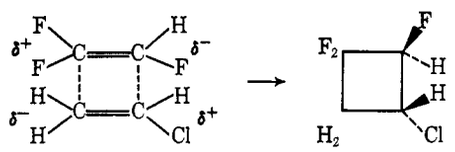
large variation of the 27° vicinal J_{HF} in the CH_2CF_2 group observed by us in I (9.16 and 15.77 Hz) and by Lambert and Roberts[10] in III (8.57 and 12.59 Hz) is probably due to small differences in C–C–F bond angles between axial and equatorial fluorines.

This is also the first determination of vicinal J_{FF} in a CF_2–CFH grouping in a cyclobutane ring. The opposite signs for the two vicinal couplings is expected from analogy to previous results for cyclobutenes and cyclobutanes.[13-15]

Conclusions

The interpretation of the nmr spectrum of 1-chloro-2,3,3-trifluorocyclobutane shows that the trifluoroethylene and vinyl chloride undergo a stereospecific 1,2 cycloaddition. Two explanations are possible for formation of only the *trans* isomer: (1) that it is an equilibrium reaction in which the most stable isomer predominates; (2) that it has an ionic rather than a diradical or a four-centered intermediate and that only the most electrostatically stable configuration of reactants leads to products.



Experimental Section

Infrared spectra were taken on a Perkin-Elmer Infracord. Nuclear magnetic resonance spectra were taken on a Varian HA-100 analytical spectrometer. Product analysis and fine scale preparations were carried out on an Aerograph Autoprep Model A-700, using a Texas Instruments Inc. Servariter model recorder. Refractive indices were taken on a Bausch & Lomb refractometer. Mass spectra were taken on a CEC 21 103C mass spectrometer equipped with an all glass heated (150°) inlet system. Microanalyses were performed by the Galbraith Laboratories, Knoxville, Tenn.

Codimerization of Trifluoroethylene with Vinyl Chloride.—Following the procedure of Park, Lacher, and Holler,[3] about 472 g of trifluoroethylene and 433 g of vinyl chloride were transferred into a sealed 1.5-l. autoclave containing 3 ml of *d*-limonene (added to prevent polymerization). The autoclave was heated to 230° for about 6 days. Upon cooling, 445 g of gaseous material and 284 g of a black liquid were obtained. Distillation of the liquid in a 3-ft glass helix packed column yielded 34.2 g (3.8% of theory) of 1-chloro-2,3,3-trifluorocyclobutane; bp 73–76° (627 mm); $n^{27}D$ 1.3683; d^{27} 1.3648. Molar refractivity: calcd, 23.76; found, 23.76.

Anal. Calcd for $C_4H_4ClF_3$: C, 33.24; H, 2.79; F, 39.44; Cl, 24.53. Found: C, 33.21; H, 2.77; F, 39.52; Cl, 24.73.

Tetramethylsilane and trichlorofluoromethane were added to the next liquid as internal reference lock signals for the nmr spectra. The sample was distilled *in vacuo* to remove oxygen.

Reaction of 1-Chloro-2,3,3-trifluorocyclobutane with Potassium Hydroxide.—Following the procedure of Park, Lacher, and Holler,[3] about 9.5 g of 1-chloro-2,3,3-trifluorocyclobutane was added dropwise over about 3 hr to a suspension of 18 g of potassium hydroxide suspended in 27 ml of heavy white mineral oil at room temperature in a 50-ml three-neck flask equipped with a stirrer and reflux condenser. After 44 hr, about 4.8 g (68% of theory) of a volatile product was obtained whose infrared spectrum was identical with that of known 2,3,3-trifluorocyclobutene. About 0.1 g each of *t*-butylpyrocatechol and diphenylamine was placed in the reaction flask and the gas trap to prevent polymerization of the cyclobutene. Catechol may be used in place of *t*-butylpyrocatechol.

Acknowledgments.—The authors wish to express their appreciation to the 3M Co., St. Paul, Minn., for their support of this work through a grant-in-aid.

Registry No.—Trifluoroethylene, 359-11-5; vinyl chloride, 75-01-4; 1-chloro-2,3,3-trifluorocyclobutane (*trans*), 20445-03-8.

(13) R. A. Newmark, *Chem. Commun.*, 1123 (1968).
(14) R. K. Harris and R. Ditchfield, *Spectrochim. Acta A*, **24**, 2089 (1968).
(15) R. E. Ernst, *Mol. Phys.*, in press.

Reactions of Dehydroacetic Acid and Related Pyrones with Secondary Amines

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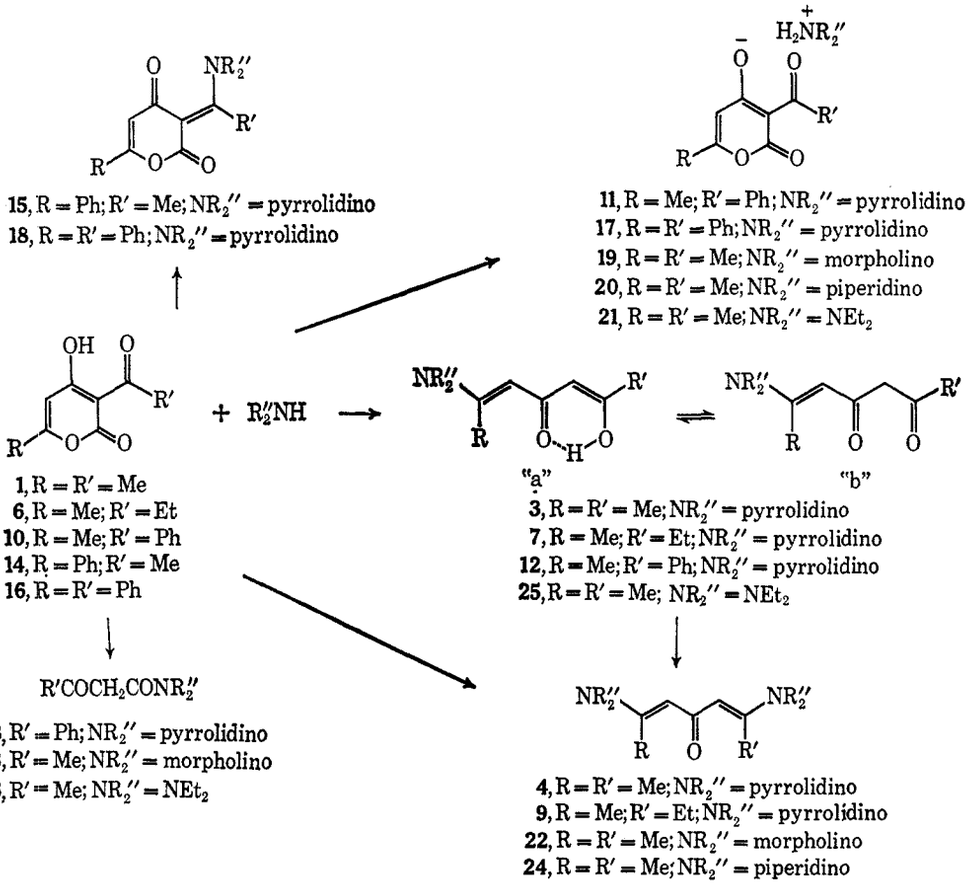
Received November 14, 1968

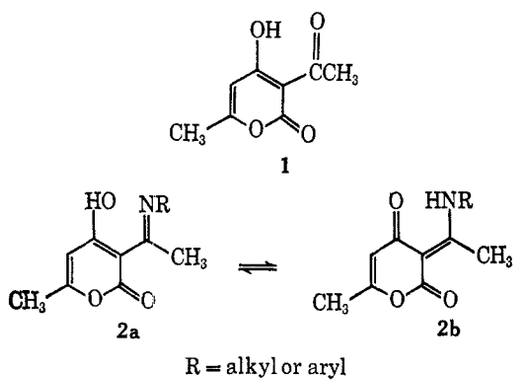
A study of the reactions of dehydroacetic acid (**1**) and related pyrones with secondary amines has been undertaken. Pyrrolidine reacts readily with dehydroacetic acid (**1**), 3-propionyl-4-hydroxy-6-methyl-2-pyrone (**6**), and 3-benzoyl-4-hydroxy-6-methyl-2-pyrone (**10**) to yield **3**, **7**, and **12**, the respective products of nucleophilic attack at the 6 position of the pyrone, followed by ring opening and decarboxylation; with 3-acetyl-4-hydroxy-6-phenyl-2-pyrone (**14**) and dehydrobenzoylacetic acid (**16**), it gives in each case the product of condensation at the carbonyl of the side chain. Reaction of enediones **3** and **7** with pyrrolidine gives the corresponding dienones **4** and **9** which could also be obtained directly from dehydroacetic acid (**1**) and 3-propionyl-4-hydroxy-6-methyl-2-pyrone (**6**) and excess pyrrolidine. Enedione **12**, however, gives **13**, the pyrrolidinamide of benzoylacetic acid, when treated with pyrrolidine. When morpholine and diethylamine are employed as amines, a more complex reaction produces in the case of dehydroacetic acid (**1**) not only enediones and dienones but also acetoacetamides formed by attack at the 2 position of the pyrone. Mechanisms for these various transformations are discussed.

A primary or secondary amine could conceivably attack dehydroacetic acid (**1**) at any of four possible sites: the carbonyl of the acetyl side chain at the 3 position, the carbon atom terminating the conjugated carbon chain at the 6 position, the lactone carbonyl at the 2 position, and the carbon atom at the 4 position (the carbon of a potential carbonyl group). Actually, primary aliphatic and aromatic amines were shown to react preferentially and exclusively with the carbonyl of the acetyl side chain at the 3 position to form the Schiff

SCHEME I



base **2a**, which probably exists in the tautomeric form **2b**.[1-6]



We recently undertook a study of the reactions of dehydroacetic acid (**1**) and related pyrones with various secondary amines. Of primary interest was whether attack at the carbonyl of the acetyl side chain at the 3 position is also a general reaction of secondary amines or whether secondary amines show a preference for reaction at one or more of the other reactive sites of this tetrafunctional molecule.

Dehydroacetic acid (**1**) reacted with 1 equiv of pyrrolidine in toluene at 50° to afford a crystalline compound with the empirical formula $C_{11}H_{17}NO_2$. This compound gave a strong enol test with ethanolic ferric chloride. Its infrared spectrum in KBr exhibited broad weak absorption in the 4-μ region and strong absorption at 6.1, 6.35, and 6.45 μ. The solution infrared spectrum in chloroform displayed an additional band at 5.85 μ. This evidence suggested that the compound had the tautomeric structure **3a** $\rightleftharpoons$ **3b** (Scheme I).[7] Furthermore, the absence of the band at 5.85 μ in the spectrum in KBr indicates that this compound, as a solid, exists entirely in the enol form **3a**. The 100-MHz nmr spectrum of a freshly prepared solution of **3a** $\rightleftharpoons$ **3b** in deuterated benzene showed four different methyl resonances occurring at δ 1.85, 2.15, 2.35, and 2.40 ppm and absorption for three different vinyl hydrogens at δ 4.58, 4.84, and 5.32 ppm. The singlets at 1.85 and 2.15 ppm are readily assigned to the enol and keto methyl groups of **3a** and **3b**, respectively,[8] and those at 2.35 and 2.40 ppm to the 1-methyl groups of **3b** and **3a**, respectively.

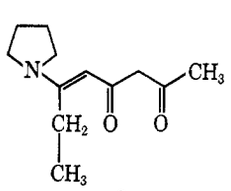
The vinyl resonances at 4.58 and 4.84 ppm can be assigned to the C-3 vinyl protons of **3a** and **3b**, respectively, the vinyl resonance at low field being due to the C-5 vinyl proton of **3a**. The two other signals in the spectrum at δ 3.43 and 17.62 ppm can be assigned to the 5-methylene group of **3b** and to the enol proton resonance of **3a**. Integrated peak areas are consistent with these assignments and indicate that enedione **3** exists to the extent of approximately 80% in the enol form

(1) S. Iguchi, K. Hisatsune, M. Himeno, and S. Muraoka, *Chem. Pharm. Bull.* (Tokyo), **7**, 323 (1959).
(2) S. Garratt, *J. Org. Chem.*, **28**, 1886 (1963).
(3) D. Cook, *Can. J. Chem.*, **41**, 1435 (1963).
(4) J. D. Edwards, J. E. Page, and M. Pianka, *J. Chem. Soc.*, 5200 (1964).
(5) R. N. Schut, W. G. Strycker, and T. M. H. Liu, *J. Org. Chem.*, **28**, 3046 (1963).
(6) D. R. Gupta and R. S. Gupta, *J. Indian Chem. Soc.*, **42**, 421 (1965).
(7) Although, for simplicity, only one enolic form is shown, other tautomeric forms, although less likely, cannot be entirely excluded.
(8) *Cf.* the spectrum of acetylacetone. L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Oxford, 1959, p 70.

3a under these conditions. A spectrum of the same sample recorded 3 hr later showed a significant reduction in the enol content. Integrated peak area ratios indicated that the tautomeric mixture now contained 70% enol **3a**.

When enedione **3** was treated with an excess of pyrrolidine in refluxing toluene, it was converted into 2,6-bis-(N-pyrrolidino)hepta-2,5-dien-4-one (**4**) in 87% yield. Similarly, reaction of dehydroacetic acid (**1**) with an excess of pyrrolidine in refluxing benzene or toluene led directly to dienone **4** in 98% yield (Scheme I). Under these conditions, none of the intermediate enedione accumulated. The structure of dienone **4** was supported by infrared and nmr spectra and elemental analysis, and was confirmed by independent synthesis which involved reaction of 2,6-dimethyl-4-pyrone (**5**) with an excess of pyrrolidine in refluxing toluene.[9]

Two mechanisms for the conversion of dehydroacetic acid (**1**) to enedione **3** are worthy of consideration. The route preferred by us involves nucleophilic attack by pyrrolidine at the 6 position of the pyrone followed by opening of the pyrone ring and decarboxylation to yield enedione **3**.[10] The alternative pathway involves condensation of pyrrolidine with the carbonyl of the acetyl side chain at the 3 position. The pyrone ring would then be opened by nucleophilic attack of HO^- at the 6 position. Subsequent decarboxylation would yield enedione **3**. Evidence that the reaction of dehydroacetic acid (**1**) with pyrrolidine involved initial attack of pyrrolidine at the 6 position of the pyrone and not at the carbonyl of the acetyl side chain was obtained from a study of the reaction of 3-propionyl-4-hydroxy-6-methyl-2-pyrone (**6**) with pyrrolidine. In this case, reaction of pyrrolidine at the 6 position of the pyrone would give rise to enedione **7**, while initial reaction of pyrrolidine at the carbonyl of the propionyl side chain would lead to enedione **8**. Actually, 3-propionyl-4-hydroxy-6-methyl-2-pyrone (**6**) was found to react with an equivalent amount of pyrrolidine in toluene at 50° to form enedione **7** in 75% yield. That the product from this reaction was **7** and not enedione **8** follows from the nmr spectrum. The spectrum of a freshly prepared solution of enedione **7** in deuterated benzene showed the following features: two overlapping triplets centered at δ 1.00 and 1.08 ppm which can be assigned to the 8-methyl groups in **7b** and **7a**, respectively;[11] two quartets centered at δ 2.17 and 2.53 ppm produced by the 7-methylene groups in **7a** and **7b**; two singlets at δ 2.38 and 2.44 ppm caused by the 1-methyl groups of **7b** and **7a**; a singlet at 3.42 ppm which can be assigned to the 5-methylene group of keto form **7b**; three singlets at δ 4.63, 4.86, and 5.34 ppm produced by the C-3 vinyl protons of **7a** and **7b** and the C-5 vinyl proton of **7a**; and a broad resonance signal at δ 17.55 ppm caused by the hydroxyl group of enol **7a**. Integrated peak areas support these assignments and indicate that enedione **7** consists of a mixture of 84% **7a** and 16% **7b** under the conditions in which the spectrum was recorded. Significant in the spectrum was the absence of methyl resonance lines in the region of 1.85–2.15 ppm. Enedione **3**, on the other hand, showed keto and enol methyl resonance lines at 2.15 and 1.85 ppm, respectively, and we would expect the keto and enol methyl of enedione **8** and its enol to resonate at similar chemical shifts. The absence of methyl resonance lines in the region of 1.85–2.15 ppm of the spectrum clearly excludes structure **8**; it establishes unequivocally that in the reaction of pyrrolidine with **6** and by analogy with **1** initial attack of pyrrolidine occurs at the 6 position of the pyrone.



8

Enedione **7** was readily transformed into dienone **9** by heating with an excess of pyrrolidine in toluene. Dienone **9** could also be obtained directly, in 63% yield, by treating pyrone **6** with an excess of pyrrolidine in refluxing toluene. The structural assignment of **9** was supported by elemental analysis and infrared and nmr spectra.

The reaction of 3-benzoyl-4-hydroxy-6-methyl-2-pyrone (**10**) (Scheme I) with pyrrolidine was also investigated. Treatment of pyrone **10** with 1 equiv of pyrrolidine in toluene at 50° afforded the salt **11** in 96% yield.

Reaction of **10** with an excess of pyrrolidine in refluxing toluene produced enedione **12** in 73% yield. The nmr spectrum of a freshly prepared solution of **12** in deuterated benzene indicated that **12** consisted of a mixture containing 85% enol tautomer **12a** and 15% keto tautomer **12b**. A spectrum of the same solution recorded 3 hr later showed no change in the composition of the tautomeric mixture.

When enedione **12** was treated with an excess of pyrrolidine in refluxing toluene, it was partially converted into **13**. The structure of **13** follows from its infrared and nmr spectra and elemental analysis. The nmr spectrum indicated that **13** consisted of a 1:1 keto–enol mixture in deuteriochloroform solution.

Next, the reaction of pyrrolidine with several 3-acyl-4-hydroxy-6-phenyl-2-pyrones was examined. Treatment of 3-acetyl-4-hydroxy-6-phenyl-2-pyrone (**14**) (Scheme I) with an equivalent amount of pyrrolidine in toluene at 50–60° yielded a crystalline compound, $C_{17}H_{17}NO_3$, indicating a 1:1 condensation with loss of one molecule of water. The ultraviolet spectrum was similar to that of pyrone **14** [λ_{max}^{MeOH} 220 mμ (log ϵ 4.18) and 354 (4.19)]. The infrared spectrum displayed strong bands at 5.9, 6.1, 6.32, 6.4, and 6.66 μ, and the compound was readily converted back into pyrone **14** in dilute hydrochloric acid. On the basis of this evidence, structure **15** was assigned to the product. The structure of **15** was further supported by the nmr spectrum in which the vinylic CH produced a signal at 6.36 ppm and the methyl group gave a singlet at 2.65 ppm.

Reaction of dehydrobenzoylacetic acid (**16**) with 1 equiv of pyrrolidine under similar conditions afforded pyrrolidinium dehydrobenzoylacetate (**17**) in 98% yield. When the condensation of **16** with pyrrolidine

(9) 2,6-Bis(N-pyrrolidino)hepta-2,5-dien-4-one has also been prepared in these laboratories from 2,4,6-heptanetrione and pyrrolidine by R. A. Langdale-Smith and D. T. Manning, unpublished work.

(10) Cleavage of 2-pyrones at the 6 position has been observed with cyanide ion and with complex metal hydrides under certain conditions: G. Vogel, *Chem. Ind.* (London), 268, 1829 (1962); *J. Org. Chem.*, **30**, 203 (1965).

(11) The nmr signal for the enol methyl in the related 3,5-heptanedione is also found at lower field than the signal for the keto methyl (see Experimental Section).

was carried out in refluxing toluene with an excess of pyrrolidine, a mixture of **17** and **18** was obtained. The yields were 60 and 11%, respectively. The structure of **18** follows from elemental analysis, ultraviolet, infrared and nmr spectra and hydrolysis back to dehydrobenzoylacetic acid (**16**) in dilute hydrochloric acid. We found that it was possible to convert the highly insoluble **17** into **18** by refluxing **17** in ethanol or 2-propanol.

Finally, the reactions of dehydroacetic acid (**1**) with morpholine, piperidine, and diethylamine were investigated. In contrast to the reaction of **1** with 1 equiv of pyrrolidine in toluene at 50°, which led to enedione **3**, treatment of **1** with an equivalent amount of either morpholine, piperidine or diethylamine under similar conditions gave the corresponding salts **19–21** (Scheme I).

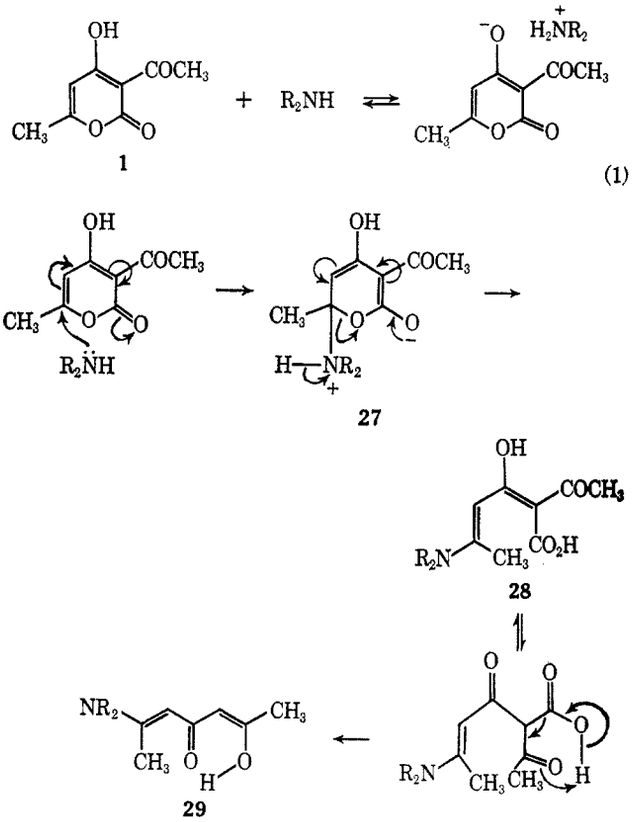
When dehydroacetic acid (**1**) was treated with an excess of morpholine in refluxing benzene, a mixture of dienone **22** and 4-acetoacetylmorpholine (**23**) was obtained. The yields were 26 and 33%, respectively. The structural assignments of **22** and **23** were substantiated by infrared and nmr spectra and elemental analysis. The structure of **23** was further confirmed by comparison of its infrared spectrum and a mixture-melting-point determination with an authentic specimen of **23** prepared by acetoacetylating morpholine with diketene.

Reaction of **1** with an excess of piperidine in benzene at 60° led to a mixture from which the only pure product isolated was 2,6-bis(N-piperidino)hepta-2,5-dien-4-one (**24**) (Scheme I). Considerable difficulty was experienced in isolating **24** owing to its apparent instability in the crude state. Treatment of **1** with an excess of the more hindered diethylamine in refluxing benzene furnished diethylammonium dehydroacetate (**21**) in 48% yield and an oil which could not be induced to crystallize. The nmr spectrum of the crude oil was examined prior to distillation and indicated that it consisted essentially of the tautomeric mixture **25a** ⇌ **25b**. Distillation of the oil, however, resulted in the separation of a third compound identified as **26** by comparison of its infrared and nmr spectra with those of an authentic sample of **26** prepared from ethyl acetoacetate and diethylamine by the method of Utzinger[12] (Scheme I). Enedione **25** decomposed during attempted distillation and purification has not been possible.

Several examples of the reactions of both 3-acyl-4-hydroxy-6-methyl-2-pyrones and 3-acyl-4-hydroxy-6-phenyl-2-pyrones with pyrrolidine have been presented in this paper. In addition, the reactions of dehydroacetic acid (**1**) with morpholine, piperidine, and diethylamine have been described. Four different modes of attack were possible in each case. The products isolated from the reactions of the 3-acyl-4-hydroxy-6-methyl-2-pyrones **1**, **6**, and **10** with pyrrolidine were the result of initial attack of pyrrolidine at only the 6 position of the pyrone, while the products isolated from the reactions of the 3-acyl-4-hydroxy-6-phenyl-2-pyrones **14** and **16** with pyrrolidine were the result of attack at the carbonyl of the acyl side chain in the 3 position. On the other hand, the products isolated from the reactions of dehydroacetic acid (**1**) with morpholine and diethylamine were the result of attack of amine at the 6 and the 2 or 4 positions.

The first step in the reactions of dehydroacetic acid and related acylpyrones with secondary amines appears to be a simple acid–base reaction which results in salt formation (eq 1) (Scheme II). The solubility of these

SCHEME II



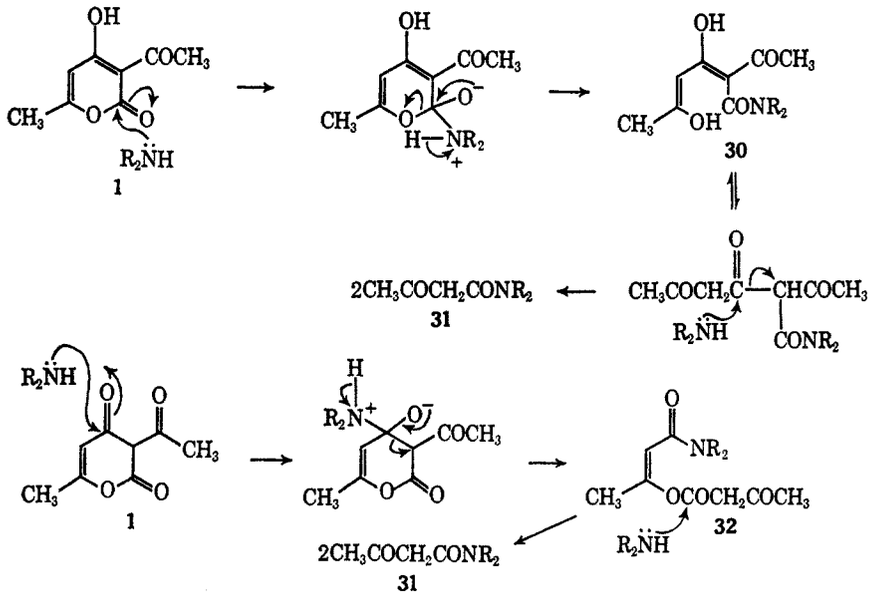
salts plays an important role in the reactions of acylpyrones with 1 equiv of amine. The low solubility of morpholinium, piperidinium and diethylammonium dehydroacetate, pyrrolidinium dehydrobenzoylacetate, and the pyrrolidinium salt of pyrone **10** results in the precipitation of these salts from solution and in effect protects the pyrone nucleus from attack. On the other hand, when the acylpyrones **1** and **6** are treated with an equivalent amount of pyrrolidine, no salt precipitation occurs and reaction proceeds presumably by dissociation of the salt into acylpyrone and free amine which then attacks the pyrone nucleus. Salt solubility becomes unimportant in reactions with excess amine since it has been observed experimentally that acylpyrone–amine salts are readily soluble in a benzene– or toluene–amine medium.

The mechanism for opening of the pyrone ring at the 6 position undoubtedly involves nucleophilic attack by the amine on the carbon atom at the 6 position to afford as an intermediate the resonance-stabilized carbanion **27**. Subsequently, **27** breaks down with expulsion of the carboxylate group to give the rather unstable β-keto acid **28**, which then undergoes facile decarboxylation to give the enol **29**.

A plausible mechanism for the formation of amides of acetoacetic acid from the reactions of dehydroacetic acid with secondary amines involves nucleophilic attack by the amine on the carbon of the lactone carbonyl at the 2 position to give the amide of α,γ-diacetylacetoacetic acid (**30**) (Scheme III). **30** is then cleaved by reaction with amine at the carbon of the β-carbonyl to afford the observed amide of acetoacetic acid (**31**).

(12) G. E. Utzinger, *Helv. Chim. Acta*, **35**, 1359 (1952).

SCHEME III

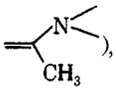
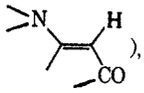


An alternative mechanism involves nucleophilic attack by pyrrolidine on the carbon atom at the 4 position to form **32**. Attack of amine at the ester carbonyl would then give the observed amide of acetoacetic acid (**31**).

The lack of reactivity of the carbonyl of the side chain in dehydroacetic acid (**1**) toward pyrrolidine is totally unexpected and could not have been predicted *a priori* in view of the affinity shown by this group for reaction with primary amines.[1-6] On the other hand, the analog **14**, which carries a phenyl substituent in the 6 position, reacts preferentially at the carbonyl of the acetyl side chain and not at the 6 position. Presumably, the steric effect of the 6-phenyl substituent in **14** is responsible for the decreased reactivity of the 6 position in **14** in comparison with **1**. The same argument applies to the reaction of dehydrobenzoylacetic acid (**16**) with pyrrolidine leading to **18**, where attack occurs preferentially at the carbonyl of the benzoyl side chain owing to the unfavorable steric situation at the 6 position.

Experimental Section

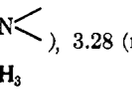
All melting points are uncorrected and were taken with a Mel-Temp capillary melting point apparatus. Infrared spectra were determined with either Baird-Atomic Models AB-2 and 4-55 or Perkin-Elmer Model 21 spectrophotometers using potassium bromide pellets of the compounds. The nmr spectra were determined at either 60 or 100 MHz with Varian Associates A-60 and HA-100 spectrometers. Chemical shifts are expressed in parts per million (ppm) downfield from an internal tetramethylsilane standard. Nmr peak multiplicities are abbreviated as follows: s (singlet), d (doublet), t (triplet), qr (quartet), and m (multiplet). The ultraviolet spectra were obtained with a Cary recording spectrophotometer, Model 14. The microanalyses were performed by Union Carbide Corp. Analytical Department, South Charleston, W. Va. Dehydroacetic acid (**1**) was the commercial product of Union Carbide Corp. 3-Benzoyl-4-hydroxy-6-methyl-2-pyrone (**10**), mp 108–110°, was prepared from 4-benzoyloxy-6-methyl-2-pyrone by Fries rearrangement with aluminum chloride. 3-Acetyl-4-hydroxy-6-phenyl-2-pyrone (**14**), mp 169–171°, was obtained by acetylating 6-phenyl-4-hydroxy-2-pyrone with acetic anhydride in the presence of sulfuric acid. Dehydrobenzoylacetic acid (**16**) was prepared from ethyl benzoylacetate by the method of Arndt.[13] The preparation of pyrones **10** and **14** has been described elsewhere.[14]

Reaction of Dehydroacetic Acid (1) with One Equivalent of Pyrrolidine.—Pyrrolidine (18 g, 0.25 mol) was added dropwise during 20 min to a stirred solution of dehydroacetic acid (42 g, 0.25 mol) in 100 ml of toluene at 50°. The reaction was mildly exothermic and the temperature rose to 55°. After the addition was complete the mixture was allowed to stand at room temperature for 40 hr. The precipitated solid (27.2 g, mp 103–106°) was collected by filtration and crystallized from benzene–cyclohexane mixture to give 20.4 g of enedione **3**, mp 110–112°. The toluene mother liquor was evaporated to dryness under reduced pressure, and the resulting semisolid residue was triturated with ether. The solid (14.8 g, mp 82–89°) which separated was collected and crystallized from benzene–cyclohexane mixture to give a second crop of **3** (11.5 g, mp 109–110°). The yield of combined recrystallized enedione **3** (31.9 g) was 65.5%. An additional crystallization from benzene–cyclohexane mixture furnished an analytical sample, mp 110–112°. Enedione **3** gave an intense green color with ethanolic ferric chloride: ir (KBr) 3.38 (CH_3 and CH_2), 3.54 (NCH_2), 4 (weak, broad, chelated OH), 6.1 (strong, C=C), 6.35 and 6.45 (very strong, chelated conjugated C=O and C=C), 7.27 (CCH_3), 7.52, 8.75, 9.70 and 12.37 μ (RR'C=CHR''). The solution ir ($CHCl_3$) shows an additional band at 5.85 μ (C=O); nmr (benzene-d_6) δ 1.05–1.35 (m, 4, CH_2CH_2), 1.85 and 2.15 (two s, 3, =C(OH)CH_3 and -$COCH_3$, respectively), 2.35 and 2.40 (two s, 3, ), 2.50–2.80 (m, 4, CH_2NCH_2), 3.43 (s, 0.4, $COCH_2CO$), 4.58 and 4.84 (two s, 1, ), 5.32 (s, 0.8, -CH=C(OH)-), and 17.62 (broad s, 0.8, intramolecularly chelated OH).

Anal. Calcd for $C_{11}H_{17}NO_2$: C, 67.66; H, 8.78; N, 7.17. Found: C, 67.98; H, 9.04; N, 7.27.

Reaction of Enedione 3 with Pyrrolidine.—A stirred mixture of enedione **3** (19.5 g, 0.1 mol) and pyrrolidine (14.2 g, 0.2 mol) in 90 ml of toluene was heated under reflux for 2 hr, water being removed with a Dean–Stark trap. Filtration of the cold solution afforded 21.5 g (87%) of 2,6-bis(N-pyrrolidino)hepta-2,5-dien-4-one (**4**), mp 205–210° dec. An analytical sample recrystallized from methanol had mp 210–215° dec; ir (KBr) 3.2 (=CH), 3.35 (CH_3 and CH_2), 3.48 (NCH_2), 6.16 (C=C), 6.55 (strong, conjugated C=O and C=C), 6.75, 6.84 (C=C), 7.06, 7.5,

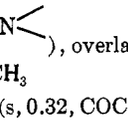
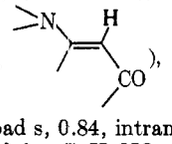
(13) F. Arndt, B. Eistert, H. Scholz, and E. Aron, *Ber.*, **69**, 2373 (1936).
(14) E. Marcus, J. F. Stephen, and J. K. Chan, *J. Heterocycl. Chem.*, **6**, 13 (1969).

9.1, 9.7, 10.85, 10.94 and 12.37 μ; nmr ($CDCl_3$) δ 1.90 (m, 8, two CH_2CH_2), 2.54 (s, 6, two ), 3.28 (m, 8, two CH_2NCH_2) and 4.91 (s, 2, =CHCOCH=).

Anal. Calcd for $C_{15}H_{24}N_2O$: C, 72.54; H, 9.74; N, 11.28. Found: C, 72.59; H, 9.88; N, 11.12.

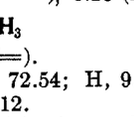
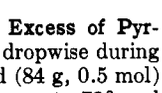
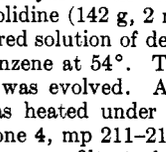
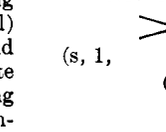
Reaction of Dehydroacetic Acid (1) with an Excess of Pyrrolidine.—Pyrrolidine (142 g, 2 mol) was added dropwise during 20 min to a stirred solution of dehydroacetic acid (84 g, 0.5 mol) in 300 ml of benzene at 54°. The temperature rose to 72° and carbon dioxide was evolved. After the addition was complete the mixture was heated under reflux for 2 hr. After cooling 115.9 g of dienone **4**, mp 211–215° dec, was collected. Concentration of the benzene filtrate furnished a second crop of 4.6 g, mp 209–215° dec. The yield was 97%. A sample of the above dienone showed no depression in melting point on admixture with a sample of dienone **4** obtained from the reaction of enedione **3** with pyrrolidine.

2,6-Bis(N-pyrrolidino)hepta-2,5-dien-4-one (4) from 2,6-Dimethyl-4-pyrone (5).—A mixture of 2,6-dimethyl-4-pyrone (31 g, 0.25 mol), pyrrolidine (71 g, 1 mol), and 100 ml of toluene was stirred and refluxed under a water separator for 25 hr. Filtration of the cold mixture gave 31.4 g (51%) of **4**, mp 200–208° dec. A single crystallization from methanol furnished 25 g of pure **4**, mp 211–215° dec.

Reaction of 3-Propionyl-4-hydroxy-6-methyl-2-pyrone (6) with One Equivalent of Pyrrolidine.—A stirred solution of pyrone **6** (18.2 g, 0.1 mol) in 60 ml of toluene at 50° was treated dropwise during 15 min with pyrrolidine (7.2 g, 0.1 mol). After the addition was complete the mixture was allowed to stand overnight at ambient temperature. The toluene was evaporated under reduced pressure, and the solid residue of 21.8 g was dissolved in 300 ml of ether. Concentration of the ether solution *in vacuo* furnished 12.6 g of enedione **7**, mp 64–70°. Further concentration of the ether afforded a second crop of 2.9 g, mp 55–62°. The yield of the combined crops (15.5 g) was 74%. Two crystallizations from ether at 0° gave an analytical sample, mp 82–86°. Enedione **7** gave an intense green color with ethanolic ferric chloride: ir (KBr) 3.4 (CH_3 and CH_2), 3.53 (NCH_2), 4 (weak, broad, chelated OH), 6.15 (C=C), 6.5 (very strong, broad, chelated conjugated C=O and C=C), 7.06, 7.5, 8.25, 8.75, 9.3, 9.9, 10.65 and 12.2 μ (RR'C=CHR''). The solution ir spectrum ($CHCl_3$) shows an additional band at 5.85 μ (C=O); nmr (benzene-d_6) δ overlapping 1.00 (t) and 1.08 (t) (3, $COCH_2CH_3$ and $=C(OH)CH_2CH_3$, respectively), 1.25–1.50 (m, 4, CH_2CH_2), 2.17 and 2.53 (two qr, 2, $=C(OH)CH_2CH_3$ and $COCH_2CH_3$, respectively), 2.38 and 2.53 (two s, 3, ), overlapping qr at 2.53, ~2.65–2.90 (m, 4, CH_2NCH_2), 3.42 (s, 0.32, $COCH_2CO$), 4.63 and 4.86 (two s, 1, ), 5.34 (s, 0.84, -CH=C(OH)-), and 17.55 (broad s, 0.84, intramolecularly chelated OH).

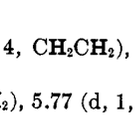
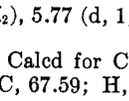
Anal. Calcd for $C_{12}H_{19}NO_2$: C, 68.86; H, 9.15; N, 6.69. Found: C, 68.60; H, 9.50; N, 6.74.

3,5-Heptanedione.—3,5-Heptanedione was prepared from ethyl propionate and methyl ethyl ketone in the presence of sodamide as described by Hauser:[15] nmr (benzene-d_6) δ overlapping 0.89 (t) and 0.97 (t) (6, $COCH_2CH_3$ and $=C(OH)CH_2CH_3$, respectively), overlapping 2.08 (qr) and 2.18 (qr) (4, $=C(OH)-CH_2CH_3$ and $COCH_2CH_3$, respectively), 3.16 (s, 0.3 $COCH_2CO$), 5.26 (s, 0.85, -CH=C(OH)-), and 15.7 (broad s, 0.85, intramolecularly chelated OH).

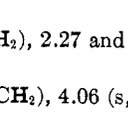
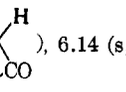
Reaction of Enedione 7 with Pyrrolidine.—A mixture of enedione **7** (5.2 g, 0.025 mol), pyrrolidine (3.5 g, 0.05 mol), and 25 ml of toluene was refluxed under a water separator for 1 hr. The toluene and excess pyrrolidine were evaporated under reduced pressure, and the residue of 7.5 g was crystallized from toluene to give 3.5 g (49%) of 2,6-bis(N-pyrrolidino)octa-2,5-dien-4-one (**9**), mp 154–156°. An analytical sample recrystallized from toluene had mp 154–156°; ir (KBr) 3.25 (=CH), 3.4 (CH_3 and CH_2), 3.53 ($N-CH_2$), 6.16 (C=C), 6.53 (strong, broad, conjugated C=O and C=C), 6.75, 6.85, 7.05, 7.45, 8.9, 9.03, 9.7, 10.75 and 12.45 μ; nmr ($CDCl_3$) δ 1.19 (t, 3, CH_2CH_3), 1.90 (m, 8, two CH_2CH_2), 2.51 (s, 3, ), overlapping 3.10 (qr) and 3.17–3.50 (m) (10,  and two CH_2NCH_2), 4.85 (s, 1, ), and 4.93 (s, 1, ).

Anal. Calcd for $C_{16}H_{26}N_2O$: C, 73.24; H, 9.99; N, 10.68. Found: C, 72.85; H, 10.04; N, 10.72.

Reaction of 3-Propionyl-4-hydroxy-6-methyl-2-pyrone (6) with an Excess of Pyrrolidine.—A solution of pyrone **6** (9.1 g, 0.05 mol) in 30 ml of toluene was treated with pyrrolidine (14.2 g, 0.2 mol), and the mixture was refluxed under a water separator. After 2 hr the solution was cooled and the crystals of 2,6-bis(N-pyrrolidino)octa-2,5-dien-4-one (8.3 g, 63%), mp 151–153°, which formed were collected. Recrystallization from toluene gave 6.2 g of dienone **9**, mp 154–156°. A mixture melting point with a sample of **9** prepared from enedione **7** and pyrrolidine was not depressed.

Reaction of 3-Benzoyl-4-hydroxy-6-methyl-2-pyrone (10) with One Equivalent of Pyrrolidine.—Pyrrolidine (3.55 g, 0.05 mol) was added dropwise during 15 min to a stirred solution of **10** (11.5 g, 0.05 mol) in 50 ml of toluene at 50°. The temperature rose to 56° and the salt precipitated from solution. After the addition was complete the mixture was stirred at room temperature for 2 hr. The precipitated salt (14.4 g, 96%), mp 155–156°, was filtered off and washed with toluene. An analytical sample recrystallized from ethanol had mp 155–156°; ir (KBr) 3.35, 3.6, 3.75, 3.85, 4.05 (NH_2^+), 5.95 (strong, lactone C=O), 6.90 (strong, conjugated C=O), 6.26, 6.37, 6.55 (C=C and NH_2^+), 7.25 (CCH_3), 12.88, 13.81 and 14.12 μ (CH, monosubstituted phenyl); nmr (D_2O with acetone as internal standard) δ 1.70–2.00 (m, 4, CH_2CH_2), 2.13 (d, 3, ), 3.00–3.25 (m, 4, CH_2NCH_2), 5.77 (d, 1, ) and 7.25–7.80 (m, 5, C_6H_5).

Anal. Calcd for $C_{17}H_{19}NO_4$: C, 67.76; H, 6.36; N, 4.65. Found: C, 67.59; H, 6.30; N, 4.58.

Reaction of 3-Benzoyl-4-hydroxy-6-methyl-2-pyrone (10) with an Excess of Pyrrolidine.—A stirred solution of pyrone **10** (11.5 g, 0.05 mol) in 50 ml of toluene at 50° was treated dropwise during 14 min with pyrrolidine (14.2 g, 0.2 mol). After the addition was complete the mixture was stirred and refluxed for 10 min. The toluene and excess pyrrolidine were removed *in vacuo* to give a yellow solid which was washed with 100 ml of ether and filtered to give 11.9 g of material, mp 135–137°. Crystallization of this solid from benzene–cyclohexane mixture afforded 9.4 g (73%) of enedione **12**: mp 140–142°; ir (KBr) 3.28 (=CH), 3.35 (CH_3), 3.48 (NCH_2), 4.0 (weak, broad, chelated OH), 6.45 (broad, strong, chelated conjugated C=O and C=C), 6.68 (aromatic C=C), 7.22 (CCH_3), 8.53, 8.73 (CN), 12.25, 12.73 (RR'C=CHR''), 13.15 and 14.4 μ (CH, monosubstituted phenyl). The solution ir spectrum ($CHCl_3$) shows additional bands at 5.95 (C=O) and 6.15 μ (C=C); nmr (benzene-d_6) δ 1.05–1.30 (m, 4, CH_2CH_2), 2.27 and 2.42 (two s, 3, ), 2.50–2.76 (m, 4, CH_2NCH_2), 4.06 (s, 0.3, $COCH_2CO$), 4.76 and 5.09 (two s, 1, ), 6.14 (s, 0.85, -CH=C(OH)-), 7.19 (broad s) and 7.80–8.10 (m, 5, C_6H_5) and 18.4 (broad s, 0.85, intramolecularly chelated OH).

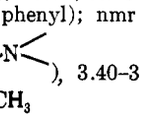
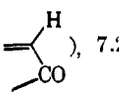
Anal. Calcd for $C_{16}H_{19}NO_2$: C, 74.68; H, 7.44; N, 5.44. Found: C, 74.89; H, 7.45; N, 5.40.

Reaction of Enedione 12 with Pyrrolidine.—A mixture of enedione **12** (8.6 g, 0.3 mol) and pyrrolidine (4.73 g, 0.06 mol) in

(15) J. T. Adams and C. R. Hauser, *J. Amer. Chem. Soc.*, **66**, 1220 (1944).

50 ml of toluene was refluxed under a water separator for 2 hr. The toluene and excess pyrrolidine were removed under reduced pressure, and the resulting oil was dissolved in 100 ml of ether. On standing for several hours at 0° the solution deposited 4.2 g of unchanged enedione **12**, mp 136–138°, which was collected by filtration. The ether filtrate was evaporated to dryness *in vacuo* to give 4.5 g of an oil. This oil was dissolved in the minimum amount of ether required for solution and the solution stored at −78° overnight. The solid of 2 g, mp 44–54°, which separated was collected. The nmr spectrum of this material indicated that it was a mixture which contained 6 mol % of enedione **12** and 94 mol % of the pyrrolidinamide of benzoylacetic acid (**13**). Recrystallization from ether at 0° afforded pure **13**: 1.6 g (22%); mp 63–66°; ir (liquid film) 3.27 (aromatic CH), 3.37 (CH_2), 3.47 (NCH_2), 3.7–4.6 (weak, broad, chelated OH), 5.92 (benzoyl C=O), 6.15 (amide C=O and aromatic C=C), 6.77 (CH_2 and aromatic C=C), 7.35 (CN), 13.1 and 14.55 μ (CH, monosubstituted phenyl); nmr ($CDCl_3$) δ 1.64–2.12 (m, 4, CH_2CH_2), 3.10–3.70 (m, 4, CH_2NCH_2), 4.0 (s, 1, $COCH_2CO$), 5.62 (s, 0.5, -CH=C(OH)-), 7.15–7.57, 7.62–7.83 and 7.90–8.05 (m, 5, C_6H_5) and 15.28 (s, 0.5, intramolecularly chelated OH).

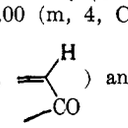
Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.96; N, 6.45. Found: C, 71.89; H, 7.09; N, 6.42.

Reaction of 3-Acetyl-4-hydroxy-6-phenyl-2-pyrone (14) with One Equivalent of Pyrrolidine.—Pyrrolidine (3.55 g, 0.05 mol) was added dropwise during 10 min to a stirred solution of pyrone **14** (11.5 g, 0.05 mol) in 120 ml of toluene at 50°. After the addition was complete the mixture was heated at 50–60° for 4 hr. Most of the toluene was evaporated under reduced pressure and cyclohexane was added to the residue. On standing the solution deposited 13.9 g of solid, mp 90–103°. Recrystallization from benzene–cyclohexane mixture furnished 10.2 g of **15**, mp 101–105°. A sample dried overnight at 60° *in vacuo* had mp 152–156°; $\lambda_{max}^{CH_3OH}$ 220 mμ (log ϵ 4.18) and 354 (4.19); ir (KBr) 3.25 (=CH), 3.34 (CH_3 and CH_2), 3.45 (NCH_2), 5.9 (strong, lactone C=O), 6.1 (conjugated C=O), 6.32, 6.4, 6.66 (C=C), 7.15, 7.26 (CCH_3), 8.17 (lactone COC), 13.0 (RR'C=CHR''), 14.1 and 14.5 μ (CH, monosubstituted phenyl); nmr ($CDCl_3$) δ 2.05 (t, 4, CH_2CH_2), 2.65 (s, 3, ), 3.40–3.94 (m, 4, CH_2NCH_2), 6.36 (s, 1, ), 7.20–7.56 and 7.68–7.93 (m, 5, C_6H_5).

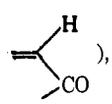
Anal. Calcd for $C_{17}H_{17}NO_3$: C, 72.06; H, 6.05; N, 4.94. Found: C, 73.64; H, 6.18; N, 4.33.

Treatment of **15** with picric acid in ethanol gave the picrate, mp 214–216° dec.

Anal. Calcd for $C_{23}H_{20}N_4O_{10}$: C, 53.91; H, 3.93; N, 10.93. Found: C, 53.79; H, 4.00; N, 10.66.

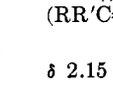
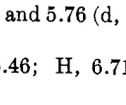
Reaction of Dehydrobenzoylacetic Acid (16) with One Equivalent of Pyrrolidine.—A stirred suspension of **16** (14.6 g, 0.05 mol) in 100 ml of toluene at 50° was treated dropwise during 19 min with pyrrolidine (3.55 g, 0.05 mol). After the addition was completed the mixture was heated at 50–60° for 2 hr. The precipitated **17**, 17.7 g (98%), mp 160–161°, was collected by filtration. An analytical sample recrystallized from ethanol had mp 164–166°; ir (KBr) 3.32, 3.63 (NH_2^+), 6.0 (conjugated lactone C=O), 6.1 (conjugated C=O), 6.21 (C=C), 6.3, 6.68 (aromatic C=C), 6.55, 7.88 (lactone COC), 12.36 (RR'C=CHR''), 12.95, 13.99 and 14.8 μ (CH, monosubstituted phenyl); nmr ($CDCl_3$) δ 1.55–2.00 (m, 4, CH_2CH_2), 2.78–3.10 (m, 4, CH_2NCH_2), 6.44 (s, 1, ) and 7.20–8.15 (m, 12, NH_2^+ and two C_6H_5).

Anal. Calcd for $C_{22}H_{21}NO_4$: C, 72.71; H, 5.82; N, 3.85. Found: C, 72.40; H, 5.84; N, 3.88.

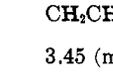
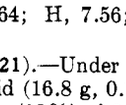
Reaction of Dehydrobenzoylacetic Acid (16) with an Excess of Pyrrolidine.—A stirred solution of dehydrobenzoylacetic acid (14.6 g, 0.05 mol) in 100 ml of boiling toluene was treated with pyrrolidine (14.2 g, 0.2 mol). The mixture was then stirred and refluxed for 5 min. The solid of 9.3 g, mp 163–165°, which had separated was collected by filtration. The toluene mother liquor was concentrated *in vacuo* to about 50 ml when a second crop of 1.5 g, mp 163–165°, precipitated from solution. A mixture melting point with authentic pyrrolidinium dehydrobenzoylacetate was not depressed. The yield was 59.5%. The toluene solution was evaporated to dryness, and the residue thus obtained was recrystallized from benzene to give 1.9 g (11%) of **18**, mp 196–199° dec. A second crystallization from benzene afforded an analytical sample: mp 200–202° dec; $\lambda_{max}^{CH_3OH}$ 275 mμ (log ϵ = 3.93) and 358 (3.89); ir (KBr) 3.25 (=CH), 3.36 (CH_2), 3.46 (NCH_2), 5.95 (strong, conjugated lactone C=O), 6.12 (strong, C=C and conjugated C=O), 6.31 6.39 (C=CN), 8.10 (lactone COC), 12.97, 13.20, 14.15 and 14.5 μ (CH, monosubstituted phenyl); nmr ($CDCl_3$) δ 1.73–2.28 (m, 4, CH_2CH_2), 3.50–4.20 (m, 4, CH_2NCH_2), 6.30 (s, 1, ), 7.18–7.53 and 7.62–7.85 (m, 10, two C_6H_5).

Anal. Calcd for $C_{22}H_{19}NO_3$: C, 76.50; H, 5.55; N, 4.06. Found: C, 76.35; H, 5.35; N, 4.00.

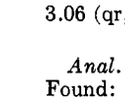
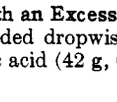
Conversion of 17 into 18.—A solution of **17** (34.8 g, 0.096 mol) in 300 ml of 2-propanol was heated under reflux for 25 hr. The 2-propanol was removed under reduced pressure, and the residue was extracted with 250 ml of boiling benzene. The insoluble solid of 18.3 g, mp 172–184° dec (a mixture of **17** and **18**), was collected by filtration. Evaporation of the filtrate afforded 12.4 g of **18**, mp 196–198° dec.

Morpholinium Dehydroacetate (19).—A stirred solution of dehydroacetic acid (21 g, 0.125 mol) in 75 ml of toluene at 53° was treated during 10 min with morpholine (11.5 g, 0.125 mol). The temperature rose to 65°; after the addition was complete the mixture was stirred at room temperature for 2 hr. The precipitated solid 30.7 g (96%), mp 114–115° dec, was filtered off. An analytical sample recrystallized from ethyl acetate had mp 114–115° dec; ir (KBr) 3.45–3.75 and 4.0–4.2 (strong, broad, NH_2^+), 5.85 (strong, lactone C=O), 6.05 (strong, conjugated C=O), 6.2 (C=C and NH_2^+), 9.0 (lactone COC) and 12.78 μ (RR'C=CHR''); nmr (D_2O with acetone as internal standard) δ 2.15 (d, 3, ), 2.49 (s, 3, $COCH_3$), 3.24–3.50 (m, 4, CH_2NCH_2), 3.90–4.17 (m, 4, CH_2OCH_2) and 5.76 (d, 1, ).

Anal. Calcd for $C_{12}H_{17}NO_5$: C, 56.46; H, 6.71; N, 5.49. Found: C, 56.80; H, 6.65; N, 5.52.

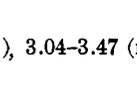
Piperidinium Dehydroacetate (20).—Under the same conditions used for **19**, dehydroacetic acid (21 g, 0.125 mol) and piperidine (10.65 g, 0.125 mol) furnished 30.7 g (97%) of **20**, mp 132–133° dec. Recrystallization from toluene furnished an analytical sample: mp 129–130° dec; ir (KBr) 3.45, 3.65, 3.81, 3.96 and 4.14 (components of a broad band, NH_2^+), 5.94 (strong, lactone C=O), 6.03 (strong, conjugated C=O), 6.25 (NH_2^+ and C=C), 6.55 (C=C), 7.27 (CCH_3) and 12.85 μ (RR'C=CHR''); nmr (D_2O with acetone as internal standard) δ 1.50–2.00 (m, 6, $CH_2CH_2CH_2$), 2.13 (d, 3, ), 2.50 (s, 3, $COCH_3$), 3.08–3.45 (m, 4, CH_2NCH_2) and 5.78 (d, 1, ).

Anal. Calcd for $C_{13}H_{19}NO_4$: C, 61.64; H, 7.56; N, 5.53. Found: C, 61.72; H, 7.46; N, 5.50.

Diethylammonium Dehydroacetate (21).—Under the same conditions used for **19**, dehydroacetic acid (16.8 g, 0.1 mol) and diethylamine (7.3 g, 0.1 mol) gave 22.2 g (92%) of **21**, mp 106–109° dec. Recrystallization from ethyl acetate afforded an analytical sample, mp 106–109° dec; ir (KBr) 3.35, 3.48 (CH_3 and CH_2), 4.0 (strong, NH_2^+), 5.93 (strong, lactone C=O), 6.04 (strong, conjugated C=O), 6.15, 6.33 (C=C), 6.55, 6.65 and 8.6 μ; nmr (D_2O with acetone as internal standard) δ 1.25 (t, 6, two NCH_2CH_3), 2.06 (d, 3, ), 2.43 (s, 3, $COCH_3$), 3.06 (qr, 4, two NCH_2CH_3) and 5.70 (d, 1, ).

Anal. Calcd for $C_{12}H_{19}NO_4$: C, 59.73; H, 7.94; N, 5.81. Found: C, 59.44; H, 7.83; N, 5.39.

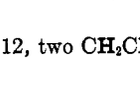
Reaction of Dehydroacetic Acid (1) with an Excess of Morpholine.—Morpholine (87 g, 1 mol) was added dropwise during 22 min to a stirred solution of dehydroacetic acid (42 g, 0.25 mol) in

150 ml of benzene at 54°. The reaction was mildly exothermic, the temperature rose to 61°, and after about one-third of the morpholine had been added morpholinium dehydroacetate precipitated from solution. When the addition was complete the mixture was heated under reflux for 4 hr and then allowed to stand overnight at room temperature. The benzene and excess morpholine were evaporated *in vacuo*, and the resulting oil was dissolved in 300 ml of ether. The ethereal solution was cooled to −78° and after standing for several hours at this temperature deposited 18.5 g (26.4%) of **22**, mp 140–163° dec. An analytical sample of dienone **22** prepared by recrystallization from benzene–hexane mixture had mp 169–175° dec; ir (KBr) 3.3 (=CH), 3.38 (CH_3), 3.55 (OCH_2 and NCH_2), 6.15 (C=C), 6.35–6.55 (broad, strong, conjugated C=O and C=C), 7.0, 8.0, 8.88, 9.03 (ether COC), 10.0, 11.03, 12.05 and 14.5 μ; nmr ($CDCl_3$) δ 2.49 (s, 6, two ), 3.04–3.47 (m, 8, two CH_2NCH_2), 3.50–3.83 (m, 8, two CH_2OCH_2) and 5.23 (s, 2, =CHCOCH=).

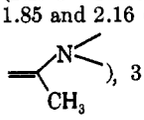
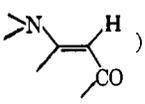
Anal. Calcd for $C_{15}H_{24}N_2O_3$: C, 64.26; H, 8.63; N, 9.99. Found: C, 64.49; H, 8.59; N, 10.11.

The original mother liquor was concentrated *in vacuo*. Crystallization of the oil thus obtained from ethyl ether–benzene–petroleum ether (bp 60–70°) mixture gave pale yellow needles of 4-acetoacetylmorpholine (12.2 g, mp 56–60°). A further crystallization from benzene–petroleum ether (bp 60–70°) mixture furnished 7.9 g of **23** as colorless needles, mp 69–71°. An additional portion of **23** was obtained by evaporating the ethyl ether–benzene–petroleum ether (bp 60–70°) mother liquor to dryness and distilling the residue at 1 mm. Crystallization of the distillate, 4 g, bp 150–160°, from benzene–petroleum ether (bp 60–70°) mixture gave 2.1 g of **23**, mp 62–66°. The yield of combined crude material (14.2 g) was 33.5%. **23** gave a violet color with ethanolic ferric chloride. A mixture melting point with an authentic sample of **23** prepared from morpholine and diketene showed no depression.

Preparation of 4-Acetoacetylmorpholine (23).—Diketene (84 g, 1 mol) was added dropwise with stirring during 1.25 hr to morpholine (109 g, 1.25 mol). During the addition the temperature was kept below 50° by use of an ice bath. After the addition was complete the mixture was allowed to stand at ambient temperature for 2.5 hr. Excess morpholine was evaporated and the residue was distilled under reduced pressure to give 118.8 g (69.5%) of **23** as a colorless liquid, bp 150–165° (2–3 mm), which solidified on cooling, Recrystallization from benzene–petroleum ether (bp 60–70°) mixture gave fine colorless needles of **23**, mp 68–70° (lit.[16] mp 71°).

Reaction of Dehydroacetic Acid (1) with an Excess of Piperidine.—A stirred solution of dehydroacetic acid (42 g, 0.25 mol) in 150 ml of benzene at 54° was treated dropwise during 20 min with piperidine (85 g, 1 mol). During the addition the temperature rose to 60°; after the addition was completed the mixture was maintained at 60° for 4 hr. The benzene and excess piperidine were removed under reduced pressure, and the resulting oil was dissolved in 100 ml of ether. On standing 21 g of a white solid, mp 70–95° dec, precipitated from solution. This material was extremely sensitive to heat and has not been identified. The ether mother liquor was evaporated to small volume, and petroleum ether (bp 60–70°) was added to the cloud point. On standing for several days at −78° the solution deposited 6.3 g (9.1%) of 2,6-bis(N-piperidino)hepta-2,5-dien-4-one (**24**), mp 82–85°. Recrystallization from benzene–petroleum ether (bp 60–70°) mixture at 0° afforded an analytical sample: mp 85–87°; ir (KBr) 3.25 (=CH), 3.43 (CH_3 and CH_2), 3.6 (NCH_2), 6.48 (strong, broad, conjugated C=O and C=C), 7.25, 7.33, 9.05 and 12.28 μ (RR'C=CHR''); nmr ($CDCl_3$) δ 1.58 (broad s, 12, two $CH_2CH_2CH_2$), 2.50 (s, 6, two ), 3.00–3.50 (m, 8, two CH_2NCH_2) and 5.20 (s, 2, =CHCOCH=).

Anal. Calcd for $C_{17}H_{28}N_2O$: C, 73.86; H, 10.21; N, 10.14. Found: C, 73.69; H, 10.26; N, 9.78.

Reaction of Dehydroacetic Acid (1) with an Excess of Diethylamine.—Diethylamine (29.2 g, 0.4 mol) was added dropwise over a period of 15 min to a stirred solution of 1 (16.8 g, 0.1 mol) in 40 ml of benzene at 50°. During the addition the temperature rose to 65° and diethylammonium dehydroacetate (**21**) precipitated from solution. After the addition was complete the mixture was stirred and refluxed for 7 hr. The benzene and excess diethylamine were evaporated under reduced pressure, and the resulting oil of 22.3 g was dissolved in 30 ml of ether. On standing the solution deposited 11.5 g (47.7%) of **21**, mp 108–110° dec. The mother liquor was concentrated *in vacuo* and afforded 10.8 g of **25** as an oil: ir (neat) 3.36 (CH_3), 3.44 (CH_3 and CH_2), 4.0 (broad, weak, chelated OH), 5.86 (C=O), 6.15, 6.47 (C=C and conjugated C=O), 7.22 (CCH_3), 7.35 ($COCH_3$), 8.74, 9.54 and 12.35 μ (RR'C=CHR''); nmr ($CDCl_3$) δ 1.15 (t, 6, two NCH_2CH_3), 1.85 and 2.16 (two, s, 3, $=C(OH)CH_3$ and $COCH_3$), 2.5 (d, 3, ), 3.3 (qr, 5.2, CH_2NCH_2 and $COCH_2CO$), 4.68 and 5.00 (two s, 0.7, ), and 5.13 (s, 0.3, –CH=C(OH)–).

The spectrum also showed weak lines at 1.2, 1.35, 2.0, 2.06, 2.2, 2.3, 2.5, and 5.52. The oil was distilled under reduced pressure and afforded 1.5 g (5%) of the diethylamide of acetoacetic acid (**26**), bp 100° (2 mm), identified by comparison of its infrared and nmr spectra with those of an authentic specimen prepared from ethyl acetoacetate and diethylamine by the method of Utzinger.[12]

Registry No.—**3b**, 20103-86-0; **4**, 20103-87-1; **7b**, 20103-88-2; **9**, 20103-89-3; **11**, 20103-90-6; **12b**, 20103-91-7; **13**, 20103-92-8; **15**, 20103-93-9; **15** picrate, 20103-94-0; **17**, 20103-95-1; **18**, 20103-96-2; **19**, 20103-97-3; **20**, 20103-98-4; **21**, 20103-99-5; **22**, 20104-00-1; **24**, 20104-01-2.

Acknowledgment.—Thanks are extended to Mr. W. H. Joyce and Mr. C. B. Strow of Union Carbide Corp. for interpretations of infrared and nmr spectra.

(16) P. Couturier, P. Blanc, and S. Frajdenrajch, *Bull. Soc. Chim. Fr.*, 594 (1962).