[FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, HEBREW UNIVERSITY]

6-Phenylazulene

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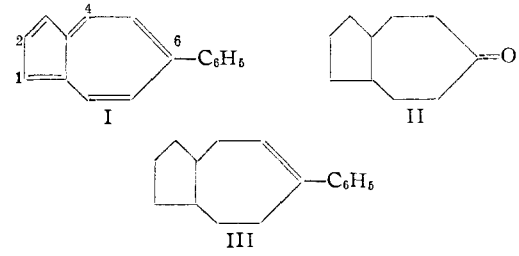
6-Phenylazulene (I) has been synthesized; contrary to the theory, the 6-phenyl group has a bathochromic effect on the longest band of azulene. A possible explanation for this discrepancy is suggested. As the unsaturated ester V gives upon hydrogenation with platinum oxide the *cis*- and in the presence of palladium–charcoal the *trans*-cyclopentane derivative, it has been possible to obtain both the *cis* and *trans* form of bicyclo[0.3.5]decan-4-one (II).

The effect of phenyl substitution on "non-alternant" hydrocarbons has been calculated by the method of linear combination of atomic orbitals (LCAO),[1] and the results have been verified in a number of cases: the fulvenes,[2,3] the heptafulvenes[3,4] and the diphensuccindadienes.[5] It appears that, even excluding effects of steric hindrance, *both* hypsochromic and bathochromic shifts can be foreseen in different molecules. In the azulene system,[1] a hypsochromic effect has been predicted for the 2- and the 6-phenyl group, while phenyl in the 1-position is expected to cause a bathochromic shift of the longest absorption band of the azulene spectrum. In view of the success of these calculations in the case of the methylated azulenes[6] it appeared of interest to verify the prediction of the theory for the phenylated azulenes. Both 1- and 2-phenylazulene[7] are known, and have been found to behave as predicted, with respect to their spectra. Whilst the longest band of azulene lies at 697 mμ,[8] those of 1- and 2-phenylazulene are located at 737 and 688 mμ, respectively,[9,10]

6-Phenylazulene (I) has now been synthesized; it is crystalline and melts at 150° (for 1- and 2-phenylazulene, melting points at 54 and 250° have been recorded, respectively). It is less basic than the alkyl-azulenes, giving no addition product with trinitrobenzene. Contrary to the theory, it shows a bathochromic effect; its longest absorption band lies at 711 mμ (log ε 2.00) (Fig. 1). Although the route employed for the synthesis of 6-phenylazulene (see below) has been used successfully for the preparation of 6-methylazulene,[11] the possibility cannot be excluded that in the dehydrogenation step of the synthesis migration of the phenyl group occurs; on the other hand, the theory may not be adequate. A closer study of the calculations, on which the prediction had been based, leads, indeed, to the following conclusions:[12] The simplest form of the LCAO calculations[1] predicts a bathochromic shift for the phenylation of all three positions, 1, 2 and 6, in the azulene system; refinement of the methods only leads to the differentiation between position 1 and positions 2 and 6. However, the introduction of these refinements in the case of the 6-phenyl-compound is accompanied by very drastic deviations from the "classical" value, indicating an extremely high polarizability of the 6-position. It is noteworthy that also in the series of the methylated azulenes,[6a] the 6-compound occupies an exceptional position. The predicted hypsochromic shift exists, but it is much larger than the one actually observed.

In the synthesis of I, some observations of more general interest have been made. The synthesis was based on the interaction between bicyclo[5.3.0]decan-4-one (II) and phenylmagnesium bromide and subsequent dehydrogenation of the hydrocarbon (III) so obtained.



The ketone II, in its *cis*-configuration, has been prepared before by Plattner and Studer[13] by cyclization of the cerium salt of *cis*-cyclopentane-1,2-dipropionic acid (IV), which in turn had been obtained from diethyl cyclopentylidene-cyanoacetate-2-acetate (V) by catalytic reduction in presence of platinum oxide (to VI), followed by hydrolysis, partial decarboxylation (to *cis*-cyclopentane-1,2-diacetic acid (VII), m.p. 170°) and double Arndt–Eistert reaction. Sorm and Fajkos,[11] on the other hand, have obtained by the same sequence a mixture of much of the *cis* and a little of the *trans* form of VII (m.p. 166 and 138°, respectively). The lat-

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

(2) E. D. Bergmann and J. Hirshberg, *Bull. soc. chim. France*, **17**, 1091 (1950).

(3) E. D. Bergmann, *Prog. Org. Chem.*, **3**, 81 (1956).

(4) E. D. Bergmann, *et al.*, *Bull. soc. chim. France*, **18**, 684 (1951).

(5) E. D. Bergmann, *Bull. Res. Council Israel*, **3**, 439 (1954).

(6) (a) B. Pullman, M. Mayot and G. Berthier, *J. Chem. Phys.*, **18**, 257 (1954); (b) B. Pullman and G. Berthier, *J. chim. phys.*, **52**, 114 (1955); (c) D. E. Mann, J. R. Platt and H. B. Klevens, *J. Chem. Phys.*, **17**, 481 (1949); (d) H. C. D. Longuet-Higgins and R. G. Sowden, *J. Chem. Soc.*, 1404 (1952).

(7) P. A. Plattner, R. Sandin and P. Wyss, *Helv. Chim. Acta*, **29**, 1604 (1946); P. A. Plattner, A. Fuerst, M. Gordon and K. Zimmermann, *ibid.*, **33**, 1910 (1950). 4-Phenylazulene has been prepared by A. St. Pfau and P. A. Plattner, *ibid.*, **19**, 858 (1936), but its spectrum has not been reported.

(8) P. A. Plattner and E. Heilbronner, *ibid.*, **30**, 910 (1947).

(9) Unfortunately, most of the published spectra data for the azulenes are of qualitative nature only; they do not permit a comparison of the intensity of the absorption bands. Only the methylazulenes are an exception: Plattner and Heilbronner (reference 8).

(10) It may be interesting to recall that annulation of a benzene ring in 1,2-position has no effect on the spectrum of azulene (longest band 697 mμ), whilst in 5,6-benzazulene a hypsochromic effect (681 mμ) is evident. The longest band of 1,2,4,5-dibenzazulene lies at 705 mμ, *i.e.*, at a slightly longer wave length than in azulene (W. Treibs, *Ann.*, **577**, 201 (1952)).

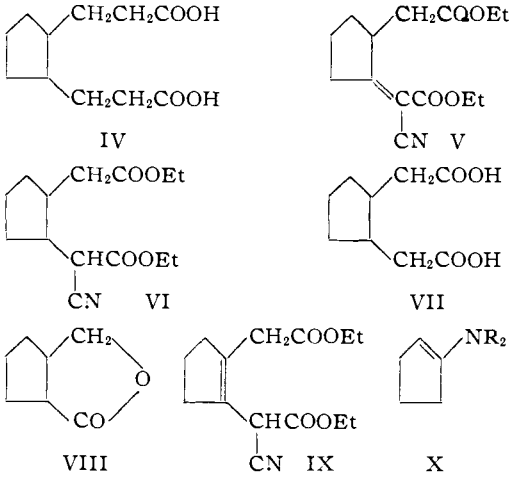
(11) F. Sorm and J. Fajkos, *Coll. Czech. Chem. Commun.*, **12**, 81 (1947) (*C. A.*, **41**, 4140 (1947)).

(12) The authors are indebted to Dr. B. Pullman, Institut du Radium, Laboratoire Curie (Paris), for his advice on this problem.

(13) P. A. Plattner and A. Studer, *Helv. Chim. Acta*, **29**, 1432 (1946).

ter had been obtained before by Linstead and Meade[14] from the lactone VIII by a sequence of reactions which gave "small and varying yields" (m.p. 132°); however, its configuration was established unequivocally.[15] It has also been prepared[11] by double Arndt–Eistert reaction with *trans*-cyclopentane-1,2-dicarboxylic acid; the observed m.p. was 135°. In the present investigation it was found that catalytic reduction of the cyano-ester V in the presence of platinum oxide gave indeed the *cis*-ester, whilst with palladium–charcoal as catalyst a different ester was obtained, which by the same sequence of reactions gave the pure *trans*-VII (m.p. 132°) and is, therefore, assumed to be, at least preponderantly, the *trans* form of VI.[15a]

The high stereospecificity of the catalysts in the hydrogenation of V is unusual; a similar case reported in the literature is the observation by Stoll, Hofmann and Petrzilka[16] that the *d*-ergot alkaloids give upon hydrogenation in the presence of palladium, the derivatives of dihydro- and dihydro-*iso*-lysergic acid in the ratio 1:1, while in the case of platinum oxide the ratio is 1:9.



One might be tempted to postulate that in one of the two instances V is isomerized to IX before it is hydrogenated, but no facts have been observed which would support this hypothesis.

The sequence of reactions which leads from *cis*-cyclopentane-1,2-diacetic acid to the *cis*-ketone II and the hydrocarbon III, has been duplicated with the *trans*-acid VII. Both the double Arndt–Eistert reaction and the successive reduction of the ester of the acid with lithium aluminum hydride, reaction with phosphorus tribromide and potassium cyanide and hydrolysis, led to the *trans*-dipropionic acid IV, which could be cyclized by heating its cerium salt to the *trans*-form of (II).[17] No difference in the ease of cyclization of the two isomeric acids IV was apparent, while according to Linstead and Meade[14] *trans*-cyclopentane-1,2-diacetic acid (VII) is cyclized to the corresponding bicyclic ketone at a higher temperature than that required in the case of the *cis*-acid. The *cis* and *trans* form of III gave the same 6-phenylazulene on dehydrogenation.

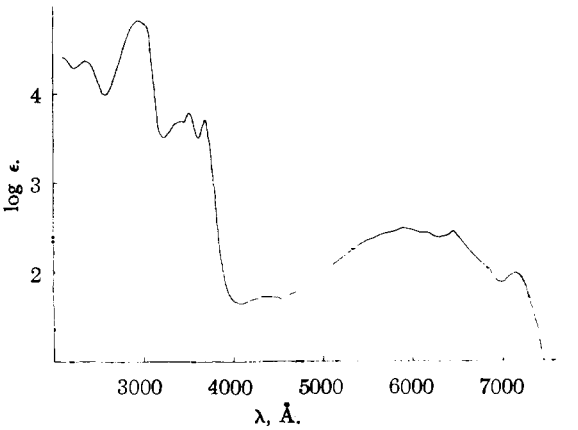


Fig. 1.—Spectrum of 6-phenylazulene.

Both ketones II show (in chloroform solution) the infrared carbonyl band at 1685 cm.$^{-1}$, while for cycloheptanone Bergmann and Pinchas[18] reported a value of 1708, and Sorm, *et al.*,[19] of 1693 cm.$^{-1}$.

In fact, the two isomeric ketones II have practically the same absorption spectrum in the infrared region; the only significant difference lies in the different location and intensity of a band in the 1200–1300 cm.$^{-1}$ region. Also the semicarbazones have identical infrared spectra; the C=N absorption lies at 1680 cm.$^{-1}$.

Throughout, the liquid *cis* compounds have a higher boiling point than the *trans* isomers: diethyl cyclopentane-1-acetate-2-cyanoacetate, *cis* 152° (0.4 mm.), *trans* 138° (0.2 mm.); ketone II, *cis* 87–88° (1.3 mm.), *trans* 73° (1 mm.); hydrocarbon III, *cis* 145° (0.4 mm.), *trans* 120° (0.4 mm.). In the 1- and 2-decalone series, no such differences appear to exist (1-decalone: *cis* 126° (20 mm.), *trans* 122° (20 mm.); 2-decalone, *cis* 121° (22 mm.), *trans* 127–128° (23 mm.); 9-methyl-1-decalone, *cis* 118° (20 mm.), *trans* 119–120° (14–15 mm.)).

The starting material for the preparation of V is ethyl cyclopentanone-2-acetate. The usual method, which consists in the reaction of the enolate of ethyl cyclopentanone-2-carboxylate with ethyl bromoacetate, hydrolysis and partial decarboxylation and re-esterification, gives an over-all yield of 42%. It appeared, therefore, interesting to apply to this synthesis the method, recently described by Stork, Terrell and Szmuszkovicz,[20] *viz.*, the direct interaction of an enamine X of cyclopentanone with ethyl bromoacetate. The preparation of these enamines with pyrrolidine or morpholine proceeded with good yields, but their reaction with ethyl bromoacetate gave only 15 and 13%, respectively, of the desired ethyl cyclopentanone-2-acetate.

(14) R. P. Linstead and E. M. Meade, *J. Chem. Soc.*, 935 (1934).

(15) In one experiment a m.p. of 137° has been observed for this acid by the British authors.

(15a) According to W. Herz (*J. Org. Chem.*, **20**, 1062 (1955)), the hydrogenation of 2-methylcyclopentylidene cyanoacetate in the presence of palladium-charcoal gives only the *cis*-dihydro derivative.

(16) A. Stoll, A. Hofmann and Th. Petrzilka, *Helv. Chim. Acta*, **29**, 635 (1946).

(17) This ketone has been obtained before, by the second of the two routes indicated, by Sorm and Fajkos, reference 11.

(18) E. D. Bergmann and S. Pinchas, *J. chim. phys.*, **49**, 537 (1952).

(19) F. Sorm, *et al.*, *C. A.*, **45**, 8482 (1951).

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

Experimental

Diethyl Cyclopentylidene-cyanoacetate-2-acetate (V).—Diethyl cyclopentanone-2-carboxylate-2-acetate was prepared in 84% yield, b.p. 170° (17 mm.), by the method of Koetz,[21] and converted into cyclopentanone-2-acetic acid by heating for 5 hours with 2 volumes of concentrated hydrochloric acid on the steam-bath.[14] After distillation (b.p. 138° (0.3 mm.)), a 55% yield, m.p. 50°, was obtained. Esterification with 3 parts of a saturated solution of hydrogen chloride in anhydrous alcohol[14] gave a 90% yield of ethyl cyclopentanone-2-acetate, b.p. 123° (13 mm.), 130° (18 mm.). For the azeotropic condensation of this ester with ethyl cyanoacetate, Plattner and Studer[13] recommend piperidine acetate as catalyst. This gave a 47% yield of the unsaturated ester V, b.p. 168° (0.5 mm.), m.p. 53°. According to Dev,[22] with benzylamine as catalyst, a yield of 92% can be obtained.

Diethyl *cis*-Cyclopentane-1-acetate-2-cyanoacetate (VI).—Hydrogenation of (V) in alcoholic solution, using platinum oxide as catalyst, at room temperature gave the *cis*-hydrogenated compound, b.p. 152° (0.4 mm.), d^{20}_4 1.0820, yield 95% (literature[14]): b.p. 170–173° (5 mm.), d^{20}_4 1.0815).

Diethyl *trans*-Cyclopentane-1-acetate-2-cyanoacetate (VI).—When the hydrogenation was carried out as above, using 10% palladium–charcoal as catalyst, the lower-boiling *trans*-ester was obtained, b.p. 138° (0.2 mm.), yield 95%, d^{25}_4 1.082, $n^{25}D$ 1.4596.

Anal. Calcd. for $C_{14}H_{21}NO_4$: C, 63.1; H, 7.9; *MR*, 67.47. Found: C, 63.2; H, 7.5; *MR*, 67.38.

cis-Cyclopentane-1,2-diacetic Acid (VII).—The *cis*-ester VI was converted into *cis*-cyclopentane-1,2-diacetic acid according to the method of Linstead and Meade.[14] The acid crystallized from nitroethane in colorless needles of m.p. 170° (literature[14] m.p. 173°), yield 75%.

Anal. Calcd. for $C_9H_{14}O_4$: C, 58.1; H, 7.5. Found: C, 58.6; H, 7.6.

trans-Cyclopentane-1,2-diacetic Acid (VII).—The same procedure applied to the *trans*-ester gave the *trans*-acid in 75% yield. From nitroethane needles, m.p. 132° (literature m.p. 132°,[14] 138°[11]), were obtained.

Anal. Calcd. for $C_9H_{14}O_4$: C, 58.1; H, 7.5. Found: C, 57.8; H, 7.2.

cis-Cyclopentane-1,2-dipropionic Acid (IV).—Ten grams of the *cis*-diacetic acid was added slowly to 13 g. of freshly distilled thionyl chloride. After 2 hours at room temperature, and heating for 15 minutes at 50°, no more hydrogen chloride was evolved. The excess thionyl chloride was removed *in vacuo* and the crude chloride dissolved in 50 ml. of anhydrous ether. This solution was added within 30 minutes to an ethereal solution of 13.6 g. of diazomethane (dried over potassium hydroxide and metallic sodium) at −10°. After 12 hours at room temperature, removal of the ether *in vacuo* (without raising the temperature) yielded 10.7 g. (92%) of the diazoketone, m.p. 67–68° (after recrystallization from ether).

For the decomposition of the diazoketone, the silver oxide–thiosulfate method[23] was first employed. A 37.4% yield of *cis*-cyclopentane-1,2-dipropionic acid (IV) was thus obtained; recrystallized from nitroethane, it melted at 128–129° (literature m.p. 130°,[11] 135°[11]).

Anal. Calcd. for $C_{11}H_{18}O_4$: C, 61.7; H, 8.4. Found: C, 62.1; H, 8.5.

A 60% yield was obtained by the method of Wilds and Meader[24] using quinoline, an 80% yield using γ-collidine as the tertiary amine.

trans-Cyclopentane-1,2-dipropionic Acid (IV).—(a) The *trans*-diazoketone (90% yield) was prepared as above from *trans*-cyclopentane-1,2-diacetic acid, recrystallized from ether and had m.p. 81–82°. The yield of the *trans*-acid obtained by the above collidine method, and recrystallized from nitroethane, m.p. 148°, was 80% (literature,[11] m.p. 165°).

Anal. Calcd. for $C_{11}H_{18}O_4$: C, 61.7; H, 8.4. Found: C, 61.7; H, 8.4.

(b) In order to verify the melting point of the *trans*-acid IV, which was much lower than that reported by Sorm and Fajkos,[11] an alternative method was applied to the synthesis of *trans*-IV. (1) Dimethyl *trans*-Cyclopentane-1,2-diacetate.—The *trans*-acid (15 g.) was esterified with 7 g. of diazomethane in ether. The ester, b.p. 105° (1 mm.), was obtained in a yield of 15.1 g. (87%), d^{25}_4 1.089, $n^{25}D$ 1.4542.

Anal. Calcd. for $C_{11}H_{18}O_4$: C, 61.7; H, 8.4; *MR*, 53.77. Found: C, 61.8; H, 8.1; *MR*, 53.21.

(2) *trans*-1,2-Di-(β-hydroxyethyl)-cyclopentane.—A solution of 15 g. of the preceding ester in 100 ml. of anhydrous ether was added within one hour to a well-agitated suspension of 3 g. of lithium aluminum hydride in 150 ml. of ether, at room temperature. The reaction product was refluxed for one hour and decomposed with ice and 10% sulfuric acid. The aqueous layer was extracted with ether and the combined ethereal solutions were washed with 5% sodium hydroxide solution and water, dried and distilled; b.p. 130° (1 mm.), yield 8.7 g. (79%), $n^{25}D$ 1.4758.

Anal. Calcd. for $C_9H_{18}O_2$: C, 68.4; H, 11.3. Found: C, 68.3; H, 11.0.

(3) *trans*-1,2-Di-(β-chloroethyl)-cyclopentane.—When 20 g. of freshly distilled thionyl chloride was added slowly to 12 g. of the preceding diol, a lively reaction set in, which was completed in refluxing the mixture for 2 hours. Benzene was added and evaporated again *in vacuo* together with the excess of the thionyl chloride. The chloride, which boiled at 92–94° (0.8 mm.), was not quite pure; yield 7.7 g. (81%), $n^{25}D$ 1.4725.

Anal. Calcd. for $C_9H_{16}Cl_2$: C, 55.7; H, 8.4. Found: C, 56.9; H, 8.5.

(4) *trans*-Cyclopentane-1,2-dipropionic Acid (IV).—Solutions of 7 g. of the dichloro compound in 30 ml. of alcohol and of 4.6 g. of potassium cyanide in 10 ml. of water were mixed and refluxed for 35 hours. The alcohol was evaporated *in vacuo* and the residue, diluted with 30 ml. of water, was extracted with ether. The ethereal solution was washed with 5% sulfuric acid, 10% sodium bicarbonate solution and water, dried and distilled. Thus, 4.5 g. (71%) of *trans*-1,2-di-(β-cyanoethyl)-cyclopentane, b.p. 135° (1.5 mm.), was obtained. This dinitrile (4 g.) was hydrolyzed by prolonged (50 hours) refluxing with a solution of 3 g. of potassium hydroxide in 40 ml. of 50% alcohol. The solution was brought to dryness *in vacuo*, the residue dissolved in water and—after extraction with ether—acidified. Extraction with ether gave the acid (m.p. 148° after recrystallization from nitroethane), which was obtained in a yield of 2.4 g. (46%).

cis-Bicyclo[5.3.0]decan-4-one (II).—To a solution of 1 g. of *cis*-cyclopentane-1,2-dipropionic acid in 30 ml. of water, there was added slowly and with vigorous agitation 1.5 g. of ceric carbonate. The reaction mixture was brought to dryness on the steam-bath and finally at 140°. The finely divided product was then pyrolyzed at 360–380° (bath temperature[11]); the ketone distilled over as a slightly bluish liquid which was directly transformed into the semicarbazone. This crystallized from nitromethane in needles of m.p. 181° (literature m.p. 183°,[13] 185°[11]), yield 700 mg. (73%).

Anal. Calcd. for $C_{11}H_{19}N_3O$: C, 63.1; H, 9.1. Found: C, 63.4; H, 8.9.

The semicarbazone was hydrolyzed by heating (with stirring) for 1 hour at 100° with the equivalent amount of oxalic acid and water. The ketone was extracted with ether, and the solution washed with 5% sodium carbonate solution and water; b.p. 87–88° (1.3 mm.), yield 48%, $n^{18}D$ 1.4907 (literature b.p. 116° (13 mm.),[13] 110° (12 mm.),[11] $n^{17.5}D$ 1.4927[13]).

trans-Bicyclo[5.3.0]decan-4-one (II).—The *trans*-cyclopentane-1,2-dipropionic acid was treated in the same manner. Again from 1 g. of the acid 700 mg. (73%) of the *trans*-semicarbazone was obtained; after recrystallization from nitroethane, m.p. 168° (literature[11] m.p. 178°).

Anal. Calcd. for $C_{11}H_{19}N_3O$: C, 63.1; H, 9.1. Found: C, 62.6; H, 9.1.

The free ketone boiled at 73° (1 mm.) (literature[11] b.p. 126° (12 mm.)), $n^{18}D$ 1.4880, yield 48%.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.9; H, 10.5. Found: C, 78.5; H, 11.0.

cis-6-Phenylbicyclo[5.3.0]-6-decene (III).—To a Grignard solution, prepared from 1.28 g. of magnesium turnings and 8.2 g. of bromobenzene, there was added at room tempera-

(21) A. Koetz, *Ann.*, **350**, 229 (1906).

(22) S. Dev, *J. Indian Chem. Soc.*, **30**, 815 (1953) (*C. A.*, **49**, 3117 (1955)).

(23) W. E. Bachmann and W. S. Struve, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 38.

(24) A. L. Wilds and A. L. Meader, *J. Org. Chem.*, **13**, 763 (1948).

ture 4.3 g. of the *cis*-ketone II. After 12 hours at room temperature, the reaction product was refluxed for 90 minutes and decomposed with ice and dilute sulfuric acid. The aqueous layer was extracted with ether, and the combined ethereal solutions were washed with 5% sodium hydroxide solution, dried and concentrated. The residue was heated for 20 minutes with a little iodine at 160°, dissolved in ether and after treatment with 5% sodium bisulfite solution, 5% sodium hydroxide solution and water and drying was distilled *in vacuo;* b.p. 145° (0.4 mm.), yield 4.4 g. (73%), $n^{19}D$ 1.5662, $n^{25}D$ 1.5610, d^{25}_4 1.012.

Anal. Calcd. for $C_{16}H_{20}$: C, 90.6; H, 9.4; *MR*, 67.54. Found: C, 91.0; H, 9.4; *MR*, 67.84.

trans-6-Phenylbicyclo[5.3.0]-6-decene (III).—From 0.7 g. of the *trans*-ketone II, 0.57 g. (68%) of the hydrocarbon was obtained, b.p. 120° (0.4 mm.), $n^{20}D$ 1.4928.

Anal. Calcd. for $C_{16}H_{20}$: C, 90.6; H, 9.4. Found: C, 90.7; H, 8.8.

6-Phenylazulene (I).—In the dynamic system described by Plattner, *et al.*,[25] 1 g. of the *cis*-hydrocarbon III was passed at 300° over 100 mg. of 10% palladium–charcoal in an atmosphere of dry nitrogen. The blue reaction product was condensed in a trap cooled with solid carbon dioxide. It was dissolved in petroleum ether and the phenylazulene extracted with 85% phosphoric acid. The unchanged starting material was recovered from the petroleum ether and subjected to the same treatment; this operation was repeated 8 times. By dilution of the phosphoric acid solutions and extraction with ether, 350 mg. of phenylazulene was obtained. The hydrocarbon does not give an addition product with trinitrobenzene; obviously, the phenyl group in the 6-position as well as in the 2-position[7] reduces the basicity of the azulene system. The crude phenylazulene was, therefore, purified by adsorption on activated alumina and elution, benzene serving as solvent. The deep blue benzene solution was concentrated *in vacuo* and the solid residue recrystallized from methanol as deep blue leaflets, m.p. 150°.

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

Anal. Calcd. for $C_{16}H_{12}$: C, 94.1; H, 5.9. Found: C, 93.4; H, 6.5.

The *trans*-hydrocarbon III gave an identical product; the dehydrogenation appeared to proceed somewhat more easily than in the case of the *cis* isomer.

Alternative Route to Ethyl Cyclopentanone-2-acetate. N-Cyclopentenyl-pyrrolidine.—The azeotropic condensation between 42 g. of cyclopentanone and 71 g. of pyrrolidine in 300 ml. of benzene was complete in 4 hours; yield 58 g. (85%), b.p. 81.5–82° (5 mm.), $n^{15}D$ 1.5144.

Anal. Calcd. for $C_9H_{15}N$: C, 78.8; H, 10.9. Found: C, 79.1; H, 10.6.

N-Cyclopentenylmorpholine.—From 42 g. of cyclopentanone and 87.1 g. of morpholine in 300 ml. of benzene, there was obtained within 3 hours, 55 g. (72%) of the enamine, b.p. 97° (7.5 mm.), $n^{16.5}D$ 1.5098.

Anal. Calcd. for $C_9H_{15}NO$: C, 70.6; H, 9.8. Found: C, 70.3; H, 9.7.

Ethyl Cyclopentanone-2-acetate.—(a) At room temperature and during 45 minutes, 71 g. of ethyl bromoacetate was added to a solution of 58 g. of N-cyclopentenyl-pyrrolidine in 200 ml. of anhydrous dioxane (with benzene, the same results were obtained). The solution turns red and a white precipitate appears. Upon refluxing for 3 hours, the precipitate disappeared; the solution was cooled and 200 ml. of water was added. The mass was stirred for 45 minutes at room temperature and extracted with benzene. The benzene layer was washed with water, dried and distilled; b.p. 105–106° (7 mm.), yield 15 g. (15%).

Anal. Calcd. for $C_9H_{14}O_3$: C, 63.5; H, 8.2. Found: C, 63.1; H, 8.2.

(b) By the same method, one obtains from 51 g. of N-cyclopentenylmorpholine, 56 g. of ethyl bromoacetate and 250 ml. of benzene, a solution which is treated with 100 ml. of water, washed with 10% hydrochloric acid, 10% sodium bicarbonate solution and water, dried and fractionated; b.p. 104° (6.5 mm.), yield 10 g. (13%).

JERUSALEM, ISRAEL

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

Azulenes. VII. A Novel Rearrangement in the Synthesis of Azulenes

BY WERNER HERZ

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The alkylation of ethyl cyclopentanonecarboxylate with several γ-bromo α,β-unsaturated esters has been studied. Chemical and spectroscopic evidence demonstrates that the products (I) have the expected structure, but attempts to utilize them as starting materials for the synthesis of 4- or 5-alkylazulenes invariably resulted in the formation of 1(or 2)-alkylazulenes. Degradation of the intermediate ε-ketoacids II obtained from I by reduction and hydrolysis showed that hydrolysis was accompanied by rearrangement, thus accounting for the structure of the azulenes finally obtained.

In order to achieve the total synthesis of azulenes derived from natural sources, a number of workers have devoted considerable effort to the development of general methods for the preparation of azulenes substituted simultaneously in the 4- and 7-positions. Application of the usual diazoacetic ester methods[1] to the ring expansion of suitably substituted indans leads to difficultly separable mixtures of azulenes[2,3] or to substances whose purity is still in question.[4] More recently Šorm and co-workers[5] have published unequivocal, if tedious, syntheses of S- and Se-guaiazulene in which appropriately substituted dicarboxylic acids were prepared by oxidation of vicinal dihydroxyhexahydroindans and cyclized to 6,10-dialkylbicyclo[5,3,0]-3-decanones.

In theory at least, the preparation of 4,7-disubstituted azulenes might be achieved by modifying an azulene synthesis developed by Šorm[6] in such a way as to afford a 2-alkylbicyclo[5,3,0]-5-decanone as the key intermediate. However, the initial alkylation of cyclopentanonecarboxylic ester by γ-bromoesters in which the bromine atom is secondary (a necessary condition for the introduction of alkyl groups in position 2) would not be expected to proceed in satisfactory yield. Similar objections might be raised to a sequence of reactions suggested by Dev.[6a]

(1) M. Gordon, *Chem. Revs.*, **50**, 127 (1952).

(2) H. Hippchen, *Z. Naturforsch.*, **1**, 325 (1946).

(3) Pl. A. Plattner, A. Fürst, L. Marti and H. Schmid, *Helv. Chim. Acta*, **32**, 2137 (1949); Pl. A. Plattner, A. Fürst and L. Marti, *ibid.*, **32**, 2452 (1949).

(4) Th. Wagner-Jauregg, H. Arnold and F. Hüter, *Ber.*, **75**, 1293 (1942); see also H. Pommer, *Ann.*, **579**, 47 (1953).

(5) F. Šorm, J. Gut, H. Hlavnička, J. Kučera and L. Sedivy, *Coll. Czech. Chem. Communs.*, **16**, 158 (1951); F. Šorm, J. Kučera and J. Gut, *ibid.*, **16**, 184 (1951); J. Novak, F. Šorm and J. Sicher, *ibid.*, **19**, 1264 (1954).

(6) F. Šorm, *ibid.*, **12**, 251 (1947).

(6a) S. Dev, *Science and Culture*, **16**, 31 (1950). The proposed synthesis of apo-S-guaiazulene outlined in this paper apparently has not been realized experimentally.