The Reaction of Enamines of Cyclic Ketones with Dimethyl Acetylenedicarboxylate[1]

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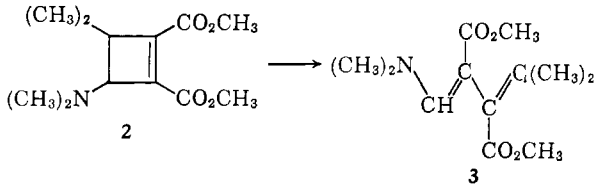
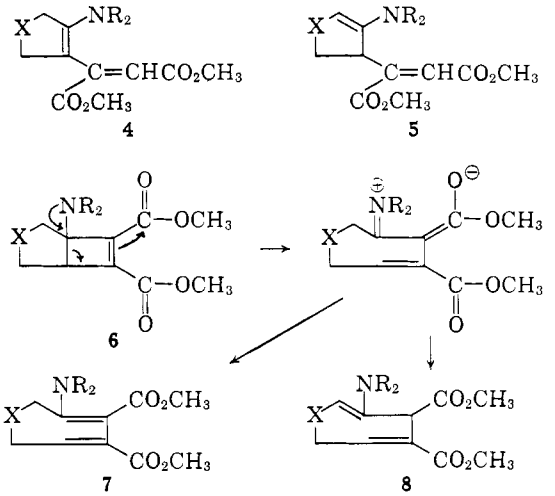
Enamines of cyclic ketones react with dimethyl acetylenedicarboxylate to yield an intermediate cyclobutene adduct which undergoes rearrangement under the conditions of the reaction with expansion of the carbocyclic ring by two carbon atoms. Hydrolysis of these products yields the corresponding keto dicarboxylic esters.

The reaction of enamines of cyclic ketones with electrophilic olefins produces an adduct which, on hydrolysis, affords the substituted ketone corresponding to the Michael addition product of the ketone and the electrophilic olefin.[2] 1-(N-Morpholino)cyclohexene and methyl acrylate, for example, produce an adduct which is converted to methyl 3-(2-oxocyclohexyl)propionate by hydrolysis in dilute acid. Brannock[3] has shown, however, that enamines derived from aldehydes react with electrophilic olefins by a cycloaddition mechanism to produce the corresponding cyclobutane derivatives. Dimethyl maleate and N,N-dimethylisobutenylamine, for example, react to form diethyl 4 - dimethylamino - 3,3 - dimethyl - 1,2 - cyclobutanedicarboxylate. The cycloaddition reaction of enamines derived from aldehydes has also been shown to occur with ketenes,[4] and with aliphatic sulfonyl chlorides[5] or acid chlorides[6] in the presence of tertiary amine. Enamines derived from cyclic ketones similarly undergo cycloaddition reactions with benzyne,[7] ketene,[6] and with aliphatic sulfonyl halides in the presence of tertiary amine.[5a] Dimethyl acetylenedicarboxylate (1) adds to N,N-dimethylisobutenylamine to produce the intermediate adduct 2 which undergoes ring opening to 3.[3a]



2 3

In view of these results the reaction of 1 with enamines derived from cyclic ketones appeared of interest since the ring opening of the cycloaddition product, should the reaction proceed in this manner, would lead to a novel method for the expansion of a carbocyclic ring by two carbon atoms. The enamines (9–14) listed in Table I reacted with 1 in toluene to produce a 1:1 adduct in all cases which were studied. The possible structures considered for these adducts were as follows: either of the tautomeric Michael-type addition products (4 and 5), the cycloaddition product (6), and either of the dienamine structures (7 and 8) resulting from ring opening of 6.[8] The product from



4 5 6 7 8

enamines 9–13 are assigned structures 15–19 corresponding to structure 7, whereas the product from enamine 14 is assigned structure 20 corresponding to the rearranged structure 8. The reaction appears, therefore, to yield the cyclobutene adduct (6) which is unstable to the conditions of the reaction and undergoes rearrangement to 7 or 8. The pyrrolidine enamines gave substantially better yields of adduct than did the morpholine enamines in the two cases where comparisons were made. The structure of 15 is established as follows: the n.m.r. spectrum shows absorption for one vinyl proton at 7.00 p.p.m. (see Table I) as a triplet (J = 7 c.p.s.). This clearly eliminates a Michael-type addition product (4 or 5) in which the long-range coupling of such a proton on the β-carbon of an α,β-unsaturated carbomethoxy system would be less than 3 c.p.s. and a cycloaddition product (6) in which there would be no vinyl proton absorption. Furthermore, the absence of any vinyl proton absorption at higher field eliminates structures of the type 5 and 8 in which the vinyl proton on the β-carbon of the enamine system would show absorption at 4–5 p.p.m. Structure 15 is in agreement with this vinyl absorption. Similar arguments may be applied to the products assigned structures 16–19 (see Table I). The product from 14, however, must be assigned structure 20 rather than the alternative con-

(1) This research has been supported by National Science Foundation, grant no. G-21443.

(2) (a) G. Stork and H. K. Landesman, *J. Am. Chem. Soc.*, **78**, 5128 (1956); (b) G. Stork, Abstracts of the 16th National Organic Symposium of the American Chemical Society, Seattle, Wash., June, 1959, p. 44; (c) L. Birkofer and C. Barnikel, *Chem. Ber.*, **91**, 1996 (1958).

(3) (a) K. C. Brannock, Enamine Symposium, 140th National Meeting of the American Chemical Society, Chicago, Ill., September, 1961; (b) K. C. Brannock, A. Bell, R. D. Burpitt, and C. A. Kelly, *J. Org. Chem.*, **26**, 625 (1961).

(4) (a) G. Opitz, H. Adolph, M. Kleemann, and F. Zimmermann, *Angew. Chem.*, **73**, 654 (1961); (b) R. H. Hasek and J. C. Martin, *J. Org. Chem.*, **26**, 4775 (1961); (c) G. A. Berchtold, G. R. Harvey, and G. E. Wilson, Jr., *ibid.*, **26**, 4776 (1961).

(5) (a) G. Stork and I. J. Borowitz, *J. Am. Chem. Soc.*, **84**, 313 (1962); (b) G. Opitz and H. Adolph, *Angew. Chem.*, **74**, 77 (1962); (c) G. Opitz and H. Adolph, *Angew. Chem., Intern. Ed.*, **1**, 113 (1962).

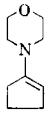
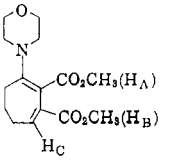
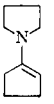
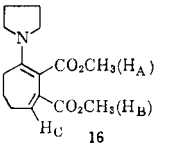
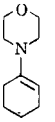
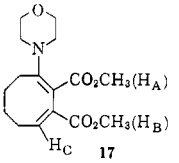
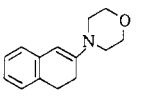
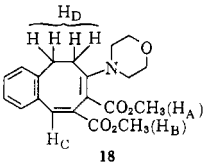
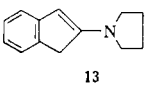
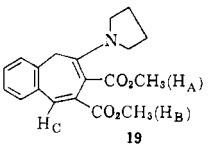
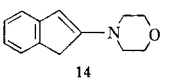
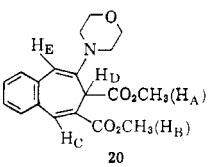
(6) (a) G. Opitz, M. Kleemann, and F. Zimmermann, *Angew. Chem.*, **74**, 32 (1962); (b) G. Opitz, M. Kleemann, and F. Zimmermann, *Angew. Chem., Intern. Ed.*, **1**, 51 (1962).

(7) M. E. Kuehne, *J. Am. Chem. Soc.*, **84**, 837 (1962).

(8) Whether isomers 5 and 8 would be formed directly or would be formed by tautomerism of 4 and 7, respectively, cannot be determined. That the position of the enamine double bond is sensitive to steric effects in β-substituted enamines derived from cyclic ketones has been demonstrated previously; see, for example, (a) G. A. Berchtold, *J. Org. Chem.*, **26**, 3043 (1961), (b) ref. 2b.

TABLE I

REARRANGED CYCLOADDITION PRODUCTS AND NUCLEAR MAGNETIC RESONANCE SPECTRAL DATA

Enamine	Rearrangement product	N.m.r. data: Proton	Chemical shift, p.p.m.	J, c.p.s.
 9	 15	H_A	3.63[a]	
		H_B	3.73[a]	
		H_C	7.00[b]	7
 10	 16	H_A	3.58[a]	
		H_B	3.70[a]	
		H_C	6.88[b]	7
 11	 17	H_A	3.62[a]	
		H_B	3.70[a]	
		H_C	6.68[c]	7.5 and 9
 12	 18	H_A	3.57[a]	
		H_B	3.80[a]	
		H_C	7.65[a]	
		H_D	2.98[d]	
		Ar–H	7.17[a]	
 13	 19	H_A	3.65[a]	
		H_B	3.85[a]	
		H_C	7.58[a]	
		Ar–H	7.1–7.5[e]	
 14	 20	H_A	3.30[a]	
		H_B	3.88[a]	
		H_C	8.02[d]	
		H_D	5.22[d]	
		H_E	5.88[f]	2
		Ar–H	7.0–7.6[e]	

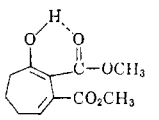
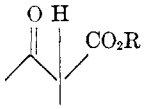
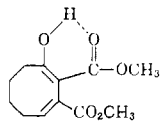
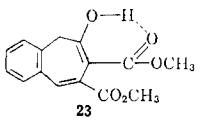
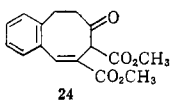
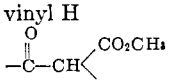
[a] Singlet. [b] Triplet. [c] Quadruplet. [d] Broad singlet. [e] Complex multiplet. [f] Doublet.

jugated structure corresponding to **19** on the basis of the resonance absorption of H_D and H_E at 5.22 and 5.88 p.p.m., respectively, with $J_{H_D - H_E} \simeq 2$ c.p.s. Structure **19** shows no absorption in this region but does show unresolved absorption in the region of 3–4.5 p.p.m. due to the methylene group of the cycloheptatriene ring and the methylene groups on the nitrogen atom of the pyrrolidine ring. In further agreement with this structure the methyl resonance of the carbomethoxy group on the saturated carbon atom of **20** has shifted to higher field as a result of shielding due to the diamagnetic field from the interatomic current of the benzene ring. This shielding effect of the aromatic nucleus allows assignment of the proton absorption of the methoxy groups of **19** and **20** as indicated in Table I. The infrared and ultraviolet spectra of these adducts are also in agreement with the proposed structures and are listed in the Experimental section.

Mild acid hydrolysis of the enamine functionality of adducts **15–20** produced the corresponding keto dicarboxylic esters **21–24** listed in Table II along with the n.m.r. spectral data for these products. The n.m.r. spectrum of **21** shows the enolic hydrogen absorption at 12.54 p.p.m. and the tertiary proton absorption of the keto form at 5.73 p.p.m. Integration of these two absorptions indicates that **21** exists in the enol form to the extent of approximately 60–70% under the conditions in which the spectrum was recorded. The spectrum of **22** shows no indication of the keto form, the enolic hydrogen absorption occurring at 12.58 p.p.m. Product **23** likewise appears to exist entirely as the enolic tautomer, the enolic hydroxyl absorption ocurring at 12.55 p.p.m. The spectrum of **24**, however, indicates the product exists entirely in the keto form, since the resonance absorption of the tertiary proton alpha to the keto group, a carbomethoxy group, and the olefinic bond appears at 4.78 p.p.m. and is split into a doublet ($J \simeq 2$ c.p.s.) by long-range coupling with the vinyl proton which absorbs at 7.95 p.p.m. The rest of the n.m.r. spectral data listed in Table II further substantiate the proposed structures. It should be noted that the hydrolysis product from the Michael-type addition products **4** and **5** would give no β-dicarbonyl system and, therefore, would not show the low field

TABLE II

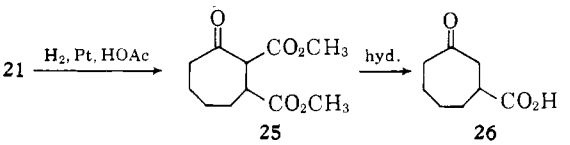
HYDROLYSIS PRODUCTS AND NUCLEAR MAGNETIC RESONANCE SPECTRAL DATA

Adduct hydrolyzed	Hydrolysis product	N.m.r. data: Proton	Chemical shift, p.p.m.	J, c.p.s.
15 or 16	 21	enolic H	12.54[a]	
		vinyl H	7.05[b]	8
		$2CH_3$—O—	3.73[a]	
			5.73[c]	
17	 22	enolic H	12.58[a]	
		vinyl H	6.90[d]	7 and 9
		$2CH_3$—O—	3.72[a]	
19 or 20	 23	enolic H	12.55[a]	
		vinyl H	7.78[a]	
		$2CH_3$—O—	3.70,[a] 3.83[a]	
		—CH_2—	3.33[a]	
		Ar—H	7.30[e]	
18	 24	vinyl H	7.95[f]	1
			4.78[f]	1
		$2CH_3$—O—	3.70,[a] 3.87[a]	
		Ar—CH_2—CH_2—CO—	2.6–3.4[e]	
		Ar—H	7.27[a]	

[a] Singlet. [b] Triplet. [c] Broad singlet. [d] Quadruplet. [e] Complex multiplet. [f] Doublet.

resonance absorption for the hydrogen-bonded enolic proton in the region of 12.5 p.p.m. The infrared and ultraviolet spectra of these hydrolysis products further support the assigned structures and are listed in the Experimental section. The hydrolysis products **21**–**24** all gave a deep violet color with ferric chloride in aqueous ethanol.

To establish further the structures of these reaction products, **21** was hydrogenated over platinum in acetic acid to **25** which was hydrolyzedand monode carboxylated to 3-carboxycycloheptanone (**26**) the infrared spectrum of which was identical to that of a sample prepared by Michael addition of hydrogen cyanide to 2-cycloheptenone and hydrolysis of the resulting 3-cyanocycloheptanone.



Experimental[9]

General Procedure for the Reaction of 1 with Enamines.—A solution of the enamine in anhydrous toluene under a nitrogen atmosphere was cooled to 0–5° in an ice bath. Compound **1** was added slowly with stirring at such a rate that the temperature never rose above 50°. When all of **1** had been added, the mixture was heated under gentle reflux for 12 hr. The mixture was cooled and the product was precipitated by the addition of excess ethyl ether. The product was then recrystallized from acetone to constant melting point.

1-(N-Morpholino)-2,3-dicarbomethoxy-1,3-cycloheptadiene (15).—This product was obtained in 48% yield from 16.2 g. (0.0774 mole) of **1** and 11.0 g. (0.0774 mole) of **9**[2c] in 40 ml. of toluene, m.p. 167–168°; $\lambda_{max}^{CH_3OH}$ 334 mμ (ε 9760); ν^{CHCl_3} 1715–1680 (s), 1610 (m), and 1540 (s) cm.$^{-1}$.

Anal. Calcd. for $C_{15}H_{21}NO_5$: C, 60.98; H, 7.17; N, 4.75. Found: C, 60.89; H, 6.94; N, 4.65.

1-(N-Pyrrolidino)-2,3-dicarbomethoxy-1,3-cycloheptadiene (16).—This product was obtained in 71% yield from 10.7 g. (0.0835 mole) of **10**[10] and 11.8 g. (0.0835 mole) of **1** in 50 ml. of toluene, m.p. 145–146°; $\lambda_{max}^{CH_3OH}$ 304 mμ (ε 11,130), 324 mμ (ε 11,030); ν^{CHCl_3} 1171 (s), 1675 (s), 1605 (m), and 1532 (s) cm.$^{-1}$.

Anal. Calcd. for $C_{15}H_{21}NO_4$: C, 64.52; H, 7.53; N, 5.02. Found: C, 64.33; H, 7.33; N, 4.91.

1-(N-Morpholino)-2,3-dicarbomethoxy-1,3-cyclooctadiene (17).—This product was obtained in 42% yield from 4.25 g. (0.030 mole) of **1** and 5.00 g. (0.030 mole) of **11**[11] in 10 ml. of toluene, m.p. 210–211°; $\lambda_{max}^{CH_3OH}$ 327 mμ (ε 10,940); ν^{CHCl_3} 1720–1680 (s), 1618 (m), and 1540 (s) cm.$^{-1}$.

Anal. Calcd. for $C_{16}H_{23}NO_5$: C, 62.11; H, 7.61; N, 4.54. Found: C, 62.55; H, 7.50; N, 4.53.

1,2-Benzo-4,5-dicarbomethoxy-6-(N-morpholino)-1,3,5-cyclooctatriene (18).—This product was obtained in 30% yield from 14.2 g. (0.0660 mole) of **12** and 9.40 g. (0.0060 mole) of **1** in 20 ml. of toluene as yellow crystals, m.p. 133–134°; $\lambda_{max}^{CH_3OH}$ 256 mμ (ε 8850) 312 mμ (ε 7640); ν^{CHCl_3} 1706–1690 (s), 1616 (m), 1598 (w), 1545 (s), and 1495 (w) cm.$^{-1}$.

Anal. Calcd. for $C_{20}H_{23}NO_5$: C, 67.22; H, 6.41; N, 3.92. Found: C, 67.01; H, 6.35; N, 3.80.

1,2-Benzo-4,5-dicarbomethoxy-6-(N-morpholino)-1,3,5-cycloheptatriene (19).—This product was obtained in 78% yield from 34.0 g. (0.183 mole) of **13**[12] and 26.0 g. (0.183 mole) of **1** in 50 ml. of toluene as yellow crystals, m.p. 159–160°; $\lambda_{max}^{CH_3OH}$ 255 mμ (ε 18,530), 287 mμ (ε 8460), 318 mμ (ε 9490), and 362 mμ (ε 7840); ν^{CHCl_3} 1710–1675 (s), 1588 (w), 1560 (m), 1530 (s), and 1485 (m) cm.$^{-1}$.

Anal. Calcd. for $C_{19}H_{21}NO_5$: C, 69.72; H, 6.42; N, 4.28. Found: C, 69.93; H, 6.30; N, 4.45.

3,4-Benzo-6,7-dicarbomethoxy-1-(N-morpholino)-1,3,5-cycloheptatriene (20).—This product was obtained in 30% yield from 8.81 g. (0.0437 mole) of **14**[12] and 6.70 g. (0.0437 mole) of **1** in 20 ml. of toluene as yellow crystals, m.p. 170–171°; $\lambda_{max}^{CH_3OH}$ 265 mμ (ε 41,150), 293 mμ (ε 9620), and 375 mμ (ε 2520); ν^{CHCl_3} 1730–1695 (s), 1635 (s), 1613 (s), 1545 (m), and 1483 (m) cm.$^{-1}$.

Anal. Calcd. for $C_{19}H_{21}NO_5$: C, 66.46; H, 6.12; N, 4.08. Found: C, 66.34; H, 6.18; N, 3.95.

(9) Melting points are corrected and boiling points are uncorrected.

(10) E. Bergmann and R. Ikan, *J. Am. Chem. Soc.*, **78**, 1482 (1956).

(11) S. Hünig, E. Benzing, and E. Lücke, *Chem. Ber.*, **90**, 2833 (1957).

(12) A. T. Blomquist and E. Moriconi, *J. Org. Chem.*, **26**, 3751 (1961).

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., $n^{25}D$ 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).

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

$$[RCH{=}CHNR_2] + RC{\equiv}CH \longrightarrow \underset{\text{II}}{RC{\equiv}C\underset{\displaystyle NR_2}{\underset{|}{C}H}CH_2R}$$

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

$$RC{\equiv}CH + \underset{\displaystyle NR_2}{\underset{|}{H}C}{=}CR_2 \longrightarrow \underset{\text{III}}{RC{\equiv}C\underset{\displaystyle NR_2}{\underset{|}{C}H}CHR_2}$$

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).