was made, using 75 g. of 6-iodo-3-hexen-1-ol and 157.5 g. of silver oxide in 1350 ml. of anhydrous ether, in which 13.4 g. of a distillate, b.p. 118–120° was obtained.

Fractional distillation of the combined 118–120° product gave 13.3 g. (23%) of the tetrahydroöxepine, b.p. 118–119°, besides 2.8 g. of a fore-run which showed the same infrared spectrum as the main product. Gas chromatography of the former fraction gave a single peak, while that of the latter one gave two peaks, one of which was definitely ascribed to ether, the other to III, $n^{25.5}$D 1.4548; infrared spectrum (NaCl plates): 3.33, 3.44, 3.51, 3.64, 5.02(w), 5.31(w), 6.02, 6.83, 7.01, 7.19, 7.45, 7.65, 7.80, 8.04(w), 8.26, 8.86, 9.48, 9.67, 10.52, 11.50, 13.12 and 14.15 μ.

Anal. Calcd. for $C_6H_{10}O$: C, 73.43; H, 10.27. Found: C, 73.27; H, 10.54.

Bromine titration of the olefinic double bond[13] gave 93.6% absorption of the calculated amount, while quantitative hydrogenation in 95% ethanol in the presence of 10% palladium-charcoal gave 98.2% absorption of the calculated amount of hydrogen.

Hexamethylene oxide[14] was isolated from the hydrogenation mixture, $n^{24.0}$D 1.4361; infrared spectrum: 3.44, 3.51, 5.71, 6.78, 6.89, 7.20, 7.28, 7.35, 7.79, 7.88, 8.05, 8.45, 8.76, 9.01, 9.66, 9.81, 10.01, 10.22, 11.90, 12.10, 12.42, 13.20 and 13.58 μ.

Fractional distillation of the higher boiling by-products using a Podbielniak column gave the following three fractions: fraction A, b.p. 59–61° (4 mm.), weighed 1.3 g.; ultraviolet absorption: λ_{max} 226 mμ, ϵ 30,900; infrared spectrum: 2.99, 3.25, 3.34, 3.43, 3.50, 5.77, 6.00, 6.25, 6.95, 7.25, 7.91, 8.39, 9.21, 9.54, 9.77, 9.95, 10.36, 11.03, 11.41, 12.30 and 12.71 μ.

Anal. Calcd. for $C_6H_{10}O$: C, 73.43; H, 10.27. Found: C, 73.24; H, 10.15.

This fraction was identified as (possibly *cis*-) 3,5-hexadien-1-ol, since quantitative hydrogenation resulted in the uptake of 97.6% of two molar equivalents of hydrogen. Isolation of the hydrogenation product, followed by the treatment with phenyl isocyanate gave *n*-hexyl phenylcarbamate, m.p. 41–42° (lit.[15] 42°).

The next higher boiling fraction B came over at about 53–63° (0.4 mm.), weighing 5.7 g., $n^{25.0}$D 1.4747–1.4754; infrared spectrum: 2.99, 3.35, 3.43, 3.50, 5.76, 6.00, 6.90, 6.99, 7.09, 7.22, 7.70, 8.05, 8.45, 8.99, 9.50, 10.28, 11.50 and 13.52–14.23 μ. This spectrum was compared to that of *cis*-3-hexene-1,6-diol prepared by the method of Raphael and Roxburgh,[4] b.p. 107–112° (0.4 mm.), $n^{25.6}$D 1.4742; infrared spectrum: 3.03, 3.35, 3.44, 3.50, 6.04, 7.04, 7.12, 7.30, 8.48, 8.96, 9.54, 11.46 and 13.90–14.60 μ. Almost all of the main absorptions showed a good agreement, but treatment of the fraction B with phenyl isocyanate did not give the crystalline bisphenylurethan, m.p. 107–108°, which was obtained easily from authentic hexenediol.

The highest boiling fraction C came over at 120–130° (0.6 mm.), and appeared to be a mixture. It was not characterized.

An attempted cyclization of X with silver oxide in acetone did not give III, but a product which showed a strong carbonyl absorption at 5.83 μ, whose structure was not determined.

Treatment of IX with potassium *t*-butoxide in diethylene glycol–diethyl ether gave a small amount of III.

Attempted Epoxidation of α-Benzene Tetrachloride (XIV).[16]—Compound XIV was found to be recoverable unchanged from treatment with either peracetic acid or perfluoroperacetic acid. Although the desired epoxide has been described by Takei, *et al.*,[8] the yield using chromic acid oxidation of XIV was too low to allow it to be a useful synthetic intermediate.

***trans*-Cyclohexen-4,5-diol Diacetate (XVI).**—1,4-Cyclohexadiene[17] was treated with 40% peracetic acid in excess acetic acid in the usual way. The crude product was isolated and acetylated by treatment with excess acetic anhydride and pyridine on the steam-bath for one hour. A 38% yield of XVI, b.p. 76–79° (0.35 mm.), n^{25}D 1.4587, was obtained.

Anal. Calcd. for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.79; H, 7.14.

1,2-Epoxy-4,5-cyclohexane Diol Diacetate (XVII).—Compound XVI was epoxidized in the usual way with perbenzoic acid in chloroform. The desired epoxide, b.p. 115–122° (0.9 mm.), n^{25}D 1.4619, was obtained in 74% yield. The structure of XVII was confirmed by acid hydrolysis and acetylation to give a product identical with authentic tetraacetate of 1,2,4,5-cyclohexanetetraol.[18]

Anal. Calcd. for $C_{10}H_{14}O_6$: C, 56.07; H, 6.59. Found: C, 56.19; H, 6.38.

Allylic Bromination of 4,5-Epoxycyclohexene.—Compound XX[19] was allowed to react with N-bromosuccinimide in carbon tetrachloride solution, with a trace of benzoyl peroxide as catalyst. The crude product, containing some succinimide, was purified by chromatography on Magnesol: Celite (1:1). The eluted product was distilled (b.p. 60–70° (bath) (0.9 mm.)) to give an analytical sample.

Anal. Calcd. for C_6H_7OBr: C, 41.17; H, 4.03; Br, 45.66. Found: C, 41.35; H, 4.21; Br, 45.54.

(13) H. J. Lucas and D. Pressman, *Ind. Eng. Chem., Anal. Ed.*, **10**, 140 (1938).

(14) A. Müller and W. Vanc, *Ber.*, **77B**, 669 (1944).

(15) E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 446.

(16) The authors are indebted to Dr. H. D. Orloff, Ethyl Corporation, for a generous supply of this material.

(17) J. P. Wibaut and F. A. Haak, *Rec. trav. chim.*, **67**, 85 (1948).

(18) G. E. McCasland and E. C. Horswill, THIS JOURNAL, **76**, 1658 (1954).

(19) M. Tiffeneau and B. Tchoubar, *Compt. rend.*, **212**, 581 (1941); *cf.* ref. 9.

ITHACA, N Y.

[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, HEBREW UNIVERSITY]

4- and 5-Phenylazulenes

BY ERNST D. BERGMANN AND RAPHAEL IKAN

RECEIVED JULY 25, 1957

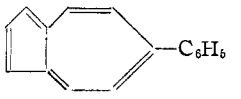
5-Phenylazulene has been prepared from bicyclo[5.3.0]decan-5-one (VIII) by reaction with phenylmagnesium bromide, dehydration and dehydrogenation. It is different from a previously described phenylazulene for which thus, indirectly, the 6-position of the phenyl group has been confirmed. The known liquid 4-phenylazulene has also been synthesized by a new route, in which 4-phenylbicyclo[5.3.0]decan-6-one (XVII) is the key substance. Whilst 4-phenylazulene absorbs at the same wave length as azulene itself, a bathochromic shift is observed for the 5- and 6-isomers, which have practically identical absorption spectra. This statement refers to the longest wave length band in the spectrum.

In a recent communication,[1] a synthesis of 6-phenylazulene (I) has been described, and it has been reported that the introduction of the phenyl group at C_6 causes a bathochromic shift in the spectrum of azulene, whilst the theory[2] predicted a hypsochromic effect. It seemed not impossible that in the preparation of 6-phenylazulene a migra-

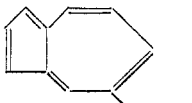
(1) E. D. Bergmann and R. Ikan, THIS JOURNAL, **78**, 1482 (1956).

(2) B. Pullman, J. Berthier and J. Baudet, *J. chim. phys.*, **50**, 69 (1953); *J. Chem. Phys.*, **21**, 187 (1953).

tion of the phenyl group had taken place, so that the compound obtained may have been 5-phenylazulene.[3] This suspicion appeared to be supported by the fact that the 6-methylazulene prepared by Arnold[4] was later[5] proved to be the 5-isomer.[6]

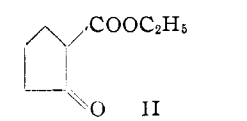


I



X

It appeared therefore interesting to synthesize 5-phenylazulene (X). The method used is illustrated by the following Chart. Up to the ketone VIII, it is a modification of the method described by Šorm.[7]



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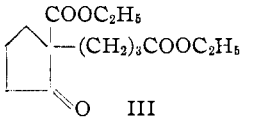

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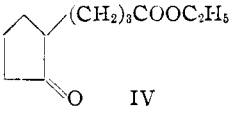

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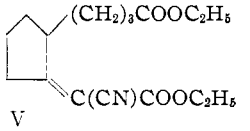
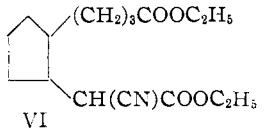


V



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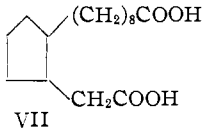
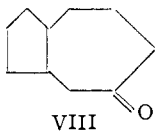
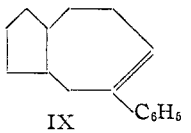


VII



VIII



IX

2-Carbethoxy-cyclopentanone (II) was alkylated with ethyl γ-bromobutyrate[8] and the product III hydrolyzed, decarboxylated and re-esterified to give IV. This was condensed with ethyl cyanoacetate in the presence of piperidine acetate and the resulting product (V) was hydrogenated (to VI), hydrolyzed and partially decarboxylated. The cerium salt of the acid VII was cyclized to bicyclo[5.3.0]-decan-5-one (VIII) and the latter treated with phenylmagnesium bromide. Thus the hydrocarbon IX was obtained, which upon dehydrogenation gave the desired 5-phenylazulene (X). The overall yield, based on II, was 2%.

Šorm[7] has assumed that the compounds VI, VII and VIII are the *cis* isomers. Of the bicyclo-[5.3.0]decan-5-one (VIII), both isomers have been prepared by a different method.[9]

(3) In fact, one of the referees had made this suggestion.

(4) H. Arnold, *Ber.*, **76**, 777 (1943).

(5) F. Šorm and J. Fajkos, *Coll. Czechoslovak Chem. Communs.*, **12**, 81 (1947).

(6) Other migrations in the last (dehydrogenation) step of azulene syntheses have been observed, but they involve the five-membered ring; W. Herz, THIS JOURNAL, **75**, 73 (1953); T. Ukita, H. Watanabe and M. Miyazaki, *ibid.*, **76**, 4584 (1954); P. A. Plattner, R. Sandrin and J. Wyss, *Helv. Chim. Acta*, **29**, 1604 (1946); P. A. Plattner, A. Fuerst, M. Gordon and K. Zimmerman, *ibid.*, **33**, 2910 (1950).

(7) F. Šorm, *Coll. Czechoslovak Chem. Communs.*, **12**, 251 (1947) (*C. A.*, **42**, 555 (1948)).

(8) *Cf.* W. E. Bachmann and W. S. Struve, THIS JOURNAL, **63**, 2589 (1941).

(9) P. A. Plattner, A. Fuerst and A. Studer, *Helv. Chim. Acta*, **30**, 1091 (1947).

Compound X melted at 100° and was therefore different from the previously[1] prepared phenylazulene (m.p. 160°).[10] The spectrum of X is given in Fig. 1; the longest absorption band lies at 7160 A. (log ε 2.16).

After this investigation had been completed, a synthesis of 5-phenylazulene (X) was reported by Treibs, Quarg and Poppe.[11] By the reaction between hydrindene and N-nitrosobenzylurethan and subsequent dehydrogenation of the product, a compound of m.p. 98–99° has been obtained by these authors. As Table I shows, the spectrum of this compound is practically identical with that of our 5-phenylazulene; furthermore both products give a trinitrobenzene derivative which contains *two* molecules of the nitro compound.

TABLE I

SPECTRA OF 4-, 5- AND 6-PHENYLAZULENE (mμ) (IN ETHANOL)

4-Phenylazulene	5-Phenylazulene (present authors)	5-Phenylazulene (Treibs, *et al.*[11])	6-Phenylazulene (Bergmann and Ikan[1])
232 (4.38)	234 (4.30)		235 (2.36)
266 (4.52)	286 (4.65)	..	294 (4.82)
345 (3.52)	349 (3.76)	..	350 (3.79)
	367 (3.82)	..	368 (3.72)
588 (2.60)	594 (2.63)	591	595 (2.50)
		613	
697 (2.15)	646 (2.60)	646	646 (2.46)
		673	
	716 (2.26)	713	716 (2.00)

It thus appears certain that the compound prepared in this study is indeed 5-phenylazulene, whilst the isomer obtained previously[1] is the 6-compound—the more so as 4-phenylazulene has been described as a blue *liquid*.[12] Its spectrum has not been reported. In order to compare the spectra of all three phenylazulenes, 4-phenylazulene (XVIII) has been prepared. Its spectrum (Fig. 1) shows the longest absorption band at 697 mμ (log ε 2.15). The comparison of the spectra in Table I shows that 5- and 6-phenylazulene have practically identical spectra and that—contrary to the theory—6-phenylazulene as well as the 5-compound absorbs at longer wave lengths than azulene itself, whilst the longest absorption band of the 4-isomer is identical with that of the unsubstituted azulene (697 mμ). Figure 2 gives the infrared spectra of the three isomers.

The synthesis of 4-phenylazulene has been carried out in a manner which differs from the route of the previous authors.[12]

Compound II was condensed with ethyl phenylbromoacetate, which had been obtained by the interaction of ethyl phenylacetate and N-bromosuccinimide. The product XI was converted to XII and the latter condensed with ethyl cyanoacetate in the presence of a mixture of piperidine and benzylamine acetates. The resulting product XIII was hydrogenated (to XIV) and hydrolyzed with simultaneous partial decarboxylation. From the dicarboxylic acid XV so obtained, the

(10) In the previous publication, the m.p. was erroneously given as 150°.

(11) W. Treibs, M. Quarg and E. J. Poppe, *Ann.*, **598**, 32 (1956).

(12) A. St. Pfau and P. A. Plattner, *Helv. Chim. Acta*, **19**, 858 (1936).

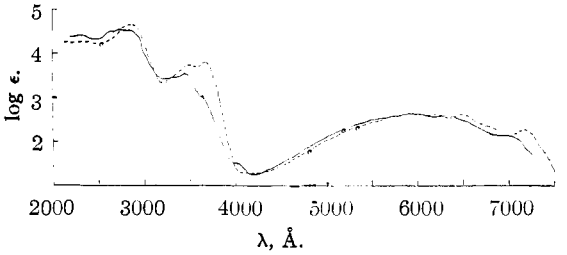
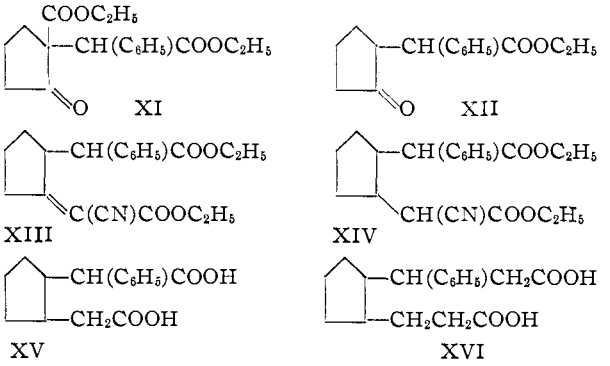
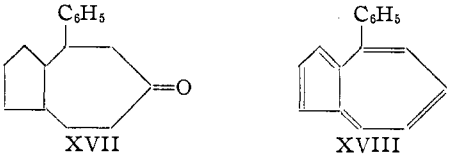


Fig. 1.—Ultraviolet and visible spectra of 4-phenylazulene (XVIII) (———) and 5-phenylazulene (X) (·····) in alcoholic solution.

homologous compound XVI was prepared by double Arndt–Eistert reaction; XVI was then cyclized to 4-phenyl-bicyclo[5.3.0]decan-6-one (XVII) *via* the cerium salt. Reduction by the method



of Huang-Minlon and subsequent dehydrogenation afforded 4-phenylazulene (XVIII), a deep-blue oil which gave a trinitrobenzene derivative of the same m.p. (86°) as indicated by the previous authors.[12]



Experimental

2-Carbethoxy-2-(γ-carbethoxypropyl)-cyclopentanone (III), b.p. 147° (0.65 mm.), $n^{15}D$ 1.4618, d^{15}_4 1.0850, was prepared in 64% yield according to Bachmann and Struve[8] and converted into **γ-(2-oxocyclopentyl)-butyric acid**[7,8] **as** (IV), in 55% yield, b.p. 134° (0.04 mm.), $n^{15}D$ 1.4748, d^{15}_4 1.1040; *MR* calcd. 43.46, found 43.28.

Ethyl γ-(2-Oxocyclopentyl)-butyrate (IV).—(1) The acid (160 g.) was esterified with 500 ml. of 96% ethanol in presence of 250 ml. of carbon tetrachloride and 5 ml. of concentrated hydrochloric acid. After refluxing the mixture for 35 hours, the volatile constituents were removed at 100° *in vacuo*, and the residue was dissolved in ether. The ethereal solution was washed with 10% sodium carbonate solution and water, dried and distilled; b.p. 109° (0.03 mm.), yield 165 g. (89%), $n^{15}D$ 1.4562, d^{15}_4 1.0180; *MR* calcd. 52.73, found 52.84.

Anal. Calcd. for $C_{11}H_{18}O_3$: C, 66.7; H, 9.1. Found: C, 67.3; H, 9.1.

Semicarbazone, from nitromethane, needles, m.p. 173° (lit.[7] 173°).

(2) According to the method of Stork,[13] 120 g. of ethyl γ-bromobutyrate was added at room temperature within 30 minutes to 90 g. of N-cyclopentenylmorpholine[1] in 200 ml. of dry benzene. The mixture was refluxed for 3 hours, cooled and decomposed with 100 ml. of water. The layers were separated, and the aqueous phase was extracted with benzene. The combined benzene solutions were washed with 5% hydrochloric acid and water, and dried. Distillation gave 16 g. (8%) of the desired IV.

(13) G. Stork, R. Terrell and J. Szmuszkovicz, THIS JOURNAL, **76**, 2029 (1954).

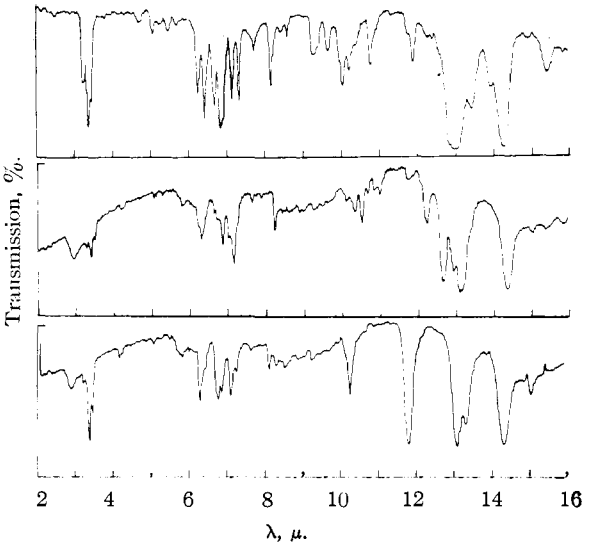


Fig. 2.—Infrared spectra of 4- (top), 5- (middle) and 6-phenylazulene (bottom) (4-phenylazulene as liquid film, 5- and 6-phenylazulene in a potassium bromide pellet).

Ethyl 2-(γ-Carbethoxypropyl)-cyclopentylidenecyanoacetate (V).—The mixture of 160 g. of IV, 140 g. of ethyl cyanoacetate, 5 ml. of piperidine acetate and 160 ml. of benzene was subjected to azeotropic distillation. The reaction was complete in 30 hours. The solvent was removed *in vacuo* and the residue dissolved in ether and washed with water; b.p. 156° (0.04 mm.) (lit.[7] 174–176° (0.6 mm.)), yield 155 g. (66%), $n^{18}D$ 1.4867, d^{18}_4 1.133; *MR* calcd., 74.15, found 74.30; ultraviolet spectrum 239 mμ (4.19) (in alcohol).

Ethyl 2-(γ-Carbethoxypropyl)-cyclopentylcyanoacetate (VI).—The preceding ester (80 g.) was hydrogenated at a pressure of 3 atmospheres and at 60°, using anhydrous ethanol (150 ml.) as a solvent and platinum oxide (250 mg.) as catalyst.[14] The reaction required 3.5 hours; b.p. 162–163° (0.5 mm.) (lit.[7] 179–181° (1.1 mm.)), yield 76 g. (95%), $n^{11}D$ 1.4712, d^{11}_4 1.072; *MR* calcd. 77.22, found 76.90.

Cyclopentane-1-acetic-2-γ-butyric Acid (VII).—A mixture of 75 g. of the ester VI and 300 ml. of concentrated hydrochloric acid was refluxed for 15 hours. On cooling, the desired acid crystallized out; it was recrystallized from nitromethane and formed colorless needles of m.p. 137° (lit.[7] 137°), yield 27 g. (52%).

Bicyclo[5.3.0]decan-5-one (VIII).—To a solution of 2.1 g. of the acid VII in 10 ml. of boiling water, 4 g. of cerium carbonate was added with stirring. The mass was brought to dryness, heated at 120° for two hours and powdered. Pyrolysis at 330–360° yielded an oil of distinct camphoraceous odor; b.p. 69° (0.6 mm.), 74° (1 mm.), yield from 23 g. of the acid VII, 12.5 g. (74%), $n^{11}D$ 1.4930, d^{11}_4 0.985; *MR* calcd. 44.50, found 44.35; ultraviolet spectrum 216 mμ (2.86) (in ethanol), infrared spectrum 1698 cm.$^{-1}$ (without solvent).

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.9; H, 10.6. Found: C, 79.5; H, 10.6.

Semicarbazone, from nitromethane, needles of m.p. 203° (lit. 204°[7], 203°[9]); ultraviolet spectrum 229 mμ (4.15) (in ethanol); infrared spectrum 1650 cm.$^{-1}$ (C=N), 1695 cm.$^{-1}$ (amide) (in KBr).[15]

5-Phenylbicyclo[5.3.0]-5-decene (IX).[16]—To a cold ethereal solution of phenylmagnesium bromide, prepared from 16.5 g. of bromobenzene and 2.6 g. of magnesium, there was

(14) According to our previous experience (ref. 1), under these conditions the *cis* form of VI should be obtained; see ref. 7, 9.

(15) *Cf.* W. H. T. Davison and P. E. Christie, *J. Chem. Soc.*, 3389 (1955).

(16) The position of the double bond has not been established.

added 8 g. of the ketone VIII. The mixture was refluxed for 6 hours and decomposed with ice and dilute sulfuric acid. The ethereal solution was washed with sodium bisulfite solution and water, dried and evaporated, and the residue heated for 3 hours with 3 g. of oxalic acid in 100 ml. of toluene under azeotropic conditions. The solution was extracted with 10% sodium hydroxide solution, washed with water, dried and distilled; b.p. 108° (0.25 mm.), yield 7.5 g. (68%) of a yellowish oil, $n^{13.5}D$ 1.5705, $d^{13.5}_4$ 1.015; *MR* calcd. 68.29, found 68.54; ultraviolet spectrum 260 mμ (3.91) (in ethanol).

Anal. Calcd. for $C_{16}H_{20}$: C, 90.5; H, 9.5. Found: C, 90.8; H, 9.3.

5-Phenylazulene (X).—By the method of Plattner, *et al.*,[17] 6.5 g. of IX was dehydrogenated. The operation was repeated 8 times and gave a yield of 2.8 g. (45%) of the azulene. After distillation (b.p. 105–115° (0.02 mm.)), it crystallized. From isopropyl alcohol, it formed blue leaflets of m.p. 100°.

Anal. Calcd. for $C_{16}H_{12}$: C, 94.1; H, 5.9. Found: C, 94.0; H, 5.7.

The trinitrobenzene derivative (2 moles TNB per mole azulene) had m.p. 102°.

Anal. Calcd. for $C_{28}H_{18}N_6O_{12}$: C, 53.3; H, 2.9. Found: C, 53.0; H, 3.2.

Ethyl Phenylbromoacetate.—The mixture of 92 g. of ethyl phenylacetate, 100 g. of N-bromosuccinimide, 400 ml. of carbon tetrachloride and 100 mg. of benzoyl peroxide was refluxed for 6 hours, cooled, filtered and distilled *in vacuo*, b.p. 117° (0.8 mm.), yield 125 g. (92%).

2-Carbethoxy-2-(α-carbethoxybenzyl)-cyclopentanone (XI).—To a cold solution of 13.2 g. of sodium in 180 ml. of anhydrous ethanol, 93 g. of 2-carbethoxycyclopentanone (II) was added with agitation within 15 minutes, followed by 154 g. of ethyl phenylbromoacetate. The mixture was refluxed for 4 hours, the alcohol distilled off on a water-bath and the residue diluted with 200 ml. of cold water and extracted with ether; b.p. 165° (0.3 mm.), yield 135 g. (72%), $n^{14}D$ 1.5110, d^{14}_4 1.1390; *MR* calcd. 83.23, found 83.62; ultraviolet spectrum (in ethanol): 253 mμ (2.45), 259 mμ (2.48), 265 mμ (2.41).

Anal. Calcd. for $C_{18}H_{22}O_5$: C, 67.9; H, 6.9. Found: C, 67.3; H, 7.3.

(2-Oxocyclopentyl)-phenylacetic Acid (as XII).—A mixture of 300 g. of the foregoing ester, 450 ml. of 48% hydrobromic acid and 450 ml. of glacial acetic acid was heated for 6 hours in an oil-bath at 150–160°. The solvent was removed *in vacuo* and the residue diluted with water, whereupon an oil separated which solidified quickly. It was brought into solution by addition of solid sodium carbonate. The solution was extracted with ether and acidified with concentrated hydrochloric acid, and the product recrystallized from nitromethane. It formed needles of m.p. 148°, yield 130 g. (63%).

Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.5; H, 6.4. Found: C, 71.5; H, 6.4.

The ethyl ester XII, prepared with alcohol, saturated with gaseous hydrogen chloride, in 91% yield, boiled at 138° (0.01 mm.), 144° (0.1 mm.), $n^{14}D$ 1.5233, d^{14}_4 1.1010; *MR* calcd. 67.76, found 68.25.

Anal. Calcd. for $C_{15}H_{18}O_3$: C, 73.1; H, 7.3. Found: C, 73.0; H, 7.4.

The 2,4-dinitrophenylhydrazone of the ethyl ester crystallized from nitromethane in orange needles, m.p. 199–200°, spectrum (in chloroform): 364 mμ (4.38).

Anal. Calcd. for $C_{21}H_{22}N_4O_6$: C, 59.1; H, 5.1. Found: C, 58.9; H, 4.9.

Ethyl [2-(α-Carbethoxybenzyl)-cyclopentylidene]-cyanoacetate (XIII).—The mixture of 115 g. of the foregoing ketoester, 77 g. of ethyl cyanoacetate, 6 ml. of piperidine, 0.9 ml. of benzylamine, 15 ml. of glacial acetic acid and 150 ml. of benzene was subjected to azeotropic distillation for 15 hours. Ether was added, and the solution washed with water, saturated sodium chloride solution and again water, dried and distilled; b.p. 205–207° (2 mm.), yield 120 g. (75%), $n^{18}D$ 1.5324, d^{18}_4 1.1560; *MR* calcd. 91.77, found 91.46; ultraviolet spectrum (in ethanol): broad maximum at 235 mμ (4.00).

Anal. Calcd. for $C_{20}H_{23}NO_4$: C, 70.4; H, 6.7. Found: C, 70.6; H, 6.7.

Ethyl [2-(α-Carbethoxybenzyl)-cyclopentyl]-cyanoacetate (XIV).—The foregoing compound (130 g.) was dissolved in 150 ml. of absolute ethanol and hydrogenated at room temperature and under 3 atm. pressure in the presence of 700 mg. of platinum oxide. The theoretical quantity of hydrogen was absorbed in 3.5 hours; b.p. 188–189° (1 mm.), yield 124 g. (95%), $n^{18}D$ 1.5150, d^{18}_4 1.117; *MR* calcd. 92.25, found 92.53; ultraviolet spectrum (in ethanol): 252 mμ (2.90), 259 mμ (2.88), 266 mμ (2.78).

Anal. Calcd. for $C_{20}H_{25}NO_4$: C, 70.0; H, 7.3. Found: C, 70.3; H, 7.3.

Cyclopentane-1-(α-phenylacetic)-2-acetic Acid (XV).—A mixture of 140 g. of the foregoing compound, 260 ml. of glacial acetic acid and 400 ml. of 48% hydrobromic acid was heated in an oil-bath (180°) for 15 hours. The solvent was removed *in vacuo* and the residue diluted wath water. The solid acid was filtered, purified by dissolution in sodium carbonate solution, acidified with concentrated hydrochloric acid, and recrystallized from nitromethane; prisms of m.p. 244°, yield 52 g. (48%); ultraviolet spectrum, (in ethanol): 253 mμ (2.32), 259 mμ (2.38), 263 mμ (2.28).

Anal. Calcd. for $C_{15}H_{18}O_4$: C, 68.7; H, 6.9. Found: C, 69.3; H, 6.7.

β-[2-(β'-Carboxyethyl)-cyclopentyl]-β-phenylpropionic Acid (XVI).—A mixture of 5 g. of the acid XV and 15 g. of thionyl chloride was heated for 3 hours at 70° and refluxed for 30 minutes. Then the excess of thionyl chloride was removed *in vacuo*, dry benzene added to the residue and the benzene evaporated again *in vacuo*. This was repeated five times. The resulting yellow oil was dissolved in 20 ml. of anhydrous ether and added slowly (within 30 minutes) to an ethereal solution of diazomethane (dried over potassium hydroxide) at −15°. The reaction mixture was kept at room temperature for 12 hours. Evaporation of the excess diazomethane and the solvent *in vacuo* (without application of heat) gave the solid bis-diazoketone, prisms of m.p. 92°, yield 4.5 g.

A solution of 4 g. of the diazoketone in 20 ml. of benzyl alcohol and 16 ml. of γ-collidine was introduced in small portions into a round-bottomed flask which had been heated at 175–180°. The reaction product was heated for an additional 10 minutes at this temperature, cooled and taken up in ether, which was then washed with 10% hydrochloric acid and water and concentrated. The residue was refluxed for 8 hours with 30 ml. of ethylene glycol monomethyl ether and 20 ml. of 50% aqueous potassium hydroxide solution, and the product was cooled, diluted with water, extracted with ether and acidified. The oily reaction product crystallized quickly upon standing; from benzene, needles of m.p. 102–103°, yield 2.8 g. (75%).

Anal. Calcd. for $C_{17}H_{22}O_4$: C, 70.3; H, 7.5. Found: C, 70.4; H, 7.3.

4-Phenylbicyclo[5.3.0]decan-6-one (XVII).—The mixture of 6 g. of the acid XVI, 20 ml. of ethanol, 10 ml. of water and 6 g. of cerium carbonate was heated with stirring on the water-bath; the salt which formed was dried thoroughly. It was then pyrolyzed over an open flame in batches of 1 g. The distillate was dissolved in ether, the solution washed with sodium bicarbonate solution and water and dried, and the ether residue distilled; b.p. 145–148° (0.7 mm.); from petroleum ether, needles of m.p. 61–62°, yield 3.4 g. (73%); ultraviolet spectrum: (in ethanol): 254 mμ (4.28), 262 mμ (4.28), 330 mμ (2.65); infrared spectrum: $\nu_{C=O}$ 1700 cm.$^{-1}$ (in carbon tetrachloride).

Anal. Calcd. for $C_{16}H_{20}O$: C, 84.2; H, 8.8. Found: C, 84.5; H, 8.6.

2,4-Dinitrophenylhydrazone, from *n*-butyl alcohol; yellow needles of m.p. 186°; spectrum (in chloroform): 368 mμ (4.34).

Anal. Calcd. for $C_{22}H_{24}N_4O_4$: C, 64.7; H, 5.9. Found: C, 64.4; H, 5.9.

4-Phenylbicyclo[5.3.0]decane.—The mixture of 8 g. of the foregoing ketone, 4 ml. of hydrazine hydrate and 36 ml. of diethylene glycol was heated at 200° for 90 minutes and after addition of 4.1 g. of powdered potassium hydroxide at 220° for another 90 minutes. After removal of the water

(17) P. A. Plattner, A. Fuerst and K. Jirasek, *Helv. Chim. Acta*, **29**, 740 (1946).

formed, the heating was continued for 4 hours at 240–250°. The reaction mixture was cooled, diluted with water, acidified and extracted with ether; b.p. 98° (0.25 mm.), yield 7 g. (93%), $n^{26}D$ 1.5450, d^{26}_4 0.9820; *MR* calcd. 68.77, found 68.94; ultraviolet spectrum (in ethanol) 252 mμ (3.26).

Anal. Calcd. for $C_{16}H_{22}$: C, 89.7; H, 10.3. Found: C, 89.6; H, 10.0.

4-Phenylazulene (XVIII).—The dehydrogenation of 4-phenylbicyclodecane (6.5 g.) was carried out in the usual manner[17] at 350–360° and the product taken up in petroleum ether from which the azulene formed was extracted with 85% phosphoric acid. The material was recycled 12 times. The acid solutions were combined, diluted with water and extracted with ether. After treatment with water, dilute bicarbonate solution and again water, the product was purified by distillation. It formed a deep-blue oil of b.p. 120–130° (0.8 mm.), yield 2.2 g. (34%). **The trinitrobenzene derivative** was prepared in alcohol and recrystallized from the same solvent. It formed needles of m.p. 86°, as indicated in the literature.

Anal. Calcd. for $C_{22}H_{15}N_3O_6$: C, 63.3; H, 3.6. Found: C, 62.8; H, 4.0.

The trinitrobenzene compound was decomposed by chromatography of its benzene solution on activated alumina; the hydrocarbon so purified was used for the determination of the spectrum.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE FLORIDA STATE UNIVERSITY]

Azulenes. IX.[1] Migration of the Isopropyl Group during the Synthesis of 1-Isopropyl-8-methylazulene

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Treatment of 1-isopropyl-7-methylindan with ethyl diazoacetate followed by hydrolysis and dehydrogenation gave 1-isopropyl-8-methylazulene and 2-isopropyl-4-methylazulene, the latter by migration of the isopropyl group. The rearrangement product was synthesized independently from 2-isopropyl-4-methylindan.

Earlier work dealing with alkyl group migrations in the azulene series was reviewed in the previous paper.[1] Isopropyl group migration, presumably due to interference between alkyl groups in the 1- and 8-positions of the azulene nucleus, was observed when attempts were made to synthesize 1-isopropyl-4,8-dimethyl-[2] and 3-isopropyl-4,5-dimethylazulene.[3] The present paper reports an analogous migration during the preparation of 1-isopropyl-8-methylazulene, the simplest member of this group.

Authentic 2-isopropyl-4-methylazulene was prepared from *o*-methylbenzyl chloride by a standard series of reactions involving condensation with diethyl isopropylmalonate, hydrolysis and decarboxylation, cyclization of the resulting acid to 2-isopropyl-4-methylindanone, Clemmensen reduction to 2-isopropyl-4-methylindan, ring expansion with ethyl diazoacetate, saponification and dehydrogenation with palladium–charcoal. The azulene, a violet liquid, was characterized through its trinitrobenzene complex and exhibited the expected[4] peaks in the visible and ultraviolet spectrum (Figs. 1 and 2).

1-Isopropyl-7-methylindan was synthesized by alkylation of *o*-tolylacetonitrile with isopropyl bromide, saponification, homologation by the method of Newman and Beal,[6] hydrolysis and cyclization and Clemmensen reduction of the resulting 3-isopropyl-4-methylindanone. Treatment of the indan with diazoacetic ester, saponification and dehydrogenation with 10% palladium–charcoal gave a mixture of 1-isopropyl-8-methylazulene and 2-isopropyl-4-methylazulene. The mixture was separated into its constituents by taking advantage of the somewhat lower basicity of 1-alkylazulenes[7] and the greater solubility of their trinitrobenzene complexes in ethanol.[1,3] Isolated in this fashion the violet 2-isopropyl-4-methylazulene which constituted the major part of the azulene mixture was identical in all respects with the authentic sample.

1-Isopropyl-8-methylazulene, a *blue* liquid, was isolated in small amount only. Its trinitrobenzene complex melted over a 3° range, which may indicate the presence of a contaminant, but the visible spectrum (Fig. 1) was sharp and exhibited bands at or near the wave lengths reported for 1,8-dimethylazulene.[4,8] Similarly, the ultraviolet spectrum (Fig. 2) exhibited a medium-intensity band at a wave length higher than 360 mμ, which seems to be characteristic of 1-alkyl substituted azulenes.[1,10]

No evidence was found for the presence of 4-methylazulene and 1,3-diisopropyl-4-methylazulene, products which might have been formed by dealkylation accompanied, or followed, by disubstitution. Although these substances might have escaped detection, their apparent absence supports the earlier suggestion[1] that migration and

(1) Paper VIII, W. Herz, THIS JOURNAL, **80**, 1243 (1958).

(2) W. Herz, *ibid.*, **75**, 73 (1953).

(3) W. Herz and B. E. Cleare, *ibid.*, **77**, 2318 (1955).

(4) For a review, see M. Gordon, *Chem. Revs.*, **50**, 127 (1952). There appears to be some question about the accuracy of the spectral data reported for 2-ethyl-4-methylazulene, the only previously synthesized 2,4-dialkylated azulene.[5]

(5) T. Wagner-Jauregg, H. Arnold, F. Hüter and J. Schmidt, *Ber.*, **74**, 1522 (1941); T. Wagner-Jauregg and H. Hippchen, *ibid.*, **76**, 694 (1943).

(6) M. S. Newman and P. F. Beal, THIS JOURNAL, **72**, 5163 (1950).

(7) Indications of this are found in the distribution studies of Pl. A. Plattner, E. Heilbronner and S. Weber, *Helv. Chim. Acta*, **32**, 574 (1949); **33**, 1663 (1950). Quantitative separation by this method is generally not feasible, but a small amount of pure 1-alkylazulene may usually be obtained by repeated extraction of the azulene mixture, dissolved in cyclohexane, with phosphoric acid (see also ref. 1).

(8) Differences in the m.p.'s of the complexes and the absorption maxima suggest that a blue azulene obtained by Hafner and Weldes[9] on treatment of 1-isopropylazulene with methyllithium and dehydrogenation with chloranil is 1-isopropyl-4-methylazulene, as might conceivably be expected by analogy with the behavior of 1-methylazulene,[8] and not 1-isopropyl-8-methylazulene.

(9) K. Hafner and H. Weldes, *Ann.*, **606**, 90 (1957).

(10) Pl. E. Plattner and E. Heilbronner, *Helv. Chim. Acta*, **31**, 804 (1948).