When a 1-g. sample of hydroxy β-diketone IV was treated with ethanolic potassium hydroxide under the same conditions, there was recovered 0.35 g. (35%) of IV, m.p. 133–135°, and 0.1 g. (9%) of its copper chelate, m.p. 171–176°. Neither dehydrated product was detected.

Pyrazoles from β-diketones. To a solution of 1 g. of hydroxy β-diketone II in 30 ml. of hot 95% ethanol was added an excess (10 drops) of Eastman 95% hydrazine. The solution was heated on the steam bath for one hour (purple color discharged). Water was added to precipitate an essentially quantitative yield of white 3-(2,2-diphenyl-2-hydroxyethyl)-phenylpyrazole (XX), m.p. 181–184° and at 182–184° after several recrystallizations from ethanol-water.

Anal. Calcd. for $C_{23}H_{20}N_2O$: C, 81.15; H, 5.92; N, 8.23. Found: C, 81.33; H, 6.08; N, 8.20.

Treating a 1-g. sample of unsaturated β-diketone XI with hydrazine in the same manner produced 0.95 g. (96%) of white 3-(2,2-diphenylethenyl)-5-phenylpyrazole (XXI), m.p. 92–98°, resolidifying at about 115°, and melting again at about 160°. After heating in *n*-hexane, XXI melted at 157–162°, and after several recrystallizations from methanol-water XXI melted at 160–162°.

Anal. Calcd. for $C_{23}H_{18}N_2$: C, 85.68; H, 5.63; N, 8.69. Found: C, 85.48, 85.64; H, 5.68, 5.63; N, 8.58, 8.74.

A 1-g. sample of pyrazole XX was refluxed 7 hr. in 15 ml. of methanol containing 1 ml. of concd. hydrochloric acid. After standing 60 hr. at room temperature, water was added, and the solution was cooled to give, after recrystallization from methanol-water, 0.2 g. (21%), of pyrazole XXI, m.p. 156–159°. Another recrystallization raised the melting point to 159–161°, which was not depressed on mixing with a sample of XXI prepared as described above. The infrared spectra of the two samples were identical.

Cleavage of hydroxy β-diketone II. To a stirred, refluxing solution of 0.013 mole of potassium *t*-butoxide (prepared from 0.5 g., 0.013 g.-atom of potassium) in 150 ml. of *t*-butyl alcohol was added 4 g. (0.012 mole) of hydroxy β-diketone II. After refluxing for 2 hr., about 120 ml. of solvent was distilled (1 hr.). The residue was cooled, and 100 ml. of ice water containing 2 ml. of concd. hydrochloric acid was added. The mixture was extracted with ether. The ether layer was extracted with fractions of cold 1% sodium hydroxide solution until the ether solution no longer gave a color with ethanolic ferric nitrate. The basic extracts were acidified and extracted with ether. This ether extract was shaken with aqueous sodium bicarbonate, washed with saturated aqueous sodium chloride, and dried over sodium sulfate. The solvent was removed on the steam bath to give 1.5 g. (80%) of benzoylacetone, m.p. 55–59° and at 58–61° after recrystallization from methanol. There was no depression in melting point on mixing with an authentic sample of benzoylacetone.

The neutral ether layer remaining after extraction with sodium hydroxide was washed with saturated aqueous sodium chloride, dried over sodium sulfate, and the solvent removed to leave 2.6 g. of a liquid residue. A 2-g. aliquot of this residue was taken up in a small amount of petroleum ether (b. p. 30–60°) and placed on an alumina column. Evaporation of the first petroleum ether eluates produced 1.1 g. (68%) of benzophenone, m.p. 46–50°. One recrystallization from petroleum ether raised the melting point to 49–50°; there was no depression on mixing with an authentic sample of benzophenone.

Similarly 0.012 mole of II was cleaved with 0.0026 and with 0.026 moles of potassium *t*-butoxide to give benzoylacetone and benzophenone in yields of 64 and 62%, and 59 and 62%, respectively.

In a blank experiment using no potassium *t*-butoxide, 73% of unchanged hydroxy β-diketone II was recovered.

Failure of monoalkalibenzoylacetone to condense with carbonyl compounds. To a stirred solution of 0.1 mole of potassium amide[3] in 300 ml. of liquid ammonia was added 0.1 mole of benzoylacetone in 50 ml. of dry ether (purple solution) followed, after 25 min., by 0.1 mole of benzophenone and 50 ml. of ether. After 6 hr., the reaction mixture was poured into a solution of 15 g. of ammonium chloride in liquid ammonia. There were recovered 87% of the benzophenone and 95% of the benzoylacetone.

Similarly monolithiobenzoylacetone was prepared from 0.1 mole each of benzoylacetone and lithium amide in 300 ml. of liquid ammonia and 50 ml. of ether (purple solution), and treated with 0.1 mole of anisaldehyde in 50 ml. of ether. After 2 hr., the reaction mixture was neutralized inversely with ammonium chloride to give 95% of recovered benzoylacetone.

DURHAM, N. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY]

Structures of the Adducts of *N*-Phenylhydroxylamine with Dimethyl Acetylenedicarboxylate

WILLIAM C. AGOSTA

Received September 28, 1960

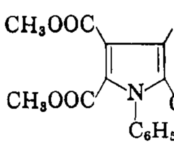
Structures II and III are proposed for the 2:2 and 2:1 adducts, respectively, of *N*-phenylhydroxylamine with dimethyl acetylenedicarboxylate. Implications of the independent formation of III from aniline, dimethyl oxalacetate, and dimethyl α-bromoxalacetate for the mechanism of the Hantzsch pyrrole synthesis are briefly discussed.

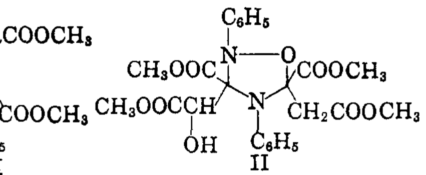
Dimethyl acetylenedicarboxylate and *N*-phenylhydroxylamine are known to react to produce two crystalline adducts, an unstable material in which the addends are present in the ratio 1 : 1, and a stable compound consisting of two molecules of ester for each one of amine.[1] Although Huntress[1] was able to obtain the latter adduct by an independent synthesis and to transform it quantitatively to tetramethyl *N*-phenylpyrrole-2,3,4,5-tetracarboxylate (I), no definite structure has been assigned to either of these compounds. On the basis of the information outlined below, we wish to propose structure II for the unstable adduct and structure III for the stable product.

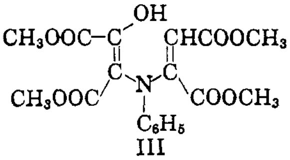
The unstable adduct slowly forms upon mixing the ester and amine in ether at 0–10°.[1] Upon

---

[1] E. H. Huntress, T. E. Leslie, and W. M. Hearon, *J. Am. Chem. Soc.*, 78, 419 (1956).

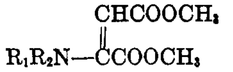

I


II


III

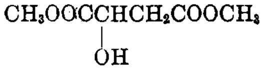
standing at 30–35° for two to three days the crystalline material is transformed to a red gum from which the stable adduct may be readily isolated.[2] The stable compound can also be obtained directly from the acetylenic ester and amine in hot benzene.[1]

The infrared spectrum[3] of the unstable material (Huntress's Adduct A) shows a broad band between 2.84 and 3.05 μ typical of a hydrogen-bonded hydroxyl group, as well as a single ester carbonyl band (5.79 μ) and aromatic ring absorptions (6–7 μ). The ultraviolet spectrum contains a single maximum at 240 mμ (ε 8640), indicating the absence of an α,β-unsaturated ester and compatible with the chromophore of a substituted aniline.[4] In contrast, the usual result of the reaction of an acetylenic ester with an amine is a simple unsaturated amino ester of the general structure IV,[5–9] as typified by the adduct of aniline with dimethyl acetylenedicarboxylate, V.[10] In this compound (V) ultraviolet maxima are found at 233 mμ (ε 9350) and 323 mμ (ε 13,800), and in the infrared ester carbonyl bands are present at 5.78 and 6.00 μ.[3] It is then clear that the reaction has in this case taken a course more complex than that customarily observed.

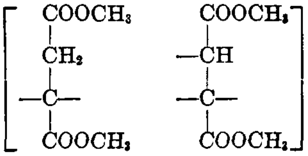

$R_1R_2N-C(COOCH_3)=CHCOOCH_3$

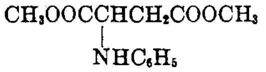
IV

V ($R_1 = C_6H_5$; $R_2 = H$)


$CH_3OOCCH(OH)CH_2COOCH_3$

VI

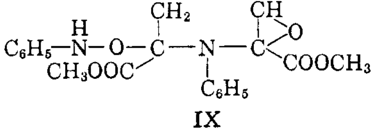

VIII

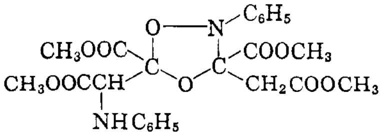

$CH_3OOCCH(NHC_6H_5)CH_2COOCH_3$

VII

Molecular weight determinations[11] indicate II to consist of two molecules each of acetylenic ester and N-phenylhydroxylamine. Since catalytic hydrogenation (*vide infra*) yields dimethyl malate (VI) and dimethyl N-phenylaspartate (VII), no new carbon-carbon bonds have formed during the addition. The NMR spectrum[12] of II shows only two proton signals besides those multiplets assignable to aromatic protons (432 c.p.s., rel. area 12.1) and hydroxyl plus methoxyl groups[13] (210 c.p.s., rel. area 13.0). Significantly each of these signals is unsplit by spin-spin coupling, a result requiring that in each case there be no protons present on the neighboring carbon atoms. One of these signals is at rather low field, 293 c.p.s., rel. area 1.1, indicating a high concentration of unshielding, electron-withdrawing groups in the vicinity of this proton; and the other is at 164 c.p.s., rel. area 2.0. Consideration of these data allows us to write as a partial expression for this 2 : 2 adduct structure VIII, in which the two halves of the molecule must be joined only by bonds involving nitrogen and/or oxygen atoms, and all valences must be satisfied without the introduction of double bonds.

Of the possible structures that can be derived from VIII, only II seems to be consistent with the origin and reactions of this material. We reject formulations containing an epoxide ring (*e.g.*


IX


X

---

[2] Huntress (ref. 1) reports a similar transformation carried out in refluxing methanol. We were unable to confirm his observation that on standing the unstable adduct reverted to its original components.

[3] Measured in carbon tetrachloride solution.

[4] *Cf.* the spectrum of N,N-dimethylaniline, $\lambda\lambda_{max}$ 251 mμ (ε 12,000) and 298 mμ (ε 1990) (H. Ley and H. Specker, *Ber.*, **72**, 192 (1939)) and that of N-phenylhydroxylamine, $\lambda\lambda_{max}$ 236 mμ (ε 9100) and 279 mμ (ε 1100) (P. Grammaticakis, *Bull. Soc. Chim.* [5], **18**, 964 (1951)).

[5] F. Straus and W. Voss, *Ber.*, **59**, 1689 (1926).

[6] H. R. Snyder, H. Cohen, and W. J. Tapp, *J. Am. Chem. Soc.*, **61**, 3560 (1939).

[7] R. M. Acheson and M. L. Burstall, *J. Chem. Soc.*, 3240 (1954); R. M. Acheson and G. F. W. Bond, *J. Chem. Soc.*, 246 (1956); R. M. Acheson and C. W. Jefford, *J. Chem. Soc.*, 2676 (1956).

[8] E. Grovenstein, Jr., W. Postman, and J. W. Taylor, *J. Org. Chem.*, **25**, 68 (1960).

[9] H. Rapoport and R. J. Windgassen, personal communication.

[10] See experimental.

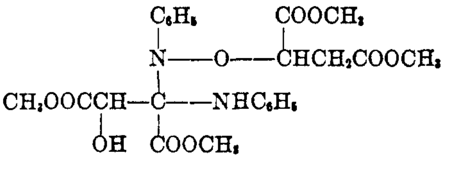
[11] We are most grateful to the California Research Corp. of Richmond, Calif., who carried out these measurements cryoscopically in benzene.

[12] NMR spectra were determined at 60 mc. r_f in deuterochloroform. Chemical shifts were measured and are reported relative to internal tetramethylsilane. We are grateful to Mr. A. J. Berlin for these measurements.

[13] Hydroxyl proton resonance appears only as a shoulder on the low field side of the methoxyl bands.

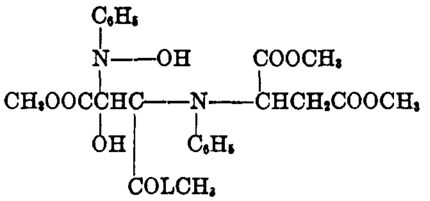
IX) as improbable of formation under the conditions of the addition. A more reasonable alternative would be X, but this structure fails to account for the ready transformation of the compound into III. *Beta*-elimination of *N*-phenylhydroxylamine from II, on the other hand, yields III directly.

Catalytic hydrogenation of II in methanol over palladium on carbon gave a complex mixture in which aniline (0.62 equivalent), dimethyl malate (VI) (0.42 equivalent), and dimethyl *N*-phenylaspartate (VII) (0.44 equivalent) were identified. These products, as well as the small amount of unidentified, base-soluble material giving a positive ferric chloride test, can be accounted for by the following considerations. Hydrogenolysis of the labile N—C—O system apparently occurs on either side to give either XI or XII. Reductive scission of the N-O bond would then give the malic ester and XIII from XI, and XIV from XII. Elimination of aniline from XIII yields XV, while the same process applied to XIV gives the aspartic ester as well as XV. Further hydrogenation and hydrogenolysis of XV and its tautomers can then account for the formation of 0.20 equivalent more aniline than dimethyl malate and also for the variable amount of hydrogen consumed. With 2% of catalyst the reaction stopped after absorption of about 2.4 equivalents of hydrogen, while use of 15% gave a quite rapid uptake of approximately this same amount followed by slow reduction to a total of 4.4 equivalents. The survival of a small portion of material in the oxidation state of XV could explain the enolic material obtained.[14]



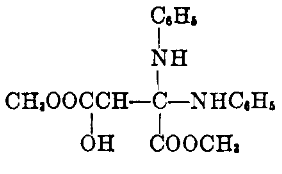
$$\begin{array}{l} \qquad\quad C_6H_5 \qquad\quad COOCH_3 \\ \qquad\quad\; | \qquad\qquad\quad | \\ \qquad\quad N\text{——O——}CHCH_2COOCH_3 \\ \qquad\quad\; | \\ CH_3OOCCH\text{—}C\text{——}NHC_6H_5 \\ \qquad\; | \qquad | \\ \qquad OH \quad COOCH_3 \end{array}$$

XI



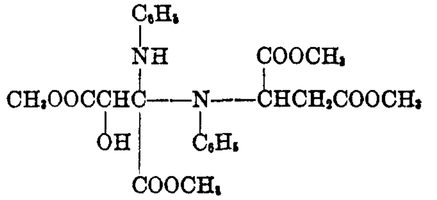
$$\begin{array}{l} \qquad\qquad C_6H_5 \\ \qquad\qquad\; | \\ \qquad\qquad N\text{——OH} \qquad COOCH_3 \\ \qquad\qquad\; | \qquad\qquad\qquad | \\ CH_3OOCCHC\text{——}N\text{——}CHCH_2COOCH_3 \\ \qquad\quad | \qquad | \qquad\; | \\ \qquad\; OH \qquad\quad C_6H_5 \\ \qquad\qquad | \\ \qquad\quad COLCH_3 \end{array}$$

XII



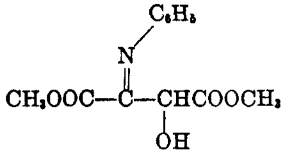
$$\begin{array}{l} \qquad\qquad\qquad C_6H_5 \\ \qquad\qquad\qquad\; | \\ \qquad\qquad\qquad NH \\ \qquad\qquad\qquad\; | \\ CH_3OOCCH\text{—}C\text{—}NHC_6H_5 \\ \qquad\; | \qquad\quad | \\ \qquad OH \qquad COOCH_3 \end{array}$$

XIII



$$\begin{array}{l} \qquad\qquad C_6H_5 \\ \qquad\qquad\; | \\ \qquad\qquad NH \qquad\qquad COOCH_3 \\ \qquad\qquad\; | \qquad\qquad\qquad | \\ CH_3OOCCHC\text{——}N\text{——}CHCH_2COOCH_3 \\ \qquad\quad | \qquad | \qquad\; | \\ \qquad\; OH \qquad\quad C_6H_5 \\ \qquad\qquad | \\ \qquad\quad COOCH_3 \end{array}$$

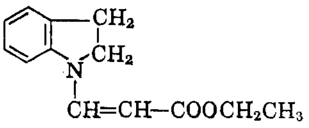
XIV



$$\begin{array}{l} \qquad\qquad\quad C_6H_5 \\ \qquad\qquad\quad / \\ \qquad\qquad N \\ \qquad\qquad \| \\ CH_3OOC\text{—}C\text{—}CHCOOCH_3 \\ \qquad\qquad\quad | \\ \qquad\qquad\; OH \end{array}$$

XV

As Huntress has pointed out,[1] the structural possibilities for the 2:1 adduct (his Adduct B) are limited by the observations that this compound may be independently synthesized by condensation of aniline, dimethyl oxalacetate, and dimethyl α-bromoxalacetate and that it is quantitatively converted to I by concentrated sulfuric acid or methanolic ammonia. The few structures alternative to III for this compound can be eliminated by consideration of the following physical data. Other than aromatic and methoxyl plus hydroxyl[13] proton resonance, the NMR spectrum[12] contains only an unsplit peak at 312 c.p.s. (rel. area 0.9 based on 13.0 for methoxyl plus hydroxyl), a region typical of vinyl protons.[15] Such an assignment is supported by the presence of a similar absorption by the model compound V at 323 c.p.s. Since no other mechanistically reasonable structure has a proton attached to a double bond, the NMR result strongly suggests III as the proper representation for this product. In the infrared the N-H absorption in V occurs at 3.08 μ,[16] but the only band beyond 3.3 μ[16] in the adduct appears at 2.87 μ, pointing to the absence of a C_6H_5—NH—C=C< system. Carbonyl absorption appears at 5.75 μ with a weaker band at 5.94 μ. This latter is compatible with the presence of an α,β-unsaturated ester bearing nitrogen on the β-carbon.[17] The ultraviolet spectrum possesses a single maximum at 307 mμ (ϵ 16,100) which is unchanged by added hydrochloric acid but changed by treatment with base to a maximum at 318 mμ (ϵ 6600) and a



i

---

[14] Clearly the steps in this reaction need not occur in the exact order outlined here. Apparently, however, the malate does not arise through the corresponding ketone, as we found oxalacetic ester unreactive under these hydrogenation conditions.

[15] L. J. Jackman, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, Pergamon Press, New York, 1959, pp. 60–62.

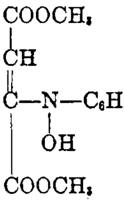
[16] Measured in chloroform.

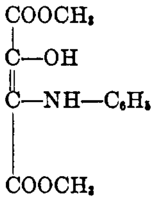
[17] *Cf.* the absorption of V at 6.01 μ,[16] and that of *i* at 5.95 μ.[9,18]

shoulder at 252 mμ (ε 9650).[18] These data also are in agreement with III rather than possible alternates. The hypsochromic shift from the value of 323 mμ found in V can be attributed to the cross-conjugated nature of the chromophore in III.

Attempts further to substantiate structures II and III by chemical means have been unsuccessful. Compound II begins to decompose almost immediately upon solution in the common organic solvents. Compound III is readily converted to I with either acidic or basic catalysis; it is unaffected by hydrogen in the presence of platinum catalyst.

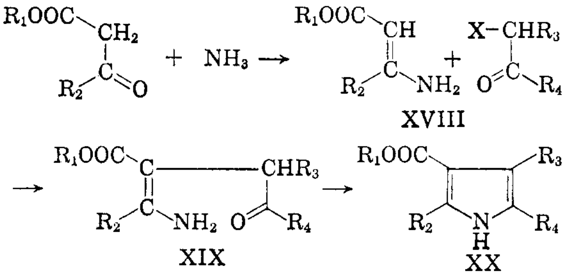
Mode of formation. Huntress's synthesis of III using aniline requires that there be a migration of hydroxyl from nitrogen to carbon at some time during the formation of this compound from N-phenylhydroxylamine and dimethyl acetylenidicarboxylate. Since our conclusions outlined above also require a carbon-bound hydroxyl in II, and since II is readily converted to III by straightforward loss of N-phenylhydroxylamine, the migration must occur under the mild conditions (0–10° in ether) leading to II. We assume that this takes place by an allylic rearrangement in the initial adduct XVI.[19] N-Arylhydroxylamines are well known to suffer transformation to *o*- and *p*-aminophenols under a variety of mild conditions.[20,21]

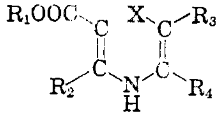

XVI

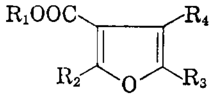

XVII

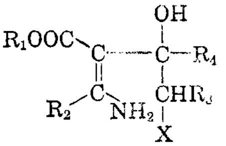
Such a reaction in XVI, with the allylic carbon rather than an *ortho* or *para* ring position as the migration terminus, would give after tautomerization XVII. Subsequent addition of another molecule of amine and of acetylenic ester can then give II.

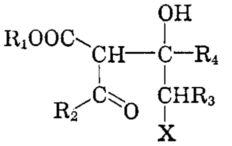
Hantzsch pyrrole synthesis. Korschun[22] showed many years ago that the first intermediate in the Hantzsch reaction between β-keto ester, amine, and α-halo ketone is probably the enamine (XVIII) formed by interaction of the first two materials. He postulated that this was subsequently alkylated by the halo ketone to give a molecule (XIX) which then cyclized to pyrrole (XX).




XXI


XXII


XXIII

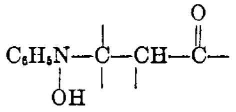

XXIV

While the evidence is certainly not compelling, the isolation of III in low yield from the condensation of dimethyl oxalacetate, dimethyl α-bromoxalacetate, and aniline[23] indicates that the enamine XVIII may condense with the halo ketone to give XXI rather than XIX, and that XXI could be the second intermediate in the sequence. It is interesting that such an intermediate would account simply for the observation that the pyrrole substituents are always oriented as in XX, while the furans simultaneously produced[24,25] are of the type XXII. If XXI is the intermediate, the control of the amine over the direction of condensation is obvious, since the orientation is established before the final, irreversible formation of the new carbon-carbon bond. On the other hand, if XIX is the intermedi-

---

[18] Neutral spectra measured in methanol, ethanol, and chloroform; acid and base effects measured in ethanol solution.

[19] *Cf.* the ready addition of N-phenylhydroxylamine to various α,β-unsaturated carbonyl compounds to give products of the general structure



$$C_6H_5N(OH)-\overset{|}{\underset{|}{C}}-\underset{|}{C}H-\overset{O}{\overset{\|}{C}}-$$

(E. Jolles, *Gazz.*, 68, 488 (1938)).

[20] (a) E. Bamberger, *Ber.*, **33**, 3600 (1900). (b) E. Bamberger, *Ber.*, **27**, 1349 and 1522 (1894). E. Bamberger and A. Rising, *Ber.*, **34**, 229 (1901). (c) C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca, N. Y., 1953, pp. 621–624, gives a discussion of the mechanism of this reaction.

[21] While most of these rearrangements have been carried out with acid catalysis (*e.g.* at room temperature in chloroform containing *p*-toluenesulfonic acid or in aqueous sulfuric acid), the rearrangement of N-(2,6-xylyl)hydroxylamine is reported to occur in distilled water (ref. 20a).

[22] G. Korschun, *Ber.*, **38**, 1125 (1905).

[23] It should be noted that the reaction yielding III was not run under the usual conditions of the Hantzsch synthesis, which involves simply heating the three starting materials together, often without solvent. Compound III was obtained by heating the components in aqueous methanolic potassium hydroxide, acidifying with acetic acid, and reheating briefly (ref. 1).

[24] F. Feist, *Ber.*, **35**, 1537 (1902).

[25] If a tertiary amine is substituted for ammonia or primary amine, the furans may be obtained in good yield. (E. W. Scoll and J. R. Johnson, *J. Am. Chem. Soc.*, **54**, 2549 (1932); A. T. Blomquist and H. B. Stevenson, *J. Am. Chem. Soc.*, 56, 146 (1934)).

ate, the orientation is probably determined by the fact that alkylation of the enamine[26] (XVIII) by the α-halo ketone is irreversible, while the supposedly competing condensation between these two molecules to yield XXIII is a reversible reaction. It should be pointed out, however, that it is just this sort of reversible condensation to give XXIV that does succeed in the sequence leading to the furan XXII.

EXPERIMENTAL[27]

Unstable (2:2) adduct of N-phenylhydroxylamine with dimethyl acetylenedicarboxylate (II). This compound was prepared as directed by Huntress.[1] The material was stored at 5° for several months without change. Since we found a melting point consistently higher than that previously reported (91–93° dec. rather than 86.1–86.6°), a sample was reanalyzed. The analytical sample was recrystallized from dichloromethane-ether.

Anal. Calcd. for $C_{24}H_{26}N_2O_{10}$: C, 57.36; H, 5.21; N, 5.58; OCH_3, 24.70; mol. wt., 502. Found: C, 57.45; H, 5.43; N, 5.62; OCH_3, 24.55; mol. wt.,[11] 482, 477.

Stable (1:2) adduct of N-phenylhydroxylamine with dimethyl acetylenedicarboxylate (III). This compound was prepared as directed by Huntress[1]; m.p. 153–154°, reported m.p. 154.4–154.9°. Attempted reduction of III with sodium borohydride in refluxing tetrahydrofuran gave a 59% yield of I as the only isolable product. An attempt to acetylate III with isopropenyl acetate containing a trace of *p*-toluenesulfonic acid gave I in good yield.

Conversion of unstable to stable adduct (II *to* III). A sample of II, m.p. 89–91°, turned to a red gum on standing at about 35° for 2 days. This gum was dissolved in ether and kept at 0° overnight. The crystalline material which separated, m.p. 149–150°, was recrystallized from aqueous methanol, m.p. 151–153°. The infrared spectrum in potassium iodide disk was identical with that of III prepared as above.

Catalytic hydrogenation of II *and identification of products.* In 400 ml. methanol 4.0 g. of II was shaken with 600 mg. of 5% palladium on carbon under 1 atm. of hydrogen until 4.2 equivalents were absorbed (197 min.). (A similar small scale experiment showed that if the reaction were continued several hours longer, a total of 4.4 equivalents was absorbed.) The filtered solution was distilled to dryness at reduced pressure and the residue dissolved in ether. This was extracted successively with 0.5*N* hydrochloric acid, saturated aqueous potassium bicarbonate, water, and brine, and then dried. The acidic and basic solutions were neutralized and extracted with ether, which was then washed with water and dried. There were thus recovered three fractions: (1) acid soluble, 863 mg.; (2) bicarbonate soluble, 241 mg. (ferric chloride test positive); (3) "neutral," 1.187 g.

By direct isolation as the hydrochloride from an aliquot of fraction 1 there was obtained the equivalent of 463 mg. (0.62 equivalent) of aniline, characterized by identity of melting point, mixture melting point, and infrared spectrum with those of authentic aniline hydrochloride. The infrared spectrum of crude fraction 1 showed dimethyl *N*-phenylaspartate to be absent.

The "neutral" fraction 2 from a similar reduction was analyzed by vapor phase chromatography (5′ silicone column with helium as eluting gas). At 220° there was eluted a material identical in retention time and infrared spectrum with authentic dimethyl *N*-phenylaspartate. A quantitative estimation of this product, made by comparison of areas on the chromatography curve with those given by known amounts of the authentic ester, indicated 0.44 equivalent in the "neutral" fraction.

Likewise vapor phase chromatography at 135° showed the presence of 0.42 equivalent of dimethyl malate in this fraction. This ester was also identified by comparison of retention time and infrared spectrum with those of the authentic ester prepared by Fischer esterification of malic acid.

Dimethyl N-phenylaspartate (VII). *N*-Phenylaspartic acid hydrochloride[28] was esterified with methanolic hydrogen chloride and the product worked up in the customary way. One molecular distillation (pot temp. 125°/0.2 mm.) gave an analytically pure, pale yellow oil.

Anal. Calcd. for $C_{12}H_{15}NO_4$: C, 60.75; H, 6.37; N, 5.90. Found: C, 61.01; H, 6.51; N, 5.76.

Adduct of aniline with dimethyl acetylenedicarboxylate (V). In 10 ml. dichloromethane were mixed 0.5 g. dimethyl acetylenedicarboxylate and 0.32 ml. aniline. After 30 min. at room temperature the solution was evaporated to dryness *in vacuo.* One molecular distillation (pot temp. 125°/0.2 mm.) of the residue gave a bright yellow oil of analytical purity.

Anal. Calcd. for $C_{12}H_{13}NO_4$: C, 61.27; H, 5.57; N, 5.96. Found: C, 60.99, H; 5.60; N, 5.64.

BERKELEY 4, CALIF.

---

[26] G. Stork, R. Terrell, and J. Szmuszkovicz, *J. Am. Chem. Soc.*, **76**, 2029 (1954).

[27] Chemical analyses were performed in the Microanalytical Laboratory of the University of California. All melting points are corrected; all boiling points are uncorrected.

[28] R. Anschütz and Q. Wirtz, *Ann.*, **239**, 137 (1887).