Apparently here the exchange of II to VIIIb is rapid as compared to the solvolysis of II, and VIIIb must solvolyze much faster than II.

It is interesting to compare the rates of acetolysis of Ia and X at constant ionic strength. Figure 5 shows the plots of rate constants of Ia and X *vs.* $\mu_{0\text{NaOTs}}$ at constant ionic strength ($\Sigma\mu_0 = \mu_{0\text{NaClO}_4} + \mu_{0\text{NaOTs}} = \text{const.}$).

The slope of the rate constant *vs.* $\mu_{0\text{NaOTs}}$ at $\Sigma\mu_0 = \mu_{0\text{NaClO}_4} = 0.063$ for Ia is 0.48×10^{-2} and for X the corresponding slope at $\Sigma\mu_0 = \mu_{0\text{NaClO}_4} + \mu_{0\text{NaOTs}} = 0.052$ is 0.726. Although the constant ionic strength at which the solvolyses reactions were investigated is higher for Ia than X, the slope is considerably steeper for X. This result again indicated that II is considerably more ionized in X than for Ia and that for X, $k_{\text{ROS}^{\text{VIII}}} >> k_{\text{ROS}^{\text{II}}}$ and $k_8/k_{-8} >> k_{\text{ROS}^{\text{II}}}$.

Salt Effects in Methanol.—The solvolysis of X in absolute methanol was strictly first order and no rate depression was observed due to common ion effect during the reaction. There was a slight increase of the rate due to primary salt effect (Table VII). An increase in $\mu_{0\text{NaOTs}}$ in $\Sigma\mu_0 = \mu_{0\text{NaClO}_4} + \mu_{0\text{NaOTs}} = \text{const.}$ did not decrease the rate, but the rate remained essentially constant. In methanol the solvolysis, therefore, appears not to proceed with anion exchange, or $k_{\text{ROS}^{\text{II}}} > k_8$.

Acknowledgments.—The author wishes to thank Dr. George R. Coraor, Prof. C. Gardner Swain and Prof. John D. Roberts for many stimulating discussions and helpful suggestions. The technical assistance of Mr. George H. Babb, Jr., is gratefully acknowledged.

WILMINGTON 98, DEL.

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

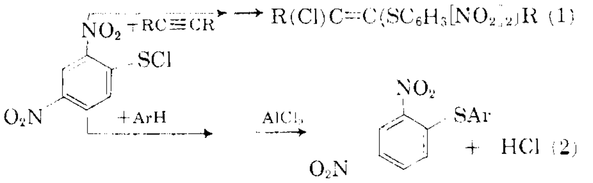
Derivatives of Sulfenic Acids. XXXII. The Synthesis of Azulenes *via* the Interactions of Arylacetylenes with Sulfenyl Halides. Part 1. 1,2,3-Triphenylazulene[1,a,b,c]

BY STEVEN J. ASSONY[2] AND NORMAN KHARASCH

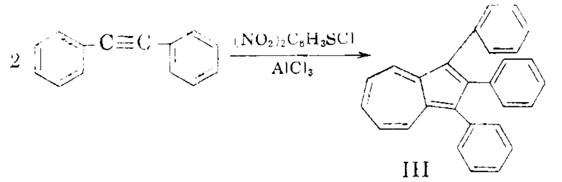
RECEIVED FEBRUARY 5, 1958

In the presence of 2,4-dinitrobenzenesulfenyl chloride and aluminum chloride, both of which are required, diphenylacetylene is dimerized to 1,2,3-triphenylazulene. This novel reaction appears to be the first recorded instance wherein a benzene ring is expanded to a seven-membered carbocyclic ring under ionizing conditions. The best yield in the one-step conversion was 25%. The structure of the azulene was established by an alternate synthesis, which involved formation and fusion of a triphenylcyclopentane ring onto the seven-membered ring of cycloheptanone.

Introduction.—In previous papers of this series, the reactions of 2,4-dinitrobenzenesulfenyl chloride (I) with symmetrical alkynes[3] and with aromatic hydrocarbons[4] were examined. It was demonstrated that I adds to symmetrical alkynes to form the 1:1 adducts (equation 1) and that the aluminum chloride-catalyzed substitution (equation 2, Ar = aryl) with aromatic hydrocarbons is a general reaction. It was also shown that the reaction of I with acetylene to yield the 1:1 adduct (equation 1, R = H) required aluminum chloride, whereas such catalysis was not required with 2-butyne, 3-hexyne or diphenylacetylene.



The present paper reports the reaction whereby, under critical conditions which require the presence of *both* the sulfenyl chloride I and aluminum chloride, diphenylacetylene (II) is dimerized to 1,2,3-triphenylazulene (III).



Initial Evidence for the Structure of III.—The following results, obtained in the initial period of study, led to the prediction[6] that the product was 1,2,3-triphenylazulene (III). In the second phase of the work, described below, the structure of III was confirmed by alternate synthesis from cycloheptanone.

(a) The molecular formula of III, a deep blue, crystalline hydrocarbon, m.p. 215.5–216°, is $C_{28}H_{20}$. It is, therefore, a dimer of diphenylacetylene, $C_{14}H_{10}$. The molecular weight was also confirmed by the mass spectral analysis of III, which was kindly carried out by the Houston laboratory group of the Shell Oil Co.

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[1] (a) Presented before the Division of Organic Chemistry, 131st Meeting of the American Chemical Society, Miami, Fla., April 11, 1957. (b) Abstracted from a dissertation presented to the Faculty of the Graduate School, University of Southern California, by Steven J. Assony, in partial fulfillment of the requirements for the degree Doctor of Philosophy, January, 1957. (c) This study was sponsored, in part, by the Office of Ordnance Research, United States Army, under Contract DA-04-495-Ord. 306.

[2] Richfield Oil Corp., Predoctoral Fellow, 1955–1956.

[3] N. Kharsch and S. J. Assony, THIS JOURNAL, **75**, 1081 (1953).

[4] C. M. Buess and N. Kharasch, *ibid.*, **72**, 3529 (1950); also ref. 5b.

[5] (a) The *trans* structure for the adducts reported has been suggested[3] but not yet fully established. The Friedel–Crafts reactions of 2,4-dinitrobenzenesulfenyl chloride with aromatic hydrocarbons and their derivatives provides an excellent method for characterizing these substances[4] and also is the first step in the synthesis of aromatic thiols by the procedure of Kharasch and Swidler, *J. Org. Chem.*, **19**, 1704 (1956). (b) *Cf.* also N. Kharasch, *J. Chem. Ed.*, **33**, 585 (1956).

[6] S. J. Assony and N. Kharasch, *Chemistry & Industry*, 1388 (1954).

(b) Aluminum chloride and I are both required to obtain III. If I is omitted, no III results, and when aluminum chloride is omitted only the 1:1 adduct of diphenylacetylene and I is obtained.

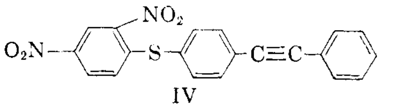
(c) The best yield, 25%, of the blue hydrocarbon III is obtained when the reaction is conducted at room temperature, in ethylene chloride solution, using the reactant ratios: one mole of I, one mole of aluminum chloride and two moles of diphenylacetylene.

(d) Compound III is not 1,2,3-triphenylnaphthalene, a colorless substance, m.p. 153–154°, which is a known compound,[7] and whose synthesis by the reaction of diphenylacetylene with lithium metal was carried out for comparison purposes (*cf.* g, below).

(e) Figure 1 shows the spectrum of III in the ultraviolet and visible regions, and for comparison the spectra of selected substituted azulenes.[8] These spectra strongly supported the initial inference that III must be a triphenylazulene.

(f) Aluminum chloride appears to be highly specific for the dimerization reaction; several other Friedel–Crafts catalysts ($AlBr_3$, $ZnCl_2$, H_2SO_4) were not effective for production of III under the conditions in which aluminum chloride is successful. An attempt to generate benzyl chloride with aluminum chloride, and to have this replace the sulfenyl chloride–aluminum chloride complex ($\mathrm{ArSCl} + \mathrm{AlCl_3} \rightarrow \overset{\delta+}{\mathrm{ArS}} - \overset{\delta-}{\mathrm{AlCl_4}}$) was not successful.[9]

(g) In the aluminum chloride-catalyzed reaction of 2,4-dinitrobenzenesulfenyl chloride and diphenylacetylene, other products are formed. The adduct of I and II, 2-chloro-1(2,4-dinitrophenylthio)-1,2-diphenylethene,[3] is obtained in considerable amounts and a colorless dimer of II, which melts at 153–154°, occurs in very low yields. Because the melting point and analysis of the latter product corresponded exactly to those of 1,2,3-triphenylnaphthalene, it was thought that this was the structure of the second dimer. Comparison with authentic 1,2,3-triphenylnaphthalene[7] (mixture melting point and infrared spectra) showed that the two were not the same. Elucidation of the exact structure of this attendant product has not, however, yet been undertaken. A search for IV, or the corresponding *m*-isomer, was made, but none was found.[10]



IV

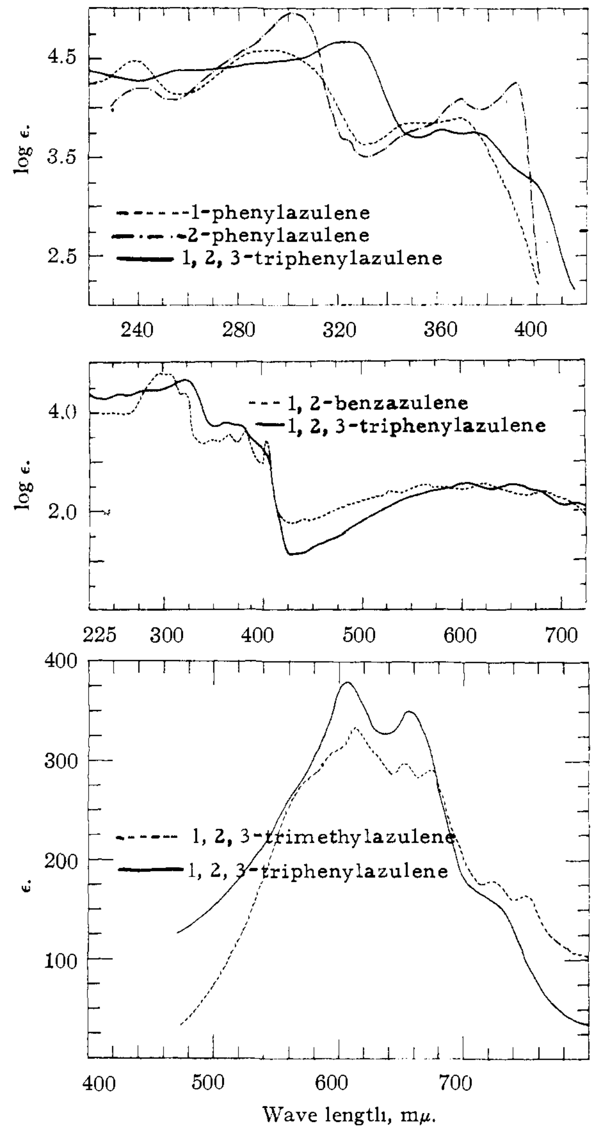


Fig. 1.—Ultraviolet and visible absorption spectra of 1,2,3-triphenylazulene and related substances; *cf.* also footnote 8.

(h) Initial studies of the chemical properties of III were made. While these supported the conclusion that III could be an azulene they offered no conclusive evidence that this was so. Thus: (1) Attempted reaction of III with sodium in amyl alcohol gave no identifiable reduction products. (2) The products of oxidation of III with chromic acid, hydrogen peroxide, potassium permanganate and ozone were small fragments which did not give suitable clues to the structure of the supposed azulene.[11] (3) Compound III dissolved in concentrated sulfuric acid and could be retrieved by dilution, but it was not soluble in 85% phosphoric acid. This behavior agrees with the basicities of other azulenes.[12] (4) Bromination of III gave a dibromo substitution product of III, $C_{28}H_{18}Br_2$, V, whose analysis helped to establish the molecular formula of III as $C_{28}H_{20}$. (5) The attempt to convert III to 1,2,3-triphenylnaphthalene, by heating in a sealed tube at 330–350° for several weeks, gave only recovered III (76%) and a small amount of tarry

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[7] W. Schlenk and E. Bergmann, *Ann.*, **463**, 77 (1928).

[8] The spectra of the comparison compounds are from the following references: 1,2-benzazulene (J. R. Nunn and W. S. Rapson, *J. Chem. Soc.*, 825 (1949); the 1- and 2-phenylazulenes (Pl. A. Plattner, A. Fürst, M. Gordon and K. Zimmerman, *Helv. Chim. Acta*, **33**, 1910 (1950)); and 1,2,3-trimethylazulene (personal communication from Drs. A. Fürst and Pl. A. Plattner).

[9] The use of other sulfenyl chlorides in the conversions of diarylacetylenes to azulenes will be described in a subsequent paper.

[10] The inference that the acetylenic linkage deactivates the benzene ring to Friedel–Crafts attack by I (*cf.* eq. 2) is supported by later observations in this Laboratory (Kharasch and Yiannios) with phenylacetylene.

[11] These results will be reported separately; *cf.* S. J. Assony, Ph.D. Dissertation, University of Southern California, 1956.

[12] M. Gordon, *Chem. Revs.*, **50**, 127 (1952).

material. No 1,2,3-triphenylnaphthalene or other definite isomerization product was found. (6) The infrared spectrum of III was examined[11] but gave no clear clues to the structure. (7) The 1:1 adduct of II and I, *i.e.*, $C_6H_5(Cl)C{=}CSC_6H_3(NO_2)_2[C_6H_5]$, eq. 1, is probably not an intermediate in the one-step synthesis of III, since treatment of this adduct with aluminum chloride under the conditions which lead to III (*i.e.*, II plus I, in presence of aluminum chloride) gave no azulene.

Alternate Synthesis of 1,2,3-Triphenylazulene.—Several approaches to the synthesis of III were tried. After repeated failures,[11] the route of Fig. 2 gave a product, which on the basis of analysis, melting point and mixture melting point, and infrared and ultraviolet spectra was identical with the product obtained from diphenylacetylene. The sequence for synthesis of III was based, in part, on the synthesis of 1,2,3-triphenylindane.[13]

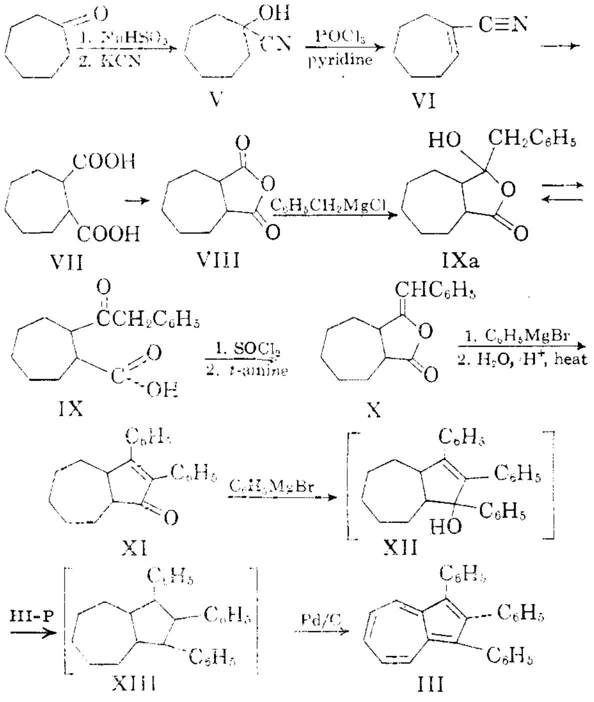

Fig. 2

The immediate aim of the present alternate synthesis was to obtain a sample of triarylazulene III for comparison with the product from diphenylacetylene. Hence, not all the intermediates were fully investigated and improvements in yields in the last steps were not sought. Compounds VI–IX were fully characterized; but the presumed intermediates X–XIII were not, although they warrant further attention in their own right. Starting with 510 mg. of intermediate XI, only about 3 mg. of III was obtained in the final dehydrogenation of supposed intermediate XIII to III. The carbon-hydrogen analyses obtained for compounds X and XI (*cf.* Experimental) would fit somewhat better for structures with two less hydrogens, as discussed in reference 11. However, since the subsequent steps lead to the fully dehydrogenated compound III, either structures X, XI or compounds of the same skeletal structure but having one more double bond (common to the two rings) would satisfy the projected synthesis of III.

Because the likelihood of rearrangements of phenyl groups from the five-membered ring to the seven-membered one is remote, and especially in view of the identity of the blue hydrocarbon from both routes, we conclude that the synthesis of the azulene by the sequence of Fig. 2 establishes its structure as 1,2,3-triphenylazulene (III). Details of the characterization of products VI–IX and the conversion to III are in the Experimental part.

Acknowledgment.—The support of the Office of Ordnance Research, United States Army, and the Richfield Oil Co. is gratefully acknowledged. We are also indebted to Dr. Adalbert Elek for microanalyses and to Messrs. Claude E. Johnson and Donald M. Frankel for assistance with the infrared determinations. The comparison spectrum of 1,2,3-trimethylazulene was kindly supplied by Drs. A. Fürst and Pl. Plattner of Basle, Switzerland.

Experimental[14]

1,2,3-Triphenylazulene *via* Diphenylacetylene.—Compound I (4.69 g., 20 mmoles) and II (7.12 g., 40 mmoles) dissolved in 75 ml. of dry ice-cold ethylene chloride. To this solution was added 2.62 g. (20 mmoles) of anhydrous aluminum chloride and a small strip of aluminum foil. The dark brown solution was shaken in the ice-bath for 10 min. and refrigerated overnight. To the cold solution was added slowly 20 ml. of ice-cold 95% ethanol, and the mixture was filtered through diatomaceous earth and washed with 1 *N* hydrochloric acid (2 × 50 ml.). Solvent was removed *in vacuo* at room temperature and the tarry residue was dissolved in 50 ml. of a solution containing 50 vol. per cent. of mixed heptanes (b.p. 80–95°) and 50 vol. per cent. of dry benzene. This solution was chromatographed on Alcoa F-20 activated alumina. A broad blue band was developed and eluted with the same solvent. The eluted solution was concentrated to dryness and the residue was crystallized from 60 ml. of nitromethane, yielding 1.75 g. (25%, based on II) of crystallized III, m.p. 209–214°. Three crystallizations from nitromethane raised the melting point to 215.5–216°. Five hundred and sixty mg. of III depressed the freezing point of 30.8 g. of pure benzene 0.287°, suggesting a molecular weight of 325 and a molecular formula of $C_{28}H_{20}$ for III. Subsequent calculations based on bromine analysis of a dibromo derivative (V) of III (see below) established conclusively that III is a dimer of II.

Anal. Calcd. for $(C_7H_5)_n$: C, 94.34; H, 5.66. Found: C, 93.87, 94.34; H, 5.59, 5.89.

In subsequent preparations, omission of the aluminum metal and use of shorter reaction periods did not appreciably lower the yields of III. However, the use of catalytic quantities of I or aluminum chloride, omission of I, substitution of aluminum bromide, zinc chloride or sulfuric acid for aluminum chloride, substitution of benzyl chloride for I refluxing the reaction mixture, or dropwise addition of a, solution of I and aluminum chloride to II, yielded either only traces of III or none at all.

A broad yellow band, observed each time a reaction mixture of III was chromatographed, was eluted and evaporated to dryness, yielding a yellowish-orange, crystalline residue of m.p. 194–201°. Recrystallization of this residue from glacial acetic acid gave chunky, yellow prisms of m.p. 205–207°. A mixture of this material with authentic 1:1 adduct (m.p. 206–207°)[3] melted at 205–207°.

In a larger-scale reaction, involving 32.0 g. of II and 21.0 g. of I, working up of the reaction mixture in the usual manner, followed by chromatography on a 4-foot activated alumina column, yielded a small amount (0.1–0.2 g.) of a colorless crystalline material as a forecut. Melting point of this substance, as isolated, was 143–148°. The analytical sample, recrystallized four times from mixed heptanes (b.p. 80–95°), melted at 154–155°.

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[13] W. Schlenk and E. Bergmann, *Ann.*, **463**, 228 (1938); *cf.* also, C. F. Koelsch, THIS JOURNAL, **56**, 1337 (1934).

[14] Melting points were taken on a Fisher-Johns Block.

Anal. Calcd. for $(C_7H_5)_n$: C, 94.34; H, 5.66. Found: C, 94.12; H, 5.90; Rast mol. wt. detn. gave values of 348, 370 and 357, average 358; $C_{28}H_{20}$ requires 356.44.

Since the elemental analysis, molecular weight and melting point of this substance agree with those reported[7] for 1,2,3-triphenylnaphthalene, an authentic sample was prepared by reaction of lithium metal and diphenylacetylene at room temperature.[7] The product melted at 151–153° (lit.[7] 153–154°).

A mixture of the colorless $C_{28}H_{20}$, isolated in this study, with authentic 1,2,3-triphenylnaphthalene melted at 137–153°. That these two substances were not identical was shown conclusively by a comparison of their infrared spectra.[11]

Bromination of III; Formation of V.—To a solution of 0.30 g. (0.84 mmole) of III, in 20 ml. of chloroform, was added 10 ml. of a 5% solution of bromine in carbon tetrachloride. Hydrogen bromide was evolved and the solution turned dark green. Solvents and excess bromine were removed by distillation and the residue dried *in vacuo*. The dark material was crystallized from mixed heptanes (b.p. 80–95°), yielding 0.39 g. of black prisms, m.p. 256–260°. A second crop of 0.02 g. was isolated from the mother liquor. Two crystallizations from mixed heptanes raised the melting point to 258–259°.

Anal. Calcd. for $C_{23}H_{18}Br_2$: C, 65.39; H, 3.53; Br, 31.08; mol. wt., 516. Found: C, 65.65; H, 3.39; Br, 31.12; mol. wt. (based on bromine content), 515.

Alternate Synthesis of 1,2,3-Triphenylazulene from Cycloheptanone. 1-Cycloheptenyl Cyanide (VI).—To a well-stirred solution of 240 ml. (244 g., 2.0 moles) of redistilled cycloheptanone in 500 ml. of ether was added a saturated solution of 250 g. (2.4 moles) of pure sodium bisulfite, and the mixture was stirred 4 hr. A saturated, aqueous solution of 160 g. (2.45 moles) of potassium cyanide was added to the thick paste, stirring was continued 5 hr. and the mixture let stand 18 hr. The organic layer was separated and the aqueous layer extracted with ether (3 × 100 ml.). These extracts were added to the organic layer and the whole was dried over magnesium sulfate. Ether was removed by distillation and the residual yellow oil dissolved in one liter of pyridine, in a 3-liter, 3-neck flask fitted with a stirrer, dropping funnel and reflux condenser. To the well-stirred solution was added 310 ml. (520 g., 3.4 moles) of phosphorus oxychloride (freshly prepared from phosphorus pentoxide and phosphorus trichloride) at such a rate that the pyridine refluxed gently from the exotherm. After complete addition, the red-brown solution was stirred for 30 minutes more on the steam-bath, then cooled to room temperature and cautiously poured onto 3 liters of ice. The organic layer was removed and the aqueous layer was extracted with benzene in a continuous extractor.

The benzene extract was added to the bulk organic material, and the whole was washed with 1 *N* hydrochloric acid (2 × 100 ml.), 10% sodium bicarbonate solution (1 × 100 ml.) and water (2 × 100 ml.), and then dried over anhydrous magnesium sulfate. Benzene was removed at the water-pump and the residual oil was distilled to give: (I), a 1–2 ml. forerun b.p. 35° (1 mm.); (II), mixed fraction, b.p. 39–40° (0.2–0.5 mm.); (III), 1-cycloheptenyl cyanide b.p. 43–44° (0.1–0.2 mm.).

Fraction II was redistilled, yielding impure cycloheptanone, b.p. 36–37° (0.1–0.2 mm.), and VI, b.p. 42–45° (0.1–0.2 mm.). The recovered cycloheptanone, contaminated with VI, weighed 55 g. The yield of colorless VI, based on cycloheptanone used, was 98 g. (53%). This product, with an odor reminiscent of benzaldehyde, darkens on storage. A freshly-distilled sample, stored in a brown bottle under nitrogen and kept in a dark cupboard, became dark overnight. However, the material could be repurified by distillation, even after storing several months.

Since cycloheptanone could not be separated from VI by distillation alone,[15] VI was not analyzed, but was characterized by hydrolysis to 1-cycloheptenoic acid.[16,17] Two grams of VI was refluxed with 4 g. of potassium hydroxide in a solution of 8 ml. of water and 20 ml. of ethanol for 72 hr. (ammonia still evolved slowly at the end of this period). Acidification and extraction gave 2.3 g. of oil which solidified on cooling in ice. The *p*-bromophenacyl ester (m.p. 95–96°) did not depress the melting point of the *p*-bromophenacyl ester prepared from an authentic sample of 1-cycloheptenoic acid.[16,17]

1,2-Cycloheptanedioic Acid (VII).—In a "citrate bottle" was placed 16.2 g. (0.134 mole) of VI, 150 ml. of 95% ethanol and a solution of 50 g. of potassium cyanide in 100 ml. of water. Diethylamine (2 ml.) was added, and the bottle was sealed with a metal crown cap, and heated at 100° for 17 hr. The reaction mixture was steam distilled (no VI was recovered), and the pot residue cooled (ice-bath), and acidified with concd. sulfuric acid, causing an oil to separate. The mixture was then extracted in a continuous extractor with ether. To the ethereal extract was added 400 ml. of water and solid sodium bicarbonate until no more carbon dioxide was evolved. The aqueous layer was separated, washed with ether (2 × 100 ml.), which was added to the main organic layer, clarified with charcoal and reduced to *ca.* 200 ml. volume, then acidified with concentrated hydrochloric acid. Evaporation was continued to dryness. The oily residue was washed with mixed heptanes (2 × 25 ml.) and triturated with ether (5 × 50 ml.). Evaporation of solvent gave 16.7 g. of oily product. Recrystallization from concentrated hydrochloric acid gave 12.2 g. VII (47%), m.p. 153–157°.

The analytical sample (m.p. 160–161°) was prepared by three recrystallizations from toluene of a product similar to the above, obtained in a previous run and of m.p. 148–152°.

Anal. Calcd. for $C_9H_{14}O_4$: C, 58.05; H, 7.59. Calcd. for $C_9H_{14}O_4 \cdot {}^1/_2H_2O$: C, 55.37; H, 7.74. Found: C, 55.15; H, 7.37.

It appears, therefore, that VII forms a very stable hemihydrate, which is not decomposed even by three recrystallizations from boiling toluene. The extreme water solubility of the product also agrees with this observation.[18]

In various attempts to prepare VII, indications of its existence in another geometric form (*cis–trans* isomers) also was obtained, and a cyclic imide, m.p. 93–94° (needles from hexane), was encountered.[11]

Anal. Calcd. for $C_9H_{13}NO_2$: C, 64.65; H, 7.83; N, 8.38. Found: C, 64.78; H, 7.97; N, 8.67.

1,2-Cycloheptanedioic Anhydride (VIII).—Two grams of VII, m.p. 158–160°, was refluxed in 25 ml. of freshly distilled decalin for 5 min. Fifteen ml. of solvent was distilled to remove water eliminated from VII, and the remaining solution was cooled, with exclusion of atmospheric moisture, and 20 ml. of mixed heptanes was added. An oil which separated was congealed by cooling with solid carbon dioxide and removed. Upon warming to room temperature, this solid reliquefied, then crystallized. The melting point of this substance (VIII) was 43–45°, raised to 50–52° upon recrystallization from mixed hexanes. The infrared spectrum showed characteristic anhydride absorption: two bands, 90 wave numbers apart in the carbonyl region. Hydrolysis of VIII in concd. HCl gave VII, m.p. 159–161°; *cf.* also ref. 18.

Another sample (15.0 g.) of VIII (m.p. 148–155°) was warmed on the steam-bath with 60 ml. of acetic anhydride for 2 hours. Excess acetic anhydride and acetic acid were removed by distillation at atmospheric pressure, and the residue distilled at the water-pump, giving 17.8 g. of anhydride, boiling at 188–192° (32 mm.).

2-Carboxycycloheptyl Benzyl Ketone (IX).—To a solution, at −70° under nitrogen, of 8.3 g. (49 mmoles) of VIII, in 50 ml. of dry ether, was added dropwise during 45 min. a solution of benzylmagnesium chloride, prepared from 6.46 g. of distilled benzyl chloride and 1.25 g. of magnesium. The mixture was stirred for 2 hours more (longer stirring, *e.g.*, 4 hr. more, decreases the yield of IX, and leads to considerable amounts of a neutral, crystalline by-product). After hydrolysis in ice-cold ammonium chloride solution, the organic layer was extracted with 10% sodium bicarbonate and acidified with concd. hydrochloric acid, to give 6.87 g. (63.5%) of a pale-orange oil. Crystallization from mixed hexanes gave white needles, m.p. 81–83°. Three more recrystallizations from the same solvent gave an analytical sample, m.p. 90.5–91.5°.

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(15) This experience differs from that reported recently by O. H. Wheeler and I. Lerner, This Journal, **78**, 63 (1956).

(16) R. S. Dale, C. Schorlemmer and A. Spiegel, *J. Chem. Soc.*, **39**, 539 (1881).

(17) E. Buchner and A. Jacobs, *Ber.*, **31**, 399 (1898).

(18) *Cf.* also D. C. Ayres and R. A Raphael, *J. Chem. Soc.*, **1779** (1958).

Anal. Calcd. for $C_{16}H_{20}O_8$: C, 73.82; H, 7.74. Found: C, 73.57; H, 7.97.

Oxidation of IX gave only benzoic acid, indicating that no ring alkylation through an "abnormal" Grignard reaction had occurred. No phthalic acid was observed. Infrared analysis showed that IX exists mainly in its tautomeric lactol form.

1,2,3-Triphenylazulene.—In an attempt to prepare the methyl pseudoester of IX (Fig. 2), X was obtained: (a) Ten grams of IX (m.p. 90–91.5°) was refluxed with 50 ml. of thionyl chloride in a 100-ml. flask protected from moisture until evolution of hydrogen chloride ceased. Excess thionyl chloride was removed *in vacuo*, the supposed pseudo-acid chloride was cooled in ice, and a mixture was kept at room temperature for 2 days, then poured into 1 liter of water. The aqueous mixture was extracted with ether, the ethereal layer was washed well with water, saturated aqueous sodium bicarbonate and saturated sodium chloride solutions, then filtered through anhydrous calcium sulfate. The dried solution was clarified with charcoal and ether was distilled. Crystallization of the residue from 20 ml. of methanol gave 4.34 g. of pale red plates, m.p. 110–112°. Chromatography of the residue obtained from the mother liquor gave 0.46 g. of yellow needles, m.p. 111–113°. An analytical sample (pale yellow plates) was recrystallized five times from methanol to m.p. 114–115°.

Anal. Calcd. for $C_{17}H_{22}O_3$ (the methyl pseudo-ester of IX): C, 74.42; H, 8.08. Found: (on different samples): C, 80.07, 80.02, 80.00; H, 6.55, 6.65, 6.49; $C_{16}H_{18}O_2$ (X) requires: C, 79.34; H, 7.85: $C_{16}H_{16}O_2$ requires: C, 80.00; H, 6.66. *Cf.* Discussion and ref. 11.

In another run compound IX (6.92 g., m.p. 88–90°) was refluxed with 25 ml. of thionyl chloride until no more hydrogen chloride was evolved. Excess thionyl chloride was removed, and 35 ml. of dry triethylamine in 35 ml. of absolute methanol was added to the residue. The dark reaction mixture was kept 2 days, then poured into 800 ml. of water. Organic material was extracted with ether, and ether was allowed to evaporate slowly. The large flat plates which deposited at the end of 7 days were separated from accompanying dark oily residue and recrystallized, with aid of charcoal, from 25 ml. of 95% ethanol, yielding 1.5 g. of feathery, almost colorless plates, melting at 112–115°. A mixture of this substance with X, as obtained above, was 112–114°.

Intermediate XI (Fig. 2) was obtained as follows. To a solution of 3.75 g. (15.6 mmoles) of X in 20 ml. of dry ether was added dropwise during 15 min. a solution of phenylmagnesium bromide, from 0.42 g. of magnesium and 2.80 g. of bromobenzene, in 50 ml. of dry ether. A yellow precipitate began to separate immediately. After full addition of the Grignard solution, the slurry was stirred for 30 min., then left overnight at room temperature. To the mixture then was added 75 ml. of cold 10% sulfuric acid to decompose the complex. The organic layer was separated, the aqueous phase extracted with ether (4 × 30 ml.), and the extracts added to the bulk organic solution. Ether was distilled and the residual oil was distilled *in vacuo*. A viscous red distillate was collected at 222–229° (2.4 mm.) and crystallized from 20 ml. of absolute methanol, yielding dark, malformed rosettes. Recrystallization, with the aid of charcoal, from 50 ml. of methanol gave large yellow-green prisms, melting at 167–170°, yield 0.51 g. (13%). Evaporation of the mother liquor gave 0.57 g. of unreacted X, m.p. 111–115°. The analytical sample of intermediate XI, prepared by three recrystallizations from absolute methanol, melted at 171–172°.

Anal. Calcd. for $C_{22}H_{24}O$: C, 86.8; H, 7.88. Found: C, 87.25; H, 6.54. The analysis fits better for a compound with two fewer hydrogen atoms (calcd. for $C_{22}H_{22}O$: C, 87.96; H, 6.71); *cf.* ref. 11.

Intermediate XII (Fig. 2) was obtained as follows: A solution of phenylmagnesium bromide was prepared in the usual manner under nitrogen from 0.2 g. of magnesium and 1.6 g. of bromobenzene in 30 ml. of dry ether. To the Grignard solution was added dropwise, during 30 min., a solution of 0.51 g. (1.7 mmoles) of XI in 60 ml. of dry ether. No violent reaction was observed, but the original pale-yellow soln. was refluxed for 1.5 hr. more, then left overnight at room temperature, before being poured into iced dilute hydrochloric acid and extracted with ether. Ether was removed on the steam-bath, leaving a red-orange oil in small amount.

To obtain intermediate XIII, Fig. 2, the above oil was refluxed with 4 ml. of freshly distilled hydriodic acid and 1.6 g. of red phosphorus, in 20 ml. of glacial acetic acid for 4 hr. The reaction mixture then was poured into 200 ml. of water to which enough solid sodium thiosulfate had been added to remove free iodine, and the solution was extracted with ether (5 × 50 ml.). The extracts were combined and washed with 10% sodium bicarbonate solution until no more gas evolved. Precipitated sulfur was removed and the ether distilled, leaving a small quantity of brown viscous oil.

The above oil was transferred, in ether soln., to a dehydrogenation apparatus and ether again was removed in a nitrogen stream. Ten grams of freshly ignited alumina was mixed thoroughly with 3 g. of 5% palladium-on-charcoal, and the mixture was poured into the dehydrogenator containing XII. The entire apparatus now was heated at 340–350° (metal-bath) under a gentle stream of nitrogen. The reaction mixture next was cooled to room temperature, extracted with chloroform (4 × 50 ml.) and the extracts were combined and filtered. The filtrate was taken to dryness and the residual oil dissolved in 40 ml. of a mixture containing 25 vol. % benzene and 75 vol. % mixed heptanes. This solution finally was chromatographed on an activated alumina column (*ca.* 1″ × 12″).

A faint blue band was eluted from the column with the same solvent and evaporated to dryness, leaving a small amount of blue-green oil. This was dissolved, with difficulty, in 10 ml. of boiling 95% ethanol. Evaporation of the solution to *ca.* 0.5 ml. caused deposition of a minute quantity of 1,2,3-triphenylazulene melting at 208–211°, with prior sintering at about 200°. A mixture of this substance with III (m.p. 212–214°) melted at 207–212°, with prior sintering at about 200°. The m.p. behavior indicates that this sample was contaminated with a small amount of difficultly-separable impurity. Further purification of the 3 mg. of final product obtained was not, however, attempted.

Infrared and ultraviolet absorption spectra of 1,2,3-triphenylazulene (III) obtained *via* diphenylacetylene and the sample obtained *via* cycloheptanone (Fig. 2) were compared and found to be completely superimposable.

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