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}_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}_D 1.5048). The sample for analysis distilled at 113° at 0.08 mm., n^{25}_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}_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}_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.

SEATTLE 5, WASHINGTON

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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).

(b) oxidative decomposition occurred on reaction with nitric acid, chromic acid or potassium permanganate; and (c) hydrogenation took place readily in the presence of catalysts. It was presumably from these results that Pommer[7] concluded that azulene had no aromatic properties.

Azulene, however, can be classified as aromatic with respect to resonance stability[8] and is the only known bicyclic non-benzenoid hydrocarbon of this type. It seemed of importance, therefore, to undertake a more extensive study of its chemistry, especially with regard to reactions characteristic of aromatic systems.

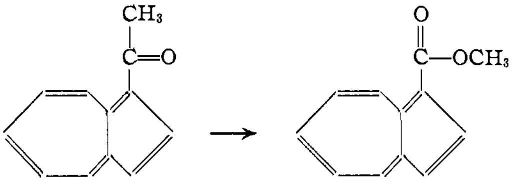
In an earlier paper[9] an improved synthesis of azulene from β-decalol was described. Subsequently two of the steps in the synthesis have been modified. A procedure has been adopted for the ozonolysis of (9,10)-octalin wherein methanol is used as the solvent and the reaction is carried out at 0° in a manner similar to that described by Criegee and Wenner.[10] The yields of 1,6-cyclodecanedione obtained ranged from 60 to 70%.

As the procedure previously described[9] for the dehydrogenation of 1,2,3,4,5,6-hexahydroazulene was subsequently found to be unsatisfactory in several respects, a more complete study of the reaction conditions was undertaken. While this work was in progress the results of a similar investigation on the dehydrogenation of an octahydroazulene and decahydroazulene by Plattner, *et al.*,[11] were reported. These authors were able to obtain an 11% yield of azulene. Our findings in the range of conditions studied agreed in general with theirs. We did, however, discover that a catalyst of 5% palladium–charcoal suspended on 40% magnesium oxide and 60% Norite was superior to others having either aluminum or Norite alone or various other combinations of the metal oxides and Norite as the carrier. An additional factor of importance was the purity of the hexahydroazulene and it was necessary for this material to be freshly distilled before dehydrogenation. Conditions were ultimately found which gave a 32% yield of azulene.

The construction of the apparatus is shown in Fig. 6. The use of an inert packing above and below the catalyst was recommended by Plattner, *et al.*[11] The apparatus and procedure as described were used in the attempted dehydrogenation of partially saturated azuloic acid esters to the corresponding azulene derivatives.[12] A special attachment for the dehydrogenation of solids is also shown. This was used in the preparation of 1-azabenz[b]azulene.[13]

By means of this modified synthesis it has been possible to prepare sufficient azulene to carry out a number of studies on the electrophilic substitution of azulene, among them the Friedel–Crafts acetylation. In our first experiments with this reaction it was found that treatment of azulene with approximately a one molar excess of acetic anhydride and aluminum chloride in carbon bisulfide at room temperature gave a 62% net yield of a diacetylazulene as red or maroon needles. The two allotropic forms were interconvertible. With an excess of azulene the reaction yielded the diacetylazulene (7% net yield) plus an unstable maroon oil (6% net yield) which could not be obtained analytically pure. The use of stannic chloride or mercuric chloride as the condensing agent under the same conditions did not greatly improve the yield of the maroon oil. Further study showed that the use of a slight excess of stannic chloride and a large excess of acetic anhydride with methylene chloride as the solvent afforded the diacetylazulene (11%) and a 57% yield of a somewhat unstable deep lavender oil which corresponded (ultraviolet and visible absorption spectra) to the maroon oil previously obtained. The lavender oil was characterized as a monoacetylazulene (I) by analysis of the stable oxime, semicarbazone and trinitrobenzene derivatives.

Attempted conversion of I to the corresponding acid by oxidation with sodium hypochlorite gave no acidic material. Sixty per cent. of the starting material was isolated plus a small amount of a green solid which proved to be identical with the dichloroazulene obtained from the reaction of azulene with N-chlorosuccinimide. When the oxidation was carried out under mild conditions (room temperature) with sodium hypoiodite an acidic product was isolated. Treatment of this material with diazomethane gave an ester (II) in 68% yield which was identical with the methyl 1-azuloate previously synthesized.[12] *This result provided the first unequivocal evidence that azulene undergoes electrophilic substitution in the 1-position.*



I II

Work on the structure of the diacetylazulene is in progress. Curiously, attempts to prepare this compound by further acetylation of the 1-acetylazulene have given very low yields.

As azulene has been reported to be oxidatively decomposed by nitric acid,[14] it was evident that successful nitration would require special conditions. Two reagents which seemed suitable were benzoyl nitrate and acetyl nitrate. While the former was found to react to give a nitroazulene, the yields were not satisfactory. However, reaction of azulene with an equivalent of cupric nitrate in acetic anhydride[15] gave a 63% yield of a red, crystalline mononitroazulene. The ultra-

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[7] H. Pommer. *Angew. Chem.*, **62**, 281 (1950).

[8] The resonance energy of azulene is *ca.* 46 kcal./mole; *cf.* E. Perretot. W. Taub and E. Briner. *Helv. Chim. Acta*, **23**, 1260 (1940): E. Heilbronner and K. Wieland, *ibid.*, **30**, 947 (1947).

[9] Paper I. A. G. Anderson, Jr., and J. A. Nelson. This Journal, **73**, 232 (1951).

[10] R. Criegee and G. Wenner. *Ann.*, **564**, 9 (1949).

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

[12] Paper II. A. G. Anderson. Jr., and J. J. Tazuma. This Journal, **75**, 4979 (1953).

[13] A. G. Anderson. Jr., and J. J. Tazuma. *ibid.*, **74**, 3455 (1952).

[14] R. E. Kremers. This Journal, **45**, 717 (1923).

[15] It has been postulated that nitrations carried out in this manner proceed *via* the intermediate acetyl nitrate: G. Bacharach. *ibid.*, **49**, 1522 (1927).

violet and visible absorption spectra of the product (Fig. 1) were unlike those of any previously known azulene derivative. This was not unexpected as the conjugative effects of auxochromic groups attached to aromatic systems are known to result in decreased fine structure and marked alteration of the hydrocarbon spectrum.[16] The infrared spectrum was taken.[3]

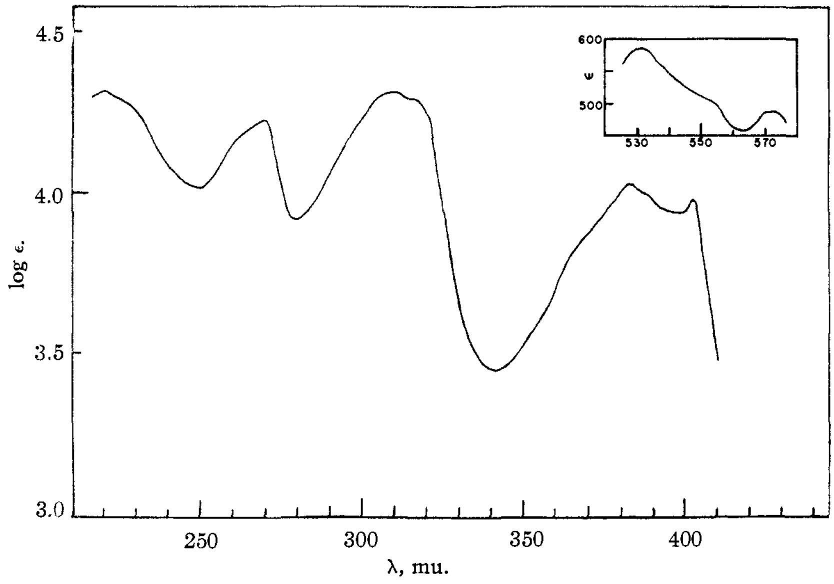

Fig. 1.—Ultraviolet and visible spectra of 1-nitroazulene.

Substitution by diazonium arylation has been postulated to occur by a radical mechanism.[17] It was initially hoped, therefore, that the reaction of azulene with a benzenediazonium salt under conditions similar to those described by Kvalnes for the arylation of quinones[18] would result in radical substitution and thus afford a test of the prediction by Brown that this type of substitution would take place in the 4-position.[19] It was found, however, that the product from the immediate reaction which took place was an azuleneazobenzene and, therefore, that electrophilic rather than radical substitution had occurred.[20] The azo compound, which was obtained in excellent yield as an opaque, yellow solid, dissolved readily in organic solvents to give yellow solutions. Treatment with concentrated inorganic acids produced a deep red color. The absorption spectrum in the ultraviolet and visible regions (Fig. 2), like that of the nitroazulene, differed markedly from typical azulene spectra. The infrared spectrum was recorded.[3]

Attempts to prepare an unsubstituted aminoazulene from both the nitroazulene and the azuleneazobenzene were unsuccessful. Although reduction apparently occurred in each case (see below), no amine could be isolated. Reduction of the nitroazulene followed by the addition of sodium nitrite and then cuprous halide failed, in separate experiments, to yield any bromo- or chloroazulene.

That nitration and diazonium coupling had effected substitution in the same position on the azulene nucleus was shown by conversion of both derivatives to the same crystalline N-acetylazulylamine. This was accomplished in 90% yield from the nitro compound by reductive acetylation and in 48% yield from the azo compound by reductive cleavage followed by acetylation. Beckmann rearrangement of the oxime of 1-acetylazulene (V) gave a 16% yield of N-acetyl-1-azulylamine (VI). This substance was identical with the products obtained from the nitro and azo derivatives thus establishing the identity of the latter as 1-nitroazulene (III) and 1-azuleneazobenzene (IV).

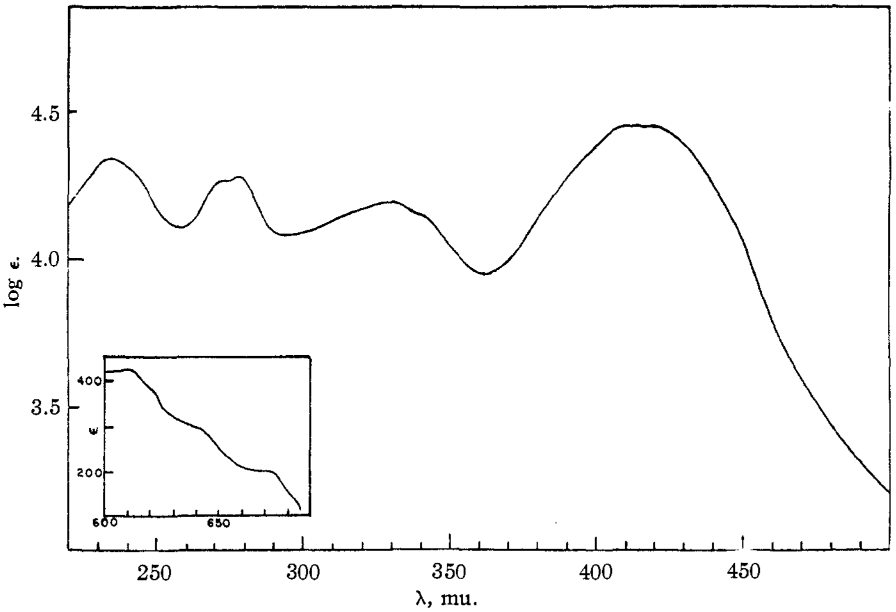

Fig. 2.—Ultraviolet and visible spectra of 1-azuleneazobenzene.

The reaction of bromine with azulene is vigorous and yields no well defined products,[14] but in view of the pronounced reactivity of azulene to other

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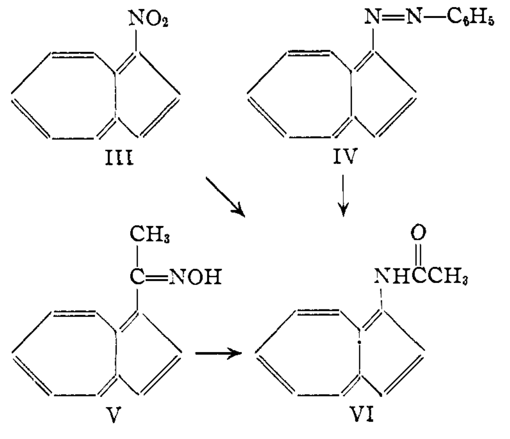
(16) R. H. Jones, *ibid.*, **67**, 2127 (1945).

(17) D. H. Hey and W. A. Waters, *Chem. Revs.*, **21**, 169 (1937); D. H. Hey, *Ann. Repts. on Progress Chem.* (*Chem. Soc. London*), **37**, 278 (1940).

(18) D. E. Kvalnes, This Journal, **56**, 2478 (1934).

(19) R. D. Brown, *Trans. Faraday Soc.*, **44**, 984 (1948).

(20) Pl. A. Plattner, *Chimia* (*Switz.*), **4**, 260 (1950), has recently reported similar results with a number of aryl diazonium salts.



electrophilic reagents it seemed likely that substitution could be effected with N-halosuccinimides.[21] Indeed, N-bromosuccinimide and azulene reacted immediately in the absence of catalysts in benzene solution or even when mixed in the solid state. From the reaction of an equimolar mixture of azulene and N-bromosuccinimide in benzene was isolated a rather unstable greenish-blue oil (66%) which could not be obtained analytically pure. The absorption spectra of the product[3] were quite similar to those characteristic of a 1-alkylazulene,[22] the essential difference consisting of the appearance of fine structure in the peak at 280 mμ. The identity of the product as a monobromoazulene was shown by the preparation of a trinitrobenzene derivative which, though unstable to heat, was obtained sufficiently pure for analysis.

A second product from the bromination was a green crystalline dibromoazulene (32% based on N-bromosuccinimide) which was also obtained in 88% yield from the reaction of the monobromoazulene with a second mole of N-bromosuccinimide or in 73% yield by direct bromination of azulene with two moles of the reagent. The dibromoazulene existed in two allotropic forms (green needles, m.p. 76–77°, and blue needles, m.p. 88–89°) which were interconvertible. The visible region of the absorption spectrum of the compound[3] closely resembled that characteristic of a 1,3-dialkylazulene.[23] The infrared spectrum is shown in Fig. 3.

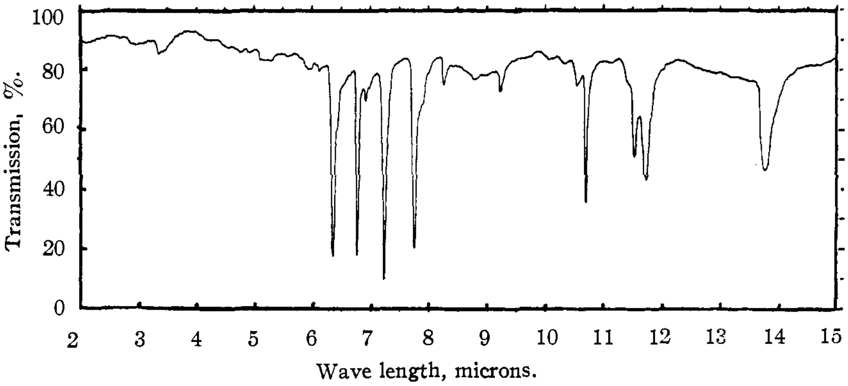


Fig. 3.—Infrared spectrum of 1,3-dibromoazulene.

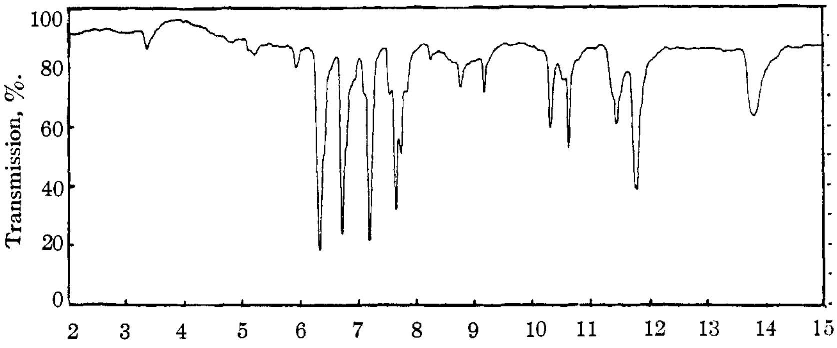


Fig. 4.—Infrared spectrum of 1,3-dichloroazulene.

The absorption spectra in the ultraviolet and visible regions corresponded exactly with those of a product previously obtained from the reaction of N-bromosuccinimide with 1,2,3,4,5,6-hexahydroazulene[9] and the latter compound is probably the same dibromoazulene.

Azulene was found to react with N-chlorosuccinimide in an analogous manner except that the rate of reaction was noticeably slower. A monochloroazulene, also a somewhat unstable oil, was obtained in 79% net yield and characterized as the trinitrobenzene derivative. The ultraviolet, visible and infrared spectra[3] of the chloroazulene were very similar to those of the bromoazulene. A crystalline dichloroazulene was obtained in 65% yield by direct chlorination of azulene with two moles of N-chlorosuccinimide or in 82% net yield from the reaction of the monochloroazulene with one mole of the reagent. The ultraviolet, visible and infrared (Fig. 4) spectra[3] of the dichloroazulene corresponded closely to those of the dibromoazulene.

As the monohaloazulenes were most probably 1-substituted derivatives, the conversion of the halogen groups to carboxyl groups was attempted. It was anticipated that this procedure would afford direct evidence for the structure of the haloazulenes as methyl 1-azuloate had been synthesized previously.[12] Both monobromo- and monochloroazulene, however, proved to be inert to metallic magnesium and lithium. Also reaction of *n*-butyllithium with the bromoazulene in an attempted metal–halogen interconversion resulted in

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(21) The reactions of N-halosuccinimides with strongly nucleophilic compounds are generally considered to be ionic and it was presumed that the halogenation of azulene would involve substitution at the 1-position.

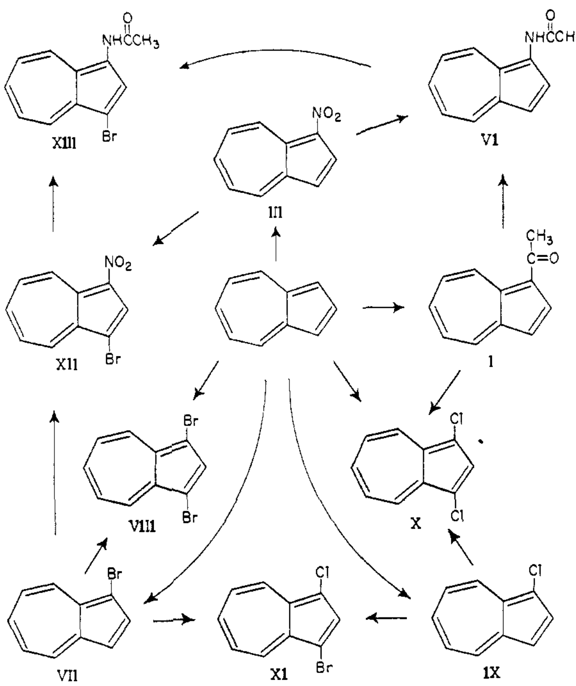
(22) Pl. A. Plattner and G. Buchi, *Helv. Chim. Acta*, **29**, 1608 (1946).

(23) Pl. A. Plattner, A. Furst and K. Jirasek, *Helv. Chim. Acta*, **30**, 1320 (1947). The ultraviolet spectrum of a 1,3-dialkylazulene has not been reported.

immediate decolorization of the blue solution but no identifiable products could be isolated after subsequent treatment with Dry Ice. The failure of the previously mentioned attempts to convert 1-nitroazulene (III) to 1-bromo- or 1-chloroazulene precluded identification in this manner.

As the above experiments were unsuccessful, other evidence for the structures of the haloazulenes was sought. Bromination of 1-nitroazulene with N-bromosuccinimide afforded a crystalline bromonitroazulene. This same product was obtained from the nitration of bromoazulene with cupric nitrate and acetic anhydride. The location of the nitro group of the bromonitroazulene in the 1-position was established by bromination of N-acetyl-1-azulylamine (VI) (obtained from 1-nitroazulene) to give a bromo-N-acetyl-1-azulylamine and the preparation of this same derivative from the bromonitroazulene by reductive acetylation. Further, bromination of chloroazulene and chlorination of bromoazulene gave identical chlorobromoazulenes and the infrared (Fig. 5), ultra violet and visible spectra of this compound[3] were very similar to those of the dichloro- and dibromoazulenes.

The above results plus a consideration of the previous observations provide, in our opinion, good evidence that the halogenation products are 1-halo- and 1,3-dihaloazulenes. First, all compounds of proven structure resulting from electrophilic substitution are 1-substituted azulenes. Second, the formation of a dichloroazulene from the action of N-chlorosuccinimide on 1-acetylazulene (I) is most reasonably interpreted as involving an electrophilic displacement of the group on the 1-position by a positive chlorine. An established example of this type of reaction has recently been reported.[24] Third, the nitro group in the bromonitroazulene obtained from both 1-nitroazulene and the bromoazulene is in the 1-position and the bromo compound is, therefore, most probably 1-bromoazulene (VII). Fourth, isolation of the same product from the bromination of chloroazulene and the chlorination of bromoazulene shows that the halogen groups in the two monohaloazulenes are in equivalent positions. Fifth, it is unlikely that the close similarity of the absorption spectra of the two monohaloazulenes and 1-methylazulene, and of the three dihaloazulenes and 1,3-dimethylazulene, plus the relative simplicity of the infrared spectra of the dihaloazulenes which would be expected for symmetrical structures, are purely fortuitous. Therefore, the most reasonable assignment of structures for the haloazulenes and their derivatives is that shown in the diagram summarizing the reactions discussed above. It is of interest that the nature of the substituent group on the 1-position apparently does not alter the position of substitution for the second entering group.



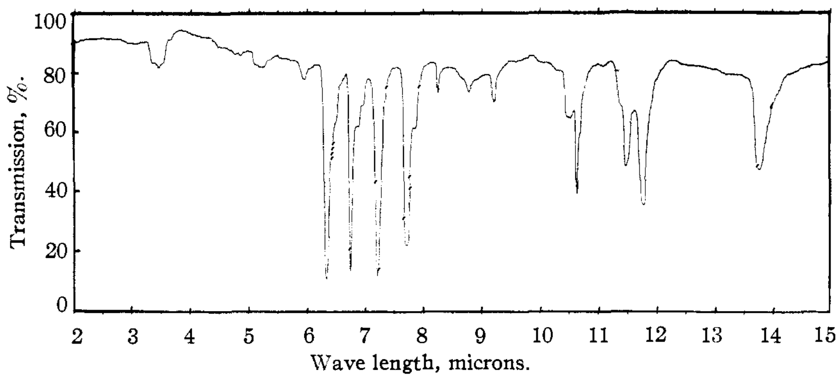
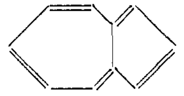
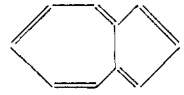


Fig. 5.—Infrared spectrum of 1-chloro-3-bromoazulene.

The ability of azulene to undergo substitution with electrophilic reagents demonstrates the aromatic character of the molecule. Azulene and other similar but hypothetical structures (*i.e.*, pentalene and heptalene) have been the subject of numerous theoretical considerations.[25] In this connection a greatly simplified quantum mechanical interpretation is pertinent to the explanation of the observed electrophilic substitution and resonance stability of azulene. The molecular systems fundamental to this viewpoint are cyclic unsaturated structures wherein 4n + 2 overlapping 2p π-atomic orbitals[26] form a topological ring which may be con-



XIV



XV

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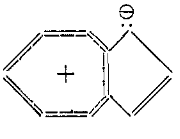
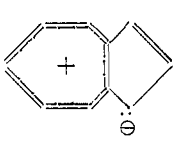
[24] N. J. Cartwright, J. I. Jones and D. Marmion, *J. Chem. Soc.*, 3499 (1952).

[25] For recent papers see: (a) D. P. Craig, *J. Chem. Soc.*, 3175 (1951); (b) R. D. Brown, *ibid.*, 2391 (1951); (c) B. Pullman, M. Mayot and G. Berthier, *J. Chem. Phys.*, **18**, 257 (1950); (d) G. Berthier and A. Pullman, *Compt. rend.*, **229**, 561 (1949); (e) G. W. Wheland and D. E. Mann, *J. Chem. Phys.*, **17**, 264 (1949); and (f) G. W. Wheland and D. E. Mann, *ibid.*, **17**, 269 (1949).

[26] C. A. Coulson, *Quart. Revs.*, **1**, 144 (1949).

sidered to be responsible for the resonance stability of such compounds.[27] As an extension of this theory, the normal or ground state of azulene may be represented by the two classical valence-bond structures (XIV and XV) and the thermodynamic stability[8] attributed to the ring of ten π-electrons in the perimeter of the molecule. If an analogous stabilization of a heptacarbocyclic ring wherein six π-electrons resonate among seven π-orbitals is accepted,[28] the theory may be applied quite successfully to explain the electrophilic substitution of azulene. In accordance with this theory formulas XVI and XVII would represent reacting structures of azulene having six π-electrons in a resonance stabilized seven-membered ring and a replaceable hydrogen at a negative position exocyclic to the stable ring. Indeed, no other structures may be drawn which possess both of these characteristics. Consequently electrophilic substitution would be expected to take place at the 1-position and also to occur more readily than if the negative position were in the stable ring (*i.e.*, as in benzene).[29] Our experimental results are in agreement with these predictions.


XVI


XVII

LCAO molecular orbital calculations of the relative stabilities of the six possible azulenium ions have led Heilbronner and Simonetta[30] to theoretical results in accord with the above discussion. Both the present reasoning and that of these authors are consistent with the observed dipole moment of azulene[25e] (which would result from any contribution of structures such as XVI and XVII to the ground state) and with other theoretical studies of the hydrocarbon.[25c,d,f]

We wish to thank Dr. W. T. Simpson for helpful discussions with regard to the qualitative application of molecular orbital theory to azulene.

Experimental[31]

1,6-Cyclodecanedione.—The ozonolysis of (9,10)-octalin[9] was conducted as described by Criegee and Wenner[10] except that the temperature was 0° and the intermediate 1-hydroperoxy-1-methoxy-6-cyclodecanone was hydrolyzed with 40% acetic acid. The yields ranged from 60 to 70%.

Dehydrogenation Catalyst.—The directions given by Linstead and Thomas[32] for the preparation of catalyst-*d* were used with the following modifications. For 1 g. of palladium chloride dihydrate, a mixture of 4 g. of C.P. magnesium oxide and 6 g. of acid-free, degassed Norite was used as the carrier. The catalyst was washed thoroughly (seven times) with distilled water by centrifugation and decantation and then washed on a sintered glass funnel with 1 liter of hot distilled water. No dilute acetic acid wash was used. The resulting wet paste was sucked partially dry and then formed into 6 × 6 mm. cylinders in a troche press made of Lucite. The catalyst was ready for use after drying in a vacuum oven at 80° and 20 mm. for 24 hours.

Azulene.—The liquid delivery apparatus was attached to the top of the dehydrogenation column, constructed and packed as shown in Fig. 6, and two side-arm receivers were connected in series at the bottom with the second one attached to a water aspirator. The receivers were cooled in a Dry Ice–acetone-bath. The apparatus was then evacuated, swept with nitrogen at a rate of 0.2 liter per minute (the rate was regulated by adjustment of valves D and E) and heated to 320–330°. The liquid 1,2,3,3,5,6-hexahydroazulene (2.3 g., 0.017 mole), prepared as previously described,[9] was admitted over a period of eight hours. A uniform rate of delivery over this period was obtained by adjusting valves C and F. A few minutes after the first portion of the diene had entered the column crystalline azulene appeared in the first receiver. The collected products were taken up in petroleum ether and chromatographed on an alumina column (27 × 200 mm.). A total of 500 ml. of petroleum ether was used to wash to column. The first eluate fraction (150 ml.) contained a small amount of unreacted diene. Evaporation of the second fraction (350 ml.) and sublimation of the residue at 10 mm. pressure yielded 715 mg. (32%) of azulene; m.p. 97–98°.

Diacetylazulene.—Azulene (19 mg., 0.15 millimole) dissolved in 10 ml. of dry C.P. carbon bisulfide was stirred vigorously at room temperature and a mixture of 50 mg. of finely powdered C.P. aluminum chloride, 5 ml. of carbon bisulfide and 30 mg. (0.29 millimole) of acetic anhydride added slowly over a period of 10 minutes. The blue color of the azulene gradually disappeared. After 1 hour, 10 ml. of ice-water was added and the mixture stirred for an additional 10 minutes. The carbon bisulfide solution was separated, washed with water (10 ml.) and the solvent evaporated in a stream of air. Unreacted azulene (13.6 mg.) was recovered by sublimation at room temperature and 10 mm. pressure and the residue taken up in benzene and chromatographed on an alumina column. Washing with benzene eluted remaining traces of azulene, then a small lavender band from which less than 1 mg. of a maroon oil was obtained and, finally, an orange-red band.

The benzene was evaporated from the orange-red eluate and the red crystals remaining were sublimed at 90° and 1 mm. pressure to give red needles (5.6 mg., 62% net yield) melting at 170–187°. Two recrystallizations from acetone raised the melting point to 189–190°. The compound was also obtained as light maroon needles, m.p. 119–120°, and the two allotropic forms were interconvertible by seeding a saturated acetone solution. The absorption spectrum of an ethanolic solution displayed maxima in mμ at 240, log ϵ 4.51; 289, log ϵ 4.69; 308, log ϵ 4.49; 382, log ϵ 4.03; and 498, log ϵ 2.85.[3]

Anal. Calcd. for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70. Found: C, 78.91; H, 5.56.

A semicarbazone derivative was obtained as orange-red needles, m.p. 184–185°.

1-Acetylazulene (I).—Azulene (0.5 g., 3.9 millimoles) was treated with a solution of 8.2 ml. (87 millimoles) of redistilled acetic anhydride and 0.8 ml. (4.1 millimoles) of anhydrous stannic chloride in 82 ml. of methylene chloride. As the solution was thoroughly mixed the color changed from blue to deep yellow and then to deep red with a green fluorescence. The mixture was shaken intermittently at room temperature for 15 minutes and the stannic chloride complex then decomposed by the addition of 50 ml. of 2 *N* hydrochloric acid. The two phases were thoroughly shaken,

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[27] For a more detailed discussion see E. Hückel, *Z. Elektrochem.*, **43**, 752 (1937), or C. A. Coulson, "Valence," Oxford University Press, London, 1952. The concept of stabilization by 4n + 2 electrons may be understood in a general way from the free-electron model: *cf.* W. T. Simpson, *J. Chem. Phys.*, **16**, 1124 (1948), and J. R. Platt, *ibid.*, **17**, 485 (1949).

[28] The one-electron energy level pattern for such a system is the same as that for six π-electrons in six π-orbitals and thus, theoretically, analogous stabilization would occur. This concept has been applied in explanations of the partial aromatic character of tropone: H. J. Dauben, Jr., and H. J. Ringold, THIS JOURNAL, **73**, 876 (1951); W. von E. Doering and F. L. Detert, *ibid.*, **73**, 876 (1951); W. von E. Doering and L. H. Knox, *ibid.*, **74**, 5683 (1952).

[29] The first prediction of electrophilic substitution in the 1-position from quantum mechanical considerations was made by R. D. Brown (ref. 19), who calculated approximate polarization energies and π-electron densities. The present discussion is a more qualitative application of molecular orbital reasoning which is felt by the authors to be of value because of its relative simplicity.

[30] E. Heilbronner and M. Simonetta, *Helv. Chim. Acta*, **35**, 1049 (1952).

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

[32] R. P. Linstead and S. L. S. Thomas, *J. Chem. Soc.*, 1127 (1940).

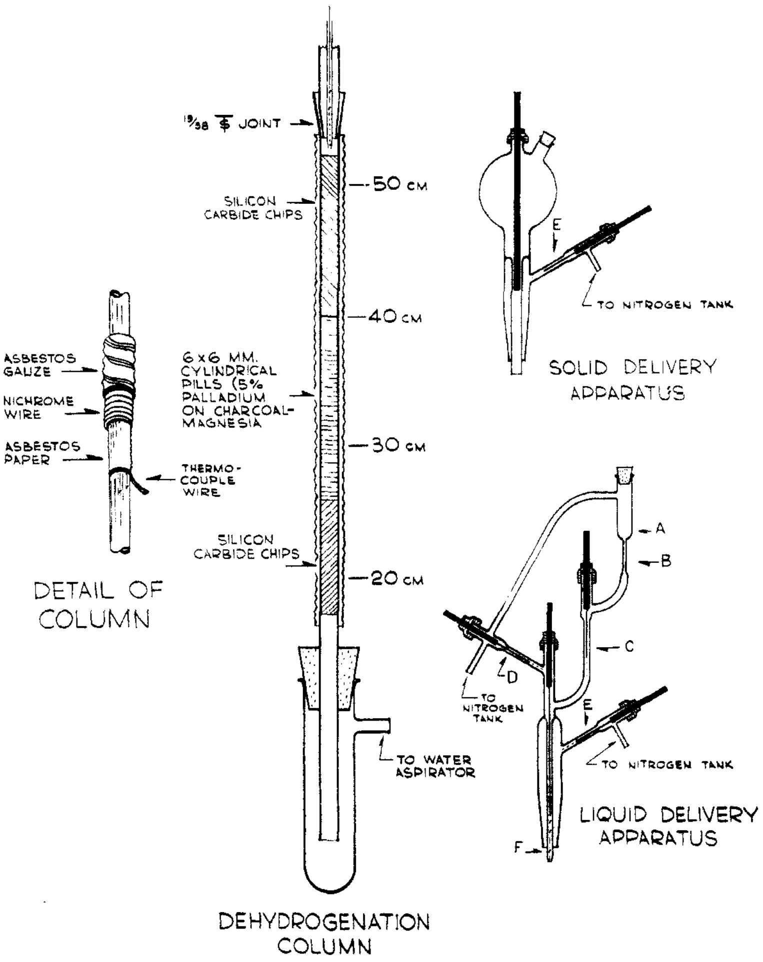

Fig. 6.—Apparatus for vapor phase catalytic dehydrogenation: A, reservoir for liquid to be dehydrogenated; B, capillary tube fitted with a nichrome wire; C, D, E and F, capillary tube—nichrome wire valves. Heavy black parts are glass rods. The silicon carbide chips used were grit No. 6.

then separated and the aqueous layer extracted with two 50-ml. portions of methylene chloride. The combined organic layers were washed with five 100-ml. portions of water and concentrated *in vacuo*. The residue was chromatographed on an alumina column. Six bands (blue, green-blue, yellow green, green-blue, yellow and orange) developed and were eluted with a mixture of 80% petroleum ether and 20% benzene. As these eluates contained only trace amounts of products they were discarded. The chromatograph was further developed with methylene chloride and three additional bands (lavender, yellow-brown and red) were eluted. The yellow-brown eluate was discarded. The material from the lavender fraction was rechromatographed twice and from the final eluate was obtained 0.375 g. (57%) of 1-acetylazulene as a lavender oil. The ultraviolet and visible absorption spectra of a *n*-hexane solution exhibited maxima in mμ at 235, log ε 4.22; 292, log ε 4.43; 297, log ε 4.41; 304, log ε 4.50; 366, log ε 3.25; 382, log ε 3.79; 550, log ε 2.50; 595, log ε 2.44 and 655, log ε 2.03.[3] The infrared spectrum was taken.[3]

The red fraction was rechromatographed and yielded 0.92 g. (11%) of diacetylazulene, m.p. 185–188°.

The lavender oil (18 mg.), which was somewhat unstable, was treated with a solution of 0.012 g. of trinitrobenzene in 1 ml. of ethanol. Warming the mixture on a steam-bath and then slowly cooling gave the trinitrobenzene derivative as brown needles, m.p. 114–115°.

Anal. Calcd. for $C_{18}H_{13}N_3O_7$: C, 56.40; H, 4.07. Found: C, 56.86; H, 3.63.

To a solution of 0.312 g. of the 1-acetylazulene in 3 ml. of alcohol was added a solution of 0.75 g. of semicarbazide hydrochloride, 1 g. of sodium acetate and 5 ml. of water. The green precipitate obtained after heating on a steam-bath for 45 minutes was recrystallized twice from alcohol to give 0.25 g. of the semicarbazone as green plates, m.p. 212–213°.

Anal. Calcd. for $C_{13}H_{13}N_3O$: C, 68.71; H, 5.77. Found: C, 68.40; H, 6.05.

To 47 mg. of 1-acetylazulene dissolved in 2 ml. of alcohol was added a solution of 98 mg. of hydroxylamine hydrochloride and 300 mg. of sodium acetate in 3 ml. of water. The mixture was warmed on a steam-bath for one hour, during which period the color gradually changed from lavender to blue. After an additional 30 minutes at room temperature more water was added and the mixture extracted with methylene chloride. The extracts were concentrated and the residue chromatographed on an alumina column with methylene chloride as the eluent. The lavender fraction, after purification by rechromatography, yielded 7 mg. of 1-acetylazulene. The blue effluent was rechromatographed and the product crystallized from petroleum ether–methylene chloride to give 37 mg. (85% net yield) of 1-acetylazulene oxime as dark blue needles, m.p. 97–98°.

Anal. Calcd. for $C_{12}H_{11}NO$: C, 77.81; H, 5.99. Found: C, 77.82; H, 6.23.

Acetylation of 1-Acetylazulene.—1-Acetylazulene (5.2 mg.) dissolved in 5 ml. of dry carbon bisulfide was heated on a steam-bath for one hour with 10 mg. of C.P. aluminum chloride and one drop of acetic anhydride. The reaction was quenched with a little water and the mixture worked up as described above for the preparation of diacetylazulene. Approximately 3 mg. of 1-acetylazulene and 0.5 mg. of red crystals identical to the diacetylazulene obtained from the acetylation of azulene were isolated.

Hypochlorite Oxidation of 1-Acetylazulene.—A solution of sodium hypochlorite was prepared from 21.8 g. of sodium hydroxide, 30 ml. of water, 125 g. of ice and 16.1 g. of chlorine as described by Newman and Holmes.[33] To 18 ml. (13 millimoles) of the hypochlorite solution heated to 60° was added dropwise with stirring a solution of 0.39 g. (2.3 millimoles) of 1-acetylazulene in 8 ml. of dioxane. The temperature of the mixture was maintained between 60 and 70° for 15 minutes and the heat then removed. After one hour the unreacted hypochlorite was decomposed with dilute sodium bisulfite, and water and methylene chloride were added. After separation of the two layers the aqueous portion was extracted with methylene chloride. The lavender organic extracts were concentrated and the residual oil chromatographed on an alumina column with benzene as the eluent. Two zones (blue-green and lavender) developed. From the lavender eluate, after purification by rechromatographing. was recovered 0.235 g. of 1-acetylazulene. Removal of the solvent from the blue-green eluate left an oily solid. Attempted sublimation at room temperature and 0.05 mm. caused a small amount of an unidentified, unstable blue oil to distil onto the cold finger and left a residue of dark green crystals. Sublimation of the green solid at 60° and 0.05 mm. gave green crystals, m.p. 85–86°, which were identical (mixed melting point and infrared spectrum) with a dichloroazulene obtained from a reaction of azulene with N-chlorosuccinimide.

Methyl 1-Azuloate (II).—In a procedure adapted from that of Morgan, Bardwell and Cullis,[34] 12.2 ml. of a solution containing 10% iodine and 20% potassium iodide was added dropwise over a period of 10 minutes to a mixture of 0.18 g. (1.06 millimoles) of 1-acetylazulene, 32 ml. of dioxane and 33.6 ml. of 10% sodium hydroxide. Iodoform separated

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[33] M. S. Newman and H. L. Holmes, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 429.

[34] K. J. Morgan, J. Bardwell and C. F. Cullis, *J. Chem. Soc.*, 3190 (1950).

from the reaction mixture during the addition and, after 20 minutes, the excess tri-iodide ions were decomposed with bisulfite solution. The cooled mixture was filtered and unreacted acetylazulene removed from the filtrate by extraction with methylene chloride. Chromatography of the residue from the organic extracts on an alumina column with methylene chloride as the eluent yielded 10 mg. of 1-acetylazulene.

Acidification of the aqueous lavender filtrate followed by extraction with three 50-ml. portions of ether and removal of the solvent from the combined extracts gave 0.158 g. of crude acidic material. Attempts to purify this substance were unsuccessful and it was taken up in 10 ml. of ether and treated with an excess of diazomethane in ether. After eight hours the excess diazomethane was destroyed with a few drops of formic acid and the solvent removed. A solution of the residue (0.16 g.) in a few milliliters of 80% petroleum ether–20% benzene solvent was chromatographed on an alumina column. Five bands (yellow, violet, lavender, orange and yellow) developed. Only the eluate from the violet zone contained an appreciable amount of material and crystallization from petroleum ether of the residue from this fraction gave 0.126 g. (68% net yield from 1-acetylazulene) of methyl 1-azuloate as dark violet needles, m.p. 56–57°. The infrared spectrum of this material was identical to that of an authentic sample[12] and a mixed melting point of the two substances gave no depression.

1-Nitroazulene (III). A.—To a stirred solution of 97 mg. (0.76 millimole) of azulene in 5 ml. of acetic anhydride cooled in a Dry Ice–acetone-bath was added a suspension of 0.19 g. of cupric nitrate and 10 ml. of acetic anhydride over a period of 10 minutes. After an additional 5 minutes the cooling bath was removed and the mixture allowed to come to room temperature. The color of the solution changed from blue to violet and, after 15 minutes, 20 ml. of water was added. The resulting mixture was shaken with 100 ml. of water and then extracted three times with 50-ml. portions of methylene chloride. The combined organic extracts were washed several times with dilute ammonium hydroxide and finally with water. After concentration under reduced pressure the residue from the organic solution was chromatographed on an alumina column (22 × 200 mm.) with methylene chloride as the eluent. An orange-red band separated from a small black band and was collected. Rechromatography of the concentrated orange-red fraction and removal of the solvent from the eluate gave a red solid. Crystallization of this material from petroleum ether–methylene chloride yielded 82 mg. (63%) of 1-nitroazulene as red needles, m.p. 106.5–107.5°. The ultraviolet and visible spectra (Fig. 1) of a *n*-hexane solution displayed maxima in mμ at 219, log ϵ 4.32; 269, log ϵ 4.23; 309, log ϵ 4.32; 382, log ϵ 4.03; 402, log ϵ 3.98; 532, log ϵ 2.77 and 572, log ϵ 2.69. The infrared spectrum was recorded.[3]

Anal. Calcd. for $C_{10}H_7NO_2$: C, 69.36; H, 4.08. Found: C, 69.15; H, 3.87.

B.—A solution of 74 mg. of benzoyl nitrate, prepared as described by Francis,[35] in 2 ml. of dry carbon tetrachloride was added under anhydrous conditions to 56 mg. (0.44 millimole) of azulene dissolved in 5 ml. of carbon tetrachloride and cooled in a Dry Ice–acetone bath. After 15 minutes the cooling bath was removed and the reaction mixture allowed to come to room temperature. The reddish-brown solution was washed with 15 ml. of ice-water and the organic layer separated. The solvent was removed and the residue taken up in benzene. After washing with sodium bicarbonate solution and water the organic solution was concentrated and chromatographed on a small alumina column with benzene as the eluent. The eluate from the first band contained 13 mg. of unreacted azulene and 9 mg. (15% net yield) of 1-nitroazulene (m.p. 105–106°) was obtained from the eluate from the second band.

1-Azuleneazobenzene (IV).—To a cold solution of aniline hydrochloride (96 mg., 0.74 millimole) diazotized in the usual manner was added a solution of 91 mg. (0.71 millimole) of azulene and 0.5 g. of sodium acetate in 5 ml. of absolute alcohol. The color of the solution changed immediately to a yellow-brown and a crystalline solid separated. After several hours, during which period no nitrogen was evolved, water was added and the mixture extracted with two 50-ml. portions of methylene chloride. The extracts were washed with saturated sodium bicarbonate and water and the solvent removed. The residue (160 mg.) was chromatographed on an alumina column (22 × 200 mm.) with methylene chloride as the eluent. A dark brown zone eluted rapidly and was collected. A second brown band remained at the top of the column. Removal of the solvent from the brown eluate afforded 150 mg. (91%) of very deep yellow opaque needles which melted at 118–120°. Rechromatography of a sample raised the melting point to 120–121°. The product gave a deep red color with concentrated inorganic acids and a yellow color with inorganic bases. It dissolved readily in common organic solvents to give yellow solutions. The ultraviolet and visible spectra (Fig. 2) showed maxima in mμ at 235, log ϵ 4.33; 278, log ϵ 428; 330, log ϵ 4.19; 414, log ϵ 4.45; 4.18, log ϵ 4.45 and 610, log ϵ 2.72.[3] The infrared spectrum was taken.[3]

Anal. Calcd. for $C_{16}H_{12}N_2$: C, 82.92; H, 5.22; N, 12.07. Found: C, 82.53; H, 5.30; N, 11.92.

N-Acetyl-1-azulylamine (VI). A. From 1-Acetylazulene Oxime (V).—To 12.4 mg. (0.67 millimole) of 1-acetylazulene oxime dissolved in 1 ml. of ethylene chloride was added a solution of 17.3 mg. (0.83 millimole) of phosphorus pentachloride in 5 ml. of ethylene chloride. The color of the solution changed immediately from lavender to brown and, subsequently, a solid separated. After 10 minutes the reaction was quenched by the addition of water, the ethylene chloride layer separated and the aqueous phase extracted with 25 ml. of methylene chloride. The combined extracts were concentrated *in vacuo* and the residue chromatographed on an alumina column (22 × 200 mm.) with an 80% petroleum ether–20% benzene solution as the eluent. A lavender zone was eluted and then methylene chloride was used to elute a slower moving blue zone. The blue effluent fraction was concentrated (reduced pressure) and the residue rechromatographed on a smaller column (8 × 100 mm.). Removal of the solvent from the blue eluate left a blue solid which, after crystallization from petroleum ether–methylene chloride, amounted to 2 mg. (16%) of product in the form of blue plates, m.p. 146–147°. This material was identical (m.m.p. and infrared spectrum) with that obtained from 1-nitroazulene and 1-azuleneazobenzene as described below.

B. From 1-Nitroazulene (III).—To a stirred solution of 53 mg. (0.31 millimole) of 1-nitroazulene and 0.2 g. of sodium acetate in 5 ml. of acetic acid and 5 ml. of acetic anhydride was added 0.5 g. of zinc dust over a period of 5 minutes. The mixture was stirred for one hour. Water was then added and the mixture extracted with two 30-ml. portions of methylene chloride. The combined extracts were washed with dilute ammonium hydroxide, then water and the solvent removed. The residue was chromatographed on an alumina column (22 × 200 mm.) and the blue zone which developed eluted with petroleum ether–methylene chloride. Evaporation of the solvent from the eluate gave 50 mg. (90%) of product as blue plates, m.p. 146–147°. The ultraviolet spectrum of an ethanol solution showed maxima in mμ at 235, log ϵ 4.19; 288, log ϵ 4.59; 360, log ϵ 3.64 and 378, log ϵ 3.63.[3] The visible spectrum had a single broad maximum at 625 mμ. The infrared spectrum was recorded.[3]

Anal. Calcd. for $C_{12}H_{11}NO$: C, 77.81; H, 5.99. Found: C, 77.94; H, 6.26.

C. From 1-Azuleneazobenzene (IV).—1-Azuleneazobenzene (40 mg., 0.17 millimole) was dissolved in a few milliliters of purified dioxane and a cold saturated solution of sodium hydrosulfite added until the color of the solution changed to a clear green. Then 300 mg. of sodium acetate and 1 ml. of acetic anhydride were added. After 30 minutes the thoroughly mixed solution was shaken with 100 ml. of water and extracted with two 25-ml. portions of methylene chloride. The combined extracts were washed with dilute ammonium hydroxide and water and the solvent removed under reduced pressure. The residue was chromatographed on an alumina column with methylene chloride as the eluent. Unreacted azo compound eluted rapidly followed by a slower moving blue zone. The effluent containing the latter fraction was rechromatographed after concentration and the solid obtained after removal of the solvent crystallized from petroleum ether–methylene chloride to give 15.4 mg. (48%) of product as blue plates, m.p. 146–147°. A mixture of this material with that from A and B above melted at 146–147°. The infrared spectra of the three products were identical.

1-Bromoazulene (VII).—A solution of 19 mg. (0.15 millimole) of azulene in 2 ml. of dry benzene was treated with 27

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[35] F. E. Francis, *J. Chem. Soc.*, **89**, 1 (1906).

mg. (0.15 millimole) of N-bromosuccinimide at room temperature. A test for active bromine with starch–iodide paper was negative after one minute. The benzene solution was evaporated in a stream of dry air and the residue taken up in 1 ml. of petroleum ether. The solution was chromatographed on a small alumina column, which also removed succinimide and any polymeric material, and the blue band which developed eluted with petroleum ether. The eluate solvent was blown off and the residue placed in a small vacuum sublimation apparatus. At room temperature and 0.1 mm. a greenish-blue liquid slowly distilled onto the cold finger and a green crystalline residue remained. The liquid fraction was chromatographed on an alumina column with petroleum ether as the eluent. The single blue band which developed was eluted, the solvent removed in a stream of dry nitrogen and the residue placed in a vacuum desiccator at 0.1 mm. pressure for 5 minutes. The product (20.5 mg., 66%) was rather unstable and could not be obtained analytically pure. The ultraviolet and visible spectra of a *n*-hexane solution showed maxima in mμ at 237, log ϵ 4.25; 280, log ϵ 4.62; 285, log ϵ 4.58; 337, log ϵ 3.56; 345, log ϵ 3.71; 362, log ϵ 3.72; 586, ϵ 294; 605, ϵ 340; 632, ϵ 312; 662, ϵ 306; 697, ϵ 149 and 736, ϵ 128.[3] The infrared spectrum was taken.[3]

A trinitrobenzene derivative was formed by warming an alcoholic solution of trinitrobenzene and a slight excess of the bromoazulene for 5 minutes and then cooling in an ice-bath. The fluffy light brown needles obtained gave no sharp melting point. The first signs of melting and simultaneous decomposition were observed at 105°.

Anal. Calcd. for $C_{16}H_{10}BrN_3O_6$: Br, 19.03; N, 10.00. Found: Br, 18.61; N, 9.95.

The crystalline fraction was sublimed at 0.1 mm. and 60–70° and a petroleum ether solution of the sublimate chromatographed on an alumina column. The single band which developed was eluted and, after removal of the solvent, gave 6.8 mg. (32% based on N-bromosuccinimide) of 1,3-dibromoazulene, m.p. 75–77°.

1,3-Dibromoazulene (VIII). A. From Azulene.—A solution of 24 mg. (0.19 millimole) of azulene in 5 ml. of dry benzene was treated with 69 mg. (0.39 millimole) of N-bromosuccinimide at room temperature for 24 hours. The reaction mixture still contained a small amount of the brominating agent (starch–iodide paper test) at this time. The benzene was removed in a stream of dry air and the residue taken up in 2 ml. of petroleum ether and chromatographed on an alumina column. Some dark, strongly adsorbed material remained at the top of the column when the blue band containing the product was eluted with petroleum ether. Evaporation of the solvent from the eluate followed by sublimation of the residue at 0.1 mm. and 60–70° afforded 39.2 mg. (73%) of green needles, m.p. 76–77°. On scratching the melt from the green needles it crystallized as blue needles, m.p. 88–89°. The two allotropic forms were interconvertible by seeding a petroleum ether solution of one with the other. The ultraviolet and visible spectra of a *n*-hexane solution displayed maxima in mμ at 239, log ϵ 4.17; 289, log ϵ 4.49; 295, log ϵ 4.42; 300, log ϵ 4.43; 338, log ϵ 3.46; 344, log ϵ 3.52; 353, log ϵ 3.71; 625, ϵ 390; 658, ϵ 341; 675, ϵ 326; 686, ϵ 337; 730, ϵ 145 and 755, ϵ 116.[3] The infrared spectrum is shown in Fig. 4.

Anal. Calcd. for $C_{10}H_6Br_2$: C, 41.99; H, 2.12. Found: C, 42.13; H, 2.24.

B. **From 1-Bromoazulene.**—A solution of 10 mg. (0.05 millimole) of 1-bromoazulene in 2 ml. of dry benzene was treated with 8.9 mg. (0.05 millimole) of N-bromosuccinimide at room temperature for 30 minutes. The solvent was evaporated in an air stream and the product (12.6 mg., 88%), which was identical (mixed melting point and infrared spectrum) to that obtained from the direct bromination of azulene, isolated as described above (A).

1-Chloroazulene (IX).—To 0.155 g. (1.2 millimoles) of azulene dissolved in 5 ml. of dry benzene was added, dropwise, a solution of 0.163 g. (1.2 millimoles) of N-chlorosuccinimide in 20 ml. of dry benzene. The solution gave a negative test with starch–iodide paper after 15 hours and was filtered through a short alumina column. The column was washed thoroughly with petroleum ether and the total filtrate concentrated *in vacuo* under nitrogen. The residue was fractionally sublimed at *ca.* 0.05 mm. with the cold finger of the apparatus cooled with ice. The first fraction consisted mainly of unreacted azulene and the final fraction consisted mainly of chloroazulene. The separate fractions were collected by washing the cold finger with petroleum ether. Resublimation of the first fraction afforded a recovery of 20 mg. of azulene. A small intermediate fraction was discarded. The final fraction was evaporatively distilled two more times and yielded 124 mg. (79% net yield) of the chloroazulene as a blue oil which was somewhat unstable and could not be obtained analytically pure. The ultraviolet and visible spectra of a cyclohexane solution showed maxima in mμ at 239, log ϵ 4.24; 275, log ϵ 4.65; 280, log ϵ 4.75; 285, log ϵ 4.65; 290, log ϵ 4.54; 324, log ϵ 3.36; 330, log ϵ 3.45; 337, log ϵ 3.50; 345, log ϵ 3.70; 353, log ϵ 3.35; 362, log ϵ 3.69; 586, ϵ 5.16; 608, ϵ 361; 637, ϵ 326; 665, ϵ 305; 702, ϵ 153 and 740, ϵ 140.[3] The infrared spectrum was taken.[3]

Heating a solution of 21 mg. of 1-chloroazulene and 20 mg. of trinitrobenzene in 12 ml. of alcohol for 5 minutes and then cooling gave the trinitrobenzene derivative as dark brown needles which had no sharp melting point. Initial melting and simultaneous decomposition occurred at 105°.

Anal. Calcd. for $C_{16}H_{10}ClN_3O_6$: Cl, 9.44; N, 11.18. Found: Cl, 9.29; N, 10.83.

1,3-Dichloroazulene (X). A. From Azulene.—A solution of 0.258 g. (1.9 millimoles) of N-chlorosuccinimide in 32 ml. of dry benzene was added to 0.122 g. (0.95 millimole) of azulene dissolved in 5 ml. of dry benzene. A starch–iodide test was negative after 24 hours and the solution was filtered through a short alumina column which was washed with petroleum ether. Concentration of the filtrate *in vacuo* left a green crystalline residue which was fractionally sublimed at *ca.* 0.05 mm. with the cold finger cooled with ice. A small amount (10 mg.) of 1-chloroazulene was collected and a small intermediate fraction discarded. The dichloroazulene (121 mg., 65%) sublimed at 60–70° as dark green needles, m.p. 85–87°. A single recrystallization from petroleum ether raised the melting point to 87–88°. The ultraviolet and visible spectra of a *n*-heptane solution exhibited maxima in mμ at 239, log ϵ 4.23; 287, log ϵ 4.61; 293, log ϵ 4.50; 337, log ϵ 3.46; 344, log ϵ 3.58; 352, log ϵ 3.81; 361, log ϵ 3.54; 369, log ϵ 3.90; 638, ϵ 386; 667, ϵ 338; 700, ϵ 318; 745, ϵ 145 and 785, ϵ 131.[3] The infrared spectrum is shown in Fig. 4.

Anal. Calcd. for $C_{10}H_6Cl_2$: C, 60.95; H, 3.07. Found: C, 60.61; H, 3.22.

B. **From 1-Chloroazulene.**—To a petroleum ether solution containing 40 mg. (0.25 millimole) of 1-chloroazulene was added 35 mg. of N-chlorosuccinimide dissolved in 5 ml. of dry benzene. A test with starch–iodide paper was negative after 12 hours and the products were isolated as described above (A) to give 7 mg. of unreacted 1-chloroazulene and 34 mg. (82% net yield) of 1,3-dichloroazulene which, after one recrystallization from petroleum ether, melted at 87–88° and was identical (mixed melting point and infrared spectrum) with the product obtained in A.

1-Chloro-3-bromoazulene (XI). A. From 1-Chloroazulene.—To 0.168 g. (1.03 millimoles) of 1-chloroazulene dissolved in 10 ml. of dry benzene was added, dropwise over a period of 20 minutes, a solution of 0.178 g. (1.0 millimole) of N-bromosuccinimide in 30 ml. of dry benzene. A starch–iodide test immediately after the addition was completed was negative and the products were isolated in the manner described above for the preparation of 1,3-dichloroazulene. 1-Chloroazulene (16 mg.) was recovered and 197 mg. (88% net yield) of 1-chloro-3-bromoazulene was isolated as dark green needles, m.p. 76–77°. A single recrystallization from petroleum ether raised the melting point to 77.5–78°. The ultraviolet and visible spectra of a cyclohexane solution showed maxima in mμ at 239, log ϵ 4.26; 289, log ϵ 4.62; 295, log ϵ 4.54; 300, log ϵ 4.51; 330, log ϵ 3.33; 338, log ϵ 3.51; 344, log ϵ 3.62; 353, log ϵ 3.83; 360, log ϵ 3.58; 371, log ϵ 3.92; 635, ϵ 388; 660, ϵ 337; 690, ϵ 326; 735, ϵ 146 and 775, ϵ 124.[3] The infrared spectrum is shown in Fig. 5.

Anal. Calcd. for $C_{10}H_6ClBr$: C, 49.70; H, 2.50; halogen, 47.80. Found: C, 50.09; H, 2.52; halogen, 47.57.

B. **From 1-Bromoazulene.**—A solution of 35 mg. (0.25 millimole) of N-chlorosuccinimide in 10 ml. of dry benzene was added to 52 mg. (0.25 millimole) of 1-bromoazulene dissolved in 5 ml. of dry benzene. After 24 hours the mixture was filtered through a short alumina column and the column washed with benzene. Removal of the solvent and sublimation of the residue *in vacuo* gave 20 mg. of recovered 1-bromoazulene and 26 mg. (69% net yield) of 1-chloro-3-bromoazulene, m.p. 76–77°, which was identical (mixed melting point and infrared spectrum) with the material obtained in A.

1-Bromo-3-nitroazulene (XII). A. From 1-Nitroazulene.—A solution of 54 mg. (0.30 millimole) of N-bromosuccinimide in 7 ml. of dry benzene was added to 52 mg. (0.30 millimole) of 1-nitroazulene dissolved in 5 ml. of dry benzene. A test with starch–iodide paper was negative after 9 hours and the reaction mixture was filtered through a short alumina column. The column was washed with benzene and the filtrate concentrated under reduced pressure. The brown-violet residue was transferred to an alumina column with a few ml. of methylene chloride and the chromatogram developed and eluted with benzene. A brown-red zone separated from a very weak red zone and the former was collected, concentrated and rechromatographed. Removal of the solvent from the desired eluate fraction gave 75 mg. (99%) of brownish lavender crystals, m.p. 181–182°. A single recrystallization from methylene chloride–petroleum ether raised the melting point to 183–184°. The ultraviolet spectrum of an alcohol solution showed maxima in mμ at 222, log ϵ 4.40; 278, log ϵ 4.36; 317, log ϵ 4.27; 410, log ϵ 4.06[3] and the visible spectrum of a solution in three parts of methylene chloride and seven parts of alcohol had a single broad maximum at 532 mμ, ϵ 1071. The infrared spectrum was recorded.[3]

Anal. Calcd. for $C_{10}H_6BrNO_2$: C, 47.64; H, 2.40; Br, 31.70. Found: C, 47.40; H, 2.55; Br, 31.86.

B. **From 1-Bromoazulene.**—To a solution of 60 mg. (0.29 millimole) of 1-bromoazulene in 5 ml. of acetic anhydride cooled in a Dry Ice–acetone-bath was added, with stirring, a suspension of 75 mg. (0.31 millimole) of cupric nitrate trihydrate in 5 ml. of acetic anhydride over a period of 5 minutes. After an additional 5 minutes the cooling bath was removed and the mixture stirred for 30 more minutes during which time the color became purple. The reaction was quenched with 20 ml. of water, the mixture shaken with an additional 100 ml. of water and the separated organic layer extracted with three 50-ml. portions of methylene chloride. The combined extracts were washed twice with dilute ammonium hydroxide and water, the solvent removed under reduced pressure and the residue chromatographed on an alumina column with 20% methylene chloride–80% petroleum ether as the eluent. Three zones (blue, brown-red and weak red) developed. From the blue eluate fraction was recovered 20 mg. of the bromoazulene. Rechromatography of the material from the brown-red fraction yielded 23 mg. (47% net yield) of 1-bromo-3-nitroazulene, m.p. 181–182°, which was identical (mixed melting point and infrared spectrum) with the product obtained in A.

N-Acetyl-3-bromo-1-azulylamine (XIII). A. From 1-Bromo-3-nitroazulene.—To a mixture of 72 mg. (0.286 millimole) of 1-bromo-3-nitroazulene, 15 ml. of acetic acid and 5 ml. of acetic anhydride was added, with stirring, 0.3 g. of zinc dust in small portions. The color of the solution changed from red to greenish blue. Stirring was continued for 1 hour, water was added and the mixture extracted with three 50-ml. portions of methylene chloride. The combined extracts were washed with cold 3 *N* ammonium hydroxide, then water and the solvent removed. The green residue was chromatographed on an alumina column with methylene chloride as the eluent. Removal of the solvent from the eluate containing the greenish blue fraction left a green solid which crystallized from petroleum ether–acetone; yield 63 mg. (83%). The product melted with decomposition at 145–150°. The ultraviolet spectrum of an alcohol solution displayed maxima at 241 mμ, log ϵ 3.40 and 294 mμ, log ϵ 4.42.[3] The visible spectrum of a solution in absolute methanol had a single broad maximum at 650 mμ, ϵ 365. The infrared spectrum of a nujol suspension was taken.[3]

Anal. Calcd. for $C_{12}H_{10}BrNO$: C, 54.56; H, 3.82; Br, 30.26. Found: C, 54.89; H, 3.60; Br, 30.28.

B. **From N-Acetyl-1-azulylamine (VI).**—A solution of 34 mg. (0.18 millimole) of N-acetyl-1-azulylamine in 10 ml. of dry benzene and 2 ml. of methylene chloride was treated with 34 mg. (0.19 millimole) of N-bromosuccinimide dissolved in 5 ml. of dry benzene. The mixture, which gave a negative starch–iodide test within a few minutes, was filtered through a short alumina column and the column washed with methylene chloride. The product (42 mg., 86%) was identical (infrared spectrum) with that obtained in A and was isolated in the same manner.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Tropolones by Isomerization. II. Substituted 3,7-Dibenzyltropolones[1,2]

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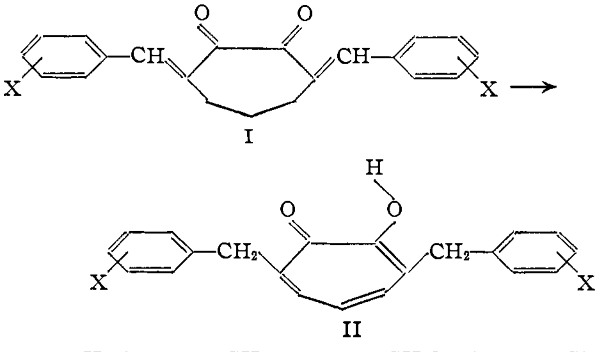
The isomerization of substituted 3,7-dibenzylidene-1,2-cycloheptanediones to the correspondingly substituted 3,7-dibenzyltropolones has been effected in triethylene glycol solution using palladium-on-charcoal. The general method has been shown to possess advantages over the isomerization as effected by hydrogen bromide–acetic acid or by palladium-on-charcoal without solvent. The ultraviolet absorption spectra of the substituted 3,7-dibenzylidene-1,2-cycloheptanediones have been related to those of the correspondingly substituted chalcones. The spectra of the substituted 3,7-dibenzyltropolones bear close resemblance to each other and to those of other known tropolones.

The finding that 3,7-dibenzylidene-1,2-cycloheptanedione (Ia) can be isomerized to 3,7-dibenzyltropolone (IIa) by means of hydrogen bromide–acetic acid[3] caused us to investigate the suggested generality of this new synthesis of tropolones. Accordingly, representative substituted 3,7-dibenzylidene-1,2-cycloheptanediones (I, also the analogous 3,7-di-(*m,p*-dimethoxybenzylidene) and 3,7-difur-



a, X = H; b, X = *p*-CH_3; c, X = *p*-CH_3O; d, X = *o*-Cl; e, X = *p*-NO_2

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[3] N. J. Leonard and G. C. Robinson, THIS JOURNAL, **75**, 2143 (1953).