[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF UTAH]

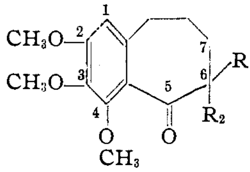
Seven-membered Ring Compounds. V.[1] The Synthesis of 2,3,4-Trimethoxybenzosuberone-6-acetic Acid and Related Compounds

BY PETE D. GARDNER[2] AND W. J. HORTON

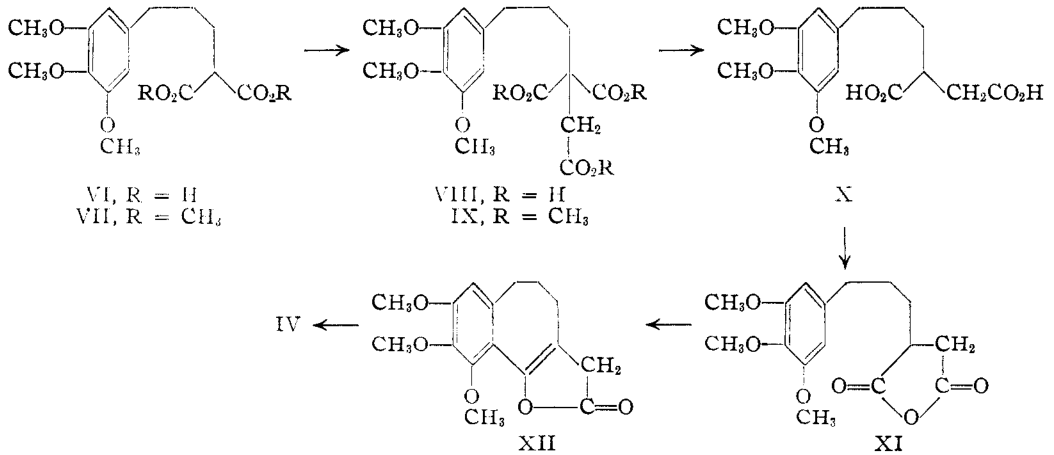
RECEIVED MARCH 16, 1953

2,3,4-Trimethoxybenzosuberone-6-acetic acid (IV) was prepared: (a) by alkylation of methyl 2,3,4-trimethoxybenzosuberone-6-carboxylate (II) and (b) by polyphosphoric acid cyclization of γ-3,4,5-trimethoxyphenylpropylsuccinic acid (X) to the enol lactone of 2,3,4-trimethoxybenzosuberone-6-acetic acid (XII). The Reformatsky reaction was successful with 2,3,4-trimethoxybenzosuberone but not with the related 6-acetic acid ester. The above enol lactone unexpectedly reacted with two moles of methyllithium.

In a search for means of obtaining a compound containing three methoxyl groups and the carbon skeleton of colchicine, the previously reported[1] β-keto-ester II was alkylated with methyl bromoacetate. Hydrolysis with loss of the carboxyl group gave 2,3,4-trimethoxybenzosuberone-6-acetic acid (IV). The acid IV was also prepared by a series of reactions from available[3] γ-3,4,5-trimethoxyphenylpropylmalonic acid (VI). The methyl ester was alkylated by methyl bromoacetate to give IX. Saponification gave a tricarboxylic acid VIII which was thermally decarboxylated and directly cyclized by phosphorus pentoxide–phosphoric acid to the enol lactone XII (Fig. 1, A).



I, $R_1 = R_2 = H$
II, $R_1 = H$; $R_2 = CO_2CH_3$
III, $R_1 = CH_2CO_2CH_3$; $R_2 = CO_2CH_3$
IV, $R_1 = H$; $R_2 = CH_2CO_2H$
V, $R_1 = H$; $R_2 = CH_2CO_2CH_3$



VI, R = H
VII, R = CH_3
VIII, R = H
IX, R = CH_3
X
XII
XI

The decarboxylation product X was also isolated and converted to the anhydride XI by acetic anhydride. This succinic anhydride, which might conceivably close to a seven- or an eight-membered ring, gave the enol lactone obtained above when polyphosphoric acid was used. The alternate cyclization to a benzocyclooctanone is a type of closure which we have not found in the literature.

When the succinic anhydride XI was cyclized, a product isomeric with the enol lactone was isolated in small amounts from the mother liquor (Fig. 1, B). A comparison of its ultraviolet spectrum with that of the parent I (Fig. 1, C) suggested that the same chromophore was present. The infrared absorption indicated that these groups were not keto groups and that a lactone was present. Cyclization in the alternate manner to yield an eight-membered enol lactone would produce a structure in violation of Bredt's rule.[4] The melting point suggested a dimer. An attempted molecular weight determination with camphor failed due to decomposition of the sample, and lack of material prevented further study.

Attempts to prepare XIII by alkylation of II with bromoacetone gave intractable gums. The enol lactone XII was therefore treated with methyllithium in order to obtain XIII.[5] The product obtained did not depress the melting point of XII but was clearly distinguished from the starting material by means of infrared absorption. The infrared curve exhibited neither carbonyl nor hydroxyl groups and analytical data supported the hypothesis that two moles of methyllithium had reacted. The ultraviolet absorption spectra of XIV (curve D) and its precursor (curve A) support

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[1] Paper IV, THIS JOURNAL, **75**, 944 (1953).

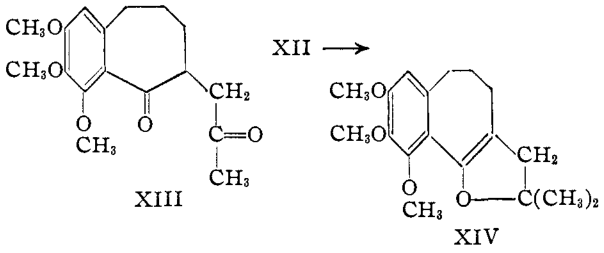
[2] From the Doctoral Dissertation of Pete D. Gardner.

[3] P. D. Gardner, W. J. Horton, G. Thompson and R. R. Twelves, THIS JOURNAL, **74**, 5527 (1952).

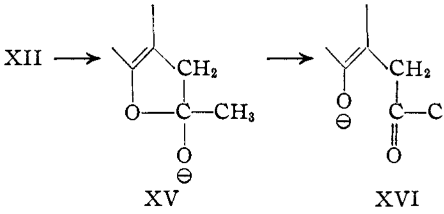
[4] The rule does not hold for [5,1,3]-bicyclic systems according to V. Prelog, L. Ruzicka, P. Barman and L. Frenkiel, *Helv. Chim. Acta*, **31**, 92 (1948); V. Prelog, P. Barman and M. Zimmermann, *ibid.*, **32**, 1284 (1949).

[5] Subsequently, R. B. Woodward, *et al.*, THIS JOURNAL, **74**, 4223 (1952), obtained a methyl ketone using one mole of methyllithium on an enol lactone.

the proposed structure. In this reaction we propose that the intermediate anion XV obtained on addition of one mole of methyllithium undergoes a



mesomeric shift to XVI[6] which allows the addition of a second mole of reagent.



The Reformatsky reaction on I using methyl bromoacetate gave the expected carbinol ester in 58% yield. All attempts to apply the reaction to V using either methyl bromoacetate or methyl γ-bromocrotonate failed presumably due to the presence of groups at positions 4 and 6. Similarly, a Darzens reaction with methyl chloroacetate and sodium methylate gave only V.

The assistance of a Frederick Gardner Cottrell grant is gratefully acknowledged. A portion of this work was completed in the laboratories of Merck and Company, Inc. We are much indebted for their coöperation.

Experimental[7]

3,4,5-Trimethoxycinnamylidenemalonic Acid Using Aqueous Choline.[8]—3,4,5-Trimethoxybenzaldehyde (100 g., 0.51 mole), 1 l. of absolute ethanol, 186 g. of ethylidenemalonic ester[3] and 532 g. of 50% aqueous choline were combined with cooling and allowed to stand at room temperature for 40 hours. The orange solid (99.8 g., 0.324 mole, 63.6%) was obtained as before[3] and melted at 201–202° dec.

Cyclization of δ-3,4,5-Trimethoxyphenylvaleric Acid.—It was found convenient to prepare I in large runs from the wet hydrogenation product of the above cinnamylidenemalonic acid. The propylmalonic acid (68.7 g., wet with acetic acid) gave 50.0 g. (0.186 mole) of the valeric acid after heating for 20 minutes at 180–190° and 13 mm. Cyclization[9] at 100° for 40 minutes gave I in 91.2% yield after recrystallization from cyclohexane (Fig. 1, C).

Cyclization of γ-3,4,5-Trimethoxyphenylpropylmalonic Acid (VI).—A solution of 12.5 g. of phosphorus pentoxide in 8 cc. of 85% phosphoric acid dissolved 0.765 g. (0.00245 mole) of VI at 100°. Gas evolution began after 4 minutes and after 20 minutes at 100° the neutral product was obtained using the reported procedure.[9] The solid (0.307 g., 0.00123 mole, 50%) melted at 96–100°, not depressed by mixing with known[3] material. A similar run in which the weight of cyclizing agent was doubled gave a 79% yield.

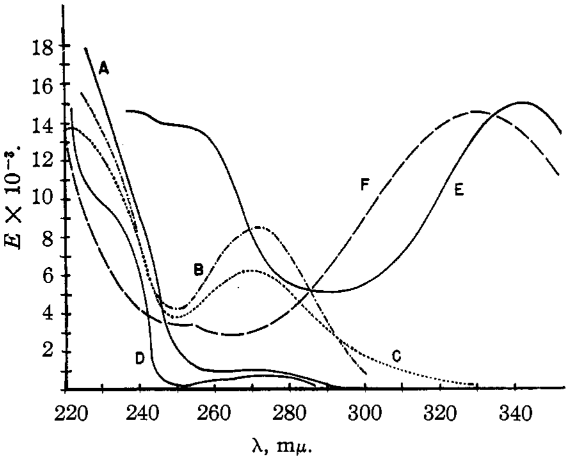


Fig. 1.—A, XII — in ethanol; B, —·—·— in isoöctane, by-product from cyclization of XI based on mol. wt. 290; C, I ------ in ethanol; D, XIV — in ethanol; E, — in chloroform, by-product from preparation of II, mol. wt. 595; F, — — — in ethanol-methyl 2,3,4-trimethoxybenzosuberone-6-glyoxylate.

An attempt to close VII using the reported procedure[10] gave unreacted diester in 95% yield, demonstrated by saponification to the crystalline acid VI.

Methyl 2,3,4-Trimethoxybenzosuberone-6-acetate (V).—A solution of 1.61 g. (0.070 mole) of sodium in 30 cc. of absolute methanol and 20 cc. of dry benzene was refluxed with 3.44 g. (0.0113 mole) of the β-keto-ester[1] II, m.p. 80–92°, for 30 minutes. The bright red mixture was cooled to 0° and 13.4 cc. of methyl bromoacetate was added in two portions over a 25-minute period followed by refluxing for 30 minutes. The cold solution was acidified with acetic acid and three-quarters of the solvent was distilled *in vacuo*. Benzene and water were added and the benzene layer was washed twice with 10% sodium hydroxide. The dried benzene solution, treated with Norite, was distilled *in vacuo* leaving a light yellow oil which gave a faint color with alcoholic ferric chloride and resisted crystallization. The oil III (3.02 g., 0.0082 mole) was refluxed for 2.25 hours with 100 cc. of methanol and 30 cc. of 45% potassium hydroxide. The methanol was distilled *in vacuo* and the alkaline solution, after washing with ether, precipitated oil on acidification. Crystalline product was obtained on rubbing the cold oil. It weighed 2.4 g. (0.0078 mole, 69% from II) and softened at 116°, m.p. 125–130°. Repeated recrystallization from benzene–petroleum ether (30–60°) gave a m.p. 131.5–132°.

Anal. Calcd. for $C_{16}H_{20}O_6$: C, 62.32; H, 6.54. Found: C, 62.74; H, 6.84.

The methyl ester V, m.p. 77–78° from cyclohexane, was obtained in 97% yield using diazomethane. Extensive recrystallization from cyclohexane and then from methanol gave thin rectangular plates, m.p. 80.8–82°.

Anal. Calcd. for $C_{17}H_{22}O_6$: C, 63.34; H, 6.88. Found: C, 63.04; H, 6.88.

On a large scale preparation of II from the glyoxylate[1] (113 g.), gas evolution, after a short induction period, was unusually rapid. The β-keto-ester II (62%) was isolated only by chromatography of the dark reaction product. From the later fractions a 6% yield of a by-product was obtained, m.p. 205.5–207° from chloroform–methanol.

Anal. Calcd. for $C_{32}H_{34}O_{11}$: C, 64.64; H, 5.76; mol. wt., 594.6. Found: C, 64.91, 64.71; H, 5.43, 5.36; mol. wt. (cryoscopic, benzil), 591.

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(6) This step is the reverse of one of the steps proposed[1] to account for the formation of enol lactones of benzosuberoneglyoxylic acids. In a reported case of addition of phenyllithium to a lactone (G. Wittig, M. Leo and W. Wiemer, *Ber.*, **64**, 2405 (1931)), the change analogous to XV → XVI did not take place. The other phenyllithium additions in this paper may be viewed as analogous to XVI → XV with stability in the form of XV.

(7) All melting points are corrected.

(8) The previously used methanolic benzyltrimethylammonium hydroxide[3] became unavailable. Similar yields were obtained with material made by distillation of 40% aqueous benzyltrimethylammonium hydroxide at 20 mm. using an oil-bath at 100–120°. The distillation was discontinued when oily drops appeared in the distillate. The residue was combined with methanol using 140 cc. per 147 g. of concentrate.

(9) R. C. Gilmore and W. J. Horton, This Journal, **73**, 1411 (1951).

(10) R. C. Gilmore, *ibid.*, **73**, 5879 (1951).

Infrared absorption suggested an unsaturated lactone or an anhydride. The ultraviolet absorption spectrum is shown (E) in Fig. 1. The related glyoxylate is curve F.

Methyl β,β-Dicarbomethoxy-ε-3,4,5-trimethoxyphenylcaproate (IX).—Reaction of 100 g. (0.324 mole) of VI with excess diazomethane gave 102 g. (0.30 mole, 92.5%), b.p. 183–185° (0.6 mm.), of **dimethyl γ-3,4,5-trimethoxyphenylpropylmalonate** VII. A center cut gave $n^{25}D$ 1.5070. The compound was not distillable without some slight decomposition.

Anal. Calcd. for $C_{17}H_{24}O_7$: C, 59.99; H, 7.11. Found: C, 60.73; H, 6.95.

A suspension of 1.36 g. (0.035 mole) of sodamide in 100 cc. of benzene and 10.0 g. (0.0294 mole) of the diester was stirred and refluxed for 95 minutes. At room temperature 4.1 cc. of methyl bromoacetate was added and the mixture was stirred for 10 minutes. The reaction was then stirred and refluxed with the addition in two portions of 4.6 cc. of the bromoester over a 25-minute period. The cooled solution was combined with 100 cc. of ether and was washed with water. Distillation of the solvent gave a yellow oil IX, b.p. 204–206° (0.8 mm.), $n^{25}D$ 1.5047. The nearly colorless distillate weighed 11.2 g. (0.0272 mole, 92.5%).

Anal. Calcd. for $C_{20}H_{28}O_9$: C, 58.24; H, 6.84. Found: C, 58.24; H, 6.71.

β,β-Dicarboxy-ε-3,4,5-trimethoxyphenylcaproic Acid (VIII).—Saponification of the triester (11.0 g., 0.0268 mole) as described above gave an oil which could not be crystallized. A methanolic solution deposited a salt of the acid when solid potassium hydroxide was added. When the salt was redissolved in water and acidified with hydrochloric acid, colorless crystals separated. If cooled overnight at 0°, 6.2 g. (0.016 mole, 61%) was obtained. The solid melted at 113°, solidified and remelted at 164° dec. Material repeatedly recrystallized from ethyl acetate and then from water gave colorless needles melting as before. A sample dried at room temperature and 1 mm. pressure contained water of crystallization, lost by drying at 100° (1 mm.). The anhydrous compound melted at 166–167°.

Anal. Calcd. for $C_{17}H_{22}O_9\cdot{}^1/_2H_2O$: C, 53.82; H, 6.11. Found: C, 53.52; H, 6.64. Calcd. for $C_{17}H_{22}O_9$: C, 55.13; H, 5.99. Found: C, 55.34; H, 5.94.

γ-3,4,5-Trimethoxyphenylpropylsuccinic Acid (X).—Decarboxylation of 8.97 g. (0.0236 mole) of the hydrate of the acid VIII was complete after 25 minutes in an oil-bath at 190°. After standing at room temperature for 2 days, nearly oil-free crystals were obtained. These dissolved in 10% sodium hydroxide and the oil obtained on acidification, when seeded with a previously prepared sample gave 6.9 g. (0.0211 mole, 89.6%), m.p. 104–105°. Several crystallizations from water were possible if the solution temperature did not exceed 40°. The colorless solid so obtained melted at 106.2–108.2°.

Anal. Calcd. for $C_{16}H_{22}O_7$: C, 58.88; H, 6.80. Found C, 58.91; H, 6.56.

The anhydride XI was prepared from 4.0 g. (0.012 mole) of the acid by heating with 20 cc. of acetic anhydride on the steam-bath for 2 hours and standing 2 days at room temperature. The colorless oil remaining when the solvent had been removed, crystallized on standing for 3 days. It weighed 3.7 g. (0.012 mole, 100%), m.p. 80–81.5°. A portion recrystallized from a large volume of petroleum ether (50–60°) gave tiny colorless needles, m.p. 82–82.6°. Repeated attempts to obtain a satisfactory analysis were unsuccessful.

Enol Lactone of 2,3,4-Trimethoxybenzosuberone-6-acetic Acid (XII).—The above anhydride (3.0 g., 0.0097 mole) was heated for 11 minutes with 60 g. of phosphorus pentoxide–phosphoric acid as described above. Isolation as reported[9] gave an oil which crystallized after 8 hours at 0° (seeded). Colorless prisms, 1.7 g. (0.0058 mole), m.p. 117–120°, were obtained. Further purification from ethyl acetate brought the melting point to 124.6–126°, not depressed when mixed with XII obtained below.

Concentration of the mother liquor gave 0.40 g., m.p. 108–130°. Three crystallizations from ethyl acetate gave colorless prisms, m.p. 164.5–166°. The compound gave a negative ferric chloride test and showed an ultraviolet absorption maximum at 271 mμ, *E* 8500 (isoöctane), Fig. 1, B.

Anal. Calcd. for $C_{32}H_{34}O_{10}$: C, 66.42; H, 5.92. Found: C, 66.53; H, 6.01.

The hydrated carboxylic acid VIII, 2.0 g. (0.0053 mole), after heating at 185° for 10 minutes, was cyclized at once as was the anhydride XI with 100 g. of phosphorus pentoxide–phosphoric acid. The oil crystallized *in vacuo* overnight. The light tan solid weighed 1.53 g. (0.0052 mole, 98%), m.p. 81–124°. Two recrystallizations from methanol and several from ethyl acetate gave colorless diamonds, m.p. 125–125.8°; ultraviolet absorption maximum at 271 mμ, *E* 1000, Fig. 1, A.

Anal. Calcd. for $C_{16}H_{18}O_5$: C, 66.19; H, 6.25. Found: C, 66.28; H, 6.09.

The enol lactone (0.201 g., 0.00069 mole), heated for 15 minutes with 0.1 g. of potassium hydroxide in 5 cc. of methanol, gave IV by acidification; 0.203 g. (0.00066 mole), m.p. 134–135°. Tiny light tan rosettes were obtained from benzene–petroleum ether (30–60°), m.p. 134.5–136°, unchanged when mixed with IV obtained above. The methyl ester V obtained using diazomethane melted at 80–81° after recrystallization from methanol and did not depress the melting point of the previously obtained material.

Methyllithium on XII.—A solution of 4.9 g. (0.017 mole) of XII in 25 cc. of dry benzene was added slowly, stirring at 0° under nitrogen, to methyllithium from 2.8 g. of lithium and 21.3 g. of methyl iodide[11] in 100 cc. of ether. A solid complex separated but rapidly dissolved. After 20 minutes at 0°, ethyl acetate was added to destroy the excess methyllithium. The washed product (1.8 g.) in benzene–petroleum ether was placed on acid-washed alumina and eluted with 90% petroleum ether–10% ether. From the initial fractions 0.559 g. (0.00183 mole) of XIV, m.p. 124–127°, was obtained. Further purification gave material melting at 125–127.6°.

Anal. Calcd. for $C_{18}H_{24}O_4$: C, 71.03; H, 7.95. Found: C, 71.19; H, 8.03.

The compound did not depress the melting point of XII. The infrared absorption curve in carbon tetrachloride solution indicated neither carbonyl nor hydroxyl groups and clearly distinguished the compound from its precursor. Attempts to prepare a 2,4-dinitrophenylhydrazone failed. The ultraviolet absorption (Fig. 1, D) exhibited a maximum at 272 mμ, *E* 690.

Methyl 2,3,4-Trimethoxy-5-hydroxy-5-benzosuberylacetate.—A solution containing 4.00 g. (0.016 mole) of I and 1.5 cc. of methyl bromoacetate in 100 cc. of 3:1 anhydrous ether–benzene was treated with 5 g. of zinc and a crystal of iodine. After refluxing for 1 hour, the additions of bromoester, zinc and iodine were repeated. Two further additions of 1.0 cc. of bromoester, zinc and iodine were made at hourly intervals and 25 cc. of ether was added after a total of 3.5 hours with more zinc and iodine. The reaction was stopped after a total of 6 hours. The product was treated in the usual manner.[12] Distillation of the washed solvents gave an oil which crystallized on standing overnight at 0° with seeding. Only chromatographic separation from impurities in a previous run made crystalline material available for seeding. The solid weighed 3.00 g. (0.00927 mole, 58%), m.p. 91–96°. Further purification from methanol gave thin plates, m.p. 102.5–103.5°, which depressed the melting point of I. The compound gave an orange-rust color in concentrated sulfuric acid.

Anal. Calcd. for $C_{17}H_{24}O_6$: C, 62.95; H, 7.46. Found: C, 62.93; H, 7.52.

The $\Delta^{5(6)}$- or $\Delta^{5(\alpha)}$-olefinic acid was obtained from 0.30 g. of ester by saponification as described previously. The alkaline solution was extracted twice with ether, acidified and the product extracted with ether. The residue from the ether solution crystallized when rubbed with petroleum ether (30–60°). The light tan solid weighed 0.14 g., m.p. 117–120°. After three recrystallizations from ethyl acetate–petroleum ether and one from cyclohexane the melting point was 119.5–121°.

Anal. Calcd. for $C_{16}H_{20}O_5$: C, 65.74; H, 6.90. Found: C, 65.97; H, 6.96.

The Reformatsky Reaction on V.—Repeated attempts to add methyl bromoacetate or methyl γ-bromocrotonate

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[11] Analogous to butyllithium, H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn and L. S. Miller, THIS JOURNAL, **71**, 1499 (1949).

[12] W. E. Bachmann, W. Cole and A. L. Wilds, *ibid.*, **62**, 824 (1940).

to V produced only unreacted material. With meticulously purified and dried reagents the reaction mixture clouded and appeared to be normal. No compound other than V could be isolated.

With similar attention to detail, methyl chloroacetate failed to add to V using sodium methylate. Unchanged crystalline material was recovered.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF WASHINGTON]

Azulene. II. Synthesis of Methyl 1-Azuloate[1]

BY A. G. ANDERSON, JR. AND JAMES J. TAZUMA

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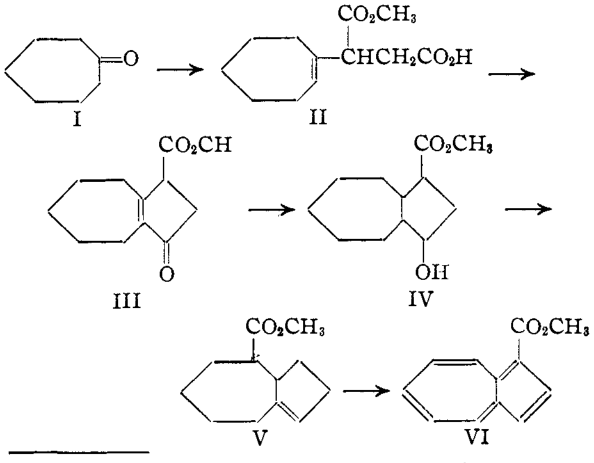
A Stobbe condensation of cycloheptanone with methyl succinate, and subsequent cyclization of the product has been shown to give methyl 3-keto-1,2,3,4,5,6,7.8-octahydro-1-azuloate. This intermediate has been converted to methyl 1-azuloate.

In connection with studies on the electrophilic substitution of azulene, 1-azuloic acid[2] or a derivative thereof was desired as a reference compound. As azulene compounds having a carboxyl group at the 1-position had not been reported in the literature, the synthesis of methyl 1-azuloate from cycloheptanone *via* the route shown (I to VI) was investigated.

Condensation of cycloheptanone (I) with dimethyl succinate in a Stobbe reaction and cyclization of the product (presumably II) gave methyl 3-keto-1,2,3,4,5,6,7,8-octahydro-1-azuloate (III) which was isolated in 27% yield and characterized by analysis. The infrared spectrum of this compound displayed a complex structure in the region between 5.5 and 6.3 μ which was interpreted to be due to the presence of both an ester and a ketone carbonyl group in the molecule.

The usual procedure for the Stobbe reaction sequence involves decarbomethoxylation of one of the intermediates (II or III) and isolation of the unsaturated cyclic ketone. For our purposes the retention of the ester group and, accordingly, the isolation of III was necessary. Johnson, *et al.*,[3] have obtained intermediates corresponding to III from other Stobbe condensations and this particular intermediate had been postulated, but not isolated, by previous workers.[4,5]



Catalytic hydrogenation of III afforded a 50% yield of IV. The infrared spectrum of this substance possessed absorption bands characteristic of hydroxyl and ester groups. Conversion of IV to V was accomplished in 50% yield by dehydration with phosphorus pentoxide. The position of the double bond in V was not established but was assumed to be as indicated from the results of Plattner and co-workers[4] on the dehydration of similar compounds.

Dehydrogenation of V was first attempted by a catalytic vapor phase method similar to that reported for the preparation of azulene.[6] The only product formed in sufficient quantity to permit isolation and identification was azulene. Subsequently it was found that a mixture of the ethyl esters of 1-methyl-5- and 1-methyl-6-azuloic acids[7] also gave a low yield of azulene when dehydrogenated by this same procedure. Treatment of V with sulfur at 180–200°, however, gave VI which was isolated as dark violet needles, m.p. 56–67°. The infrared, ultraviolet and visible absorption spectra of this new azulene derivative were recorded.[8]

Experimental[9]

Methyl 3-Keto-1,2,3,4,5,6,7,8-octahydro-1-azuloate (III).—In a procedure adapted from that of Plattner, *et al.*,[4] 56 g. (0.5 mole) of cycloheptanone[10] was allowed to react with 146 g. (1.0 mole) of methyl succinate in the presence of potassium *t*-butoxide (from 23 g. of potassium) in anhydrous *t*-butyl alcohol (400 ml.). Our procedure differed from that described[4] in that the reaction mixture was permitted to

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[1] From the Ph.D. thesis of James J. Tazuma. This work was supported in part by a grant from the Research Corporation.

[2] The name azuloic acid is proposed for an azulene monocarboxylic acid. This nomenclature corresponds to that used for the analogous compounds of benzene, naphthalene, *etc.*

[3] W. S. Johnson, H. C. E. Johnson and J. W. Peterson, THIS JOURNAL, **67**, 1360 (1945); W. S. Johnson, V. L. Stromberg and J. W. Peterson, *ibid.*, **71**, 1384 (1949).

[4] Hs. H. Günthard, R. Süess, L. Marti and Pl. A. Plattner, *Helv. Chim. Acta*, **34**, 959 (1951).

[5] J. W. Cook, R. Philip and A. R. Sommerville, *J. Chem. Soc.*, 164 (1948).

[6] Paper I, A. G. Anderson, Jr. and J. A. Nelson, THIS JOURNAL, **73**, 232 (1951). The details of the modified apparatus, catalyst and procedure used will be described in the next paper in this series.

[7] A sample of this mixture was kindly provided by Dr. E. J. Cowles.

[8] Absorption spectra have been deposited as Document number 3991 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35 mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

[9] All melting points were taken on a Fisher–Johns block and are uncorrected.

[10] H. J. Dauben, Jr., H. J. Ringold, R. H. Wade and A. G. Anderson, Jr., THIS JOURNAL, **73**, 2359 (1951).