ml. of absolute ethanol. The autoclave was then shaken under 1,000 lb. of hydrogen pressure at 100° for 1 hr.

After filtration, the solution was concentrated *in vacuo* and the oily residue taken up in ether and separated into basic and neutral fractions. The basic fraction was converted to its hydrochloride salt and recrystallized from ethanol–ether to give 5.8 g. (50%) of analytically pure ethyl α-diphenylmethyl-β-alaninate hydrochloride, m.p. 200–202°; λ_{max}^{KBr} 3.50, 5.80, 6.15, 6.22, 6.29, 6.65, 6.84 μ; λ_{max}^{MeOH} 258 mμ, ε 475.

Anal. Calcd. for $C_{18}H_{21}NO_2 \cdot HCl$: C, 67.59, H, 6.94; N, 4.38. Found: C, 67.89; H, 7.01; N, 4.36.

Acknowledgment.—We wish to thank Dr. George I. Poos who suggested the original problem for helpful discussions, and Mrs. Mary Christie for the spectroscopic data and nitrogen analyses.

Reactions of Acetylenic Esters with Enamines

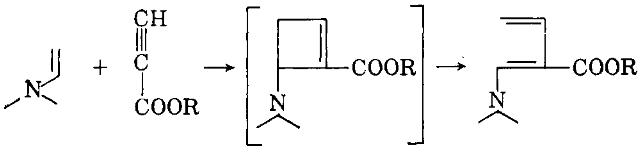
CHARLES F. HUEBNER, L. DORFMAN, MICHAEL M. ROBISON, ELLEN DONOGHUE, WILLIAM G. PIERSON, AND PATRICIA STRACHAN

Research Department, Ciba Pharmaceutical Company, Division of Ciba Corporation, Summit, New Jersey

Received June 10, 1963

Enamines derived from cyclic ketones react with ethyl propiolate or dimethyl acetylenedicarboxylate to produce intermediate cyclobutene adducts which have, in several cases, been isolated. These cyclobutenes on heating, undergo bond rearrangement with expansion of the cyclic ketone ring by two carbon atoms. In at least one case, however, treatment with dilute acid in the cold results in a second reaction course to form a Michael-type adduct of the ester and cyclic ketone. Reactions of dimethyl acetylenedicarboxylate with enamines derived from β-diketones and β-keto esters also are described.

Since the introduction by Stork and co-workers[1] in 1954 of a relatively general procedure for the alkylation of carbonyl compounds *via* their enamine derivatives, reactions of the latter with a wide variety of electrophiles have been studied by various investigators.[1] Although alkylations with electrophilic olefins, reported in 1956[2], have been widely studied,[1] little, until recently, has been known about the corresponding reactions of enamines with electrophilic acetylene compounds. The earliest report of such a reaction, in abstract form,[3] indicates that enamines react with conjugated acetylenic esters to produce an intermediate cyclobutene adduct, which rearranges in such a manner as to interpose the two acetylenic carbon atoms between the erstwhile olefinic carbons of the enamine. We had been independently studying this reaction for some time with both cyclic and acyclic[4] enamines when we became aware of the activities of two other groups of investigators in this field. Bose and Minah[5] have reported on reactions of enamines of cyclic ketones with dimethyl acetylenedicarboxylate and with methyl propiolate to yield ring-expanded products by an analogous process, and a pending paper by Berchtold[6] is concerned with the dimethyl acetylenedicarboxylate reaction in similar cases. In spite of some duplication in these investigations, we present our findings on reactions of cyclic enamines here, for they include certain unique results, among these the *isolation of several of the intermediate cyclobutene adducts.* In addition we have found that the cyclobutenes may, at least in certain cases, be converted *either* to the ring-expanded derivatives,[5,6] *or* (on hydrolysis) *to the unsaturated keto esters corresponding to Michael-type additions of acetylenic esters to ketones.* In addition, we report here reactions of acetylenic esters with various acyclic enamines derived from β-diketones or β-keto esters, the courses of which are widely diverse in nature.



The early experiments with ethyl propiolate were carried out by addition of the ester to a dioxane solution of 1-pyrrolidinocyclopentene (**1a**) at ambient temperature, and subsequent heating of the mixture on the steam bath. Removal of solvent allowed isolation of the crystalline 1-pyrrolidino-2-carbethoxy-1,3-cycloheptadiene (**3**). The structure of this substance was indicated by infrared bands at 1661 and 1605 cm.$^{-1}$ (Nujol) representing C=O and C=C absorptions, respectively. In the n.m.r. spectrum[7] the C-3 proton was observed as a doublet at 6.45 δ ($J_{3,4}$ = 10.1) and H-4 as a triplet of a doublet at 5.70 δ ($J_{3,4}$ = 10.1, $J_{4,5,5}$ = 6.4). Chemical confirmation of the structure was obtained in several ways. Mild acid hydrolysis of the enamine group resulted in the formation of the keto–enol mixture (**4**), which was reduced catalytically to the known[8] 2-carbethoxycycloheptanone (**6**). This keto ester was identified by its reaction with phenylhydrazine to yield the solid phenylpyrazolone derivative,[8] and by its hydrolysis and decarboxylation to cycloheptanone, the semicarbazone of which was compared with an authentic sample. The sequence of reactions also was carried out in reversed order, partial hydrogenation preceding the mild hydrolysis to yield the same product.

When, on the other hand, ethyl propiolate and **1a** were allowed to react below room temperature and the

---

[1] *Cf.* G. Stork, A. Brizzolara, H. Landesman, J. Smuszkovicz, and R. Terrell, *J. Am. Chem. Soc.*, **85**, 207 (1963), for a recent survey.

[2] G. Stork and H. Landesman, *ibid.*, **78**, 5128 (1956).

[3] K. C. Brannock, Abstracts of Papers, 140th National Meeting of the American Chemical Society, Chicago, Ill., September, 1961, p. 450.

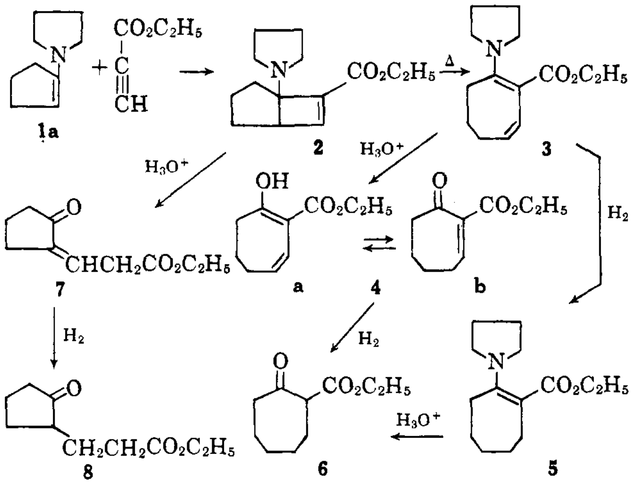
[4] *Cf.* C. F. Huebner and E. Donoghue, *J. Org. Chem.*, **28**, 1732 (1963).

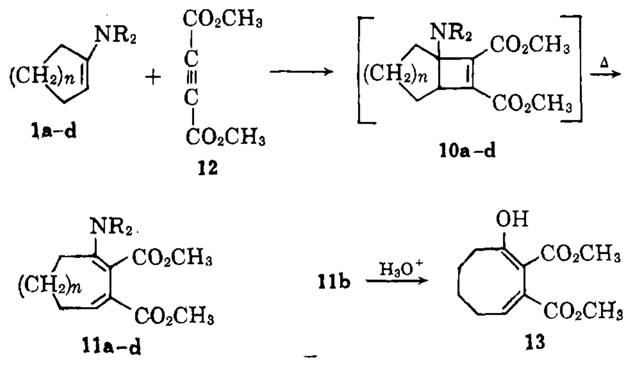
[5] A. K. Bose and G. L. Minah, Metropolitan Regional Meeting of the American Chemical Society, Newark, N. J., January 28, 1963.

[6] G. A. Berchtold and G. F. Uhlig, *J. Org. Chem.*, **28**, 1459 (1963). We wish to thank Dr. Berchtold who, through Dr. F. Greene, made a copy of his paper available to us before publication, on submission of the previous manuscript[4] from this laboratory.

[7] Spectra were obtained with the Varian A-60 spectrometer at 60 Mc./sec. using tetramethylsilane as internal reference. Chemical shifts are quoted in field-independent δ-units (p.p.m.) where δ is defined by the relationship $\delta = 10^6 |H_{ref} - H| / H_{ref}$; coupling constants (*J*) are expressed in c.p.s.

[8] W. Dieckmann, *Ber.*, **55** 2485 (1922).





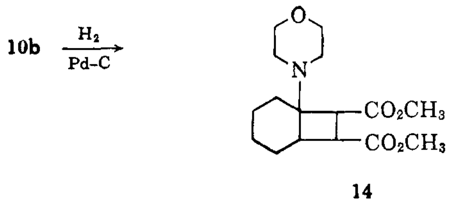
a, $n = 1$, $R_2 = -CH_2CH_2CH_2CH_2-$
b, $n = 2$
c, $n = 3$ } $R_2 = -CH_2CH_2OCH_2CH_2-$
d, $n = 4$

reaction mixture was treated with dilute acetic acid *without heating*, the Michael-type adduct **7** was obtained. Its structure, indicated by infrared absorption bands at 1730 (ester C=O) and 1660 cm.$^{-1}$ (C=C—C=O) and by a single vinyl proton signal appearing in the n.m.r. spectrum as a triplet at 6.37 δ ($J = 7$), was further established by partial hydrogenation to ethyl β-(2-oxocyclopentyl)propionate (**8**). The identity of this reduction product with the substance as prepared unequivocally by reaction of **1a** with ethyl acrylate[1] was demonstrated by comparison of spectra and of solid derivatives.

Isolation of 5-pyrrolidino-6-carbethoxybicyclo[3.2.0]-hept-6-ene (**2**) was effected by reaction of **1a** and the acetylenic ester in absolute ether at about 15°. Removal of the solvent at low temperature yielded essentially pure **2** as an oil. The n.m.r. spectrum of the compound in deuteriobenzene solution showed one vinyl proton which appeared as a *singlet* ($J < 1$) 41 c.p.s. upfield from the benzene proton (impurity in C_6D_6). Such a signal is to be expected for the vinyl proton in **2**, since its dihedral angle with the bridgehead proton is close to 90°, as seen on examination of models. Heating the deuteriobenzene solution resulted in a change of the spectrum and the appearance of signals characteristic of **3**. Treatment of the oily cyclobutene **2** with dilute acetic acid, on the other hand, resulted in the formation of the cyclopentanone **7**, isolated and characterized by the usual criteria. In this connection it is of interest that treatment of **2** with dilute *hydrochloric* acid under similar conditions did not effect this rearrangement and hydrolysis; little or no nonbasic material could be extracted from the acidic medium. Although it was not possible to crystallize **2** as such, or to prepare a solid acid salt as a derivative, the substance was readily converted to a crystalline, stable methiodide **9**. The n.m.r. spectrum of this derivative again showed the single vinyl proton as a single (δ = 7.35) and the other spectral data were consistent with the proposed structure.

Reactions of enamines (**1a–d**) were also carried out with dimethyl acetylenedicarboxylate (**12**)[9] to yield, after heating, the corresponding ring expansion products **11**. One such material (**11b**) was hydrolyzed by mild acid to produce the corresponding enol **13**.

In another experiment, the acetylenic ester and 1-morpholinocyclohexene (**1b**) were allowed to react in deuteriobenzene below 25°. The n.m.r. spectrum of the solution, determined 30 min. after mixing, showed the complete absence of vinyl protons, a finding consistent only with structure **10b**. Refluxing an aliquot of the solution produced **11b**, isolated, in this case, in 21% yield. Another portion of the solution was evaporated at low temperature to produce **10b** as an oil. Hydrogenation resulted in the uptake of one mole of hydrogen to yield the corresponding cyclobutane **14**, isolated as the hydrochloride. The cyclobutene **10b** is apparently stable indefinitely in benzene, but in diglyme solution even at room temperature, conversion to **11b** takes place in good yield within several days.



14

Reactions of dimethyl acetylenedicarboxylate with enamines derived from β-diketones and β-keto esters were also studied. It was not necessarily expected that these reaction courses would be analogous to those described, since the more complex enamines, being vinylogous amides, differ considerably from the simpler vinylamines in their reactivities.[10] In the event, the reactions were found to be diverse and complex in nature, and indeed, the structures of some of the products cannot yet be formulated with complete certainty.

The first of these transformations was found to lead to a new synthesis of the benzene ring under unusually mild conditions.[4] Thus, addition of **12** to 4-pyrrolidinopenten-3-one-2 (**15**)[10,11] in tetrahydrofuran results in an

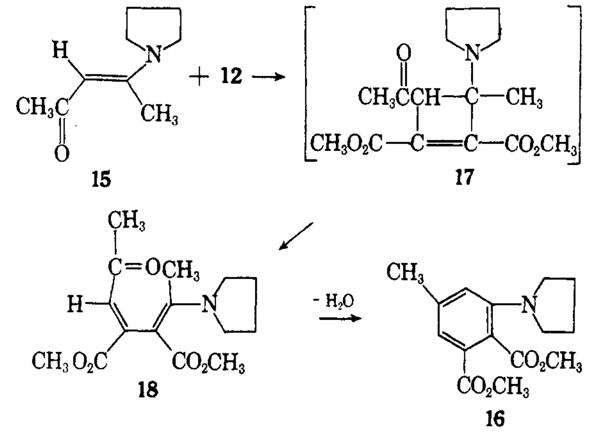
---

[9] After this report had been submitted, a detailed paper by Brannock [K. C. Brannock, R. D. Burpitt, V. W. Goodlett, and J. G. Thweatt, *J. Org. Chem.*, **28**, 1464 (1963)] appeared in print. Since this, together with the work of Berchtold [G. A. Berchtold and G. F. Uhlig, *ibid.*, **28**, 1459 (1963)], is concerned with these same reactions, we limit our description here to significant variations in approach.

[10] N. J. Leonard and J. A. Adamik, *J. Am. Chem. Soc.*, **81**, 595 (1959).

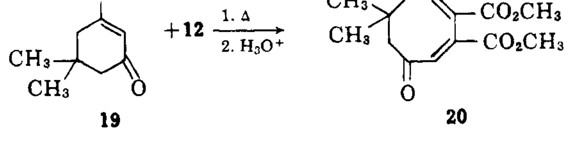
[11] Ultraviolet and n.m.r. data indicate that β-dialkylamino-α,β-unsaturated ketones and esters exist predominantly in the geometric form with the amino and carbonyl groupings *trans* to one another, unlike the corresponding incompletely alkylated amines, which exist in a *cis*, chelated configuration [*cf.* G. O. Dudek and R. H. Holm, *J. Am. Chem. Soc.*, **83**, 3914 (1961)]. Thus, the *trans* configuration of **15** is reflected in its high extinction coefficient [λ_{max} 310 mμ (ε 32,900)] relative to that of 4-aminopenten-3-one-2 [*vide infra*, λ_{max} 298 mμ (ε 18,310)]. Further, deshielding of the methyl group protons by the adjacent (*cis*) acetyl function in the former is reflected in a downfield shift of the n.m.r. signal (2.52 *vs.* 1.90 δ). Several other examples of this preferred configuration, not directly pertinent to this investigation, have been observed in this laboratory.

exothermic reaction. Dilution of the mixture with water yields dimethyl-3-pyrrolidino-5-methylphthalate (**16**) in 60% yield. The reaction presumably proceeds *via* the cyclobutene **17** and diolefin **18**. The presence of water appears to accelerate the conversion of **18** to **16**, since evaporation of the tetrahydrofuran yields an oil which only slowly produces crystalline **16**. The structure of the product was indicated by the n.m.r. spectrum, which revealed signals for two isolated aromatic protons at 6.94 and 6.62 δ with indications of *meta* splitting, and a three-proton singlet at 2.27 δ attributable to an aromatic methyl group.

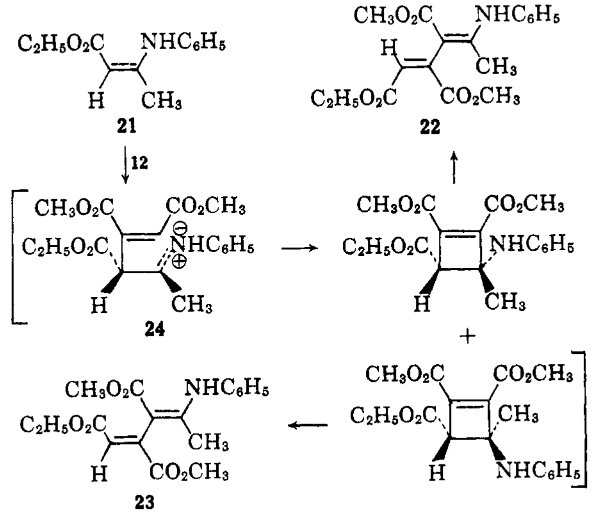


A detailed n.m.r. study of the reaction course was carried out as described for the preparation of 2. Molar equivalents of **15** and **12** were mixed in deuteriobenzene at a temperature below 25°, and the spectrum was measured at intervals. The vinyl proton signal of **15** at 4.78 δ disappeared slowly as the strength of the vinyl proton signal of **18** (6.63 δ) increased. After 20 min. the conversion to **18** was 27% complete and after 2 hr., 67%. The sum of the two protons taken at different times was always equal to 1/21 of the total proton count, thus indicating that no measurable concentration of the cyclobutene **17** accumulated. The formation of **17** is thus slower and its breakdown much more rapid than in the case of the cyclobutenes derived from simple enamines. The geometric structure indicated for **18** is preferred, since the position of the vinyl proton signal indicates deshielding by the β-carbomethoxyl group. Further, the shift of the $CH_3C{=}C$ signal from 2.48 for **15** to 1.80 δ for **18** indicates a marked change in environment, implying that the CH_3 is no longer *cis* to a $C{=}O$ group. It is noteworthy that **18** is the only one of the four possible geometric isomers which can undergo direct ring closure.

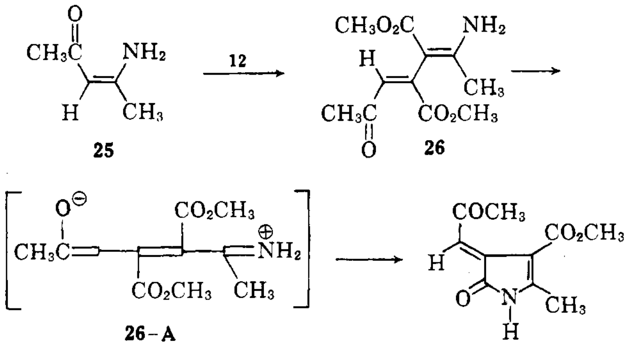
Reaction of an enamine of a cyclic β-diketone was exemplified in 5,5-dimethyl-1-pyrrolidinocyclohexen-1-one-3 (**19**), which on treatment with dimethyl acetylenedicarboxylate and subsequent hydrolysis yielded 2,3-dicarbomethoxy-7,7-dimethyl-1-hydroxy-5-oxo-1,3-cyclooctadiene (**20**). The structure of the product follows from spectral data (*vide infra*).



The reaction of ethyl 3-anilinocrotonate (**21**) with **12** in deuteriobenzene was characterized by the slow disappearance of the vinyl proton signal of **21** at 4.86 δ and no measurable accumulation of a cyclobutene. Two new vinyl proton signals appeared, the stronger at 5.92 and a second at 6.87 δ. As estimated by the disappearance of **21**, reaction was 25% complete after 2.5 hr., and 68% complete after 6 hr. On work-up of the reaction mixture it was possible to isolate **22**, the major diene, by crystallization. When the reaction was run in diglyme solution and the temperature was allowed to reach 85°, on the other hand, the diene **23** was formed in larger amount. Structural assignments are based on spectral measurements. The infrared spectra of both **22** and **23** show strongly bonded NH groups, even in dilute solution. This result was confirmed by the positions of the NH signals in the n.m.r. spectra. These were observed at 11.45 and 11.33 δ, respectively. The carbomethoxyl and amino groups must therefore be *cis*. The vinyl proton of **23** appears farther downfield in the n.m.r. spectrum; this proton is therefore *cis* to the β-carbomethoxy group and more deshielded. Corroborative evidence is obtained from the ultraviolet spectra. Diene **22** with an all *trans* extended chromophore would be expected to have the larger extinction coefficient, as is observed.[11] It may be noted that the two geometric isomers **22** and **23** cannot arise from a single cyclobutene intermediate unless partial inversion at a carbon atom takes place during its breakdown. Another possibility would be intervention of **24**, a type of intermediate proposed by Stork,[1] which can lead to the two cyclobutenes, and, in turn, yield **22** and **23**.

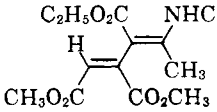


Reaction of **12** with 4-aminopenten-3-one-2 (**25**) was followed by n.m.r. measurements in a similar manner, and the slow formation of two dienes was again noted. These were characterized by vinyl proton signals at 5.89 and 7.21 δ, in a ratio of 2.1 to 1. In this case only the former compound (**26**) was isolated in pure form. Assignment of structure is analogous to that for **22**. Although **26** may be recrystallized from anhydrous ethanol, treatment with water at room temperature converts it to the amide **27**. Seemingly water must function as a proton-donating solvent facilitating the conversion of **26** *via* **26-A** to a geometric isomer capable of ring closure. The depicted stereochemistry of **27** is preferred, since the position of the vinyl proton signal far downfield at 7.13 δ indicates strong deshielding by a β-carbonyl group. It may be noted that neither **22** nor **23** undergoes lactamization under the conditions used in formation of **27**.

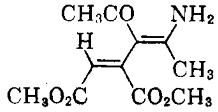


25 **26** **26-A** **27**

It must be mentioned that reaction of **21** and **25** with dimethyl acetylenedicarboxylate by the Michael route, rather than *via* the cyclobutenes can not be entirely excluded by these data. The products which would be obtained, **28** and **29**, are isomeric with the above structures, and it has not been possible to distinguish chemically between the possibilities. However, since all of the enamines derived from simple ketones as well as **15** derived from a diketone react *via* the cyclobutene with interposition of two carbon atoms in the chain, it is more satisfactory to view the reactions of **21** and **25** in the same way.

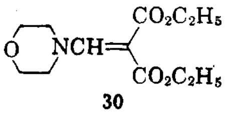


28



29

Finally, it may be noted that while reactions of **12** with enamines derived from β-diketones or β-keto esters proceed much more slowly than with simple enamines, introduction of another electronegative group, as in the case of **30**, prevents reaction altogether. No temperature rise was noted on mixing **30** and **12** in diglyme, and the malonic ester derivative was recovered from the reaction mixture after twenty-four hours.



30

Experimental[12]

1-Pyrrolidino-2-carbethoxy-1,3-cycloheptadiene (3).—Ethyl propiolate (9.80 g.) in 40 ml. of dioxane (purified by passage through alumina) was added slowly under nitrogen to a solution of 13.75 g. of 1-pyrrolidinocyclopentene[1] and a trace of hydroquinone in 40 ml. of purified dioxane. Heat was evolved and a small quantity of solid precipitated from the solution. The mixture was warmed on the steam bath for 15 min., during which period it turned red and the solid redissolved. Removal of solvent *in vacuo* left, after thorough drying *in vacuo*, 23.75 g. of semicrystalline solid. This was triturated thoroughly with cold, low-boiling petroleum ether. The resulting yellow crystals were separated by filtration and recrystallized from cyclohexane; yield of pure product 8.53 g., m.p. 100.5–101.5°; λ_{max} (log ε) 220 (3.87), 271 (4.00), and 340 mμ (4.04); λ_{min} (log ε) 243 (3.66), 295 mμ (3.29).

Anal. Calcd. for $C_{14}H_{21}NO_2$: C, 71.45; H, 9.00; N, 5.95. Found: C, 71.17; H, 9.01; N, 5.56.

Hydrolysis of 3.— Compound **3** (5.88 g.) was stirred under nitrogen for 12–18 hr. with a mixture of 5 ml. of glacial acetic acid, 25 ml. of water, and a trace of hydroquinone. The product was extracted into ether and the extracts were washed successively with 5% hydrochloric acid, water, and saturated brine. The dried extract was filtered through a pad of Darco, the solvent was evaporated, and the residue distilled to yield 2.99 g. of colorless liquid **4**, b.p. 85–88° (0.5 mm.). This product, like the other cyclic β-keto esters, gives a dark blue color with ferric chloride. The ultraviolet spectrum exhibited maxima at 229 (3.92), and 287 (3.65), while a minimum was observed at 252 mμ (3.05). The infrared spectrum (liquid film) showed strong absorption bands at 1640 and 1605 cm.$^{-1}$ and a shoulder at 1728 cm.$^{-1}$. The n.m.r. spectrum reveals that **4** is about 70% in the enolic form **4a**, as indicated by the intensity of the OH proton signal far downfield (12.9 δ). For the enolic modification H-3 is revealed as a doublet at 6.12 δ ($J_{3,4}$ = 12) which, in turn, is split into two triplets (J = 1.2), presumably because of long-range coupling with C-5. The vinyl proton at C-4 appears as a triplet of a doublet at 5.53 δ ($J_{4,3}$ = 12, $J_{4,5,5}$ = 4.5). The ketonic modification is best formulated as **4b**, as seen by the signal of a single vinyl proton at C-3, a poorly resolved triplet at 7.17 δ. Two CH_3 groups are seen as triplets at 1.27 and 1.30 δ (J = 6.5) as a consequence of the equilibrium mixture.

Anal. Calcd. for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 66.20; H, 7.83.

Hydrogenation of 4.—The mixture of tautomers (895 mg.) was hydrogenated in ethanol solution at atmospheric pressure in the presence of 0.25 g. of 10% palladium on carbon. Hydrogen uptake was quantitative in 1 hr. Separation of the catalyst and removal of solvent afforded a quantitative yield of 2-carbethoxycycloheptanone as a pale yellow oil, which was hydrolyzed and decarboxylated by refluxing for 2 hr. with a mixture of 25 ml. of 5% aqueous sulfuric acid and 0.5 ml. of ethanol. The resulting 0.5 g. of cycloheptanone was converted to the semicarbazone, m.p. 161–164° (lit.[13] m.p. 163°), undepressed on admixture with an authentic sample.

In another experiment, 85 mg. of hydrogenation product was heated with 55 mg. of phenylhydrazine in 1 ml. of ethanol for 45 min. at steam-bath temperature, during which period the ethanol was allowed to evaporate. The resulting solid mass was washed with ether and recrystallized from ethanol to yield 20 mg. of the phenylpyrazolone derivative, m.p. 213–214° (lit.[8] m.p. 210°).

1-Pyrrolidino-2-carbethoxycycloheptene (5).—Compound **3** (4.70 g.) was hydrogenated at atmospheric pressure using 0.25 g. of 10% palladium on carbon in 50 ml. of absolute ethanol. The reduction was interrupted when 1 mole of hydrogen had been absorbed. The usual work-up afforded an oily residue which crystallized on standing. Recrystallizations from *n*-hexane (Darco) afforded 1.38 g. of colorless plates, m.p. 63.5–64.5°. The ester carbonyl was observed at 1662 cm.$^{-1}$ (Nujol), and the ultraviolet spectrum showed a maximum at 322 (3.67) and a minimum at 265 mμ (2.61).

Anal. Calcd. for $C_{14}H_{23}NO_2$: C, 70.85; H, 9.77; N, 5.90. Found: C, 70.92; H, 9.83; N, 5.77.

Mild acid hydrolysis of the cycloheptene produced 2-carbethoxycycloheptanone, as shown by its conversion to the phenylpyrazolone derivative.

Formation of 7.—Ethyl propiolate (2.45 g.) in 10 ml. of purified dioxane was added under nitrogen with swirling to 3.44 g. of 1-pyrolidinocyclopentene (**1a**) in 10 ml. of dioxane, the temperature being maintained at about 15°. The mixture was allowed to stand for 45 min. at this temperature, then 10 ml. of water and 3 ml. of acetic acid were added, and the solution was stirred overnight. After evaporation of the dioxane *in vacuo*, the residue was extracted into ether, and the extracts were washed successively with 5% HCl, water, and saturated brine. Evaporation of the dried extracts after addition of

---

[12] Melting points and boiling points are uncorrected. Ultraviolet spectra (wave lengths expressed in mμ, extinction coefficients as log ε) were determined in ethanol, and n.m.r. spectra, in deuteriochloroform, unless otherwise indicated.

[13] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 316.

hydroquinone left a residue which could be only partially distilled. Considerable decomposition and polymerization took place on heating. The product was obtained as a yellow oil, b.p. 108–112° (0.55 mm.). The ultraviolet spectrum of the somewhat impure material exhibited maxima at 240 (3.93) and 315 (2.64) and a minimum at 228 mμ (2.35). The single vinyl proton appeared as a triplet at 6.37 δ (J = 7). Each band of the triplet was split again into a triplet by long-range coupling with the adjacent ring CH_2 (J = 2.5). The side-chain CH_2 appeared as a doublet at 3.11 δ (J = 7).

Anal. Calcd. for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 64.83; H, 7.44.

For characterization **7** was converted to its 2,4-dinitrophenylhydrazone by conventional methods.[14] The orange-red plates, m.p. 138.5–139.5° from ethanol, showed infrared absorption (Nujol) at 1744 cm.$^{-1}$. In the ultraviolet, maxima were observed at 240–255 (4.21), 266 (417), 290 (3.97), and 384 (4.51), while the minimum appeared at 312 mμ (3.76).

Anal. Calcd. for $C_{16}H_{18}N_4O_6$: C, 53.03; H, 5.01; N, 15.46. Found: C, 53.30; H, 5.10; N, 15.41.

Ethyl β-(2-Oxocyclopentyl)propionate (**8**).—The unsaturated keto ester (365 mg.) was hydrogenated at atmospheric pressure in the presence of 0.1 g. of 10% palladium-on-carbon in 50 ml. of 95% ethanol. The usual work-up afforded **8** as a colorless oil which was converted to its 2,4-dinitrophenylhydrazone, m.p. 88–89.5°, from ethanol. Compound **8** was also prepared by reaction of **1a** with ethyl acrylate by the method employed by Stork[1] for the corresponding methyl ester. The infrared spectrum was identical with that of the reduction product. The dinitrophenylhydrazone had m.p. 90–90.5°, undepressed on admixture with the derivative from the reduction product.

Anal. Calcd. for $C_{16}H_{20}N_4O_6$: C, 52.74; H, 5.53; N, 15.38. Found: C, 52.44; H, 5.45; N, 15.25.

5-Pyrrolidino-6-carbethoxybicyclo[3.2.0]hept-6-ene (**2**).—Compound **1a** (13.75 g.) and ethyl propiolate (9.80 g.) were separately dissolved in 50-ml. portions of anhydrous ether, and the solutions were chilled in an ice bath. The ester solution was added over a 10-min. period to the enamine in a nitrogen atmosphere. A small quantity of amorphous, polar solid precipitated, which was separated by filtration. The orange filtrate was kept at ice-bath temperature for 1 hr. and then filtered through a pad of Darco. The solvent was evaporated *in vacuo* at ice-bath temperature. The resulting oil resisted crystallization, but was relatively pure **2**, as shown by spectral examination. The infrared spectrum of the liquid showed a carbonyl band at 1710 cm.$^{-1}$ and a C═C band at 1610 cm.$^{-1}$. The ultraviolet spectrum exhibited maxima at 220 (3.78) and 283 (3.12) and a minimum at 260 mμ (2.95).

Conversion of 2 to the Michael Adduct 7.—A mixture of 2.36 g. of the cyclobutene, 8 ml. of purified dioxane, 4 ml. of water, and 1.2 ml. of acetic acid was stirred overnight at room temperature in a nitrogen atmosphere. The mixture, initially homogeneous, separated into two layers during the reaction. Evaporation of the dioxane *in vacuo* was folllowed by addition of water and extraction into ether, washing the extracts with 5% hydrochloric acid, water, and brine, and drying and evaporation of solvent to yield 1.6 g. of oil. Distillation *in vacuo* yielded 0.42 g. of yellow oil, b.p. about 94° (0.2 mm.), together with considerable polymeric residue. The infrared spectrum of the liquid was identical with that of the adduct prepared earlier. The keto ester was converted to its 2,4-dinitrophenylhydrazone, m.p. 138–139.5°. The infrared spectrum of this derivative also agreed in all details with the compound referred to above.

In a separate experiment 7.05 g. of the cyclobutene was stirred for 4 hr. with 35 ml. of 5% hydrochloric acid. Extraction of the solution with ether yielded only a very small quantity of polar oil and none of the desired keto ester.

5-Pyrrolidino-6-carbethoxybicyclo[3.2.0]hept-6-ene Methiodide (**9**).—A solution of 0.47 g. of the amine in 10 ml. of dry benzene was added to a solution of 0.56 g. of methyl iodide in the same solvent. The mixture was allowed to stand overnight and the resulting dirty yellow needles were separated by filtration and washed with benzene. There was obtained 0.43 g. of crude product, m.p. 100–104°. The analytical sample was prepared by recrystallizations from ethyl acetate containing a little isopropyl alcohol. The resulting white needles had m.p. 116–117.5°. The infrared spectrum showed bands at 1710 and 1610 cm.$^{-1}$. In the n.m.r., aside from the vinyl proton singlet mentioned earlier, a feature of interest was the N-methyl group signal at 3.60 δ.

Anal. Calcd. for $C_{15}H_{24}NO_2I$: C, 47.75; H, 6.42; N, 3.72. Found: C, 47.56; H, 6.38; N, 3.67.

1-Morpholinocyclooctene (**1d**).—This enamine, b.p. 147–149° (14 mm.), was prepared in 50% yield by the method used by Djerassi and Tursch[15] for 1-morpholinocyclohexene.

Anal. Calcd. for $C_{12}H_{21}NO$: C, 73.79; H, 10.84; N, 7.19. Found: C, 73.18; H, 10.47; N, 7.59.

1-Morpholino-2,3-dicarbomethoxy-1,3-cyclooctadiene (**11b**).—Dimethyl acetylenedicarboxylate (2.55 g.) was carefully added to 3.0 g. of 1-morpholinocyclohexene[1] (**1b**) in 3 ml. of "diglyme." A spontaneous exothermic reaction ensued with the temperature rising to *ca.* 105°. The solution was allowed to cool, and the product was separated by filtration and recrystallized from chloroform–acetone; yield 50%, m.p. 210–212°. The ultraviolet spectrum exhibited λ_{max} (log ϵ) 303 (4.06) and a plateau at 312–324 mμ (4.05), while the infrared spectrum (Nujol) showed carbonyl absorptions at 1714 and 1680 cm.$^{-1}$ and C═C absorption at 1614 cm.$^{-1}$. In the n.m.r. spectrum the vinyl proton appeared as a quartet at 6.75 δ (J = 7.3, 9.6).[16]

Anal. Calcd. for $C_{16}H_{23}NO_5$: C, 62.12; H, 7.49; N, 4.53. Found: C, 61.87; H, 7.72; N, 4.60.

1-Pyrrolidino-2,3-dicarbomethoxy-1,3-cycloheptadiene (**11a**). From the requisite enamines this product, as well as **11c** and **11d** (*vide infra*), were prepared in like manner and in similar yield. Compound **11a** had m.p. 135–138° after recrystallizations from ethanol–water. The ultraviolet spectrum showed λ_{max} (log ϵ) 324 (4.04), while infrared bands were found at 1718, 1683, and 1605 cm.$^{-1}$. The vinyl proton signal appeared as a triplet (or a quartet with the center peaks superimposed) at 6.83 δ (J = 7).

Anal. Calcd. for $C_{15}H_{21}NO_4$: C, 64.49; H, 7.58; N, 5.01. Found: C, 64.76; H, 7.60; N, 4.98.

1-Morpholino-2,3-dicarbomethoxy-1,3-cyclononadiene (**11c**).—This compound, after recrystallization from methanol, had m.p. 152–155°, but was contaminated by an unknown impurity, as shown by the n.m.r. spectrum. In this case the vinyl proton signal was observed at 6.05 δ (J = 4, 12).[16] The ultraviolet maximum was observed at 328 mμ (4.11).

Anal. Calcd. for $C_{17}H_{25}NO_5$: C, 63.14; H, 7.79; N, 4.33. Found: C, 63.20; H, 7.59; N, 4.43.

1-Morpholino-2,3-dicarbomethoxy-1,3-cyclodecadiene (**11d**).—After recrystallizations from ethanol–water the compound had m.p. 114–115°, λ_{max} (log ϵ) 326 mμ (4.14). The infrared absorptions were observed at 1722, 1690, and 1630 cm.$^{-1}$ and the vinyl proton signal at 5.82 δ (J = 4, 12).[16]

Anal. Calcd. for $C_{18}H_{27}NO_5$: C, 64.07; H, 8.06; N, 4.15. Found: C, 63.83; H, 8.05; N, 4.11.

1-Hydroxy-2,3-dicarbomethoxy-1,3-cyclooctadiene (**13**).—One-half gram of **11b** was allowed to stand for several hours at room temperature in 5 ml. of 15% aqueous hydrochloric acid, with occasional swirling. Momentary solution was followed by turbidity and crystallization of the enolic product, which was separated by filtration and recrystallized from acetone–water; yield, 95%. The substance, m.p. 60–64°, gave a deep purple color with ferric chloride. The infrared spectra in chloroform and in Nujol gave no indication of hydroxyl absorption, apparently because of strong internal hydrogen bonding. Infrared bands were observed at 1725, 1663, and 1609 cm.$^{-1}$, while the ultraviolet maximum was seen at 254 mμ (4.00). In the n.m.r. the chelated hydroxyl proton appeared at 12.7 and the vinyl proton at 6.98 δ (J = 7.1, 9.4).

Anal. Calcd. for $C_{12}H_{16}O_5$: C, 59.99; H, 6.71. Found: C, 60.26; H, 6.95.

6-Morpholino-7,8-dicarbomethoxybicyclo[4.2.0]oct-7-ene (**10b**).—A solution of 0.234 g. of dimethyl acetylenedicarboxylate in 2.34 ml. of deuteriobenzene was mixed with a solution of 0.25 g. of **1b** in 2.5 ml. of the same solvent. The characteristic triplet at 4.68 δ (J = 3.1) due to the vinyl proton of **1b** was completely absent from the n.m.r. spectrum determined 30 min. after mixing, and no new vinyl proton signals appeared.

Based on these observations, a large-scale preparative experiment was run in an attempt to isolate the cyclobutene or a derivative. A solution of 7.6 g. of the ester in 75 ml. of benzene was added slowly with cooling (5–7°) to 8.0 g. of **1b** in 30 ml. of

---

(14) Ref. 13, p. 219.

(15) C. Djerassi and B. Tursch, *J. Org. Chem.*, **27**, 1041 (1962).

(16) These coupling constants must retain a certain degree of uncertainty because of the extreme difficulty in analyzing the remainder of the complex spectrum.

benzene. The final volume of the solution was 168 ml. A 25-ml. aliquot of the solution was refluxed for 4 hr. and evaporated to dryness. The crystals of **11b**, after filtration and washing with ether, weighed 0.51 g. (21%), m.p. 210–212°. Another 38-ml. aliquot of the benzene solution was evaporated at reduced pressure to yield crude **10b** as an orange oil. Attempts to crystallize the product as the base or as its hydrochloride or methiodide salt were unsuccessful. Although the preparation contained neither starting material nor eight-membered enamine **11b**, as shown by thin-layer chromatography, purification by chromatography on alumina was not successful. The major component, though obtained in a fairly pure state, appeared to generate another minor component on further treatment. The nature of these transformations is unknown.[17]

In another experiment 2.34 g. of the acetylenic ester in 2.5 ml. of diglyme was added dropwise to a solution of 2.5 g. of **1b** in 2.5 ml. of the same solvent, keeping the temperature at 5–7°. The mixture (9.5 ml.) was placed in the refrigerator overnight. An aliquot (7.5 ml.) was then heated to 130° for 10 min. On cooling, 1.22 g. (34%) of **11b** was obtained, m.p. 210–212°. The remainder of the solution was allowed to stand at room temperature for 3 days, during which period **11b** was slowly produced. The yield of crystalline material at the end of this period was 0.52 g.

6-Morpholino-7,8-dicarbomethoxybicyclo[4.2.0]octane Hydrochloride (**14**).—The remainder of the benzene solution referred to in the previous section (105 ml.) was shaken with hydrogen at 40 p.s.i. in the presence of 1 g. of 10% palladium on charcoal for 3 hr. After separation of the catalyst the benzene was stirred with 12 ml. of 15% aqueous hydrochloric acid for 2 hr. The aqueous extract was made alkaline with ammonia, the product was extracted into ether, and the solvent was removed from the dried extracts. Addition of 6 *N* ethanolic hydrogen chloride to the residue yielded a solid hydrochloride which, after recrystallization from ethanol weighed 4 g. and had m.p. 193–194°. The ultraviolet spectrum showed only end absorption, while in the infrared ester carbonyl absorptions were observed at 1754 and 1740 cm.$^{-1}$.

Anal. Calcd. for $C_{16}H_{25}NO_5.HCl$: C, 55.31; H, 7.48; N, 4.03. Found: C, 55.06; H, 7.31; N, 4.23.

Dimethyl 3-Pyrrolidino-5-methylphthalate (**16**).—Dimethyl acetylenedicarboxylate (4.7 g.) was added over a period of several minutes to a solution of 5 g. of 4-pyrrolidinopenten-3-one-2 (**15**)[10] in 10 ml. of warm tetrahydrofuran. An exothermic reaction took place, after which the mixture was heated 15 min. on the steam bath, then poured into water. The resulting solid was collected by filtration and recrystallized from methanol to yield 5.4 g. of **16**, m.p. 82–84°. The ultraviolet spectrum had λ_{max} (log ϵ) 236 (4.21), 274 (3.90), and 347 (3.54), and λ_{min} (log ϵ) 259 (3.86) and 301 mμ (2.89). The infrared spectrum (Nujol) showed ester carbonyl absorptions at 1732 and 1713 with aromatic absorption at 1605 cm.$^{-1}$.

Anal. Calcd. for $C_{15}H_{10}NO_4$: C, 64.96; H, 6.91; N, 5.05. Found: C, 65.25; H, 6.85; N, 5.01.

For the spectral studies a solution of 0.18 g. of dimethyl acetylenedicarboxylate in 1.8 ml. of deuteriobenzene was added over a period of several minutes to a solution of 0.15 g. of **15** in 1.5 ml. of deuteriobenzene while keeping the temperature at 5°. After mixing, the reaction was warmed to 25° and the n.m.r. spectrum was measured at intervals.

2,3-Dicarbomethoxy-7,7-dimethyl-1-hydroxy-5-oxo-1,3-cyclooctadiene (**20**).—To a solution of 5 g. of **19**[10] in 20 ml. of diglyme maintained at 60°, 3.68 g. of dimethyl acetylenedicarboxylate was added dropwise, after which the mixture was heated at steam-bath temperature for 30 min. The contents were poured into water and the oil was extracted into ether, the ether removed, and the residue treated with 15 ml. of 15% hydrochloric acid for 1 day. A crystalline material gradually separated which was recrystallized from ethanol; m.p. 147–149°. The n.m.r. spectrum of **20** indicates a chelated hydroxyl proton at 13.1 δ, split by long-range coupling with one of the adjacent methylene protons (J = 1.6). The vinyl hydrogen signal appears at 6.55 δ (J = 1.4), coupled with a C-6 proton. The C-6 methylene signal was observed as a quartet (AB type) at 2.50 δ (J = 12.1). The high field proton of this quartet was split into a doublet by long-range coupling (J = 1.4) with H-4. The C-8 methylene signal was also observed as a quartet (AB type) at 2.30 δ (J = 11.4). The lowfield proton in this case was split into a doublet (J = 1.6) by coupling with the hydroxyl proton. This long-range coupling disappears on addition of deuterium oxide. Strong infrared bands are observed at 1745, 1727, and 1603 cm.$^{-1}$.

Anal. Calcd. for $C_{14}H_{18}O_6$: C, 59.56; H, 6.43. Found: C, 59.83; H, 6.39.

Ethyl 5-Anilino-3,4-dicarbomethoxy-*trans,cis*-2,4-hexadienoate (**22**) **and Ethyl 5-Anilino-3,4-dicarbomethoxy-*cis,cis*-2,4-hexadienoate** (**23**).—A solution of 0.19 g. of **12** in 1.9 ml. of deuteriobenzene was added to a solution of 0.25 g. of ethyl 3-anilinocrotonate (**21**) in 2.5 ml of deuteriobenzene under the conditions described in the preceding experiment. Since the downfield band in the n.m.r. spectrum was somewhat obscured by incompletely deuterated solvent, the deuteriobenzene was removed after the reaction was complete (24 hr.) and the spectrum determined in deuteriochloroform. Integration of the vinyl protons showed **22** and **23** to be present in a ratio of 1.4 to 1.0. A solution of 6.1 g. of **12** in 60 ml. of benzene was then added dropwise to a solution of 8.0 g. of **21** in 80 ml. of benzene while keeping the reaction temperature at 5°. The mixture was then allowed to warm to room temperature. After allowing it to stand for 48 hr., the solvent was removed *in vacuo*, and the residue was recrystallized twice from methanol–water to yield 5.0 g. of **22**, m.p. 88–90°. The ultraviolet spectrum showed maxima at 256 (4.07), 302 (3.73), and 342 (3.74) and minima at 230 (3.93), 289 (3.70), and 318 mμ (3.71). The infrared spectrum in methylene chloride showed a broad bonded NH band at 3250 to 3000 cm.$^{-1}$ which was unaltered on dilution. Pertinent features of the n.m.r. spectrum were the vinyl proton signal at 6.00 δ and the $CH_3—C=C$ signal at 2.08 δ.

Anal. Calcd. for $C_{18}H_{21}NO_6$: C, 62.24; H, 6.10; N, 4.03. Found: C, 62.43 H, 6.16; N, 3.95.

A solution of 5.0 g. of **12** in 5 ml. of diglyme was added to 7.2 g. of **21** in 5 ml. of diglyme in small portions; the temperature rose to 85°. The mixture was then heated on the steam bath for 15 min. and poured into water. The resulting oil was extracted with ether and the extract was dried and evaporated. The residue crystallized on standing. Recrystallization from methanol gave 5.7 g. of **23**, m.p. 72–74°, depressed to 55–65° on admixture with **22**. The ultraviolet spectrum showed maxima at 254 (4.07), 312 (3.49), and 336–360 plateau (3.46); and minima at 230 (3.99) and 294 mμ (3.45). The infrared spectrum in methylene chloride showed a broad band at 3250 to 3000 cm.$^{-1}$ which was unaltered on dilution. Features of the n.m.r. spectrum were the vinyl proton signal at 6.89 δ and the $CH_3—C=C$ signal at 2.08 δ.

Anal. Calcd. for $C_{18}H_{21}NO_6$: C, 62.24; H, 6.10; N, 4.03. Found: C, 62.10; H, 6.04; N, 4.02.

6-Amino-4,5-dicarbomethoxy-*trans,cis*-3,5-heptadien-2-one (**26**).—A solution of 18.6 g. of **12** in 10 ml. of anhydrous tetrahydrofuran was added in small portions to 13.0 g. of **25** in 10 ml. of tetrahydrofuran over several minutes. The temperature rose to 85°. After an hour, about half of the tetrahydrofuran was removed by distillation, and the residue was chilled to effect crystallization. Recrystallization from ethyl acetate gave 12 g. of **26**, m.p. 115–116°. The ultraviolet absorption spectrum was characterized by a maximum at 300 (4.12) and a minimum at 257 mμ (3.34). The infrared spectrum in methylene chloride showed a strongly-bonded NH at 3140 and a weakly bonded NH at 3430 cm.$^{-1}$, neither of which changed on dilution. The n.m.r. spectrum showed a vinyl proton signal at 5.92 δ and a $CH_3—C=C$ signal at 2.12 δ.

Anal. Calcd. for $C_{11}H_{15}NO_5$: C, 54.76; H, 6.27; N, 5.83. Found: C, 54.46; H, 6.50; N, 5.73.

Methyl 2-Methyl-5-oxo-4-(2-oxo-propylidene)-2-pyrroline-3-carboxylate (**27**).—When a portion of the tetrahydrofuran reaction mixture containing **26** was poured into water, a pale yellow, crystalline substance separated. Recrystallization from ethanol yielded **27**, m.p. 179–181°. Conversion of **26** to **27** could also conveniently be carried out in 90% yield by solution of the former in minimum boiling water and collection of product on cooling. The ultraviolet spectrum showed maxima at 267 (3.98) and 363 (3.69), and minima at 224 (3.35) and 306 mμ (3.16). The compound dissolved in aqueous sodium hydroxide with a deepening of the color-maximum 434. The n.m.r. spectrum showed the vinyl proton signal at 7.14 δ.

Anal. Calcd. for $C_{10}H_{11}NO_4$: C, 57.41; H, 5.30; N, 6.70. Found: C, 57.57; H, 5.35; N, 6.57.

Attempted Reaction of Diethyl 4-Morpholinylmethylene-

---

(17) Compound **10b** had an R_f value of 0.47, while the minor component ran at 0.56 on aluminum oxide G, using 1:1 benzene–methylene chloride as solvent.

malonic Ester (30) with 12.—A mixture of 5 g. of **30**[18] and 2.76 g. of **12** were mixed in 10 ml. of diglyme. No temperature rise was noted. After 24 hr. at room temperature, the reaction was diluted with water and unchanged **30** recovered, m.p. 58–61°.

Acknowledgment.—The authors wish to express their sincere appreciation to Miss Natalie Cahoon and co-workers for spectra determinations and to Mr. George Robertson and co-workers for analytical results.

---

[18] C. D. Hurd and L. T. Sherwood, *J. Org. Chem.*, **13**, 471 (1948).

Reactions of Mercaptoamines. I. With Isocyanates and Isothiocyanates[1]

ARTHUR F. FERRIS AND BEVERLY A. SCHUTZ

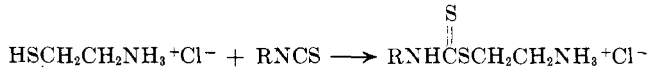
Midwest Research Institute, Kansas City 10, Missouri

Received May 3, 1963

Isothiocyanates reacted with 2-mercaptoethylamine hydrochloride to give S-substituted products, the hydrochlorides of S-2-aminoethyl N-alkyldithiocarbamates. With free 2-mercaptoethylamine, one mole of phenyl isothiocyanate gave the N-substituted product, 1-(2-mercaptoethyl)-3-phenyl-2-thiourea, and two moles gave the N,S-disubstituted product. All aliphatic isothiocyanates gave disubstituted products, the 1-[2-(N-alkyldithiocarbamoyl)ethyl]-3-alkyl-2-thioureas, regardless of the relative amount of isothiocyanate. The disubstituted products were cleaved by silver nitrate to one mole of the isothiocyanate and the silver mercaptide of the 1-(2-mercaptoethyl)-3-alkyl-2-thiourea, from which the free thiourea was obtained by treatment with sodium sulfide. Isocyanates, regardless of relative amount, reacted with 2-mercaptoethylamine to give the N,S-disubstituted products. Cleavage with silver nitrate afforded the 1-(2-mercaptoethyl)-3-alkylureas.

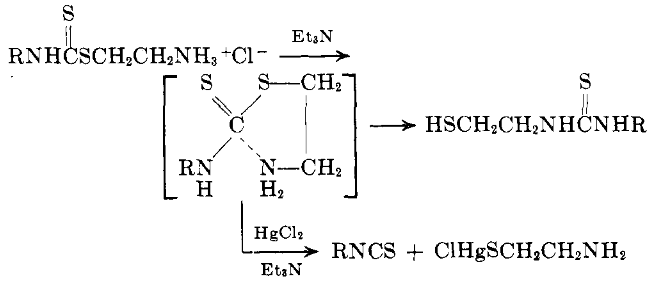
The behavior of isocyanates and isothiocyanates toward active hydrogen compounds has been studied since the earliest days of organic chemistry, and it is well known that both react vigorously with amines, and that isocyanates also react, somewhat less vigorously, with alcohols and water.[2] In contrast, isothiocyanates are so relatively unreactive toward hydroxyl-containing compounds that aqueous media often are used in their preparation,[3] and their reaction with hydroxyalkyl amines gives hydroxyalkyl thioureas.[4] Both isocyanates and isothiocyanates have been reported to react with thiols,[5] but there is no evidence to indicate how readily these reactions proceed relative to reaction with the amino group. Consequently there was no *a priori* way of predicting how compounds containing both the thiol and the amino function would react with isocyanates and isothiocyanates. This question became of importance in connection with the proposed preparation of a number of 2-mercaptoethyl ureas and thioureas for testing as radioprotective drugs, and an examination of the reaction of 2-mercaptoethylamine with isocyanates and isothiocyanates was undertaken.

The reaction with isothiocyanates was studied first, since there seemed to be a better chance of directing this reaction preferentially to one or the other functions of the 2-mercaptoethylamine molecule. When a solution of 2-mercaptoethylamine hydrochloride in ethanol (pH 5 to Hydrion test paper) was treated with phenyl or *n*-butyl isothiocyanate, there was no reaction. However, when a few drops of aqueous sodium hydroxide were added, raising the pH to 6–6.5, vigorous exothermic reaction took place and solid products crystallized. Analysis indicated that these products were the result of reaction at the thiol function, that is, that they were the hydrochlorides of S-2-aminoethyl N-phenyldithiocarbamate (72% yield) and N-*n*-butyldithiocarbamate (74%), respectively. This structure assignment was confirmed by their chemical behavior and by the fact that 2-dimethylaminoethanethiol hydrochloride, which can react only at the thiol function, reacted vigorously with phenyl isothiocyanate at pH 6. Treatment of an aqueous solution of the product with base gave free S-(2-dimethylamino)ethyl N-phenyldithiocarbamate in 66% yield.



$$HSCH_2CH_2NH_3^+Cl^- + RNCS \longrightarrow RNH\overset{S}{\overset{\|}{C}}SCH_2CH_2NH_3^+Cl^-$$

The dithiocarbamates derived from 2-mercaptoethylamine were much less stable. The hydrochlorides dissolved in water to give clear solutions, but the solutions underwent rapid hydrolysis. In a few minutes cloudiness appeared, and the characteristic odor of the parent isothiocyanate became strongly noticeable. When the hydrochlorides were treated with an equivalent of weak base, they rearranged to the corresponding N-substituted derivatives of 2-mercaptoethylamine, giving 1-(2-mercaptoethyl)-3-phenyl-2-thiourea (77%) and somewhat impure 1-(2-mercaptoethyl)-3-*n*-butyl-2-thiourea (77%). This rearrangement appears to be exactly analogous to the known rearrangement of S-acyl 2-mercaptoethylamine derivatives.[6,7] As a preparative route to 2-mercaptoethylthioureas this reaction was less satisfactory than other techniques to be de-



---

[1] This work was supported by the U. S. Army Medical Research and Development Command, Department of the Army, under Contract No. DA-49-193-MD-2174.

[2] I. D. Morton and E. Hoggarth, "Chemistry of Carbon Compounds," Vol. IB, E. H. Rodd, Ed., Elsevier Publishing Co., Amsterdam, The Netherlands, 1952, p. 939.

[3] M. L. Moore and F. S. Crossley, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 599.

[4] F. B. Dains, R. Q. Brewster, I. L. Malm, A. W. Miller, R. V. Maneval, and J. A. Sultzaberger, *J. Am. Chem. Soc.*, **47**, 1981 (1925).

[5] E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. IV, Chemical Publishing Co., Inc., New York, N. Y., 1962, pp. 201 and 238.

[6] J. Baddiley and E. M. Thain, *J. Chem. Soc.*, 3425 (1951).

[7] T. Wieland and E. Bokelmann, *Ann.*, **576**, 20 (1952).