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
RESEARCH DIVISION
AMERICAN CYANAMID COMPANY
STAMFORD, CONNECTICUT

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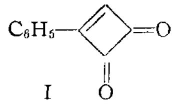
RECEIVED MAY 11, 1955

PHENYLCYCLOBUTADIENOQUINONE

Sir:

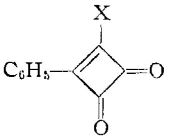
No authentic cylobutadiene derivatives appear to have yet been prepared except for biphenylene[1a] and related substances[1b,2,3] where the four-membered rings are part of fused-ring systems.[4] The failure to detect cyclobutadiene or its non-fused ring derivatives among the products of appropriate synthetic 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}_{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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RECEIVED MAY 20, 1955

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.

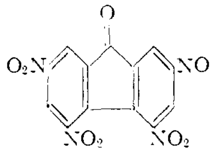
[5] For references and discussion see J. D. Roberts, A. Streitwieser, Jr., and Clare M. Regan, THIS JOURNAL, **74**, 4579 (1952).

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

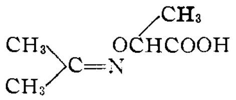
[7] L. E. Miller, H. B. Staley and D. J. Mann, *ibid.*, **71**, 374 (1949).

[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.

(−) and (+)-(isopropylideneaminoöxy)-propionic acid, II, respectively, in the presence of *p*-toluenesulfonic acid

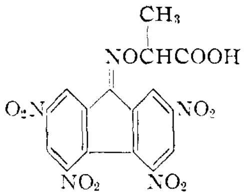


I



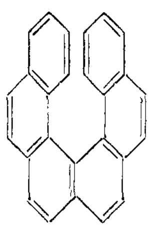
II

$(CH_3)_2C{=}NOCH(CH_3)COOH$



III

When a solution of two equivalents of 1-naphthyl-*sec*-butyl ether and one equivalent of (−)-III, $[\alpha]^{29}D$ −91.4° (*c*. 1.6, dioxane), in acetic acid was cooled a purple complex separated. The ethers recovered from the complex and the mother liquor were optically active, $[\alpha]^{31}D$ −7.8° (*c*, 6.4 ethyl acetate) and $[\alpha]^{32}D$ +6.4° (*c*, 11, ethyl acetate), respectively. Similarly, methyl 2-(1-anthryl)-propionate was partly resolved into the corresponding (+)- and (−)-forms, $[\alpha]^{24}D$ +101° and $[\alpha]^{27}D$ −66.0° by means of (+)-III, $[\alpha]^{23}D$ +84° (*c*, 1.5, dioxane). The above rotations are undoubtedly not maximal but represent the result of a single separation of complex.



IV

When a solution of phenanthro[3,4-*c*]phenanthrene,[2] IV, m.p. 231–231.5° (uncor.), in benzene was treated with one-half equivalent of the complexing agent the solution became dark red. Upon the addition of ethanol, the hydrocarbon separated as hexagonal plates. Three further applications of this treatment followed by nine conventional recrystallizations afforded IV, m.p. 263–267°, $[\alpha]^{24}D$ −3640° (*c*, 0.0988, chloroform). The optical stability of this compound is indicated by the fact that it remelts at 234–250°, showing that even at its m.p. racemization is not complete. This is the first example of the resolution of a hydrocarbon which owes its asymmetry to intramolecular overcrowding.

N-*sec*-Butylpicramide, a compound which might have been used for resolution by means of complex formation has been prepared.[3] Racemic N-*sec*-butylpicramide was partially resolved by complex formation with (+)-β-naphthylcamphylamine but the partially resolved reagent was never used to resolve any other compound.

Because of the considerable complexing ability of III, this reagent should prove valuable for the resolution of a variety of racemic aromatic compounds. The extensions and limitations in the use of III and analogous compounds is under study as well as the exchange reaction represented by equation (1).

The reagent II was made by treating the sodium salt of acetoxime with methyl 2-bromopropionate.[4] 2-(Isopropylideneaminoöxy)-propionic acid, II, m.p. 58–61°, (Found: C, 49.5; N, 9.7), was resolved by treating two equivalents of racemic II with 1.5 equivalents of (−)-ephedrine in 1:1 benzene–Skellysolve B. The resulting salt, m.p. 116–119°, was decomposed with hydrochloric acid. The acid thus produced was recrystallized from 5:1 Skellysolve B–acetone to give (+)-II, m.p. 83.5–85.5°, $[\alpha]^{26}D$ +30.8° (*c*, 7.6, water, 2 dm.).

(−)-2-(2,4,5,7-Tetranitro-9-fluorenylideneaminoöxy)-propionic acid, m.p. 198–200° cor.,[5] (Found: C, 43.0, H, 2.0, N, 15.8), $[\alpha]^{28}D$ −97.1° (*c*, 1.5, dioxane), was made by gently refluxing a mixture of one equivalent of 2,4,5,7-tetranitrofluorenone, 1.5 equivalents of (+)-2-(isopropylideneaminoöxy)-propionic acid and 1.7 equivalents of *p*-toluenesulfonic acid monohydrate, in glacial acetic acid. The product was then precipitated with water and the yellow solid recrystallized from a mixture of acetic acid and butyl chloride. The (+)-III was made similarly by starting with I and (−)-II.

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[2] The synthesis of this hydrocarbon will be described later.

[3] R. Weiss and A. Abeles, *Monatsh.*, **59**, 238 (1932).

[4] Compare E. Borek and H. T. Clark, THIS JOURNAL, **58**, 2020 (1936).

[5] The substance also melts and resolidifies or sinters between 125° and 135°.

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RECEIVED APRIL 21, 1955

BISCYCLOPENTADIENYLRHENIUM HYDRIDE—A NEW TYPE OF HYDRIDE

Sir:

When rhenium pentachloride (0.03 mole) is allowed to react with sodium cyclopentadienide (0.2 mole) in tetrahydrofuran solution and the evaporated purple reaction mixture is heated at 120–170° in vacuum, a yellow crystalline sublimate, m.p., 161–162°, is obtained in yields ~20% based on the halide. The molecular weight of the compound by the isothermal distillation method in benzene and ether is 312 ± 5. The compound cannot, however, be biscyclopentadienylrhenium, $(C_5H_5)_2Re$, since it is diagmagnetic in the crystal and the melt from 77 to 510°K., and in organic solvents. The only reasonable explanation of this fact is that the compound is a hydride. Chemical analysis does not, however, provide an unequivocal answer [*Anal.* Found: C, 37.7; H, 3.6; Re, 58.75. Required for $(C_5H_5)_2ReH$; C, 37.85; H, 3.49; Re, 58.66; mol. wt., 317.5].

Proof of the hydridic nature of the compound comes from studies with a Varian Associates high resolution nuclear magnetic resonance spectrometer. In carbon disulfide solutions, a resonance peak attributable to the protons of the cyclopentadienyl rings is observed with a shift relative to the reference, water, of −1.17 p.p.m. $(H–H_r/H_r)$; a second resonance peak of approximately one-tenth the intensity is observed with a displacement of