Procedure for the Hydrolysis of Adducts 15–20.—Each of the adducts (1.00 g.) was dissolved in 5.0 ml. of methanol and 1.0 ml. of concentrated hydrochloric acid and heated on a steam bath to reflux. Water (2–5 ml.) was added and the solution was heated on a steam bath for 10 min. The solution was allowed to cool and precipitation was induced by scratching the wall of the flask. The product was collected by suction filtration, washed thoroughly with 2:1 aqueous methanol, and recrystallized from aqueous methanol to obtain the analytically pure hydrolysis product.

2,3-Dicarbomethoxy-3-cycloheptenone (**21**).—This product was obtained in 89–92% yield from the hydrolysis of **15** or **16**, m.p. 63.5–64.0°; $\lambda_{max}^{CH_3OH}$ 260 mμ (ε 8030); ν^{CHCl_3} 1712 (s), 1650 (s), 1600 (s) cm.$^{-1}$.

Anal. Calcd. for $C_{11}H_{14}O_5$: C, 58.37; H, 6.24. Found: C, 58.66; H, 6.24.

2,3-Dicarbomethoxy-3-cyclooctenone (**22**).—This product was obtained in 86% yield from the hydrolysis of **17**, m.p. 75.4–76.3°; $\lambda_{max}^{CH_3OH}$ 256 mμ (ε 9880); ν^{CHCl_3} 1720 (s), 1662 (s), 1653 (s), 1618 (s) cm.$^{-1}$.

Anal. Calcd. for $C_{12}H_{16}O_5$: C, 60.00; H, 6.70. Found: C, 59.83; H, 6.53.

5,6-Benzo-2,3-dicarbomethoxy-3,5-cycloheptadienone (**23**).—This product was obtained in 90% yield from the hydrolysis of **19** or **20**, m.p. 103–104°; $\lambda_{max}^{CH_3OH}$ 244 mμ (ε 18,400); 287 mμ (ε 7610); ν^{CHCl_3} 1715 (s), 1654 (s), 1595 (s), 1490 (w) cm.$^{-1}$.

Anal. Calcd. for $C_{15}H_{14}O_5$: C, 65.69; H, 5.11. Found: C, 65.57; H, 5.17.

5,6-Benzo-2,3-dicarbomethoxy-2,5-cycloöctadienone (**24**).—This product was obtained in 87% yield from the hydrolysis of **18**, m.p. 103–104°; $\lambda_{max}^{CH_3OH}$ 266 mμ (ε 9420); ν^{CHCl_3} 1740 (s), 1710 (s), 1655 (s), 1615 (m), 1493 (s) cm.$^{-1}$.

Anal. Calcd. for $C_{16}H_{16}O_5$: C, 66.67; H, 5.55. Found: C, 66.91; H, 5.63.

2,3-Dicarbomethoxycycloheptanone (**25**).—A solution of **21** (9.60 g., 43 mmoles) in 10 ml. of glacial acetic acid was stirred hydrogen at atmospheric pressure and room temperature with prereduced catalyst prepared from 96 mg. of platinum oxide. In 4 hr. 43 mmoles of hydrogen had been absorbed. The solvent was removed by distillation and the residue was distilled to obtain 3.8 g. (40%) of **25**, b.p. 134–138° at 0.65 mm., $n^{26}D$ 1.4785; ν^{CHCl_3} 1730 (s), 1705 (s), 1640 (w), 1610 (w) cm.$^{-1}$.

Anal. Calcd. for $C_{11}H_{16}O_5$: C, 57.90; H, 7.02. Found: C, 57.72; H, 6.96.

3-Carboxycycloheptanone (**26**).—(a) **Preparation from 25.**—Compound **25** (3.98 g., 0.0174 mole) was added to 10 ml. of a solution containing 29% potassium hydroxide in methanol and the mixture was refluxed for 6 hr. The methanol was evaporated and the residue was extracted once with chloroform. Acidification of the residue with hydrochloric acid effected spontaneous decarboxylation. The acid solution was extracted with three 20-ml. portions of ether. The ether extracts were dried over anhydrous sodium sulfate. The ether was removed under reduced pressure and the residue distilled at 200° at 0.65 mm. Crystallization was induced from a 1:1 mixture of benzene–cyclohexane to give 1.66 g. (61%) of a colorless crystalling product, m.p. 40–41°; ν^{CHCl_3} 2920 (s), 1700 (s), 1550 (m) cm.$^{-1}$.

Preparation from Cycloheptenone.—A solution of 2- and 3-cycloheptenone[13] (4.25 g., 0.0385 mole) and 2 ml. of glacial acetic acid in 27 ml. of 95% ethanol was cooled in an ice bath with stirring while a solution of 7.15 g. of potassium cyanide in 13 ml. of water was added over a period of 35 min. The mixture was stirred in an ice bath for 8 hr. after the addition was complete. A saturated sodium chloride solution (75 ml.) was added and the product was extracted with three 50-ml. portions of ether. The combined extracts were washed with 75 ml. of saturated sodium chloride solution, dried over sodium sulfate, and the ether removed under reduced pressure. Distillation gave 1.9 g. (38%) of nitrile, b.p. 131–134° at 10 mm. Hydrolysis of 0.765 g. (5.6 mmoles) of nitrile was effected by refluxing in 10 ml. of 20% methanolic potassium hydroxide for 12 hr. The reaction mixture was extracted with chloroform, acidified with hydrochloric acid, extracted with three 10-ml. portions of ether, and dried over anhydrous sodium sulfate. The ether was evaporated and the residue distilled in a Hickman still to obtain 0.250 g. (28%) of 3-carboxycycloheptanone, the infrared spectrum of which was identical to the sample prepared by the hydrolysis and monodecarboxylation of **25**.

(13) R. Belcher, W. Hoyle, and T. West, *J. Chem. Soc.*, 2743 (1958).

Enamine Chemistry. I. Reactions with Nonactivated Terminal Acetylenic Compounds[1]

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The addition, preferably catalyzed by copper(I) chloride, of a variety of nonactivated terminal acetylenic compounds to the double bonds of enamines derived from isobutyraldehyde and butyraldehyde is described.

The reaction between acetylenic compounds and secondary amines is well known, and it has been postulated that this reaction proceeds *via* an enamine intermediate (I)[2] which then reacts with more of the acetylenic compound to give the adduct (II).

$$\mathrm{RC{\equiv}CH + HNR_2 \longrightarrow \underset{\textstyle I}{[RCH{=}CHNR_2]}}$$

$$\mathrm{[RCH{=}CHNR_2] + RC{\equiv}CH \longrightarrow RC{\equiv}C\underset{\underset{\textstyle II}{NR_2}}{\underset{|}{C}}HCH_2R}$$

We have found that nonactivated terminal acetylenic compounds (those with no electron-withdrawing group adjacent to the acetylenic linkage) do indeed react with enamines to give products (III) arising from

$$\mathrm{RC{\equiv}CH + \underset{NR_2}{\underset{|}{H}}C{=}CR_2 \longrightarrow RC{\equiv}C\underset{\underset{\textstyle III}{NR_2}}{\underset{|}{C}}HCHR_2}$$

the addition of the acetylenic compounds to the double bonds of the enamines.

To effect the uncatalyzed addition of acetylenic compounds to enamines, prolonged heating was necessary. However, with the addition of a catalytic amount of copper(I) chloride, the reaction time was greatly decreased and, in some cases, the reaction proceeded exothermically and spontaneously.

The structure of the adduct (IV) from ethynylbenzene and N,N-dimethylisobutenylamine was based on its conversion to 4-methyl-2-pentenophenone (V).

The structures of the other adducts were assigned by analogy.

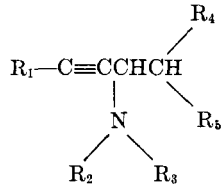
Table I is a list of products obtained during this investigation from the reaction of various enamines with terminal acetylenic compounds.

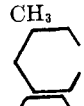
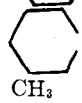
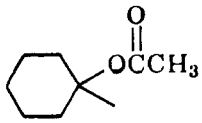
(1) A portion of the material in this paper was presented at the Enamine Chemistry Symposium, 140th National Meeting of the American Chemical Society, Chicago, Ill., September, 1961.

(2) W. Reppe, *Ann. Chem.*, **596**, 12 (1955); J. D. Rose and R. A. Gale, *J. Chem. Soc.*, **792** (1949); C. W. Kruse and R. F. Kleinschmidt, *J. Am. Chem. Soc.*, **83**, 216 (1961).

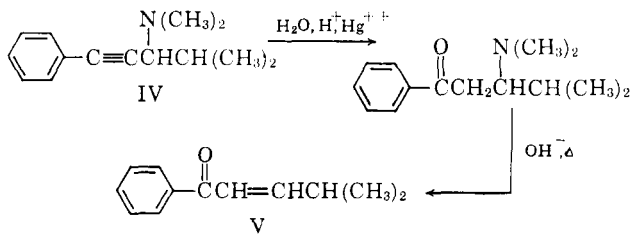
TABLE I

ADDITION PRODUCTS OF ENAMINES AND TERMINAL ACETYLENIC COMPOUNDS



Structure	R_1	R_2	R_3	R_4	R_5	B.p., °C. (mm.)	$n^{20}D$	Yield, %	Method[a]	Anal. Calcd.	Anal. Found
VI	H	CH_3	CH_3	CH_3	CH_3	68–69 (100–109)	...	21	A	N, 11.2	N, 11.4
VII	$(CH_3)_2CHCH(N(CH_3)_2)$—	CH_3	CH_3	CH_3	CH_3	106 (9)	1.4575	47	A	N, 12.5	N, 12.5
VIII	C_6H_5	$R_2 + R_3$ = 		CH_3	CH_3	118–124 (1.5)	1.5393	64	B	C, 84.6 H, 9.6	C, 84.3 H, 9.3
	C_4H_9	CH_3	CH_3	CH_3	CH_3	45–50 (0.5)	1.4453	76	C	C, 79.5 H, 12.8	C, 79.8 H, 12.7
	C_4H_9	$R_2 + R_3$ = 		CH_3	CH_3	67–77 (0.5–1.5)	1.4688	72	C	C, 81.4 H, 12.3	C, 81.7 H, 12.0
	C_4H_9	$R_2 + R_3$ = 		H	C_2H_5	75–77 (0.5)	1.4708	77	C	C, 81.4 H, 12.3	C, 81.2 H, 11.9
	C_6H_5	CH_3	CH_3	CH_3	CH_3	70–75 (*ca.* 0.5)	1.5258	86	C	C, 83.5 H, 9.5	C, 83.8 H 9.7
	CH_3COOCH_2—	CH_3	CH_3	CH_3	CH_3	57–60 (*ca.* 0.5)	1.4523	79	C	C, 67.0 H, 9.7	C, 67.3 H, 9.9
	$CH_3COOC(CH_3)_2$—	CH_3	CH_3	CH_3	CH_3	45–53 (0.5–1)	1.4451	75	C	C, 69.3 H, 10.3	C, 69.4 H, 10.3
IX	$CH_3COOC(CH_3)(CH_2CH_3)$—	CH_3	CH_3	CH_3	CH_3	60–65 (*ca.* 0.5)	1.4477	89	C	C, 70.3 H, 10.5	C, 70.2 H, 10.6
	$CH_3COOC(CH_3)(CH_2CH(CH_3)_2)$—	CH_3	CH_3	CH_3	CH_3	68–74 (*ca.* 0.5)	1.4498	88	C	C, 71.9 H, 10.9	C, 72.3 H, 11.2
		CH_3	CH_3	CH_3	CH_3	83–89 (*ca.* 0.5)	1.4714	89	C	C, 72.4 H, 10.3	C, 72.8 H, 10.3
X	$HOC(CH_3)_2$—	CH_3	CH_3	CH_3	CH_3	58–67 (1–1.5)	1.4570	76	D	C, 72.1 H, 11.6	C, 71.9 H, 11.3

[a] For a detailed example of each method, see Experimental.



Experimental[3]

Materials.—N,N-Dimethylisobutylamine was prepared as previously described.[4] 1-Isobutenylpiperidine was prepared as described by Benzing[5] and 1-butenylpiperidine was prepared by the method of Mannich.[6]

The following examples illustrate the methods of preparation used in this investigation.

1-Isopropyl-N,N-dimethyl-2-propynylamine (VI) and N,N,N′,N′,2,7-Hexamethyl-4-octyne-3,6-diamine (VII). Method A.—A mixture of N,N-dimethylisobutenylamine (99 g., 1 mole), copper(I) chloride (0.5 g.), and benzene (125 ml.) was heated to 100° in an autoclave under 7 atm. of nitrogen pressure. Acetylene was added until the pressure was 14 atm. As the reaction proceeded, the pressure dropped to 7 atm. and more acetylene was added until the pressure was again 14 atm. This was repeated until the pressure remained constant. After the mixture was cooled to room temperature, the catalyst was removed by

(3) Boiling points and melting points are uncorrected. Melting points were determined using a Fisher-Johns melting point apparatus.

(4) K. C. Brannock and R. D. Burpitt, *J. Org. Chem.*, **26**, 3576 (1961).

(5) E. Benzing, *Angew. Chem.*, **71**, 521 (1959).

(6) C. Mannich and H. Davidsen, *Ber.*, **69**, 2106 (1936).

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]

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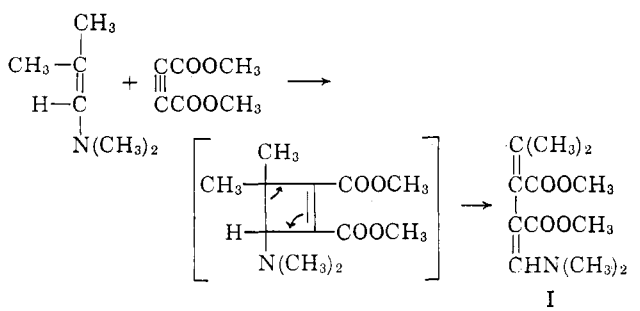
The reaction of a variety of enamines with acetylenedicarboxylates was studied. The reaction products are those derived from the cyclobutene rearrangement of cycloaddition adducts initially formed. In the case of enamines derived from alicyclic ketones, the net result of the reaction is a ring enlargement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

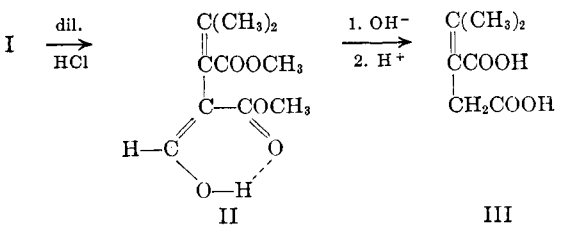
The cycloaddition of electrophilic olefins to enamines, leading to cyclobutanes, has been reported.[2] The reactions of a variety of enamines derived from acyclic aldehydes and ketones and cyclic ketones with both acetylenedicarboxylates and propiolates have now been investigated. The reactions involving 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).