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.

SALT LAKE CITY 1, UTAH

[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

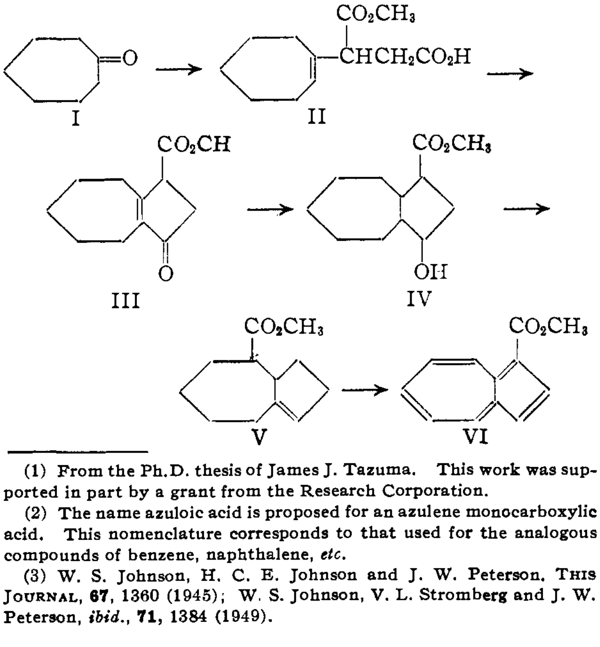
RECEIVED FEBRUARY 13, 1953

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).

stand overnight after refluxing and the ether extracts, after acidification, were extracted with 1 N ammonium hydroxide rather than sodium bicarbonate. The crude yellow oil (presumably II) thus obtained (86 g., 0.38 mole) was added over a period of 10 minutes to a solution of 26 g. (0.19 mole) of anhydrous zinc chloride, 900 ml. of acetic anhydride and 350 ml. of acetic acid in a 3 l., three-necked flask fitted with a dropping funnel and reflux condenser. The contents of the flask were protected from moisture under a dry nitrogen atmosphere. The resulting solution was heated at 40° for two days and then at 120° for 4 hours. After distillation of *ca.* 1200 ml. of the solvent, 500 g. of ice was added to the cooled residue and the solution made basic with dilute ammonium hydroxide. The oily layer which formed was separated and the aqueous phase extracted with three 200 ml. portions of ether. The combined oil and ether extracts were dried, the solvent removed and the residue distilled under reduced pressure. The fraction (11 g.) boiling at 120–130° at 0.15 mm. was collected and redistilled to give 7 g. of III, b.p. 110–113° at 0.06 mm., $n^{25}\mathrm{D}$ 1.5062. Redistillation of a higher boiling (130–140° at 0.15 mm.) fraction gave an additional 1.5 g. (total yield 7.9%) of slightly less pure product ($n^{25}\mathrm{D}$ 1.5048). The sample for analysis distilled at 113° at 0.08 mm., $n^{25}\mathrm{D}$ 1.5071.

Anal. Calcd. for $C_{12}H_{16}O_3$: C, 69.21; H, 7.75. Found: C, 69.53; H, 7.81.

A 2,4-dinitrophenylhydrazone of III, prepared in the usual manner and recrystallized from alcohol, was obtained as orange prisms, m.p. 185–187°.

Anal. Calcd. for $C_{18}H_{20}N_4O_6$: C, 55.66; H, 5.19. Found: C, 55.20; H, 5.26.

Methyl 3-Hydroxydecahydro-1-azuloate (IV).—A solution of 14.4 g. (0.69 mole) of the redistilled keto ester (III) in 25 ml. of ethanol was hydrogenated at 100° and 1500 lb. pressure in the presence of Raney nickel catalyst.[11] The catalyst and solvent were removed and the residue distilled under reduced pressure. The fraction (10 g.) boiling at 97–102° at 0.04 mm. was collected and redistilled to give 8.7 g. (60%) of IV, b.p. 96–99° at 0.03 mm., $n^{25}\mathrm{D}$ 1.4913.

Anal. Calcd. for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 68.24; H, 9.59.

Methyl 1,2,4,5,6,7,8,9-Octahydro-1-azuloate (V).—Phosphorus pentoxide (4 g.) was suspended in 25 ml. of dry benzene under a nitrogen atmosphere in a small three-necked flask equipped with a dropping funnel and stirrer. A solution of 3.7 g. (0.017 mole) of the hydroxy ester (IV) in 15 ml. of dry benzene was added dropwise to the rapidly stirred suspension. After 3 hours 2 g. of phosphorus pentoxide was added and the stirring continued for 8 hours. After separation of the benzene layer, the residue was dissolved in water and extracted with ether, the ether extracts being combined with the original benzene layer. The organic solution was dried, the solvent removed and the residue distilled. The fraction (1.8 g., 55%) boiling at 65–68° at 0.15 mm. was collected, $n^{25}\mathrm{D}$ 1.4901.

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 73.59; H, 9.01.

Methyl 1-Azuloate (VI).—In a small one-piece distilling apparatus was placed a mixture of 1 g. (5.1 millimoles) of the unsaturated ester (V) and 0.65 g. (20.4 millimoles) of flowers of sulfur. The bulb of the apparatus was heated to 180–200° in a salt-bath for 30 minutes under a slight vacuum. When the evolution of hydrogen sulfide had ceased the bath temperature was raised to 280° and the pressure lowered to *ca.* 10 mm. The deeply violet-colored distillate obtained was dissolved in a small volume of petroleum ether and the mixture filtered through a small, short alumina column to remove unreacted sulfur. The filtrate was concentrated and chromatographed on an alumina column (8 × 200 mm.) with a mixture of 80% petroleum ether and 20% benzene as the eluent. Four zones (lavender, violet, blue and orange) developed and were collected. The eluates from the first, third and fourth zones were very weakly colored and were discarded. The violet eluate fraction was concentrated and rechromatographed to give, after crystallization from petroleum ether, 25 mg. (2.6%) of VI as violet needles, m.p. 56–57°. The absorption spectrum[8] of a cyclohexane solution of VI showed maxima in mμ at 235, log ϵ 4.28; 287, log ϵ 4.63; 292, log ϵ 4.63; 298, log ϵ 6.72; 352, log ϵ 3.78; 370, log ϵ 3.98; 544, ϵ 411; 590, ϵ 358 and 650, ϵ 146. The infrared spectrum was taken.[8]

Anal. Calcd. for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.30; H, 5.55.

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[11] A. A. Pavlic and H. Adkins, *ibid.*, **68**, 1471 (1946).

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

Azulene. III. Electrophilic Substitution[1-3]

BY A. G. ANDERSON, JR., JERRY A. NELSON[4] AND JAMES J. TAZUMA

RECEIVED MAY 15, 1953

Friedel–Crafts acetylation of azulene has been shown to give 1-acetylazulene and a diacetylazulene. The structure of the 1-acetylazulene was established by conversion to methyl 1-azuloate. 1-Nitroazulene has been obtained from the treatment of azulene with cupric nitrate and acetic anhydride and reaction of the hydrocarbon with benzenediazonium chloride has been shown to give 1-azuleneazobenzene. These results constitute the first conclusive demonstration that azulene undergoes electrophilic substitution in the 1-position. Reaction of azulene with one equivalent of N-bromo- or N-chlorosuccinimide has been shown to give the corresponding monohaloazulene plus some dihaloazulene. The latter was also obtained in good yield from the monohalogen derivative by further halogenation or directly from azulene by the use of two equivalents of the halogenating agent. A number of other new azulene derivatives have been prepared and evidence has been obtained which indicates the halogenation products to be 1-halo- and 1,3-dihaloazulenes. Two improvements in the method used for the synthesis of azulene are described. The resonance stability and electrophilic substitution of azulene are considered from a simplified molecular orbital standpoint.

Prior to the report of our first results from a study of the electrophilic substitution of azulene,[5] knowledge of the chemical properties of this unique hydrocarbon was limited to a few experiments which demonstrated the unsaturated character of the molecule.[6] It was observed that (a) vigorous reactions yielding no well defined products resulted from treatment with bromine or nitrosyl chloride;

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

[2] Presented in part at the 118th Meeting of the American Chemical Society, Chicago, Illinois, September, 1950.

[3] Absorption spectra not shown have been deposited as Document number 3992 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 $5.00 for photoprints, or $2.25 for 35 mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

[4] Shell Oil Fellow, 1949–1950.

[5] A. G. Anderson, Jr., and J. A. Nelson, THIS JOURNAL, **72**, 3824 (1950).

[6] A. E. Sherndal, *ibid.*, **37**, 167 (1915); L. Augsburger, *Science*, **42**, 100 (1915); L. Ruzicka and A. J. Haagen-Smit, *Helv. Chim. Acta*, **14**, 1104 (1931).