filtration, and the benzene was removed by distillation to a base temperature of 155° at 200 mm. The distillation was continued to give, after removal of an intermediate fraction, 26.2 g. (21%) of 1-isopropyl-N,N-dimethyl-2-propynylamine, b.p. 68–69° at 100–109 mm.

The distillation was continued and, after collection of an intermediate fraction, there was obtained 53 g. (47%) of N,N,N′,N′,-2,7-hexamethyl-4-octyne-3,6-diamine, b.p. 106° at 9 mm., $n^{20}D$ 1.4575.

1-(1-Isopropyl-3-phenyl-2-propyn-3-yl)piperidine (VIII). Method B.—Ethylnylbenzene (27 g., 0.26 mole) and 1-isobutenylpiperidine (40 g., 0.29 mole) were combined and heated at 145–150° for 15 hr. Distillation of the reaction mixture through a 6-in. Vigreux column gave, after removal of 15 g. of forerun, 40.5 g. (64%) of 1-(1-isopropyl-3-phenyl-2-propyn-3-yl)piperidine, b.p. 118–124° at 1.5 mm., $n^{20}D$ 1.5393.

6-Dimethylamino-3,7-dimethyl-4-octyn-3-yl Acetate (IX). Method C.—N,N-Dimethylisobutenylamine (200 g., 2.02 moles) and copper(I) chloride (3 g.) were placed in a three-necked reaction flask equipped with a mechanical stirrer, thermometer, and dropping funnel. The stirrer was started and 3-methyl-1-pentyn-3-yl acetate (280 g., 2 moles) was added dropwise. An exothermic reaction occurred and the temperature of the mixture was maintained at 40–45° by intermittent cooling. The mixture was stirred for 2 hr. after the addition was completed and the catalyst was then removed by filtration. Distillation of the reaction mixture through a 6-in. Vigreux column gave, after removal of a 15-g. forerun, 428 g. (89%) of 6-dimethylamino-3,7-dimethyl-4-octyn-3-yl acetate, b.p. 60–65° at *ca.* 0.5 mm., $n^{20}D$ 1.4477.

5-Dimethylamino-2,6-dimethyl-3-heptyn-2-ol (X). Method D.—N,N-Dimethylisobutenyl amine (50 g., 0.5 mole), copper(I) chloride (3 g.), and hydroquinone (0.1 g.), were placed in a three-necked reaction flask and heated to reflux (86°). The mixture was stirred while 2-methyl-3-butyn-2-ol (42 g., 0.5 mole) was added dropwise. The mixture was heated during the addition and the temperature rose to 110° and refluxing ceased. The temperature was kept at 110° for 10 min. The mixture was then cooled to room temperature, filtered, and distilled through a 6-in. Vigreux column to give, after removal of a 1-g. forerun, 70 g. (76%) of 5-dimethylamino-2,6-dimethyl 3-heptyn-2-ol, b.p. 58–67° at 1–1.5 mm., $n^{20}D$ 1.4570.

Transformation of 1-Isopropyl-N,N-dimethyl-3-phenyl-2-propynylamine (IV) to 4-Methyl-2-pentenophenone (V).—To a solution of 60 ml. of concentrated sulfuric acid and 15 ml. of water was added 1-isopropyl-N,N-dimethyl-3-phenyl-2-propynylamine (27 g., 0.137 mole). To this mixture was added mercury(II) sulfate (1 g.). The resulting mixture was heated on the steam bath for 4 hr. and then poured onto ice and extracted once with ether (200 ml.). Evaporation of the ethereal extract on the steam bath gave less than 1 g. of residue. The remaining aqueous layer was made basic with sodium hydroxide (12 g., 0.3 mole) and extracted once with ether (400 ml.). Evaporation of the ether on the steam bath to 75° gave 26.5 g. of residue. The residue was combined with 10% sodium hydroxide solution (10 ml.), water (10 ml.), and ethyl alcohol (75 ml.) and was heated on the steam bath for 5.5 hr. During this time dimethylamine was evolved. After the mixture was chilled, a solid separated which was collected, washed with aqueous ethyl alcohol, and dried to give 9.5 g. (41%) of 4-methyl-2-pentenophenone, m.p. 142–143° (reported[7] m.p. 139–140°).

(7) W. D. Emmons, *J. Am. Chem. Soc.*, **79**, 5739 (1957).

Enamine Chemistry. II. Reactions with Acetylenedicarboxylates[1]

KENT C. BRANNOCK, ROBERT D. BURPITT, V. WILSON GOODLETT, AND JOHN G. THWEATT

Research Laboratories, Tennessee Eastman Company, Division of Eastman Kodak Company, Kingsport, Tennessee

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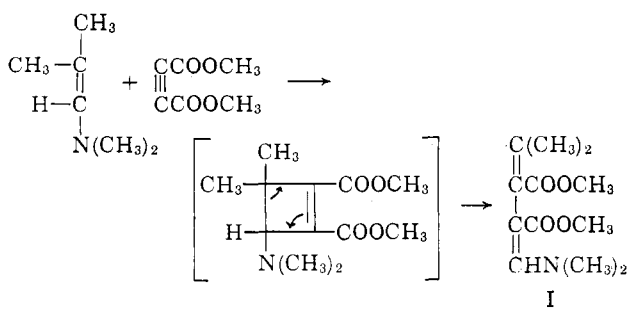
The reaction of a variety of enamines with acetylenedicarboxylates was studied. The reaction products are those derived from the cyclobutene rearrangement of cycloaddition adducts initially formed. In the case of enamines derived from alicyclic ketones, the net result of the reaction is a ring enlargement in which two carbon atoms are inserted into the ring. Some further transformations of the reaction products are described.

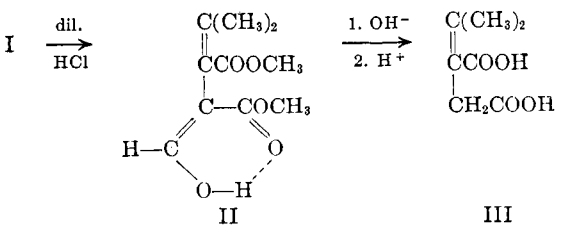
The cycloaddition of electrophilic olefins to enamines, leading to cyclobutanes, has been reported.[2] The reactions of a variety of enamines derived from acyclic aldehydes and ketones and cyclic ketones with both acetylenedicarboxylates and propiolates have now been investigated. The reactions involving acetylenedicarboxylates proved to be more straightforward and will be discussed in this paper.

The reaction of enamines derived from butyraldehyde, isobutyraldehyde, and 3-pentanone with acetylenedicarboxylates gives products derived from ring opening of the expected cyclobutene intermediates. The reaction sequence is shown for N,N-dimethylisobutenylamine and dimethyl acetylenedicarboxylate.



I

The enamine function of the product (I) was hydrolyzed with dilute acid to give the hydroxymethylene ester (II) which in turn was cleaved by aqueous alkali to give teraconic acid (III).



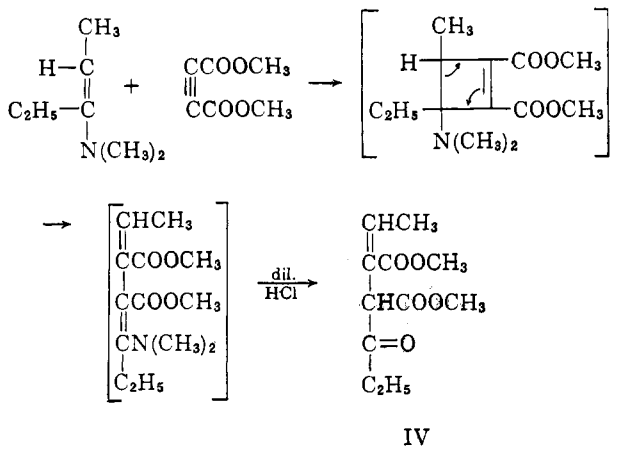
II III

Similar transformations were carried out with the product derived from butyraldehyde, whereas the product derived from 3-pentanone was converted directly to the keto diester (IV) without the isolation of intermediates.

A similar reaction of enamines derived from cyclic ketones with acetylenedicarboxylates, the net result of

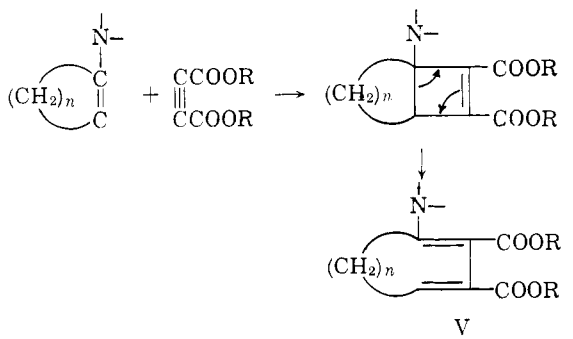
(1) A portion of the material in this paper was presented at the Enamine Chemistry Symposium, 140th National Meeting of the American Chemical Society, Chicago, Ill., September, 1961.

(2) K. C. Brannock, A. Bell, R. D. Burpitt, and C. A. Kelly, *J. Org. Chem.*, **26**, 625 (1961).



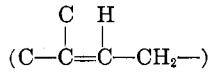
IV

which would be a ring enlargement with insertion of two carbons in the ring, appeared especially attractive to us.



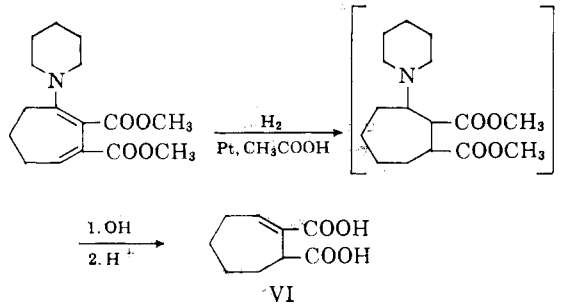
V

This sequence occurred smoothly with enamines derived from cyclopentanone, cycloheptanone, cyclooctanone, and cyclododecanone, that is, when n = 3, 5, 6, or 10. The structures of the five adducts were assigned, in part, on the basis of their hydrolysis to the corresponding unsaturated keto esters, and, in part, on the basis of their n.m.r. spectra, which showed a single olefinic proton as a triplet.



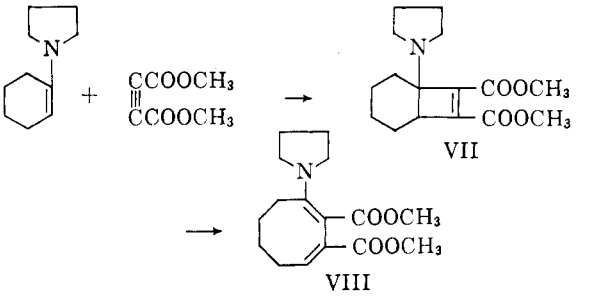
In addition, all of the adducts showed very similar infrared absorptions in the C=O and C=C range [maxima at 5.75–5.80 μ, 5.95–6.0 μ, 6.1–6.3 μ (weak), and 6.45–6.5μ].

The adduct (V) derived from cyclopentanone (n = 3), was further converted by hydrogenation and digestion of the crude product with aqueous alkali to 2-cycloheptene-1,2-dicarboxylic acid (VI). On hydrogenation, VI gave the known *cis*-1,2-cycloheptanedicarboxylic acid which was isomerized to the known *trans*-1,2-cycloheptanedicarboxylic acid by heating it with dilute sulfuric acid.

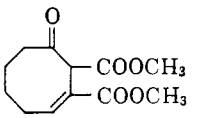


VI

Reaction of the pyrrolidine enamine of cyclohexanone with dimethyl acetylenedicarboxylate gave a heat-sensitive solid in good yield to which we have assigned the bicyclooctene structure (VII). No vinyl protons



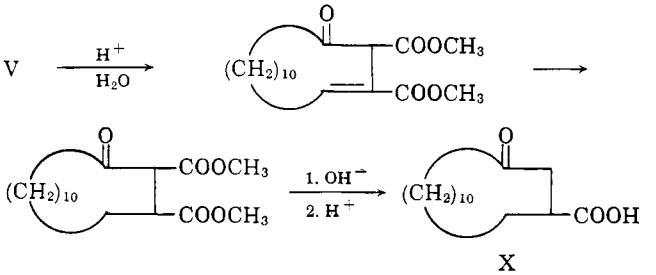
were indicated in the n.m.r. spectrum of VII and its infrared spectrum was compatible with the proposed structure. The compound undergoes considerable decomposition on melting (77–81°) or on attempted recrystallization from hexane. It could be recrystallized from ether, however. After heating VII for eighteen hours on a steam bath, the ring enlargement product (VIII) was obtained in 11% yield. In another case, VIII was obtained fortuitously in 33% yield when VII was subjected to an unsuccessful series of transformations. A significant amount of rearrangement of VII occurs when it is treated with dilute acid since the keto ester (IX) was obtained in 21% yield after this treatment; hydrolysis of VIII under similar conditions gave IX in 53% yield.



IX

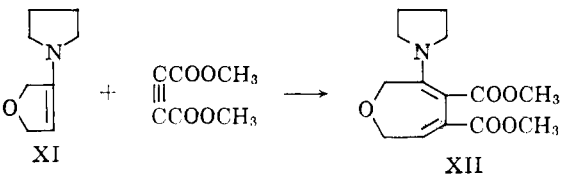
We believe that the reluctance of VII to undergo the cyclobutene rearrangement may be due to the 6/4 ring fusion forcing the cyclobutene ring into nonplanarity, and thus making the rearrangement less favorable. The nature of the thermal decomposition products of VII, other than VIII, has not been determined.

The product derived from cyclododecanone (V. n = 10) was converted by hydrolysis, hydrogenation, saponification, and decarboxylation to 3-oxocyclotetradecanecarboxylic acid (X).



X

In one case, the heterocyclic enamine (XI) obtained from dihydro-3(2*H*)-furanone gave the ring enlargement product (XII) in poor yield.



Experimental[3]

Materials.—1-Ethyl-N,N-dimethylpropenylamine was prepared by a slight modification of the method of Stork and Landesman.[4] The methiodide salt of the N-methylimine of 3-pentanone was treated with a twofold excess of triethylamine in benzene. After the mixture had stood at room temperature for 24 hr., it was filtered and the filtrate was distilled to give 1-ethyl-N,N-dimethylpropenylamine, b.p. 127–128° (atm. pressure), $n^{20}D$ 1.4479, in 46% yield.

Anal. Calcd. for $C_7H_{15}N$: C, 74.2; H, 13.3. Found: C, 73.9; H, 13.2.

1-(1-Cyclododecenyl)pyrrolidine was prepared by refluxing, for 3 days, a mixture of cyclododecanone (182 g., 1 mole), pyrrolidine (213 g., 3 moles), 0.25 g. of *p*-toluenesulfonic acid, 200 ml. of xylene, and 25 ml. of hexane under a column topped with a Dean–Stark trap. After distillation, the enamine, b.p. 120–125° at 0.4–0.5 mm., $n^{20}D$ 1.5237, was obtained in 77% yield.

Anal. Calcd. for $C_{16}H_{29}N$: C, 83.1; H, 10.9. Found: C, 82.9; H, 10.8.

1-(2,5-Dihydro-3-furyl)pyrrolidine.—Dihydro-3(2*H*)-furanone[5] (36.5 g., 0.4 mole) was added to a slurry of 5 g. of anhydrous potassium carbonate in pyrrolidine (28.4 g., 0.4 mole) at 0° and the mixture was allowed to stand for 3 hr. at 0°. It was then filtered and the filtrate was distilled to give 18 g. (32%) of 1-(2,5-dihydro-3-furyl)pyrrolidine, b.p. 55–59° at 0.2 mm., $n^{20}D$ 1.5148. This enamine was quite sensitive to heat and much of it was lost during distillation. For most purposes, the crude material can be used without distillation. The alternative structure, 1-(4,5-dihydro-3-furyl)pyrrolidine, was excluded on the basis of the n.m.r. spectrum (determined at 40 Mc. with a Varian Associates 4300B instrument) which showed an olefinic proton singlet (as does 2,5-dihydrofuran) at 4 p.p.m. (relative to tetramethylsilane) and a single absorption for the two methylene groups at 4.7 p.p.m. In the alternative structure, the absorptions due to the two methylene groups would be expected to be resolved.

Anal. Calcd. for $C_8H_{13}NO$: N, 10.0. Found: N, 9.8.

1-(1-Cyclooctenyl)piperidine, b.p. 87–88° at 1 mm., $n^{20}D$ 1.5164, was prepared in 72% yield by the method of Kuehne.[6]

Anal. Calcd. for $C_{13}H_{23}N$: N, 7.3. Found: N, 7.1.

N,N-Dimethylisobutenylamine,[7] 1-butenylpiperidine,[8] and the pyrrolidine enamines of cyclopentanone, cyclohexanone, and cycloheptanone[6] were prepared as described in the literature.

Dimethyl 2-Dimethylaminomethylene-3-isopropylidenesuccinate.—N,N-Dimethylisobutenylamine (45.5 g., 0.46 mole) was added dropwise to dimethyl acetylenedicarboxylate (65.3 g., 0.46 mole) in 50 ml. of ether with cooling to keep the temperature at 25–30°. The mixture was allowed to reflux spontaneously (about 1 hr.) and was then heated at reflux for 0.5 hr. On distillation, there was obtained 54.2 g. (49%) of crude dimethyl 2-dimethylaminomethylene-3-isopropylidenesuccinate, b.p. 119–121° at 0.55 mm., which crystallized, m.p. 65–75°. A sample for analysis, recrystallized from hexane, melted at 83.5–84.5°.

Anal. Calcd. for $C_{12}H_{19}NO_4$: C, 59.3; H, 7.9; N, 5.8. Found: C, 59.7; H, 7.8; N, 5.6.

Dimethyl 2-Formyl-3-isopropylidenesuccinate.—Dimethyl 2-dimethylaminomethylene-3-isopropylidenesuccinate (16 g., 0.066 mole) was added to a solution of 25 ml. of concentrated hydrochloric acid in 175 ml. of water and warmed gently on the steam bath until solution was complete. The mixture rapidly became turbid and an oil layer separated. The mixture was allowed to stand 1 hr. and was then extracted with ether. Distillation of the extract gave 9 g. (64%) of dimethyl 2-formyl-3-isopropylidene succinate, b.p. 93–96° at 0.8 mm., $n^{20}D$ 1.4909 (supercooled), which crystallized, m.p. 56–58°.

Anal. Calcd. for $C_{10}H_{14}O_5$: C, 56.1; H, 6.6. Found: C, 55.8; H, 6.6.

This material gave an intense violet color with iron(III) chloride solution and its infrared spectrum showed that it was, for the most part, the enol or hydroxymethylene form.[9] This material did not give a solid 2,4-dinitrophenylhydrazone.

Diethyl 2-Dimethylaminomethylene-3-isopropylidenesuccinate.—Diethyl acetylenedicarboxylate (170 g., 1.0 mole) was added dropwise to N,N-dimethylisobutenylamine (120 g., 1.2 moles) in 150 ml. of ether over a 2-hr. period, at such a rate that the mixture was maintained at reflux (44–46°). The temperature was allowed to decrease slowly to room temperature over the next hour and the mixture stood overnight. It was then distilled to remove excess N,N-dimethylisobutenylamine by heating it to 65° at 2 mm. When cooled, the entire residue (270 g.; theoretical yield, 269 g.) crystallized.

The product was treated with Darco and recrystallized from hexane to give 197 g. (73%) of diethyl 2-dimethylaminomethylene-3-isopropylidenesuccinate, m.p. 57–58°. A sample for analysis, recrystallized from hexane, melted at 59°.

Anal. Calcd. for $C_{14}H_{23}NO_4$: C, 62.4; H, 8.6; N, 5.2. Found: C, 62.3; H, 8.5; N, 5.1.

This material did not give a solid 2,4-dinitrophenylhydrazone.

Diethyl 2-Formyl-3-isopropylidenesuccinate.—Diethyl 2-dimethylaminomethylene-3-isopropylidenesuccinate (100 g., 0.37 mole) was dissolved in a solution of 150 ml. of concentrated hydrochloric acid in 850 ml. of water. An oil layer separated after a short time. The mixture was allowed to stand, with occasional shaking, for 1 hr. and was then extracted with ether. Distillation of the ether layer gave 64 g. (70%) of diethyl 2-formyl-3-isopropylidenesuccinate, b.p. 110–112° at 3 mm.

Anal. Calcd. for $C_{12}H_{18}O_5$: C, 59.5; H, 7.5. Found: C, 59.6; H, 7.6.

This product gave an intense violet color with iron(III) chloride solution and its infrared spectrum showed that it was, for the most part, the enol form. It did not give a solid 2,4-dinitrophenylhydrazone, but did give a semicarbazone, m.p. 144–146°.

Anal. Calcd. for $C_{13}H_{21}N_3O_5$: C, 52.2; H, 7.1. Found: C, 52.1; H, 7.2.

Teraconic Acid.—Diethyl 2-formyl-3-isopropylidenesuccinate (30 g., 0.124 mole) was refluxed with 20 g. of sodium hydroxide in 75 ml. of water for 3 hr. The solution was acidified with concentrated hydrochloric acid, cooled, and filtered to give 19 g. (97%) of crude teraconic acid, m.p. 168–171° dec. A sample for analysis, recrystallized from water, melted at 174° dec.

Anal. Calcd. for $C_7H_{10}O_4$: C, 53.2; H, 6.3; neut. equiv., 79.08. Found: C, 53.2; H, 6.4; neut. equiv., 78.8.

An authentic sample of teraconic acid prepared by the method of Kloetzel[10] melted at 174° and showed no depression of the melting point when admixed with the teraconic acid obtained previously.

Dimethyl 2-Piperidinomethylene-3-propylidenesuccinate.—Dimethyl acetylenedicarboxylate (14 g., 0.1 mole) was added dropwise with stirring to 1-(1-butenyl)piperidine (14 g., 0.1 mole) in ether (25 ml.) at such a rate that gentle refluxing of the ether was maintained. Distillation of the mixture through a 3-in. Vigreux column gave, after removal of ether and a 4-g. forerun, 14 g. (50%) of dimethyl 2-piperidinomethylene-3-propylidenesuccinate, b.p. 150–156° at 1.5 mm., $n^{20}D$ 1.5354.

Anal. Calcd. for $C_{15}H_{23}NO_4$: C, 64.0; H, 8.2. Found: C, 63.9; H, 8.1.

Dimethyl 2-Formyl-3-propylidenesuccinate.—Dimethyl 2-piperidinomethylene-3-propylidenesuccinate (11 g., 0.04 mole) was dissolved in a solution of concentrated hydrochloric acid (16 ml.) in water (90 ml.). The mixture was allowed to stand, with occasional shaking, for 1.5 hr. and was then extracted with ether and the etheral extract was distilled to give 4 g. (48%) of dimethyl 2-formyl-3-propylidenesuccinate, b.p. 93–96° at 1 mm., $n^{20}D$ 1.4833.

Anal. Calcd. for $C_{10}H_{14}O_5$: C, 56.0; H, 6.6. Found: C, 55.8; H, 6.7.

2-Propylidenesuccinic Acid.—Dimethyl 2-formyl-3-propylidenesuccinate (3 g., 0.014 mole) was refluxed wth a solution of sodium hydroxide (2.5 g., 0.063 mole) in water (20 ml.) for 1.5 hr. The resulting solution was acidified with concentrated hydrochloric acid and extracted with ether. Evaporation of the ether on a steam bath gave 1.7 g. (77%) of crude 2-propylidenesuccinic acid. A small sample, recrystallized from water, melted at 166–167° (reported[10] m.p. 163–166°).

Dimethyl 2-Ethylidene-1-propionylsuccinate.—To a solution of 1-ethyl-N,N-dimethylpropenylamine (28.3 g., 0.25 mole) in

(3) Melting points are uncorrected and were determined using a Fisher-Johns melting point apparatus.
(4) H. K. Landesman, P.D. thesis, Columbia University, 1956.
(5) H. Wynberg, *J. Am. Chem. Soc.*, **80**, 364 (1958).
(6) M. E. Kuehne, *ibid.*, **81**, 5400 (1959).
(7) K. C. Brannock and R. D. Burpitt, *J. Org. Chem.*, **26**, 3576 (1961).
(8) C. Mannich and H. Davidsen, *Ber.*, **69**, 2106 (1936).
(9) W. J. Croxall and J. O. Van Hook, *J. Am. Chem. Soc.*, **72**, 803 (1950)
(10) M. C. Kloetzel, *ibid.*, **70**, 3571 (1948).

ether (100 ml.) was added, over 1 hr., dimethyl acetylenedicarboxylate (35.5 g., 0.25 mole). The temperature of the reaction mixture was maintained below 35° by intermittent cooling. After the reaction mixture had stood for 2 hr., the ether was evaporated on a steam bath and the residual oil was dissolved in a solution of concentrated hydrochloric acid (30 ml.) and water (150 ml.). The mixture stood for 18 hr.; the oil which had separated was removed by extraction with ether. Distillation of the etheral extract gave, after removal of ether, 50.8 g. (89%) of dimethyl 2-ethylidene-1-propionylsuccinate, b.p. 102–104° at 1.2 mm., $n^{20}D$ 1.4743. The infrared spectrum was consistent with the assigned structure.

Anal. Calcd. for $C_{11}H_{16}O_5$: C, 57.8; H, 7.1. Found: C, 58.0; H, 7.0.

Dimethyl 3-(1-Pyrrolidinyl)-2,7-cycloheptadiene-1,2-dicarboxylate.—Dimethyl acetylenedicarboxylate (28.4 g., 0.2 mole) was added, over 10 min., to 1-(1-cyclopentenyl)pyrrolidine (30.2 g., 0.22 mole) in ether (150 ml.) with cooling to keep the temperature at 25–35°. The mixture was allowed to stand for 0.5 hr. and the ether was removed by evaporation on a steam bath. On cooling, the residue crystallized. Recrystallization of the product from a hexane–benzene mixture gave 39.8 g. (71%) of dimethyl 3-(1-pyrrolidinyl)-2,7-cycloheptadiene-1,2-dicarboxylate, m.p. 147–148°.

Anal. Calcd. for $C_{15}H_{21}NO_4$: C, 64.5; H, 7.6. Found: C, 64.9; H, 7.8.

Dimethyl 7-Oxo-2-cycloheptene-1,2-dicarboxylate.—Dimethyl-3-(1-pyrrolidinyl)-2,7-cycloheptadiene-1,2-dicarboxylate (11.5 g., 0.041 mole) was dissolved in a solution of concentrated hydrochloric acid (10 ml.) and water (40 ml.). After the mixture had stood for 15 hr., the oil layer which had separated was removed by extraction with ether. Distillation of the etheral extract gave, after removal of ether, 4.6 g. (49%) of dimethyl 7-oxo-2-cycloheptene-1,2-dicarboxylate, b.p. 101–106° at 0.4–0.5 mm. This compound crystallized on standing and melted at 55–57°. Its n.m.r. spectrum showed that it was, for the most part, the enol form.

Anal. Calcd. for $C_{11}H_{14}O_5$: C, 58.4; H, 6.2. Found: C, 58.5; H, 6.5.

2-Cycloheptene-1,2-dicarboxylic Acid.—Dimethyl 3-(1-pyrrolidinyl)-2,7-cycloheptadiene-1,2-dicarboxylate (42 g., 0.15 mole) was dissolved in acetic acid (350 ml.) and hydrogenated at 40 p.s.i. at room temperature, using 0.5 g. of platinum(IV) oxide as a catalyst, until hydrogen absorption had stopped. The catalyst was removed by filtration and most of the acetic acid was removed by distillation under reduced pressure. The residue was treated with excess aqueous 20% sodium hydroxide in methanol, and heated on a steam bath for 2 hr. The solution was acidified with concentrated hydrochloric acid and was extracted three times with ether. Evaporation of the combined etheral extracts gave 7 g. (25%) of 2-cycloheptene-1,2-dicarboxylic acid. A sample, recrystallized from water, melted at 168–170°. N.m.r. spectrum showed one olefinic proton absorption as a triplet.

Anal. Calcd. for $C_9H_{12}O_4$ C, 58.7; H, 6.6; neut. equiv., 92.1. Found: C, 58.5; H, 6.5; neut. equiv., 92.2.

2-Cycloheptene-1,2-dicarboxylic acid was obtained in 73% yield from a similar hydrogenation using 0.25 mole of dimethyl 3-(1-pyrrolidinyl)-2,7-cycloheptadiene-1,2-dicarboxylate, 500 ml. of acetic acid, and 2 g. of platinum(IV) oxide. Treatment was then the same as that used previously.

***cis*-1,2-Cycloheptanedicarboxylic Acid.**—2-Cycloheptene-1,2-dicarboxylic acid (15 g., 0.082 mole) was dissolved in a solution of water (100 ml.) and sodium hydroxide (6.6 g., 0.165 mole) and hydrogenated at 125° and 1500 p.s.i., using 5 g. of Raney nickel as a catalyst. The catalyst was removed by filtration and the filtrate was evaporated on a steam bath to one-third the original volume. The solution was acidified with concentrated hydrochloric acid and filtered to give 12 g. of *cis*-1,2-cycloheptanedicarboxylic acid. Extraction of the filtrate with ether and evaporation of the etheral extract gave an additional 2.5 g. of product. The yield was 95%. A sample for analysis, recrystallized from toluene, melted at 130–131° (reported[11] m.p. 133–135°).

The infrared spectrum of the acid was identical with that of a sample of authentic *cis*-1,2-cycloheptanedicarboxylic acid.[12]

Anal. Calcd. for $C_9H_{14}O_4$: C, 58.0; H, 7.6. Found: C, 58.0; H, 7.5.

***trans*-1,2-Cycloheptanedicarboxylic Acid.**—*cis*-1,2-Cycloheptanedicarboxylic acid (5 g., 0.027 mole) was combined with 25 ml. of a 30% (by volume) solution of concentrated sulfuric acid in water and heated for 12 hr. in a bomb at 150°. The mixture was cooled and filtered to give 4 g. (80%) of *trans*-1,2-cycloheptanedicarboxylic acid. A sample, recrystallized three times from acetonitrile, melted at 156–157° (reported m.p. 157–158.5°,[11] 145–147[13]). A stable hemihydrate, m.p. 160–161°, has been reported[14] but was not encountered by us. The infrared spectrum of our material was identical with that of a sample supplied by Dr. R. A. Raphael.[15] We found the melting point of this sample to be 155–156°. On one occasion, we obtained a small amount of the *trans*-1,2-cycloheptanedicarboxylic acid, which melted at 116–120°. This may have been due to polymorphism, since the optically active *trans* acid has been reported to melt at 115–116°.[11]

Dimethyl 1-(1-Pyrrolidinyl)bicyclo[4.2.0]oct-7-ene-7,8-dicarboxylate.—Dimethyl acetylenedicarboxylate (28.4 g., 0.2 mole) was added over 10 min. to 1-(1-cyclohexenyl)pyrrolidine (30.2 g., 0.2 mole) in 150 ml. of ether with cooling to keep the temperature at 25–35°. Toward the end of the addition, a crystalline precipitate appeared. The mixture was allowed to stand for 10 min. and 150 ml. of pentane was added. The mixture was chilled and filtered to give 41 g. (70%) of dimethyl 1-(1-pyrrolidinyl)bicyclo[4.2.0]-oct-7-ene-7,8-dicarboxylate, m.p. 77–81°. This compound is thermally unstable and undergoes considerable change on melting or on attempted recrystallization from hexane. It could, however, be recrystallized from ether.

Anal. Calcd. for $C_{16}H_{23}NO_4$: C, 65.5; H, 7.9. Found: C, 65.6; H, 7.9.

Dimethyl 3-(1-Pyrrolidinyl)-2,8-cyclooctadiene-1,2-dicarboxylate.—Dimethyl 1-(1-pyrrolidinyl)bicyclo[4.2.0]oct-7-ene-7,8-dicarboxylate (37 g., 0.126 mole) was heated on a steam bath for 18 hr. The material was cooled, and ether (100 ml.) was added. It was then chilled and filtered to give 4 g. (11%) of dimethyl 3-(1-pyrrolidinyl)-2,8-cyclooctadiene-1,2-dicarboxylate, m.p. 138–140°. After recrystallization of the product from ether, the melting point was 141–142°.

Anal. Calcd. for $C_{16}H_{23}NO_3$: C, 65.5; H, 7.9. Found: C, 65.5; H, 7.9.

Dimethyl 3-(1-pyrrolidinyl)-2,8-cyclooctadiene-1,2-dicarboxylate was obtained fortuitously in 33% yield from dimethyl 1-(1-pyrrolidinyl)bicyclo[4.2.0]oct-7-ene-7,8-dicarboxylate when the latter compound was subjected to an unsuccessful series of transformations.

On standing, the bicyclooctene undergoes a significant amount of rearrangement, as shown by the fact that a 21% yield of dimethyl 8-oxo-2-cyclooctene-1,2-dicarboxylate was obtained from treatment of the bicyclooctene with dilute hydrochloric acid.

Dimethyl 8-Oxo-2-cyclooctene-1,2-dicarboxylate.—Dimethyl 3-(1-pyrrolidinyl)-2,8-cyclooctadiene-1,2-dicarboxylate (4 g., 0.017 mole) was dissolved in 25 ml. of 10% hydrochloric acid solution and allowed to stand for 24 hr. at room temperature. The oil which had separated was extracted with ether and the ether was evaporated on a steam bath, leaving 1.75 g. (53%) of dimethyl 8-oxo-2-cyclooctene-1,2-dicarboxylate, which crystallized on standing. A sample for analysis, recrystallized from hexane, melted at 74–75°. The n.m.r. spectrum showed that it was, for the most part, the enol form.

Anal. Calcd. for $C_{12}H_{16}O_5$: C, 60.0; H, 6.7. Found: C, 59.8; H, 6.7.

Dimethyl 3-(1-Pyrrolidinyl)-2,9-cyclononadiene-1,2-dicarboxylate.—To a solution of 1-(1-cycloheptenyl)pyrrolidine (3.3 g., 0.02 mole) in ether (25 ml.) was added, over 5 min., dimethyl acetylenedicarboxylate (2.8 g., 0.02 mole) with cooling to keep the temperature at 30–35°. The reaction mixture was allowed to stand at room temperature for 0.5 hr. and then cooled to 10°. After filtration, 3.9 g. of dimethyl 3-(1-pyrrolidinyl)-2,9-cyclononadiene-1,2-dicarboxylate, m.p. 109.5–110.5°, was obtained. Evaporation of the filtrate and addition of pentane gave an additional 1.8 g. of the same product. The combined yield was 93%.

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(15) We are indebted to Dr. R. A. Raphael, University of Glasgow, for supplying us with a sample of *trans*-1,2-cycloheptanedicarboxylic acid.

Anal. Calcd. for $C_{17}H_{25}NO_4$: C, 66.4; H, 8.2. Found: C, 66.7; H, 8.4.

Diethyl 3-Piperidino-2,10-cyclodecadiene-1,2-dicarboxylate.—1-(1-Cyclooctenyl)piperidine (3.86 g., 0.02 mole) and diethyl acetylenedicarboxylate (3.40 g., 0.02 mole) were allowed to react in ether as described in the preceding example. There was obtained 4.4 g. (60%) of diethyl 3-piperidino-2,10-cyclodecadiene-1,2-dicarboxylate, m.p. 91–92°.

Anal. Calcd. for $C_{21}H_{33}NO_4$: C, 69.4; H, 9.2. Found: C, 69.5; H, 9.2.

Dimethyl 3-Pyrrolidinyl-2,14-cyclotetradecadiene-1,2-dicarboxylate.—To 1-(1-cyclododecenyl)pyrrolidine (8.5 g., 0.036 mole) in 25 ml. of ether was added, portionwise, dimethyl acetylenedicarboxylate (5.15 g., 0.036 mole) with cooling to keep the temperature at 30–35°. The ether was removed on a steam bath and the residue was crystallized from pentane to give 12.35 g. (90.5%) of crude dimethyl 3-pyrrolidinyl-2,14-cyclotetradecadiene-1,2-dicarboxylate. A sample for analysis, recrystallized from ether, melted at 94–95°.

Anal. Calcd. for $C_{22}H_{35}NO_4$: D, 70.0; H, 9.3. Found: C, 69.9; H, 9.1.

Hydrolysis of dimethyl 3-pyrrolidinyl-2,14-cyclotetradecadiene-1,2-dicarboxylate with dilute hydrochloric acid gave dimethyl 14-oxo-2-cyclotetradecene-1,2-dicarboxylate, m.p. 73–74° (recrystallized from ether), in 83% yield.

Anal. Calcd. for $C_{18}H_{28}O_5$: C, 66.6; H, 8.7. Found: C, 66.6; H, 8.8.

Hydrogenation of dimethyl 14-oxo-2-cyclotetradecene-1,2-dicarboxylate in methanol over 5% palladium on alumina at room temperature and 3 atm. gave dimethyl 3-oxocyclotetradecane-1,2-dicarboxylate, m.p. 93° (recrystallized from methanol), in 84% yield.

Anal. Calcd. for $C_{18}H_{30}O_5$: C, 66.2; H, 9.3. Found: C, 66.3; H, 9.3.

Treatment of dimethyl 3-oxocyclotetradecane-1,2-dicarboxylate (32.6 g., 0.1 mole) with a solution of 15 g. of sodium hydroxide in 250 ml. of methanol and 250 ml. of water at reflux for 5 hr., followed by acidification with concentrated hydrochloric acid, gave 21.5 g. (85%) of 3-oxocyclotetradecanecarboxylic acid, m.p. 142.5–143.5° (recrystallized from toluene).

Anal. Calcd. for $C_{15}H_{26}O_3$: C, 70.8; H, 10.3. Found: C, 70.6; H, 10.5.

Dimethyl 2,7-Dihydro-3-pyrrolidinyl-4,5-oxepindicarboxylate.—Dimethyl acetylenedicarboxylate (15.2 g., 0.107 mole) was added portionwise to 1-(2,5-dihydro-3-furyl)pyrrolidine (14.9 g., 0.107 mole) in 75 ml. of ether with cooling to maintain the temperature at 25–30°. The mixture was allowed to stand overnight and the ether was removed on a steam bath. After addition of more ether and chilling, 5 g. (17%) of dimethyl 2,7-dihydro-3-pyrrolidinyl-4,5-oxepindicarboxylate was obtained. A sample for analysis, recrystallized from a benzene–hexane mixture, melted at 162–163°.

Anal. Calcd. for $C_{14}H_{19}NO_5$: C, 59.8; H, 6.6. Found: C, 59.9; H, 6.7.

Ketenes I. Cycloaddition of Ketene and Dialkylketenes to Enamines

ROBERT H. HASEK AND JAMES C. MARTIN

Research Laboratories, Tennessee Eastman Company, Division of Eastman Kodak Company, Kingsport, Tennessee

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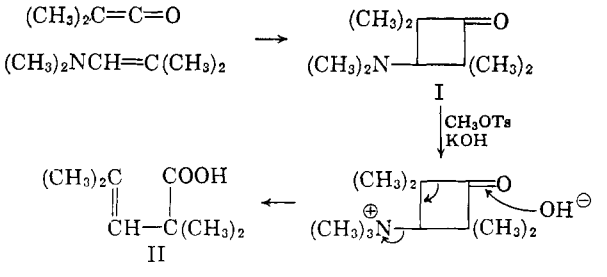
The cycloaddition of dialkylketenes to enamines derived from secondary aldehydes takes place readily to form 3-dialkylamino-2,2,4,4-tetraalkylcyclobutanones. When the cycloaddition involves enamines containing a β-hydrogen and/or ketene, the enolizable cyclobutanones are unstable and are isomerized thermally to dialkylaminovinyl ketones. A number of cyclobutanones and their rearrangement and reduction products are described.

Ketenes add to a number of olefinic compounds to form cyclobutane derivatives.[1] Ketene[2] and diphenylketene[3] have been studied more than any other member of the series; cycloadditions of dialkylketenes with olefinic compounds have been reported only for dimethylketene with ethyl vinyl ether[4] and cyclopentadiene.[4,5] In a study of the scope of the cycloaddition reactions of dialkylketenes, we observed the particularly facile addition of dimethylketene to enamines. This reaction, noted independently by other workers,[6,7] was reported briefly in a Communication.[8] The present paper is a more detailed account of our work.

Stable cyclobutanone derivatives were obtained by addition of dialkylketenes to enamines lacking any β-hydrogen atoms. Dimethylketene and N,N-dimethylisobutenylamine, mixed in isopropyl acetate at room temperature, reacted to give 3-dimethylamino-2,2,4,4-tetramethylcyclobutanone (I) in 64% yield. The structure of I was consistent with infrared and n.m.r. spectral data, and was confirmed by quaternization with methyl tosylate and alkaline degradation to 2,2,4-trimethyl-3-pentenoic acid (II).

The cycloaddition reaction was carried out with several dialkylketenes and a variety of enamines derived



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