

actions using anhydrous sodium iodide in the absence of any solvent. Carbon dioxide evolved during the reaction was absorbed in two Friedrichs absorption bottles connected in series and previously weighed. All the condensates, except that resulting from the reaction with unsubstituted acetoacetic ester, consisted of two layers. They were made homogeneous by addition of appropriate amounts of dioxane. Samples were taken from the homogeneous condensate, or condensates made homogeneous by addition of dioxane, for the analysis of water content by Karl Fischer's aquametric method. A weighed portion of the condensate from the reaction with the unsubstituted ester was fractionated; the fraction boiling below 90° was collected and weighed. Similar portions were taken from the homogenized condensates from the reaction with the methylated esters were also fractionated, and the fractions boiling below 110° were collected and weighed. Samples were taken from these distillates for the analyses of ethyl iodide, ketones, ethyl alcohol, and esters. The analyses of ethyl iodide and ketones were carried out in the same way as in the previous work. Ethyl alcohol was estimated exclusively by acetylation with a weighed amount of acetic anhydride, followed by hydrolysis of the excess of the anhydride and alkalimetry. For the analysis of esters, weighed samples of the distillates were saponified with an excess of alcoholic sodium hydroxide. The resulting alkaline solutions were evaporated to dryness, and the residues were dissolved in water, neutralized, acidified with dilute sulfuric acid in amounts slightly more than sufficient to liberate the organic acids, and steam distilled. Each of the distillates was absorbed in an excess of standard alkali and titrated back with standard acid. The identification of the products in the condensates was performed by gas-liquid partition chromatography as well as by chemical means, as described in the previous paper.

Action of Hydrated Sodium Iodide on Ethyl Acetoacetate.—Ethyl acetoacetate (65 g, 0.5 mole) and 93 g (0.5 gfw) of pulverized hydrated sodium iodide were placed in the reaction flask and heated. Complete dissolution of the salt soon occurred. When the temperature reached 150°, a vigorous reaction took place. The reaction temperature was maintained at 155° most of the time. Toward the end of the reaction, the temperature was raised to 160°. The reaction ended in 2.5 hr. Homogeneous condensate, weighing 55.6 g, was collected. The amount of carbon dioxide evolved was 11.6 g (0.53 mole/mole of ester). The yield of acetone amounted to 12.8 g (0.56 mole/mole of ester). The residue consisted of a brownish yellow crystalline paste which on acidification gave small amounts of unidentified brownish oil with evolution of a little carbon dioxide.

Action of Hydrated Sodium Iodide on Ethyl Methylacetoacetate.—The reaction was conducted in a manner similar to that for expt. 1 except that 72 g (0.5 mole) of methylacetoacetic ester was used instead of the unsubstituted ester. Reaction began when the temperature reached 140°. It became vigorous at 150°, but thereafter it slowed down, and at the end of 3 hr subsided almost completely. The condensate, weighing only 18.2 g, was made homogeneous by adding 10 g of dioxane. The yield of methyl ethyl ketone amounted to 3.3 g (0.092 mole/mole of ester). The amount of carbon dioxide evolved during the reaction was 3.4 g (0.16 mole/mole of ester). Acidification of the residue did not give much more carbon dioxide. About 0.3 mole of the unreacted ester was recovered.

Action of Hydrated Sodium Iodide on Ethyl Dimethylacetoacetate.—The reaction was performed in the same manner as in expt. 1, except that 79 g (0.5 mole) of dimethylacetoacetic ester was used in place of the unsubstituted ester. The temperature was held at 150–160°. The reaction first took place at a moderate rate, then slowed down. It subsided almost completely at the end of 3 hr. The condensate, which was collected in a receiver cooled in ice and salt, consisted of crystals of ice and organic liquid, and weighed 19 g. It was warmed to room temperature, and made homogeneous by addition of 25 g of dioxane. The yield of methyl isopropyl ketone amounted to 4.5 g (0.11 mole/mole of ester). No ethyl alcohol was present in the condensate. The amount of carbon dioxide evolved was 2.5 g (0.11 mole/mole of ester). From the residue was recovered 36 g (about 0.25 mole) of the unreacted ester.

Action of Hydrated Calcium Iodide on Ethyl Acetoacetate.—Ethyl acetoacetate (65 g, 0.5 mole) and 92 g (0.25 gfw) of hydrated calcium iodide were introduced in the reaction flask and heated. Complete dissolution of the salt rapidly occurred. Vigorous reaction took place when the temperature

reached 140°. Subsequently the temperature was maintained at 145–155°. At the end of 2 hr the reaction was complete, and crystalline paste was left in the reaction flask. The amount of carbon dioxide evolved during the reaction was 9.7 g. Acidification of the residue produced 3.8 g more, making a total of 13.5 g (61.4 moles/mole of ester). The condensate collected, weighing 86.8 g, consisted of two layers. It was made homogeneous by adding 37.2 g of dioxane. The yield of acetone amounted to 35.1 g (0.607 mole/mole of ester). Serious foaming might occur at the latter phase of the reaction. This can be suppressed by addition of a little anisole.

Action of Hydrated Calcium Iodide on Ethyl Methylacetoacetate.—Ethyl methylacetoacetate (72 g, 0.5 mole) and 92 g (0.25 gfw) of hydrated calcium iodide were placed in the reaction flask and heated. Dissolution of the salt soon occurred. A vigorous reaction began when the temperature reached 140°. The temperature was maintained at 145–155°. At the end of 1.5 hr the reaction was complete. The condensate, consisting of two layers, weighed 108 g. It was made homogeneous by adding 88 g of dioxane. The yield of methyl ethyl ketone was 26.1 g (0.725 mole/mole of ester). The amount of carbon dioxide evolved during the reaction was 8.3 g. Acidification of the residue gave 7.0 g more, making a total of 15.3 g (0.70 mole/mole of ester).

Action of Hydrated Calcium Iodide on Ethyl Dimethylacetoacetate.—Ethyl dimethylacetoacetate (79 g, 0.5 mole) and 92 g (0.25 gfw) of hydrated calcium iodide were introduced into the reaction flask and were heated. At 140°, a vigorous reaction began to take place. The temperature was maintained at 145–155°. The reaction was complete at the end of 1.5 hr. The condensate, when cooled in ice and salt, consisted of a mixture of large crystals of ice and organic liquid and weighed 121 g. The freshly collected condensate, when stored in a well-stoppered flask and warmed to room temperature, built up a pressure inside the flask, showing the presence of ethylene. To make the condensate homogeneous, 137 g of dioxane was added. The yield of methyl isopropyl ketone attained 33.3 g (0.775 mole/mole of ester). Butyl alcohol was absent in the condensate. The amount of carbon dioxide evolved during the reaction was 6.7 g; acidification of residue gave 8.7 g more, making a total of 15.4 g (0.71 mole/mole of ester).

Registry No.— $\text{CH}_3\text{COCH}_2\text{COOEt}$, 141-97-9; $\text{CH}_3\text{COCHMeCOOEt}$, 609-14-3; $\text{CH}_3\text{COCMe}_2\text{COOEt}$, 597-04-6; $\text{NaI}\cdot 2\text{H}_2\text{O}$, 13517-06-1; $\text{CaI}_2\cdot 4\text{H}_2\text{O}$, 13640-62-5.

The Reaction of Benzyne with Benzene¹

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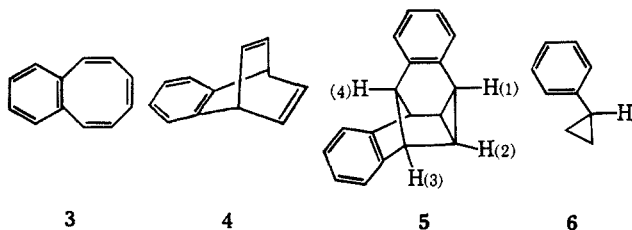
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The thermal decomposition of benzenediazonium-2-carboxylate (1) in benzene was reported² to produce a mixture of hydrocarbons from which three 1:1 adducts of benzyne and benzene were characterized, namely, biphenyl (2), benzocyclooctatetraene (3), and benzobicyclo[2.2.2]octatriene (4). Further examination of this hydrocarbon mixture has revealed a 2:1 adduct as well. Elemental analysis and molecular weight determination indicated the molecular formula $\text{C}_{18}\text{H}_{14}$ for the new hydrocarbon, mp 154°. The ultraviolet spectrum above 220 μ contained only the bands expected for benzenoid chromophores. The compound readily absorbed 1 molar equiv of hydrogen (Pd-C) to form a dihydro derivative.

(1) Financial support by the Petroleum Research Fund (2363-C) of the American Chemical Society is gratefully acknowledged.

(2) R. G. Miller and M. Stiles, *J. Am. Chem. Soc.*, **85**, 1798 (1963).

The nuclear magnetic resonance spectrum of the $C_{18}H_{14}$ hydrocarbon consisted of an aromatic multiplet at τ 2.8 (eight protons) and the following signals in the aliphatic proton region: τ 6.99 (unresolved multiplet, one proton), 7.14 (triplet, one proton), 7.37 (unresolved multiplet, two protons), and 8.37 (pair of multiplets, two protons).



The spectroscopic data and chemical information are consistent with structure **5** for this 2:1 adduct.^{3,3a} Spin-decoupling experiments at 100 Mc indicated a 6.6 cycle coupling between H_1 and H_2 , and a 1.5 cycle coupling between H_3 and H_4 . Proton 2 appears to be weakly coupled to both $H(3)$ and $H(3')$ with couplings of approximately 1.8 and 0.8 cycles.

The chemical shift of $H(1)$ (τ 7.14) is at lower field than the corresponding proton in phenylcyclopropane (**6**) by approximately 1 ppm.⁴ This difference may be taken to indicate that phenylcyclopropane exists as a mixture of conformers, subjecting the tertiary proton to less deshielding, on the average, than is exerted by the aromatic ring in the rigid structure (**5**). Electron diffraction studies⁵ have led to the conclusion that phenylcyclopropane exists predominantly in the conformation in which the two rings lie in perpendicular planes. The ultraviolet spectrum of the rigid compound (**5**) (Table I) resembles fairly closely that of **6**.

TABLE I

ULTRAVIOLET SPECTRUM OF THE DIADDUCT **5**^a

Wavelength, $m\mu$	$10^4 \epsilon$
195.8 max	176
198.3 max	169
220 sh	40
259.0 sh	1.0
264.0 max	1.4
267.7 max	1.3
274.6 max	1.1

^a In absolute ethanol at 25°, as recorded with Cary Model 14 spectrometer.

The formation of the 2:1 adduct **5** is assumed to result from the addition of benzyne to **4**. The parent compound (barrelene) has been shown⁶ to react with dimethyl acetylenedicarboxylate and with dicyano-

acetylene to form adducts with structures analogous to **5**.

The formation of the silver nitrate complex of benzocyclooctatetraene (**3**)⁷ was utilized previously² in the isolation of this compound from the benzyne-benzene reaction. In the present work it was found that both **3** and **4** are extracted from organic solutions by aqueous silver nitrate, and that silica gel chromatography was a more efficient means of separating the hydrocarbon products. This procedure also led to the isolation of small amounts of an ester which was identified as phenyl *o*-phenylbenzoate.

Experimental Section⁸

Thermolysis of Benzenediazonium 2-Carboxylate in Benzene.—The diazonium carboxylate (**1**)⁹ (2.16 g, 0.0145 mole) was added in one portion to 300 ml of benzene, and the suspension was stirred at 45° for 24 hr. The evolution of nitrogen and carbon dioxide was complete after approximately 20 hr. The reaction mixture was cooled to room temperature, filtered from 30 mg of insoluble material, reduced in volume to *ca.* 10 ml at the rotary evaporator, and applied to the top of a 1-m column (19-mm diameter) of silica gel prepared with petroleum ether (bp 40–60°). Elution of the chromatogram with 3.5 l. of petroleum ether containing 100 ml of benzene, followed by a second 3.5-l. portion containing 200 ml of benzene, yielded a total of 0.494 g of hydrocarbon, spread over 71 fractions of 63 ml each, collected automatically. Fractions 13–22 consisted of 0.262 g of a mixture of biphenyl (**2**) and benzocyclooctatetraene (**3**), which were not completely separated, but which could be analyzed (nmr) as an 8:5 ratio of **2**:**3**. Fractions 35–50 yielded 160 mg of pure **4**. Fractions 60–71 yielded 63 mg of a new hydrocarbon (**5**), mp 153–154°. The ultraviolet spectrum of the new hydrocarbon is recorded in Table I.

Anal. Calcd for $C_{18}H_{14}$: C, 93.87; H, 6.13; mol wt, 230.3. Found: C, 93.88; H, 6.17; mol wt, 219 (Rast).

The new hydrocarbon did not readily decolorize bromine in carbon tetrachloride or permanganate in acetone. It proved stable to heating at 210–220° for 24 hr. It readily (10 min) absorbed 1 equiv of hydrogen at 1 atm in ethyl acetate solution (10% Pd on C) to form a dihydro derivative, mp 93.5–94.0°.

Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 93.10; H, 7.02.

The reaction of the diazonium carboxylate with benzene at 80° appeared to be complete in approximately 10 min. Work-up of the reaction mixture as described above yielded a much smaller quantity of hydrocarbon products. From 2.14 g (0.0144 mole) of **1** and 300 ml of benzene there were obtained 36 mg of **2**, 36 mg of **3**, 42 mg of **4**, and no more than a trace of the diadduct **5**.

Isolation of Phenyl *o*-Phenylbenzoate.—Following removal of hydrocarbon products by the chromatographic procedure described above, small amounts of one or more products, exhibiting infrared spectra suggestive of esters, could be eluted from the column. Combination of this small ester fraction from several reaction mixtures led to the crystallization of a compound, mp 61°. The following hydrolysis experiment indicated it to be phenyl *o*-phenylbenzoate.

Anal. Calcd for $C_{19}H_{14}O_2$: C, 83.20; H, 5.14. Found: C, 83.02; H, 5.19.

Alkaline hydrolysis (1% KOH; 2-hr reflux) of 18 mg of the ester led to phenol (sublimed and identified by infrared spectrum) and 9 mg of *o*-phenylbenzoic acid (mp 107–109°) which proved identical with a sample prepared by alkali fusion of fluorenone, as described by Fittig.¹⁰

Registry No.—**5**, 13811-18-2; benzene, 462-80-6; benzene, 71-43-2; phenyl *o*-phenylbenzoate 13811-19-3.

(7) G. Wittig, H. Eggers, and P. Duffner, *Ann.*, **619**, 10 (1958).

(8) Melting points are corrected. Microanalyses were by Spang Microanalytical Laboratory, Ann Arbor, Mich.

(9) M. Stiles, R. G. Miller, and U. Burckhardt, *J. Am. Chem. Soc.*, **85**, 1792 (1963).

(10) R. Fittig and E. Ostermayer, *Ann.*, **166**, 374 (1873).

(3) Structure **5** was confirmed by an X-ray crystallographic study. See J. W. Schilling and C. E. Nordman, Abstracts, American Crystallographic Association Meeting, Atlanta, Ga., Jan 1967, p 22.

(3a) NOTE ADDED IN PROOF.—This compound has also been reported by L. F. Friedman, *J. Am. Chem. Soc.*, **89**, 3071 (1967).

(4) N. S. Bhacca, D. P. Hollis, L. J. Johnson, and E. A. Pier, NMR Spectrum Catalog, Vol. 2, Varian Associates, Palo Alto, Calif., 1963, Spectrum No. 528.

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(6) H. E. Zimmerman and G. L. Grunewald, *J. Am. Chem. Soc.*, **86**, 1434 (1964).