Lack of time and material does not permit us to obtain additional evidence regarding these alternate linkages. Logical approaches would be by the use of the Edman method on the aspartyl-glutaminyl-leucine peptide[1] and by partial acid degradation of the nonapeptide mentioned above. Details of this and the earlier work will be reported shortly.

EXPERIMENTAL THERAPEUTICS AND MEDICINAL CHEMICAL SECTIONS
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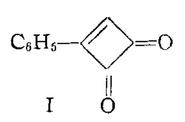
RECEIVED MAY 11, 1955

PHENYLCYCLOBUTADIENOQUINONE

Sir:

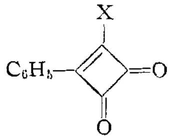
No authentic cylobutadiene derivatives appear to have yet been prepared except for biphenylene[1a] and related substances[1b,2,3] where the four-membered rings are part of fused-ring systems.[4] The failure to detect cyclobutadiene or its non-fused ring derivatives among the products of appropriate synthetic reactions can be ascribed either to excessive ring strain or unfavorable electronic configurations.[3,5] Strong evidence that ring strain is not the most important factor is now provided by a synthesis of the quite stable phenylcyclobutadienoquinone (phenylcyclobutendione, I) which to a first approximation is expected to have the same degree of ring strain as phenylcyclobutadiene.



I

Phenylacetylene with trifluorochloroethylene at 120° for 24 hours gave 1,1,2-trifluoro-2-chloro-3-phenylcyclobutene[6]; b.p. 52–53° (0.4 mm.), $n^{25}\text{D}$ 1.5117. *Anal.* Calcd. for $C_{10}H_8F_3Cl$: C, 54.92; H, 2.77. Found: C, 54.83; H, 2.89. Hydrolysis[6] of the adduct with 92% sulfuric acid at 100° afforded bright-yellow crystalline I in 75% yield; m.p. 152–153° (dec.) after recrystallization from acetone. *Anal.* Calcd. for $C_{10}H_6O_2$: C, 75.94; H, 3.82; mol. wt., 158. Found: C, 76.00; H, 3.85; mol. wt. (Rast), 151. I had $\lambda_{\max} = 286$ mμ, ϵ 2.3×10^5 and strong infrared absorption at 5.6 μ. A chloroform solution of I with 30% hydrogen peroxide yielded phenylmaleic anhydride, m.p. 119–120°, which did not depress the m.p. of an authentic sample.[7] Reduction of I with amalgamated zinc and hydrochloric acid yielded phenylcyclobutane which was identified by comparison of its infrared spectrum with material previously prepared.[6] I is much more stable to water and oxygen than *o*-benzoquinone. It is apparently not reduced by agents such as hydrogen over platinum to the corresponding hydroquinone.

I can be converted to a variety of stable substitution products (II–VII) which have some chemical properties analogous to those of substituted benzo- and naphthoquinones.



II, X = Cl
III, X = Br
IV, X = I
V, X = -OCH_3
VI, X = -NH_2
VII, X = -OH

I reacted with chlorine or bromine in acetic acid to yield the yellow halogen derivatives II and III, respectively. II had m.p. 114–115°. *Anal.* Calcd. for $C_{10}H_5O_2Cl$: C, 62.36; H, 2.62. Found: C, 62.20; H, 2.54. III had m.p. 128–129°. *Anal.* Calcd. for $C_{10}H_5O_2Br$: C, 50.66; H, 2.13. Found: C, 50.64; H, 2.13. Reduction of III with amalgamated zinc and hydrochloric acid gave phenylcyclobutane. III reacted rapidly with alcoholic silver nitrate and, with sodium iodide in acetone, yielded IV, m.p. 163–165° (dec.). *Anal.* Calcd. for $C_{10}H_5O_2I$: C, 42.26; H, 1.77. Found: C, 42.38; H, 1.87. Methanolysis of III afforded pale yellow V, m.p. 151–152° (*Anal.* Calcd. for $C_{11}H_8O_3$: C, 70.20; H, 4.28. Found: C, 69.51; H, 4.16) while ammonia in dry benzene gave the colorless essentially neutral amino derivative (VI), m.p. 279–281° (dec.). *Anal.* Calcd. for $C_{10}H_7O_2N$: C, 69.36; H, 4.07; N, 8.09. Found: C, 69.37; H, 4.04; N, 8.08. With dilute acetic acid, III was hydrolyzed to colorless VII, m.p. 205–208° (dec.). VII is soluble in water, is an exceptional strong acid for a C, H, O compound ($pK_A \sim 1$) and gives a magenta color with ferric chloride solution. *Anal.* Calcd. for $C_{10}H_6O_3$: C, 68.96; H, 3.48; neut. equiv., 176. Found: C, 68.87; H, 3.61; neut. equiv., 174. VII is converted to V with diazomethane.

The stable existence of I–VII suggests the possibility that quinone-type derivatives of unknown cyclic polyolefins such as pentalene and heptalene might be more stable than the parent hydrocarbons.

Investigation of the chemical and physical properties of I–VII is being continued.

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A NEW REAGENT FOR RESOLUTION BY COMPLEX FORMATION; THE RESOLUTION OF PHENANTHRO-[3,4-*c*]PHENANTHRENE[1]

Sir:

We wish to report the synthesis of 2-(2,4,5,7-tetranitro-9-fluorenylideneaminoöxy)-propionic acid, III, a useful reagent for the optical resolution of certain aromatic compounds which do not have the functional groups usually needed to effect resolution by conventional reagents.

The dextro and levo forms of III were made by condensing 2,4,5,7-tetranitrofluorenone, I, with

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(1) (a) W. C. Lothrop, THIS JOURNAL, **63**, 1187 (1941); (b) **64**, 1698 (1942).

(2) R. F. Curtis and G. Viswanath, *Chem. and Ind.*, 1174 (1954).

(3) M. P. Cava and J. F. Stucker, *ibid.*, 446 (1955).

(4) An excellent survey of attempts to prepare non-fused ring cyclobutadiene derivatives was recently presented by E. R. Buchman, Abst. of A.C.S. meeting, Sept. 13, 1954, p. 9-O.

(5) For references and discussion see J. D. Roberts, A. Streitwieser, Jr., and Clare M. Regan, THIS JOURNAL, **74**, 4579 (1952).

(6) *Cf.* J. D. Roberts, G. B. Kline and H. E. Simmons, Jr., *ibid.*, **75**, 4765 (1953).

(7) L. E. Miller, H. B. Staley and D. J. Mann, *ibid.*, **71**, 374 (1949).

(1) A part of this material was presented before the Division of Organic Chemistry at the 127th meeting of the American Chemical Society, Cincinnati, Ohio, March, 1955.