the steam bath for one hour (purple color discharged). Water was added to precipitate an essentially quantitative yield of white 3-(2,2-diphenyl-2-hydroxyethyl)-phenylpyrazole (XX), m.p. 181–184° and at 182–184° after several recrystallizations from ethanol-water.

Anal. Calcd. for $C_{23}H_{20}N_2O$: C, 81.15; H, 5.92; N, 8.23. Found: C, 81.33; H, 6.08; N, 8.20.

Treating a 1-g. sample of unsaturated β-diketone XI with hydrazine in the same manner produced 0.95 g. (96%) of white 3-(2,2-diphenylethenyl)-5-phenylpyrazole (XXI), m.p. 92–98°, resolidifying at about 115°, and melting again at about 160°. After heating in *n*-hexane, XXI melted at 157–162°, and after several recrystallizations from methanol-water XXI melted at 160–162°.

Anal. Calcd. for $C_{23}H_{18}N_2$: C, 85.68; H, 5.63; N, 8.69. Found: C, 85.48, 85.64; H, 5.68, 5.63; N, 8.58, 8.74.

A 1-g. sample of pyrazole XX was refluxed 7 hr. in 15 ml. of methanol containing 1 ml. of concd. hydrochloric acid. After standing 60 hr. at room temperature, water was added, and the solution was cooled to give, after recrystallization from methanol-water, 0.2 g. (21%), of pyrazole XXI, m.p. 156–159°. Another recrystallization raised the melting point to 159–161°, which was not depressed on mixing with a sample of XXI prepared as described above. The infrared spectra of the two samples were identical.

Cleavage of hydroxy β-diketone II. To a stirred, refluxing solution of 0.013 mole of potassium *t*-butoxide (prepared from 0.5 g., 0.013 g.-atom of potassium) in 150 ml. of *t*-butyl alcohol was added 4 g. (0.012 mole) of hydroxy β-diketone II. After refluxing for 2 hr., about 120 ml. of solvent was distilled (1 hr.). The residue was cooled, and 100 ml. of ice water containing 2 ml. of concd. hydrochloric acid was added. The mixture was extracted with ether. The ether layer was extracted with fractions of cold 1% sodium hydroxide solution until the ether solution no longer gave a color with ethanolic ferric nitrate. The basic extracts were acidified and extracted with ether. This ether extract was shaken with aqueous sodium bicarbonate, washed with saturated aqueous sodium chloride, and dried over sodium sulfate. The solvent was removed on the steam bath to give 1.5 g. (80%) of benzoylacetone, m.p. 55–59° and at 58–61° after recrystallization from methanol. There was no depression in melting point on mixing with an authentic sample of benzoylacetone.

The neutral ether layer remaining after extraction with sodium hydroxide was washed with saturated aqueous sodium chloride, dried over sodium sulfate, and the solvent removed to leave 2.6 g. of a liquid residue. A 2-g. aliquot of this residue was taken up in a small amount of petroleum ether (b. p. 30–60°) and placed on an alumina column. Evaporation of the first petroleum ether eluates produced 1.1 g. (68%) of benzophenone, m.p. 46–50°. One recrystallization from petroleum ether raised the melting point to 49–50°; there was no depression on mixing with an authentic sample of benzophenone.

Similarly 0.012 mole of II was cleaved with 0.0026 and with 0.026 moles of potassium *t*-butoxide to give benzoylacetone and benzophenone in yields of 64 and 62%, and 59 and 62%, respectively.

In a blank experiment using no potassium *t*-butoxide, 73% of unchanged hydroxy β-diketone II was recovered.

Failure of monoalkalibenzoylacetone to condense with carbonyl compounds. To a stirred solution of 0.1 mole of potassium amide[3] in 300 ml. of liquid ammonia was added 0.1 mole of benzoylacetone in 50 ml. of dry ether (purple solution) followed, after 25 min., by 0.1 mole of benzophenone and 50 ml. of ether. After 6 hr., the reaction mixture was poured into a solution of 15 g. of ammonium chloride in liquid ammonia. There were recovered 87% of the benzophenone and 95% of the benzoylacetone.

Similarly monolithiobenzoylacetone was prepared from 0.1 mole each of benzoylacetone and lithium amide in 300 ml. of liquid ammonia and 50 ml. of ether (purple solution), and treated with 0.1 mole of anisaldehyde in 50 ml. of ether. After 2 hr., the reaction mixture was neutralized inversely with ammonium chloride to give 95% of recovered benzoylacetone.

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Structures of the Adducts of *N*-Phenylhydroxylamine with Dimethyl Acetylenedicarboxylate

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Structures II and III are proposed for the 2:2 and 2:1 adducts, respectively, of *N*-phenylhydroxylamine with dimethyl acetylenedicarboxylate. Implications of the independent formation of III from aniline, dimethyl oxalacetate, and dimethyl α-bromoxalacetate for the mechanism of the Hantzsch pyrrole synthesis are briefly discussed.

Dimethyl acetylenedicarboxylate and *N*-phenylhydroxylamine are known to react to produce two crystalline adducts, an unstable material in which the addends are present in the ratio 1 : 1, and a stable compound consisting of two molecules of ester for each one of amine.[1] Although Huntress[1] was able to obtain the latter adduct by an independent synthesis and to transform it quantitatively to tetramethyl *N*-phenylpyrrole-2,3,4,5-tetracarboxylate (I), no definite structure has been assigned to either of these compounds. On the basis of the information outlined below, we wish to propose structure II for the unstable adduct and structure III for the stable product.

The unstable adduct slowly forms upon mixing the ester and amine in ether at 0–10°.[1] Upon

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(1) E. H. Huntress, T. E. Leslie, and W. M. Hearon, *J. Am. Chem. Soc.*, 78, 419 (1956).