

Anal. Calcd. for $C_{16}H_{14}O_6S$: C, 60.36; H, 4.43. Found: C, 60.53; H, 4.63.

The amide was prepared in the usual manner using thionyl chloride and aqueous ammonia. The product was recrystallized from aqueous ethanol to give fine white needles, m.p. 151–151.5°.

Anal. Calcd. for $C_{16}H_{14}O_4NS$: C, 60.52; H, 4.76. Found: C, 60.61; H, 4.55.

p-Vinylphenyl Tosylate.—A mixture containing 100 ml. of freshly distilled quinoline and 5 g. of copper powder was heated to 220°. With stirring, 50.0 g. (0.157 mole) of the tosylate of *p*-hydroxycinnamic acid was added, in small portions; the addition was complete in 15 minutes. Stirring and heating were continued for 1 hr. The crude reaction mixture was distilled, and the fraction boiling at 90–180° (1 mm.) was retained. This fraction solidified when cooled and was recrystallized from aqueous ethanol to give 12.7 g. (30%) of white crystalline product, m.p. 67–68°. A second experiment gave a 33% yield of product. Further recrystallization from aqueous ethanol gave flat white needles, m.p. 68–68.5°.

Anal. Calcd. for $C_{16}H_{14}O_3S$: C, 65.67; H, 5.14. Found: C, 65.40; H, 5.26.

The dibromide derivative was prepared by dissolving the compound in chloroform, adding bromine until the bromine color persisted; evaporation of the solvent left a pale yellow solid. Recrystallization from aqueous ethanol gave fine white needles, m.p. 74–75°.

Anal. Calcd. for $C_{16}H_{14}O_3SBr_2$: C, 41.48; H, 3.25. Found: C, 41.45; H, 3.44.

The Addition of the Tosylate of *p*-Hydroxybenzaldehyde to Methylmagnesium Iodide.—To 0.203 mole of methylmagnesium iodide was added dropwise with stirring an ethereal solution of 56.0 g. (0.203 mole) of the tosylate of *p*-hydroxybenzaldehyde. No sludge formed during this addition, in marked contrast to the behavior of the inverse addition. The reaction mixture was purified in the same manner as the anomalous reaction. Distillation of the crude product under diminished pressure gave a trace of yellow solid distillate before sudden decomposition occurred, leaving a non-distillable purple tar.

COLUMBIA, MISSOURI

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF BRYN MAWR COLLEGE AND THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

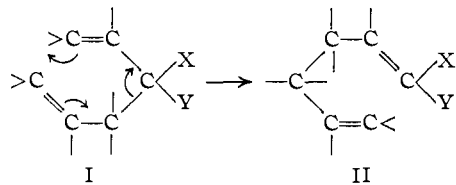
The Rearrangement of Allyl Groups in Three-carbon Systems. VI. Benzene and Phenanthrene Derivatives

BY ARTHUR C. COPE, LAMAR FIELD, D. W. H. MACDOWELL AND MARY ELIZABETH WRIGHT

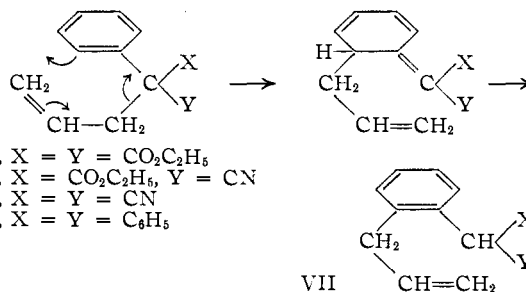
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Compounds III–VI and VIII containing an allyl group and a benzenoid ring attached to a carbon atom substituted by two electron-attracting groups failed to rearrange on heating with migration of the allyl group to an *ortho* position. Such rearrangements do occur with migration of an allyl group to the β -carbon atom of an aliphatic vinyl group (*i.e.* I \rightarrow II). Diethyl α -allyl-9-phenanthrenemalonate (IX) was observed to rearrange on heating, and evidence has been obtained indicating that the rearrangement product is the diethyl ester of 1-carboxy-2,3-dihydro-1H-cyclopenta(*l*)phenanthrene-2-acetic acid (XI).

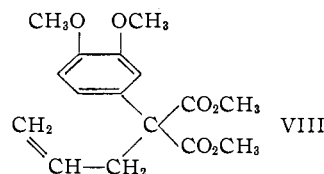
Earlier papers in this series¹ have described the thermal intramolecular rearrangement of allyl groups in three-carbon systems. The allyl group has been shown to migrate with inversion from a carbon atom which in most instances was attached to one or more electron-attracting groups to the β -carbon atom of an aliphatic vinyl group, as shown in the equation



This paper reports an investigation of the behavior on heating of a number of similar compounds in which the two carbon atoms comprising the vinyl group form part of an aromatic ring. Rearrangement of such compounds would be similar to the Claisen rearrangement of allyl aryl ethers² and would be expected to occur with a shift of hydrogen to reform the aromatic nucleus as shown in the equation



When the compounds III–VI were heated at temperatures of 190–290° in an atmosphere of nitrogen, partial decomposition occurred, but no evidence of rearrangement was obtained, for only the unchanged compounds III–VI could be isolated after heating. The absence of any substantial amount of a rearrangement product corresponding to VII was shown by oxidation with potassium permanganate of the samples of III, IV and V recovered after heating, which yielded benzoic acid but no *o*-phthalic acid. Dimethyl (3,4-dimethoxy-



(1) Preceding paper: A. C. Cope and L. Field, *THIS JOURNAL*, **71**, 1589 (1949).

(2) D. S. Tarbell, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 1.

phenyl)-allylmalonate (VIII) was prepared as a compound in which rearrangement of the allyl group to an *ortho* position might be facilitated by the increased electron densities caused by the methoxyl substituents. However, the ester VIII did not undergo rearrangement when heated at 190 to 246°.

Since the 9,10-double bond of phenanthrene possesses more double bond character³ than the corresponding bond in benzene derivatives, it appeared that rearrangement would be more likely to occur in the case of diethyl α -allyl-9-phenanthrenemalonate (IX) than in compounds III-VI and VIII.

Diethyl α -allyl-9-phenanthrenemalonate (IX), m.p. 62-63°, was prepared from diethyl 9-phenanthrenemalonate in 62% yield. The structure of IX was confirmed by quantitative hydrogenation to diethyl α -propyl-9-phenanthrenemalonate (X), which was shown to be identical with an authentic sample prepared by alkylation of diethyl 9-phenanthrenemalonate.

Attempts to rearrange IX at 165-215° (5.8 hr.) and at 240-242° (3.6 hr.) resulted in a recovery of 80 and 20%, respectively, of the unchanged ester. Heating at 266-296° (3.5 hr.), however, formed an isomer, XI, in a yield of 28%. The ultraviolet spectra of the ester IX and its rearrangement product XI were almost identical and very similar to the spectrum of phenanthrene⁴ itself (Fig. 1). The failure of the rearrangement product to reduce potassium permanganate or to be reduced catalytically, contrary to the behavior of the ester IX, indicated that the allyl group had become saturated in the isomerization and accordingly that cyclization had occurred. This evidence and the absence of active hydrogen in the isomerization product XI (Zerewitinoff determination) indicated that it could not have the structure of the rearrangement product which might be expected, diethyl 10-allyl-9-phenanthrenemalonate (analogous to VII).

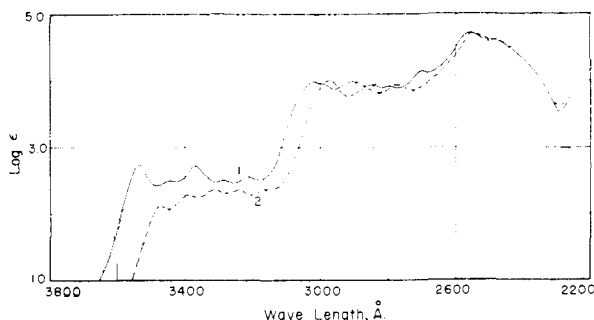


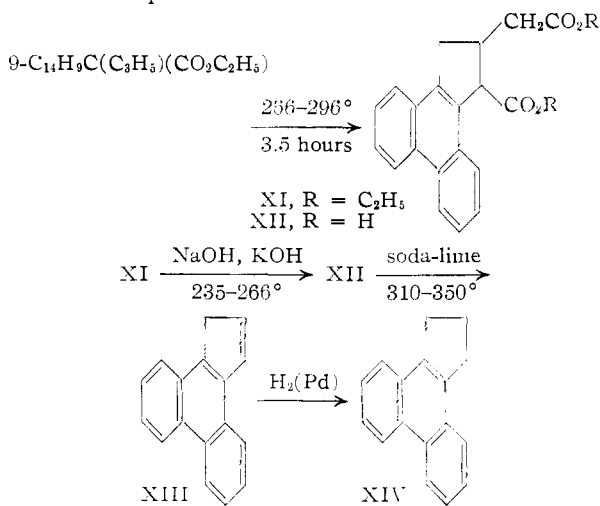
Fig. 1.—Ultraviolet absorption spectra in 95% ethanol, determined with Beckman model DU spectrophotometer: curve 1, XI; curve 2, IX.

The isomerization product XI, when heated with a mixture of potassium hydroxide and sodium hydroxide, yielded a dibasic acid XII. When the disodium salt of XII was mixed with soda-lime and pyrolyzed at 310-350° and 0.1 mm., an unsaturated hydrocarbon C₁₇H₁₂ (XIII) was obtained in 63%

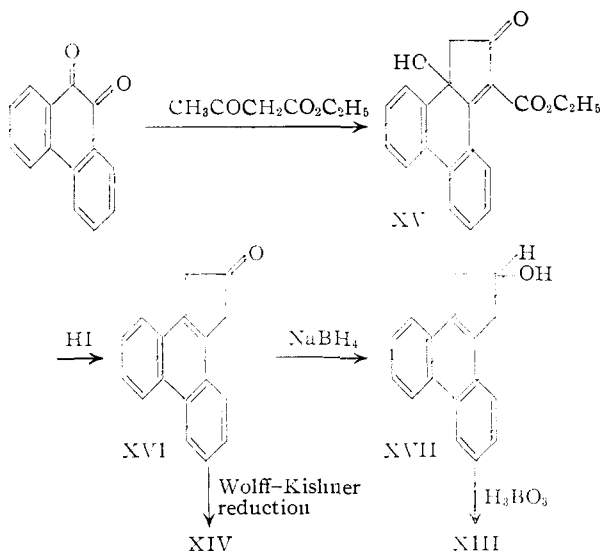
(3) L. Pauling, "The Nature of the Chemical Bond," 2nd Ed., Cornell Univ. Press, Ithaca, N. Y., 1942, p. 142.

(4) M. S. Newman and A. S. Hossey, THIS JOURNAL, **69**, 3023 (1947).

yield. Quantitative hydrogenation of this hydrocarbon in the presence of a palladium catalyst formed 2,3-dihydro-1H-cyclopenta(*l*)phenanthrene (XIV), which was shown to be identical with an authentic sample.



Authentic samples of the hydrocarbons XIII and XIV were prepared as follows. 9,10-Phenanthrenequinone and ethyl acetoacetate were condensed in ethanolic suspension containing a small amount of piperidine⁵ to give a 72% yield of ethyl 3,3a-dihydro-3a-hydroxy-2-oxo-2H-cyclopenta(*l*)phenanthrene-1-carboxylate (XV).⁶ Treatment of XV with hydriodic acid at 110-120° yielded the ketone, 2,3-dihydro-2-oxo-1H-cyclopenta(*l*)phenanthrene (XVI).⁷ Reduction of the ketone with sodium borohydride yielded the corresponding alcohol, 2,3-dihydro-2-hydroxy-1H-cyclopenta(*l*)phenanthrene (XVII), which was dehydrated by heating with boric acid to give the hitherto unknown 1H-cyclopenta(*l*)phenanthrene (XIII), identical in all respects with the sample of XIII obtained by decarboxylation



(5) B. Lachowicz, *Monatsh.*, **17**, 344 (1896).

(6) The proof of structure of XV, first synthesized by F. R. Japp and P. W. Streatfield, *J. Chem. Soc.*, **43**, 27 (1883), will be described in a forthcoming publication by A. C. Cope and D. W. H. MacDowell.

(7) E. Beschke, *Ann.*, **398**, 265 (1916).

of XII. The ketone XVI was reduced by the Wolff-Kishner method to yield the known 2,3-dihydro-1H-cyclopenta(l)phenanthrene⁸ (XIV), which was similarly shown to be identical in all respects with the saturated hydrocarbon produced by hydrogenation of XIII.

A study of acids analogous to XII containing benzene and naphthalene rather than phenanthrene nuclei⁹ has provided evidence that supports formula XI for the rearrangement product and XII for the corresponding acid. No conclusions can be drawn at present concerning the way in which the rearrangement of IX to XI occurs.

Experimental¹⁰

Attempted Rearrangement of Diethyl Phenylallylmalonate (III) and Ethyl Phenylallylcianoacetate (IV).—Diethyl phenylallylmalonate¹¹ (III) was prepared from the sodium enolate of diethyl phenylmalonate and allyl bromide in 78% yield, b.p. 117–119° (1 mm.), n_D^{25} 1.4970. Samples of the ester were heated under reflux in a nitrogen atmosphere at 295° for 1 hr., either alone or in the presence of small amounts of metaphosphoric acid or *p*-toluenesulfonic acid. The ester underwent partial decomposition under these conditions, but 30 to 60% of it was recovered unchanged in each instance.

To a solution of sodium (10.1 g.) in anhydrous ethanol (250 ml.) cooled to –5°, ethyl phenylcyanoacetate¹² (83.4 g.), was added dropwise with stirring. The solution was stirred at –5° for 0.3 hr., and then allyl bromide (58.6 g.) was added in one portion and the mixture was heated under reflux for 0.5 hr. The mixture was cooled, water (500 ml.) was added and the ester was extracted with benzene. The benzene extract was washed with water, and after removal of the benzene under reduced pressure, the residue was distilled to give crude IV, 88.7 g., b.p. 163–176° (22 mm.), n_D^{25} 1.5013. The ester was purified by redistillation to yield pure IV (55.7 g., 55%), b.p. 174–175° (20 mm.), n_D^{25} 1.5034, d_4^{25} 1.0511; M_D calcd. 64.27, M_D found 64.46.

Anal. Calcd. for C₁₄H₁₆O₂N: N, 6.11. Found: N, 6.10.

Samples of ethyl phenylallylcianoacetate were heated at 226–246° for 12 hr. or in the presence of a small amount of benzoyl peroxide at 246° for 8 hr. As in the case of the malonic ester derivative III, partial decomposition occurred, but the greater part of the ester IV was recovered.

Attempted Rearrangement of Phenylallylmalononitrile (V).—To a stirred suspension of sodamide in liquid ammonia prepared from sodium (5.4 g.), was added a solution of phenylmalononitrile¹³ (33.1 g.) in anhydrous ether (75 ml.). The brown mixture was stirred until most of the ammonia had evaporated, and then anhydrous benzene (200 ml.) was added. The mixture was heated under reflux for 6 hr. and cooled to room temperature. Allyl bromide (33.8 g.) was added in one portion to the cooled solution, and the mixture was heated overnight under reflux. The mixture was cooled, water (800 ml.) was added and the phenylallylmalononitrile was isolated by extraction with benzene and distillation. The yield was 36.4 g. (87%), b.p. 119–121° (3.9 mm.), n_D^{25} 1.5131, d_4^{25} 1.0258; M_D calcd. 53.20, M_D found 53.39.

Anal. Calcd. for C₁₂H₁₀N₂: N, 15.37. Found: N, 15.19.

A 7-g. sample of V was heated at 180–200° in a nitrogen atmosphere for a period of 40 hr. Distillation of the compound after heating gave 1.8 g. of a crude distillate, n_D^{25} 1.5187. Oxidation with potassium permanganate gave only benzoic acid and no *o*-phthalic acid.

(8) J. W. Cook, G. M. Badger, W. Carruthers and R. Schoental, *J. Chem. Soc.*, 169 (1949).

(9) A. C. Cope, J. E. Meili and D. W. H. MacDowell, *THIS JOURNAL*, **73**, 2551 (1956).

(10) Melting points are corrected and boiling points are uncorrected. We are indebted to Dr. S. M. Nagy and his associates for analyses.

(11) W. Wislicenus and R. Goldstein, *Ber.*, **29**, 2600 (1896); R. H. Pickard and J. Yates, *J. Chem. Soc.*, **95**, 1011 (1909).

(12) W. L. Nelson and L. H. Cretcher, *THIS JOURNAL*, **50**, 2758 (1928).

(13) J. C. Hessler, *Am. Chem. J.*, **32**, 123 (1904).

Preparation and Attempted Rearrangement of Dimethyl (3,4-Dimethoxyphenyl)-allylmalonate (VIII). Dimethyl 3,4-dimethoxyphenylmalonate.—To a solution of sodium methoxide prepared from sodium (3.8 g.) and methanol (100 ml.) heated to 60° was added a solution of dimethyl oxalate (19.6 g.) in methanol (20 ml.) with vigorous stirring. Methyl 3,4-dimethoxyphenylacetate¹⁴ (34.8 g.) was then added in one portion, and the mixture was allowed to stand at room temperature for 6 hr. Removal of the methanol under reduced pressure left the sodium derivative as a crystalline solid. The solid was washed several times with anhydrous ether and dissolved in water. Acidification of the aqueous solution with sulfuric acid caused separation of an oil, which was extracted with ether. The ether extracts were washed with water, and the ether was removed under reduced pressure. The residual oil was heated at 125–175° and 16 mm. for 4 hr. in the presence of 25 g. of ground soft glass. The product was then distilled; dimethyl 3,4-dimethoxyphenylmalonate was obtained in a yield of 24.5 g. (55%), b.p. 160–166° (1.5 mm.), m.p. 61.5–69.5°. Recrystallization from hexane-benzene gave the pure ester (20.7 g., 46%), m.p. 69.5–70.5°.

Anal. Calcd. for C₁₃H₁₆O₆: C, 58.20; H, 6.01. Found: C, 58.22; H, 6.09.

Dimethyl (3,4-Dimethoxyphenyl)-allylmalonate.—To a suspension of sodamide in liquid ammonia prepared from sodium (0.54 g.) was added a solution of dimethyl 3,4-dimethoxyphenylmalonate (6.3 g.) in ether (100 ml.). The mixture was stirred until most of the ammonia had evaporated and was then heated under reflux for 3 hr. The mixture was cooled, and a solution of allyl bromide (3.4 g.) in toluene (100 ml.) was added. The suspension was heated overnight under reflux, cooled, diluted with water and the product extracted with benzene. Recrystallization from ether-pentane gave pure dimethyl (3,4-dimethoxyphenyl)-allylmalonate (5.0 g., 69%), m.p. 62–63°.

Anal. Calcd. for C₁₆H₂₀O₆: C, 62.32; H, 6.54. Found: C, 62.16; H, 6.56.

Oxidation of VIII (0.3 g.) with boiling potassium permanganate solution gave veratric acid (0.08 g.), m.p. 180–181°. Isolation of this acid and no other product on oxidation indicated that no alkylation had occurred on the aromatic nucleus.

A 1-g. sample of VIII when heated in a nitrogen atmosphere for a total of 7 hr. at 190–246° gave only unchanged VIII, identified by melting point and mixed melting point. Heating to temperatures above 260° resulted in almost complete decomposition, but crystallization of the product from pentane gave only VIII. Thus, no indication of any rearrangement was obtained.

Attempted Rearrangement of Allyltriphenylmethane (VI).—Allyltriphenylmethane¹⁵ (0.20 g.) was heated for a total of 7 hr. at 180–290° in a nitrogen atmosphere. During this period the compound was cooled to room temperature several times to give a crystalline solid which was shown to be allyltriphenylmethane by its melting point and mixed melting point. Heating at 280 to 290° for 3 hr., however, caused nearly complete decomposition. The oily product when crystallized from *n*-propyl alcohol gave 0.05 g. of unchanged allyltriphenylmethane, m.p. 68–69°.

Diethyl α -Allyl-9-phenanthrenemalonate (IX).—To a solution of sodium (1.1 g.) in absolute ethanol (35 ml.) at 50° was added diethyl 9-phenanthrenemalonate¹⁶ (15.0 g.). After stirring the mixture at 45–50° for 0.5 hour, allyl bromide (7.6 g.) was added in one portion. The mixture was heated and stirred under reflux for 0.8 hr. and was then cooled to 5°, poured into 200 ml. of ice-water and extracted with ether. Removal of the ether left a viscous yellow oil (16.3 g.) which was dissolved in hexane containing 10% of ether and seeded. White prisms (13.7 g., 82%), m.p. 58.5–62°, were removed by filtration. An additional 0.8 g. (5%), m.p. 59.5–62.5°, was obtained from the mother liquor.

A solution of the first crop of crystals in 70 ml. of 95% ethanol was boiled with Darco (activated charcoal). The mixture was filtered and the Darco was washed with 10 ml. of ethanol. The filtrate was diluted with 15 ml. of water and 20 ml. of ethanol. The solution was then cooled to

(14) H. R. Snyder, J. S. Buck and W. S. Ide, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 333.

(15) W. E. Bachmann and R. F. Cockerill, *THIS JOURNAL*, **55**, 2932 (1933).

(16) A. C. Cope and L. Field, *J. Org. Chem.*, **14**, 856 (1949).

about 40° and the oil (about 1 ml. in volume) which first separated was removed. The clear solution was seeded and allowed to stand first at 25° and then at 5°. The product, obtained as large colorless prisms (10.5 g., 62%), was removed by filtration and washed with 10 ml. of cold 50% ethanol; m.p. 62–63°. After several recrystallizations from hexane and hexane-ether mixtures, the melting point was unchanged.

Anal. Calcd. for $C_{24}H_{24}O_4$: C, 76.57; H, 6.43. Found: C, 76.49; H, 6.57.

Diethyl α -Propyl-9-phenanthrenemalonate (X).—A solution of IX (3.0 g.) in anhydrous ethanol (70 ml.) containing 0.30 g. of 10% palladium on Norit was shaken with hydrogen at atmospheric pressure. During 45 minutes 103% of one molar equivalent of hydrogen was absorbed and there was no further absorption. The catalyst was removed by filtration and the filtrate concentrated under reduced pressure, leaving 2.96 g. (98%) of fine colorless crystals, m.p. 94.5–95.5°. After one recrystallization from ether-hexane (1:1) and two from ethanol, colorless prisms of X were obtained, m.p. 95–96°, undepressed on admixture with the authentic sample described below.

Anal. Calcd. for $C_{24}H_{26}O_4$: C, 76.16; H, 6.93. Found: C, 75.94; H, 7.08.

An authentic sample of X was prepared by alkylating diethyl 9-phenanthrenemalonate (2.5 g.) with *n*-propyl iodide in the presence of sodium ethoxide in ethanol. The product was purified by crystallization from ethanol and treatment with Darco. The yield of X was 1.4 g. (50%), m.p. 94–95°.

Rearrangement of Diethyl α -Allyl-9-phenanthrenemalonate (IX).—The ester IX (4.00 g.) was sealed in a Pyrex tube under nitrogen and heated at 266–296° for 3.5 hr. The tube was then cooled and opened (considerable gas was present), and the fluorescent red-green glass was distilled in a short-path still at 0.35 mm. with a heating block temperature of 199–206°. A small fore-run was removed before collection of the main portion.

The fluorescent yellow-green distillate was dissolved in 20 ml. of ethanol and treated with Darco. The filtered solution was seeded and allowed to stand at 25° until crystallization was well advanced, and then at 5°. The solid thus obtained was recrystallized from 20 ml. of hexane containing 20% of ether and yielded 1.11 g. (28%) of the rearrangement product XI as clusters of colorless needles, m.p. 92–94°. A similar product, that was recrystallized from cyclohexane-hexane containing 20% ether and several times from ethanol, had a constant m.p. of 92.5–94° and was analyzed.

Anal. Calcd. for $C_{24}H_{24}O_4$: C, 76.57; H, 6.43; active hydrogen, none; mol. wt., 376. Found: C, 76.35; H, 6.44; active hydrogen, 0.02 (methylmagnesium iodide at 25° for 2.3 hr.), 0.53 (80–100° for 1.5 hr.); mol. wt., 383 (Rast method in borneol).

The product gave a negative olefin test with potassium permanganate in ethanol.¹⁷ The compound also failed to absorb hydrogen in the presence of 10% palladium on Norit.

Saponification of XI to the Acid XII.—An intimate mixture of the rearrangement product XI (0.78 g.) with sodium hydroxide (2.0 g.) and potassium hydroxide (2.0 g.) was heated in an iron tube under a positive pressure of nitrogen at 235–266° for 10 hr. The cooled melt was treated with 100 ml. of water and heated on a steam-bath for 1.5 hr. The solid which was present was removed by centrifugation and sublimed at 145° (0.2 mm.) to give 11 mg. (2%) of a crystalline solid, m.p. 150.5–156°, which reduced 2% aqueous potassium permanganate solution and which was proved by mixed melting point to be the hydrocarbon XIII described below.

The supernatant layer was acidified with hydrochloric acid and allowed to stand overnight. The solid which precipitated was separated and washed well with water. A solution of the solid in 20 ml. of 5% aqueous potassium hydroxide solution was extracted with ether, treated with Darco and precipitated by adding hydrochloric acid. After repeating this precipitation procedure, 519 mg. (78%) of a cream-colored powder was obtained, m.p. 237–248.5° dec. A sample that was recrystallized once from methanol and four times from aqueous acetic acid had a m.p. of 242.5–244° dec.

(17) V. N. Ipatieff, W. W. Thompson and H. Pines, *THIS JOURNAL*, **70**, 1658 (1948).

Anal. Calcd. for $C_{20}H_{16}O_4$: C, 74.98; H, 5.04; neut. equiv., 160.1. Found: C, 74.82; H, 5.22; neut. equiv., 162.6.

Decarboxylation of XII Forming an Unsaturated Hydrocarbon XIII.—The acid XII (411 mg.) was converted to the sodium salt by evaporation of a solution in 10.4 ml. of 0.298 *N* aqueous sodium hydroxide. An intimate mixture of the salt with soda-lime (2.47 g.) was heated in a sublimation apparatus during 45 minutes to 310° at 0.1 mm., then at 310–320° for 11 hr. and finally at 320–350° for 2 hr. There was obtained as a sublimate 174 mg. (63%) of the hydrocarbon XIII as pale yellow clusters of rods, m.p. 151–154°. Resublimation of a 131-mg. portion, followed by crystallization from aqueous isopropyl alcohol, gave nearly colorless silky needles (117 mg.), m.p. 151–153.5°, which decolorized 2% aqueous potassium permanganate solution. A sample that was recrystallized twice from a mixture of equal parts of ethanol and ether gave fine colorless needles of XIII having a constant m.p. of 150.2–152.8°.

Anal. Calcd. for $C_{17}H_{12}$: C, 94.44; H, 5.55. Found: C, 94.11; H, 5.83.

In a similar experiment, an intimate mixture of 0.144 g. of the rearrangement product XI with potassium hydroxide (0.5 g.) and sodium hydroxide (0.5 g.) was heated at 255–265° for 7 hr. This reaction mixture also yielded the unsaturated hydrocarbon XIII (35 mg., 42%), m.p. 148.5–153°.

Reduction of the Unsaturated Hydrocarbon XIII to XIV.—A 97-mg. sample of XIII in ethyl acetate (12 ml.) was hydrogenated in the presence of 22 mg. of 10% palladium on Norit. After 1 hr., 98% of one molar equivalent of hydrogen had been absorbed, and there was no further absorption. The catalyst was removed by filtration and washed with ethyl acetate, and the filtrate was concentrated. The residue consisted of nearly colorless needles of XIV (95 mg., 97%), m.p. 148.5–150.5° (depressed to 145–149° by XIII), which did not decolorize a 2% aqueous potassium permanganate solution. Recrystallization from aqueous isopropyl alcohol, and then from a mixture of equal parts of ethanol and ether, gave long colorless needles of XIV, m.p. 149.5–150°, undepressed on admixture with an authentic sample of XIV described below.

Condensation of 9,10-Phenanthrenequinone with Ethyl Acetoacetate.—To 9,10-phenanthrenequinone¹⁸ (30 g.) suspended in commercial absolute ethanol (25 ml.) was added ethyl acetoacetate (37.5 g.) in commercial absolute ethanol (50 ml.). A further portion of ethanol (25 ml.) together with 6 drops of piperidine was added to the resulting mixture, which was then heated under reflux on a steam-bath. After heating for 40 minutes, a further 6 drops of piperidine was added. Again, after heating for 2 hr. more, ethanol (25 ml.) and piperidine (12 drops) were added. Fifteen minutes later the mixture suddenly turned solid. After heating for an additional period of 30 minutes, the mixture was cooled and filtered. The solid on the filter was washed with cold ethanol and then with cold benzene, leaving pale yellowish-green needles (37 g., 82%), m.p. 190–191°. Recrystallization from acetonitrile (Norit) gave 32.5 g. (72%) of faintly yellow tinged needles, m.p. 190–191.6°. Repeated recrystallizations from benzene gave almost colorless needles of ethyl 3,3a-dihydro-3a-hydroxy-2-oxo-2H-cyclopenta(l)phenanthrene-1-carboxylate (XV), melting at 190–191°; the melting points previously reported are 184.5–185.5°⁶ and 188°.⁵

Anal. Calcd. for $C_{20}H_{16}O_4$: C, 75.01; H, 5.03. Found: C, 75.02; H, 5.05.

2,3-Dihydro-2-oxo-1H-cyclopenta(l)phenanthrene (XVI).—To the condensation product XV described above (8.0 g.) was added 20 ml. of hydriodic acid (sp. gr. 1.7, 55–58% HI). The resulting brown slurry was heated under reflux in an oil-bath at 110–120° for 1.3 hr. Water (30 ml.) was added and the resulting black solid was removed by filtration. This product was boiled with a 10% sodium bisulfite solution for 5 minutes, the solid particles being broken up with a spatula. The mixture was filtered and the precipitate was washed well with water. Air-drying gave a green powder (7.1 g.), which was digested under reflux with 95% ethanol (500 ml.) for 12 hr. Norit was added to the solution, heating was continued for 30 minutes and the solution was filtered. The pale yellow filtrate was cooled in ice and the product, 2,3-dihydro-2-oxo-1H-cyclopenta(l)phenanthrene,

(18) R. Wendland and J. La Lande, *Org. Syntheses*, **34**, 76 (1954).

threne (XVI), separated as white shiny needles (2.27 g., 39%), m.p. 219–220.8°. Concentration of the mother liquor gave a further 0.8 g. (14%) of a light tan solid, m.p. 218–221°. Recrystallization from dioxane gave shiny needles melting at 223–223.6° (lit.⁷ 219°).

2,3-Dihydro-2-hydroxy-1H-cyclopenta(l)phenanthrene (XVII).—To a suspension of the ketone XVI (0.75 g.) in methanol (50 ml.) was added a solution of sodium borohydride (1.0 g.) in methanol (30 ml.). A vigorous effervescence occurred, and after about 30 seconds all of the suspended solid material had gone into solution. The resulting solution was allowed to stand at room temperature for 2 days, and the solution was brought to pH 7 by addition of dilute hydrochloric acid. The solution was poured into water (300 ml.), and the dense white precipitate was removed by filtration and washed well with water. On air-drying, impure XVII was obtained as a fine white powder (0.72 g., 95%), m.p. 184.6–186.1°. Two recrystallizations from 95% ethanol gave fine colorless needles of XVII (0.6 g., 80%), m.p. 187.1–188.0°.

Anal. Calcd. for $C_{17}H_{14}O$: C, 87.16; H, 6.02. Found: C, 87.11; H, 5.82.

When the above alcohol (100 mg.) was heated under reflux on a steam-bath for 3 hr. with 100% formic acid and then poured into water, the corresponding formate separated (103 mg., 92%). Recrystallization from 95% ethanol gave long white needles (59 mg., 53%), m.p. 179.5–180°.

Anal. Calcd. for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.30; H, 5.53.

When the alcohol XVII (1.0 g.) was warmed at 100° with acetic anhydride and then poured onto ice, the corresponding acetate (1.19 g., 98%), m.p. 158–159.2°, was obtained. Recrystallization from 95% ethanol gave white needles, m.p. 160–161° (685 mg., 57%).

Anal. Calcd. for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.40; H, 5.96.

1H-Cyclopenta(l)phenanthrene (XIII).—A mixture of the alcohol XVII (0.5 g.) and boric acid (2.0 g.) was heated at atmospheric pressure in a metal-bath until a liquid melt was obtained. The tube was cooled, the pressure reduced and the solid mass was heated slowly at first to 180–190° (0.4 mm.) and then to 300° (0.1 mm.). A brownish-yellow sublimate (370 mg., 79%) was collected. It was resublimed at 100–120° (0.05 mm.), the sublimate weighing 101 mg. (22%), m.p. 143–147.5°. This product was dissolved in benzene and passed through a column of activated alumina. Elution of the column with benzene afforded 94 mg. of a white solid, m.p. 146.1–148.5°. Three recrystallizations from isopropyl alcohol gave 27 mg. of XIII, m.p. 149.9–151.9°. A mixture of this product with XIII, obtained by degradation of XII (m.p. 150.2–152.8°), melted at 150–152.7°. The synthetic sample of XIII and the sample obtained by degradation had identical infrared spectra.

2,3-Dihydro-1H-cyclopenta(l)phenanthrene (XIV).—To a solution of potassium hydroxide (1.2 g.) in diethylene glycol (6 ml.) was added the ketone XVI (1.0 g.) and 2 ml. of 85% hydrazine hydrate. The mixture was heated at 160–165° for 1.5 hr. The excess hydrazine hydrate was removed by heating to 205–210° and the mixture was heated at 205° for an additional period of 3.5 hr. The mixture was diluted with water and acidified with hydrochloric acid. A brown powder that weighed 0.96 g. after air-drying was obtained. Recrystallization from 95% ethanol (Norit) yielded XIV (0.57 g., 58%) as colorless needles, m.p. 145.1–147.9°. Two more recrystallizations from absolute ethanol raised the melting point to 149.1–149.9° (420 mg.) (lit.⁸ 150°). The hydrocarbon XIV synthesized by this method and the sample obtained by the degradation $XI \rightarrow XII \rightarrow XIII \rightarrow XIV$ described above were identical according to mixed melting point and comparison of infrared spectra.

CAMBRIDGE 39, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Rearrangement of Allyl Groups in Three-carbon Systems. VII. Diethyl α -Allyl-2-naphthalenemalonate

BY ARTHUR C. COPE, JAY E. MEILI AND D. W. H. MACDOWELL¹

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Diethyl α -allyl-2-naphthalenemalonate (I) has been observed to rearrange on heating at 273° to the diethyl ester of 3-carboxy-2,3-dihydro-1H-benz(e)indene-2-acetic acid (II). Evidence establishing the structure of II was obtained by degrading the corresponding acid III to 1,2-naphthalenedicarboxylic acid and to 2,3-dihydro-1H-benz(e)indene (VII). The conversion of III to a geometric isomer VI and an intramolecular anhydride IV was found to parallel exactly transformations of related model compounds in the indan series (XI, XII and XIII). Final proof of structure of the acid III was obtained by synthesis.

The preceding paper² reports the thermal rearrangement of diethyl α -allyl-9-phenanthrenemalonate to an isomeric ester containing the 2,3-dihydro-1H-cyclopenta(l)phenanthrene ring system. Before the structure of the rearrangement product was known, the thermal rearrangement of diethyl α -allyl-2-naphthalenemalonate (I) was studied as an analogous case in which the structure of the product might be established more simply. The results obtained and an investigation of some indan derivatives that are structurally related to the rearrangement product are described in this paper.

Ethyl 2-naphthaleneacetate was condensed with diethyl carbonate in the presence of dry sodium ethoxide with removal of the ethanol formed by distillation,³ and the resulting enolate was alkylated

with allyl bromide to give diethyl α -allyl-2-naphthalenemalonate (I) (97%). This ester was converted to diethyl α -propyl-2-naphthalenemalonate by quantitative hydrogenation. Saponification of the ester I followed by acidification at 0–5° resulted in decarboxylation and formed α -allyl-2-naphthaleneacetic acid (70%), from which the ethyl ester was prepared.

When diethyl α -allyl-2-naphthalenemalonate was heated at 273° for 24 hr., an isomeric ester II was formed in 65% yield. This ester gave negative unsaturation tests with potassium permanganate and on saponification yielded a crystalline dicarboxylic acid, III, m.p. 235.0–235.8° dec. Esterification of the acid III with ethanol re-formed the ester II.

The dicarboxylic acid III was not decarboxylated by heating alone or mixed with copper powder at 220–250°, or by boiling with copper powder in quinoline, and accordingly could not be a malonic

(1) Visking Corporation Fellow, 1953–1954.

(2) A. C. Cope, L. Field, D. W. H. MacDowell and M. E. Wright, *THIS JOURNAL*, **76**, 2547 (1956).

(3) A procedure described for similar cases by V. H. Wallingford, A. H. Homeyer and O. M. Jones, *ibid.*, **63**, 2056 (1941).