Schaffer, Quebec, Canada, ionizing energy 70 ev. Nmr spectra were obtained on a Varian A60A spectrometer (Sadtler Research Corp.) and data are expressed in parts per million downfield from an internal tetramethylsilane standard.

Materials.—N-Methylglycine (sarcosine) (mp 210–211°) was obtained from Nutritional Biochemicals Co., Cleveland, Ohio. N-Phenylglycine (mp 125–127°) and N-acetyl-N-phenylglycine (mp 190–192°) were obtained from Eastman Organic Chemicals, Rochester, N. Y. N-Benzoyl-N-methylglycine (N-benzoylsarcosine) was prepared using O'Brien and Niemann's procedure,[6] mp 104–105°. N-Acetyl-N-methylglycine (N-acetylsarcosine) was prepared according to Southwick's procedure[7] (mp 136–137.5°) and N-benzoyl-N-phenylglycine was obtained by Rebuffat's method.[8]

Anhydro-2,3-dimethyl-4-trifluoroacetyl-5-hydroxy-1,3-oxazolonium Hydroxide (2b).—N-Acetylsarcosine (1 g, 0.007 mole) was added to 10 ml of trifluoroacetic anhydride and the mixture was stirred for 1.5 hr at room temperature. The resulting solution was then poured into 50 ml of dry ether, thereby precipitating 1.21 g (83%) of white crystals, mp 128–131°. Several recrystallizations from benzene–petroleum ether (bp 30–60) gave 0.96 g (65%) of white crystals, mp 133–135°. The ultraviolet spectrum showed λ_{max} at 310 mμ (ϵ 1.83 × 10^3) and 263 mμ (ϵ 7.5 × 10^4).

Anal. Calcd for $C_7H_6F_3NO_3$: C, 40.20; H, 2.89; F, 27.25; N, 6.70. Found: C, 40.36; H, 3.09; F, 27.51; N, 6.54.

Anhydro-3-phenyl-4-trifluoroacetyl-5-hydroxy-2-methyl-1,3-oxazolonium hydroxide (2c) was prepared as above using 2 g (0.010 mole) of N-acetyl-N-phenylglycine in 20 ml of trifluoroacetic anhydride. The crude yield of crystals (mp 202–205°) was 2.4 g (88.4%). Several recrystallizations from a minimum volume of boiling ethyl acetate gave 0.6 g (22%) of crystals, mp 211–212°. The ultraviolet spectrum showed λ_{max} at 264 mμ (ϵ 6.47 × 10^3) and 312 mμ (ϵ 1.43 × 10^4).

Anal. Calcd for $C_{12}H_8F_3NO_3$: C, 53.14; H, 2.97; F, 21.02; N, 5.17. Found: C, 53.15; H, 3.01; F, 21.05; N, 5.18.

Anhydro-2,3-diphenyl-4-trifluoroacetyl-5-hydroxy-1,3-oxazolonium hydroxide (2d) was prepared as was **2b** whereby 1.0 g (0.0039 mole) of crude N-benzoyl-N-phenylglycine was added to 10 ml of trifluoroacetic anhydride. The crude yield of bright yellow crystals which precipitated was 1.19 g (91%), mp 185–190°. Several recrystallizations from benzene–petroleum ether gave 1.10 g (84%) of yellow crystals, mp 193–195° (lit.[4] value 195°). The ultraviolet spectrum showed λ_{max} at 367 (ϵ 1.86 × 10^4), 276 (1.26 × 10^4), and 246 mμ (1.36 × 10^4).

Anal. Calcd for $C_{17}H_{10}F_3NO_3$: C, 61.27; H, 3.02; F, 17.10; N, 4.20. Found: C, 61.17; H, 3.32; F, 16.84; N, 4.23.

Anhydro-3-methyl-4-trifluoroacetyl-5-hydroxy-2-phenyl-1,3-oxazolonium hydroxide (2e) was prepared as was **2b** using 1.0 g (0.005 mole) of N-benzoylsarcosine in 10 ml of trifluoroacetic anhydride. The crude yield of yellow crystals was 1.30 g (96%), mp 161–164°. Several recrystallizations from benzene–petroleum ether gave 0.90 g (66%) of yellow crystals, mp 161.5–163°. The ultraviolet spectrum showed λ_{max} at 347 (ϵ 2.29 × 10^4), 276 (1.24 × 10^4), and 243 mμ (1.14 × 10^4).

Anal. Calcd for $C_{12}H_8F_3NO_3$: C, 53.15; H, 2.97; F, 21.02; N, 5.17; mol wt, 271.2. Found: C, 53.10; H, 3.03; F, 20.77; N, 5.29; mol wt, 260 (Rast).

Anhydro-2,3-dimethyl-4-(N-acetylsarcosyl)-5-hydroxy-1,3-oxazolonium Hydroxide (5a).—To 4.24 g (0.034 mole) of N-acetylsarcosine in 50 ml of nitromethane was added 7.00 g (0.034 mole) of DCC dissolved in 50 ml of nitromethane. After 2 hr of stirring the solution was filtered and the solid remaining behind was rinsed with nitromethane to give 7.13 g (94%) of dicyclohexylurea, mp 232.5–234.5° (lit.[9] value 234°). The filtrate was evaporated *in vacuo* to give an oil. Ethyl acetate (15 ml) was added and after a few days' refrigeration, off-white crystals deposited. They were filtered to give 2.15 g (56%), mp 134–137°. After two recrystallizations from a minimum volume of boiling ethyl acetate, 1.00 g (26%) was recovered, mp 137–138°. The ultraviolet spectrum showed λ_{max} at 300 mμ (ϵ 1.35 × 10^4) and 260 mμ (ϵ 9.78 × 10^3).

Anal. Calcd for $C_{10}H_{14}N_2O_4$: C, 53.08; H, 6.24; N, 12.38; mol wt, 226. Found: C, 53.11; H, 6.27; N, 12.21; mol wt, 207 (thermoelectric).

Anhydro-3-methyl-4-(N-benzoylsarcosyl)-5-hydroxy-2-phenyl-1,3-oxazolonium Hydroxide (5b). A. Using DCC.—To 6.55 g (0.034 mole) of N-benzoylsarcosine in 50 ml of nitromethane was added 7.00 g (0.034 mole) of DCC dissolved in 50 ml of nitromethane. After 2 hr of stirring the solution was filtered and the solid remaining behind was rinsed with nitromethane to give 6.90 g (91%) of DCU, mp 232–235°. The filtrate was evaporated *in vacuo* to give a dark red oil. Ethyl acetate (25 ml) was added, the solution was boiled, and upon cooling crystals were deposited, yield 2.18 g (37%), mp 169–172°. The solid was recrystallized from a minimum volume of boiling ethyl acetate to give 1.32 g (22%) of yellow crystals, mp 175–176°. The ultraviolet spectrum showed λ_{max} at 352 (ϵ 1.61 × 10^4), 268 (1.24 × 10^4), and 244 mμ (1.24 × 10^4).

Anal. Calcd for $C_{20}H_{18}N_2O_4$: C, 68.55; H, 5.18; N, 8.00; mol wt, 350. Found: C, 68.43; H, 5.25; N, 8.26; mol wt, 380 (Rast), 388 (thermoelectric), 350 (mass spectrometry).

B. Using Acetic Anhydride.—To 5.0 g (0.026 mole) of N-benzoylsarcosine in a 100-ml round-bottom flask was added 50 ml of acetic anhydride and the mixture was stirred at 55° for 1 hr in an oil bath. After overnight refrigeration, the excess acetic anhdride was evaporated *in vacuo*. To remove excess anhydride residue, the oil was washed several times with dry ether. The resulting yellow solid was dissolved in boiling ethyl acetate and the solution was evaporated on a steam bath to a volume of 50 ml. After several days' refrigeration, a solid was deposited, yield 2.15 g (44%), mp 165–169°. Two recrystallizations from a minimum volume of boiling ethyl acetate gave 1.15 g (39%) of yellow crystals, mp 175.5–177°.

A mixture melting point with the anhydro-3-methyl-4-(N-benzoylsarcosyl)-5-hydroxy-2-phenyl-1,3-oxazolonium hydroxide (5b) made using DCC showed no depression.

The ultraviolet (as well as infrared) spectrum showed the same absorptions as compound (5b).

Anal. Calcd for $C_{20}H_{18}N_2O_4$: C, 68.55; H, 5.18; N, 8.00; mol wt, 350. Found: C, 68.88; H, 5.10; N, 8.14; mol wt, 375 (thermoelectric).

Registry No.—**2b**, 14119-97-2; **2c**, 14119-98-3; **2d**, 14172-82-8; **2e**, 14119-99-4; **5a**, 14120-00-4; **5b**, 14120-01-5.

(6) J. O'Brien and C. Niemann, *J. Am. Chem. Soc.*, **79**, 84 (1957).
(7) P. Southwick, H. Diamond, and R. Stansfield, *ibid.*, **78**, 1609 (1956).
(8) G. Rebuffat, *Gazz. Chim. Ital.*, **17**, 232 (1887).
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Synthesis and Properties of Fluorine-Containing Heterocyclic Compounds. IV. An N,N′-Unsubstituted Imidazolidine[1]

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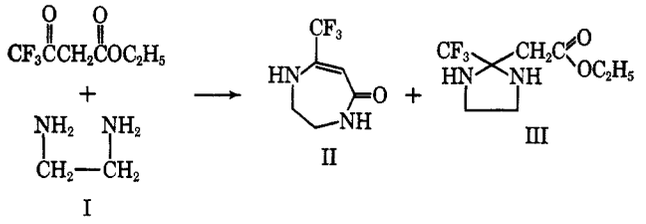
The reaction of ethyl acetoacetate with *o*-phenylenediamine may yield several products depending upon conditions.[3,4] In contrast, only diethyl (3,3′-ethylenedimino)dicrotonate was isolated from the reaction with 1,2-ethylenediamine (I);[5] no product was isolated from the reaction of I and ethyl trifluoroacetoacetate.[6a] In continuation of our previous studies,[7] we have now re-

(1) Part III in this series: A. S. Dey and M. M. Joullié, *J. Org. Chem.*, **30**, 3237 (1965).
(2) To whom all correspondence should be addressed.
(3) J. Davoll, *J. Chem. Soc.*, 308 (1960).
(4) A. Rossi, A. Hunger, J. Kebrle, and K. Hoffmann, *Helv. Chim. Acta*, **43**, 1298 (1960).
(5) C. M. Hofmann and S. R. Safir, *J. Org. Chem.*, **27**, 3565 (1962).
(6) (a) A. E. Martell, R. L. Belford, and M. Calvin, *J. Inorg. Nucl. Chem.*, **5**, 170 (1958); (b) G. O. Dudek and R. H. Holm, *J. Am. Chem. Soc.*, **83**, 2099 (1961).
(7) (a) M. M. Joullié, S. Násfay, and L. Rypstat, *J. Org. Chem.*, **21**, 1358 (1956); (b) F. B. Wigton and M. M. Joullié, *J. Am. Chem. Soc.*, **81**, 5212 (1959); (c) A. S. Dey and M. M. Joullié, *J. Heterocyclic Chem.*, **2**, 113, 120 (1965); (d) D. K. Wald and M. M. Joullié, *J. Org. Chem.*, **31**, 3369 (1966).

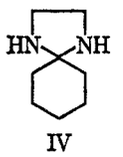
examined the latter reaction and obtained not only the expected 1,2,3,4-tetrahydro-7-trifluoromethyl-1,4-diazepin-5-one (II) but also a compound which we formulate as ethyl 2-(trifluoromethyl)-2-imidazolidineacetate (III).



I II III

The assignment of the enamine[5] (II) rather than the ketimine[3,8] structure to the tetrahydrodiazepinone is based on spectroscopic evidence. The ultaviolet maximum at 280 mμ (log ε 4.80, in ethanol) is very close to that observed by Hofmann and Safir[5] for the 7-methyl analog (λ_{max}^{MeOH} 285 mμ, log ε 4.18). The slight hypsochromic shift would be expected upon trifluoromethyl substitution. The nmr spectrum (in acetone-d_6) shows resonances at τ 3.08 (1 H, br) and 2.67 (1 H, br) assigned to the N–H protons of the amide and amine and at τ 5.07 (1 H) and 6.52 (4 H, multiplet) of the vinylic and methylene protons, respectively.[6b] The infrared spectrum, in a very dilute chloroform solution, shows N–H stretch at 3424 and 3452 cm^{-1}, which are reasonably assigned[9] to *cis*-amide and secondary amine, respectively.

The only report of an N,N′-unsubstituted imidazolidine is the condensation product of cyclohexanone with ethylenediamine which has been formulated by Bergmann, *et al.*,[10] as 1,4-diazaspiro[4.5]decane (IV) on evidence of molecular refractivity and absence of C=N absorption in the infrared. Since the analytical



IV

data reported for compound IV were incomplete, we have repeated this condensation and, although the compound was difficult to purify, we obtained a product with similar physical constants.

The band positions at 1092, 1113, and 1155 cm^{-1} were assigned as characteristic of the imidazolidine ring; these values correspond very closely to those of compound III, with absorptions at 1090, 1115 sh, and 1158 cm^{-1}. The lack of significant absorption above 3000 cm^{-1} in the infrared spectrum of IV, although not unknown in secondary amines,[11] made the imidazolidine structure appear suspect, particularly since compound III showed N–H stretch at 3380 cm^{-1}. This enhancement of N–H intensity could be rationalized by the presence of the $-CF_3$ group,[12] but a more firm confirmation of the imidazolidine structure in IV seemed desirable.

The nmr spectrum of compound IV, in carbon tetrachloride, showed three peaks at τ 7.15, 8.55, and 8.84 (2:5:1). This spectrum supports the imidazolidine structure. Deuteration studies to conclusively establish the presence of amine protons could not be successfully carried out since the compound rapidly decomposes in presence of water, acid, or base. The position of the peak at τ 8.84 was, however, concentration dependent. In concentrated solution (~30%) it appeared at τ 8.68 and moved to higher field upon dilution. The other two peaks did not change their positions (±2 Hz). This supports the assignment of this peak to N–H protons. Additional evidence was furnished by the mass spectrum of IV: molecular ion, M^+ 140.1314 (M, calcd for $C_8H_{16}N_2$: 140.1313); base peak, m/e 30 (CH_3CH_3), 28 ($CH_2{=}CH_2$), 139 (M − 1, loss of H on N), 110 (M − 2H and $-CH_2CH_2-$), 97 ($M - {>}NCH_2CH_2-$), 84 (M − $>NCH_2CH_2N<$). These fragments are consistent with the spiro structure proposed by Bergmann, *et al.*[10]

The structural assignment of III as an imidazolidine derivative is substantiated by following chemical and spectral evidence. With acetic anhydride, benzoyl and acetyl chlorides, and picric acid only derivatives of ethylenediamine were isolated.[13] With phenyl isocyanate only the monourea was formed, possibly because it precipitated. The nmr spectrum of III shows a quadruplet at τ 5.85 (2 H, J = 7 Hz) and a triplet at τ 8.74 (3 H, J = 7 Hz) of the ethyl ester group, single peaks at τ 6.95 (4 H) and 7.34 (2 H) assigned to the two kinds of methylene protons, and a broad peak at τ 7.39 (2 H) to the amine hydrogens. The infrared spectrum (in carbon tetrachloride) shows the N–H stretch at 3380 cm^{-1}, the ester carbonyl at 1729 cm^{-1}, and, except for three strong peaks at 1140, 1158, and 1175 cm^{-1} ($-CF_3$), only weak absorptions appear in the fingerprint region. The mass spectrum of III is also consistent with the proposed structure: molecular ion, M^+ 226 (M, calcd for $C_8H_{13}N_2F_3O_2$: 226); base peak, m/e 157 (M − Cw_3), 139 (M − $CH_2COOC_2H_5$), 181 (M − OC_2H_5), 197 (M − C_2H_5).

Experimental Section[14]

1,2,3,4-Tetrahydro-7-trifluoromethyl-1,4-diazepin-5-one (II).—To 6.0 g (0.1 mole) of ethylenediamine, dissolved in 100 ml of xylene refluxing in a flask equipped with a Dean–Stark trap, was added dropwise 18.4 g (0.1 mole) of ethyl trifluoroacetoacetate. The solution was refluxed for 1 hr after the separation of water was completed and left standing overnight. An amber oil with some colorless crystals separated on the bottom. The xylene layer was decanted, the residual xylene removed *in vacuo*, and the mixture of oil and solid crystallized from methanol to yield 16% of II, mp 191.5–192.5°. *Anal.* Calcd for $C_6H_7F_3N_2O$: C, 40.14; H, 4.01; F, 31.76; N, 15.46. Found: C, 40.01; H, 3.92; F, 31.64; N, 15.56.

Ethyl 2-(Trifluoromethyl)-2-imidazolidineacetate (III).—The supernatant xylene layer from the preparation of II was evaporated and the residual oil fractionated *in vacuo*. The fraction boiling at 77–78° (2.0 mm) was collected. It solidified upon standing and was crystallized from carbon tetrachloride to yield 25% of III, mp 40.5–41.0° (*Anal.* Calcd for $C_8H_{13}N_2F_3O_2$: C, 42.48; H, 5.79; F, 25.20, N, 12.38; mol wt, 226. Found: C, 42.38; H, 5.86; F, 25.34; N, 12.35; mol wt, 230 (osmotic), 226 (mass spectral)) and phenylurea, mp 152–152.5° (from methanol) (*Anal.* Calcd for $C_{15}H_{18}N_3F_3O_3$: C, 52.17; H, 5.25;

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(9) C. N. R. Rao, "Chemical Applications of Infrared Spectroscopy," Academic Press Inc., New York, N. Y., 1963, pp 258–260.

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(11) (a) L. Marion, D. A. Ramsay, and R. N. Jones, *J. Am. Chem. Soc.*, **73**, 305 (1951); (b) R. A. Russell and H. W. Thompson, *J. Chem. Soc.*, 483 (1955); (c) R. A. Heacock and L. Marion, *Can. J. Chem.*, **34**, 1782 (1956).

(12) D. A. Barr and R. N. Haseldine, *J. Chem. Soc.*, 4169 (1955).

(13) J. L. Riebsomer, *J. Org. Chem.*, **15**, 241 (1950).

(14) Melting points were determined on a Thomas-Hoover apparatus and are corrected. Analyses are by Galbraith Laboratories, Knoxville, Tenn.

N, 12.17; F, 16.51. Found: C, 52.10; H, 5.28; N, 12.23; F, 16.57).

1,4-Diazaspiro[4.5]decane (IV).—To 9.8 g (0.1 mole) of redistilled cyclohexanone dissolved in 100 ml of refluxing benzene in a flask with a Dean–Stark trap was added dropwise 6.0 g (0.1 mole) of ethylenediamine. After the separation of water was completed, the benzene was removed under reduced pressure and the residue distilled in a short-path distillation apparatus. The material boiling above 65° (0.1 mm) was collected. The distillate was rapidly redistilled on a spinning-band column and the fraction boiling at 71–72° (0.05 mm) collected. The yield of IV was 37%: $n^{30}D$ 1.4978; mp 30–31° (lit.[10] bp 61–61.5° (0.01 mm); mp 28.5–30°; $n^{30}D$ 1.4962). This product is stable for several weeks if kept in a refrigerator, but it turns into a yellow liquid in 2–3 days at room temperature. It is rapidly decomposed by water. *Anal.* Calcd for $C_8H_{16}N_2$: C, 68.52; H, 11.50; N, 19.98; mol wt, 140. Found: C, 68.50; H, 11.57; N, 19.96; mol wt, 142 (osmotic), 140 (mass spectral).

Registry No.—II, 14120-51-5; III, 14120-52-6; phenylurea derivative of III, 14120-53-7; IV, 177-03-7.

Synthesis of 2-Methyl-4H-pyran-4-one

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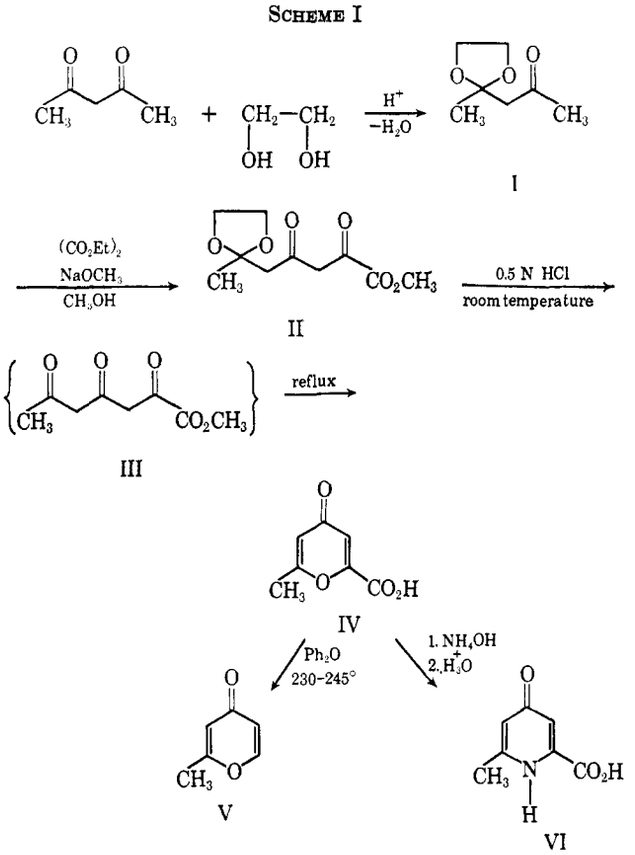
Although 2-methyl-4H-pyran-4-one has been cited in the literature,[1] a synthesis of this compound apparently has never been reported. We now wish to present a convenient total synthesis of 2-methyl-4H-pyran-4-one in four steps starting from acetylacetone. The synthesis is outlined in Scheme I.

In the first step, one of the keto functions of acetylacetone was rendered inactive by ketal formation[2] with ethylene glycol to form I.[3]

2-Methyl-2-acetonyl-1,3-dioxolane (I) was acylated with diethyl oxalate and sodium methoxide in methanol to form methyl 2,4-diketo-6-ethylenedioxyheptanoate (II) in a crude yield of 89%. This intermediate was characterized by its infrared spectrum [$\lambda_{max}^{CCl_4}$ = 5.72 ($-C(=O)OCH_3$), 6.1 and 6.8 μ (β-diketone carbonyls, and 9.55 (ethylenedioxy ether linkages)] and by analysis of its copper chelate. Crude II was treated with 0.5 *N* hydrochloric acid at room temperature to effect hydrolysis of the ketal group. The intermediate triketone (III) was not isolated; instead, the reaction mixture was refluxed to complete ring closure and subsequent ester hydrolysis, forming 6-methyl-4H-pyran-4-one-2-carboxylic acid (IV) in 45–50% yield from crude II. The structure of IV was established by its spectral properties, analytical data, and its conversion to 6-methyl-4-pyridone-2-carboxylic acid (VI).

SCHEME I



In the final step IV was decarboxylated by heating in diphenyl ether at 230–245° followed by partial distillation of the reaction mixture under slight vacuum. 2-Methyl-4H-pyran-4-one (V) was obtained in the distillate as a 10–15% diphenyl ether solution. After separation from diphenyl ether, crude V was obtained in an approximate quantitative conversion and 93% purity. Analytical material[4] was readily obtained by glpc fractionation. Unlike 4H-pyran-4-one and 2,6-dimethyl-4H-pyran-4-one the 2-methyl derivative is a liquid at room temperature. The nmr spectrum of V has a rather simple appearance, though somewhat more complex when examined in detail since the 3-H appears to be involved in spin coupling with the remaining protons in the molecule. The 5-, 3-, and 6-hydrogens exhibit an ABX-type spectrum with further splitting of the 3-hydrogen by the 2-methyl hydrogens. The apparent coupling constants (in cycles per second) are $|J_{2,3}| \leqslant 0.7$, $|J_{3,5}| = 2.5$, $|J_{3,6}| \leqslant 0.6$, and $|J_{5,6}| = 5.7$.

In retrospect, going from acetylacetone to methyl 2,4,6-triketoheptonoate (III) was, in essence, an acylation of acetylacetone at the terminal methyl position, though indirect. Since Hauser and co-workers[5] have shown that acetylacetone dicarbanion can be acylated at the methyl position, it might appear preferable to obtain III directly from acetylacetone by acylation of its dicarbanion with dimethyl oxalate. This reaction, however, does not appear feasible since the dicarbanion product VII would be expected to undergo facile

(1) Use of 2-methyl-4H-pyran-4-one as a reactant was described by L. L. Woods (*J. Org. Chem.*, **27**, 696 (1962)); in a private communication Woods informed us that he had obtained a sample from Monsanto Chemical Co. of Texas City, Texas. We subsequently obtained a sample of 2-methyl-4H-pyran-4-one from Dr. R. J. Evans of Monsanto. We wish to thank Dr. Woods for his correspondence and Dr. Evans for the sample.

(2) H. Stetter and S. Vestner, *Ber.*, **97**, 169 (1964).

(3) In our initial procedure (see Experimental Section), glycol monoacetate, which is also formed in the reaction, *i.e.*, by alcoholic cleavage of acetylacetone (H. Adkins, W. Kutz, and D. C. Coffman, *J. Am. Chem. Soc.*, **52**, 4391 (1930)), proved rather difficult to separate from I by fractional distillation. Subsequent use of a procedure similar to one described by P. C. Dutta, P. K. Dutta, and K. N. S. Sastry [*J. Ind. Chem. Soc.*, **31**, 881 (1954)] led to a substantial reduction of glycol monoacetate in the crude reaction mixtures.

(4) This material was identical with the 2-methyl-4H-pyran-4-one obtained from Monsanto.[1]

(5) (a) C. R. Hauser and T. M. Harris, *J. Am. Chem. Soc.*, **80**, 6360 (1958); (b) S. D. Work and C. R. Hauser, *J. Org. Chem.*, **28**, 725 (1963).