until all of the diphenylcyclooctatetraene fractions had been removed from the instrument (a total of 1300 transfers). From this distribution, 1,2-diphenylcyclooctatetraene (I), $K \sim 0.77$, and 1,3-diphenylcyclooctatetraene (II), $K \sim 1.08$, were isolated as pure compounds. A third broad band contained the remaining isomers, $K \sim 0.58$. They were separated by 1655 fundamental transfers in a second solvent system, composed of methyl-cyclohexane-nitromethane, into pure 1,4-diphenyl-cyclooctatetraene (III), $K \sim 1.23$ and 1,5-diphenyl-cyclooctatetraene (IV), $K \sim 1.47$. There was no evidence in the distributions for the presence of a second 1,2- or a second 1,4-diphenylcycloocta-tetraene, which theoretically are possible, unless the double and single bonds in the cyclooctatetraene nucleus assume a preferred position with relation to the phenyl substituents, rather than both possible positions.

The identity of the crystalline 1,2-isomer I was established by direct comparison with an authentic sample.[4] After short-path distillation at 55° and 0.01 mm. the 1,3-isomer II was obtained as a golden yellow liquid that failed to crystallize; its homogeneity was established by the distribution curve and the results of hydrogenation described below (Anal. Calcd. for $C_{20}H_{16}$: C, 93.71; H, 6.29. Found: C, 93.36; H, 6.32). Crystallization from aqueous methanol yielded the 1,4-isomer III as canary yellow needles, m.p. 47.7–48.8° (Anal. Found: C, 93.98; H, 6.34). Crystallization from ethanol yielded the 1,5-isomer IV as pale yellow prisms, m.p. 102.1–102.6° (Anal. Found: C, 93.52; H, 6.24). The ultraviolet and infrared absorption spectra of the isomers showed significant differences.

Microhydrogenation of II, III and IV in ethanol in the presence of 10% palladium on Norit resulted in the absorption of 98.5 to 100.8% of the theoretical four molar equivalents of hydrogen. In each case the two isomeric (cis and trans) diphenyl-cyclooctanes that were formed were separated by chromatography on alumina and fractional crystallization, and their identities were established by comparison with authentic samples. Hydrogenation of II gave both 1,3-diphenylcyclooctanes,[5] while IV yielded both 1,5-diphenylcyclooctanes,[6] m.p. 80–81° and 62–62.5°. From the mixture of cis and trans isomers obtained by hydrogenation of III, a single crystalline 1,4-diphenylcyclooctane was isolated, which was identical with an authentic sample synthesized as follows. Phenyllithium was added to cyclooctane-1,4-dione,[7] and the resultant glycol was dehydrated by boiling in benzene containing a trace of iodine. After chromatography on alumina and crystallization from methanol, pure 1,4-diphenylcycloocta-1,3-diene was obtained, m.p. 65.9–66.3° (Anal. Calcd. for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.16; H, 7.75). Hydrogenation of the diene formed a mixture of cis- and trans-1,4-diphenylcyclooctanes, which were

separated by chromatography on alumina and recrystallization from methanol. One crystalline isomer was obtained, m.p. 58.5–59.5° (Anal. Calcd. for $C_{20}H_{24}$: C, 90.85; H, 9.15. Found: C, 90.85; H, 9.31).

In a preliminary study, it has been found that the copolymerization of phenylacetylene with acetylene, previously reported to yield phenyl-cyclooctatetraene,[8] also can be employed to prepare polyphenyl substituted cyclooctatetraenes. With a higher concentration of phenylacetylene than was used previously,[8] a mixture of hydrocarbons was obtained that was partially separated by countercurrent distribution with the first solvent system described above. The pure 1,4- and 1,5-diphenylcyclooctatetraenes III and IV have been isolated as crystalline solids, and more complete separation of the mixture by countercurrent distribution is in process.

(8) A. C. Cope and H. C. Campbell, THIS JOURNAL, **73**, 3536 (1951); **74**, 179 (1952).

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THE THEORETICAL OPTICAL ROTATION OF PHEN-ANTHRO[3,4-c]PHENANTHRENE

Sir:

The optical rotation of phenanthro[3,4-c]phenanthrene in chloroform solution was recently reported by Newman and co-workers[1] to be $-3640°$. We have calculated a theoretical value for this rotation using Kirkwood's polarizability theory of optical activity,[2] which states that

$$[\alpha]_D = 4.930 \times 10^{37}(n^2 + 2)g/3M \qquad (1)$$

Here M is the molecular weight of the compound (328.4) and n is the refractive index of the solution. The refractive index of the chloroform solution used in the experimental determination can be approximated by that of pure chloroform, 1.45.

The factor g is related to the molecular configuration and is approximated by the polarizability theory as

$$g^{(0)} = \frac{\alpha^2\beta^2}{6} \sum_{i>k=1}^{6} \frac{R_{ik} \cdot (n_i \times n_k)}{R_{ik}^3} \left[n_i \cdot n_k - 3 \frac{(n_i \cdot R_{ik})(n_k \cdot R_{ik})}{R_{ik}^2} \right] \qquad (2)$$

$$R_{ik} = R_k - R_i \qquad (3)$$

For benzene, the mean polarizability, α, and the anisotropy ratio, β, are 9.89×10^{-24} cc. and -0.58 respectively. R_i is the position vector of the center of the i-th benzenoid ring and n_i is the unit vector normal to the plane of the i-th ring. The sum taken over each pair of rings has fifteen terms.

We placed the centers of the six benzenoid rings on a left-handed cylindrical helix $x = a \cos \theta$, $y = a \sin \theta$, $z = -b \theta$ at $\theta = 0°, 60°, 120°, 180°, 240°$, and $300°$. The unit normal, n, to each ring, assumed perpendicular to the radius vector drawn normally outward from the z-axis, was found from the cross product of the unit radius vector by the

(4) A. C. Cope and D. S. Smith, THIS JOURNAL, **74**, 5136 (1952).

(5) A. C. Cope, F. S. Fawcett and G. Munn, ibid., **72**, 3399 (1950); A. C. Cope, M. R. Kinter and R. T. Keller, ibid., **76**, 2757 (1954).

(6) A. C. Cope and R. J. Cotter, to be published.

(7) A. C. Cope, A. H. Keough, H. E. Simmons, Jr., and G. W. Wood, to be published.

(1) M. S. Newman, W. B. Lutz and D. Lednicer, THIS JOURNAL, **77**, 3420 (1955).

(2) J. G. Kirkwood, J. Chem. Phys., **5**, 479 (1937).

unit tangent to be $-\mathbf{i}\,b\sin\theta + \mathbf{j}\,b\cos\theta + \mathbf{k}\,a/(a^2 + b^2)^{1/2}$. The trigonometric functions in $g^{(0)}$ combine so that the resulting expression is a function of $\theta_{ik} \equiv \theta_k - \theta_i$ only

$$g^{(0)} = \frac{-\alpha^2\beta^2\gamma}{6a^2(1+\gamma^2)^2} \sum_{i>k=1}^{6} f(\theta_{ik}) \qquad (4)$$

where $\gamma \equiv b/a$ and

$$f(x) = \frac{2(1-\cos x)+\gamma^2 x\sin x}{[2(1-\cos x)+\gamma^2 x^2]^{3/2}}\left[1+\gamma^2\cos x - \frac{3\gamma^2(x-\sin x)^2}{2(1-\cos x)+\gamma^2 x^2}\right] \qquad (5)$$

If a bond length of 1.40 Å. is used, the radius a is 2.42 Å. Lacking an X-ray analysis, we estimated the value of b by assuming the distance between the nearest pair of non-bonded carbon atoms at the ends of the helix to be 3.80 Å., which is the packing distance between neighboring molecules in benzene crystals.[3]

The calculated results are $g^{(0)} = -1.46 \times 10^{-32}$ and $[\alpha]_D = -3010°$. The close agreement between the calculated and experimental rotations demonstrates the applicability of the polarizability theory to compounds which owe their asymmetry to steric interference. The agreement in sign indicates that the molecules of the compound isolated[1] have a left-handed helical configuration.

(3) E. G. Cox, Proc. Roy. Soc. (London), A135, 491 (1932).

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DISTINCTION BETWEEN CYCLOHEPTATRIENE AND BICYCLOHEPTADIENE STRUCTURES BY NUCLEAR MAGNETIC RESONANCE

Sir:

The finding that certain substitution reactions of eucarvone also involve bridging across the ring to form bicyclo[4.1.0]heptene (carene) derivatives[1] prompted us to investigate the possibility that eucarvone enol, eucarvone enolate ion and related structures which are subject to cycloheptatriene $\rightleftarrows$ bicycloheptadiene equilibria may be more stable as the bicyclic than as the monocyclic valence tautomers. This Communication describes the application of nuclear magnetic resonance (NMR) to this hitherto unsolved problem. A complete account of the work together with its bearing on the mechanism of bridging reactions of eucarvone will be presented later.

A number of the enol esters of eucarvone which might have either mono- or bicyclic structures (I or II) were prepared (as models of eucarvone enol) by acylation of sodioeucarvone, e.g. the enol

I   II
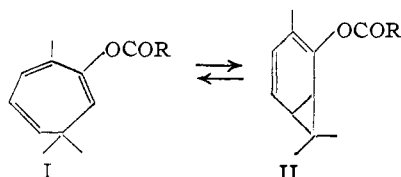
acetate, b.p. 64–66° (1 mm.), $n^{20}D$ 1.4942, λ_{max} 273, 207 mμ (log ϵ 3.42, 4.09), ν_{max} 1762, 1685, 1649 cm.$^{-1}$. Found: C, 75.10; H, 8.42. These were

(1) E. J. Corey and H. J. Burke, THIS JOURNAL, 76, 5257 (1954).

found to be homogeneous and not subject to a valence tautomeric change upon heating. The NMR spectrum[2] of the enol acetate shows that it is a cycloheptatriene rather than a caradiene type. The ethylenic hydrogen absorption (at A) is well separated from the hydrogen absorption due to CH_3—C=X (at B) and this, in turn, from the *gem*-dimethyl hydrogen absorption (at C).[3] There is no absorption in the place expected for two tertiary bridge hydrogens of a caradiene structure (see below). Furthermore, the ratio of the integrated absorption area for the hydrogens in the *gem*-dimethyl groups (obtained by integration under the curve at C) to that for the ethylenic hydrogens (area under curve at A) is 1.55 in agreement with the cycloheptatriene (calcd. 1.50), but not with the caradiene structure (calcd. 3.0).
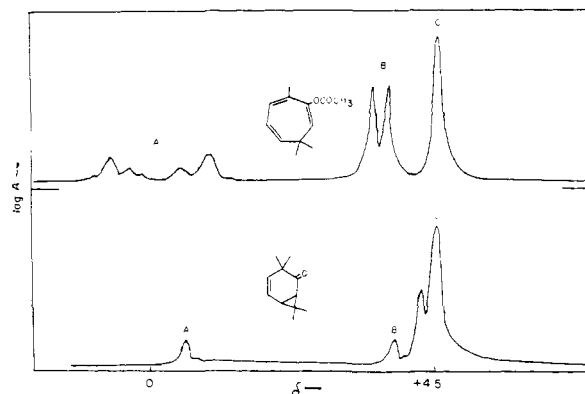

Fig. 1.—A = electromagnetic absorption; δ = change, relative to water as the standard, in magnetic field necessary for hydrogen absorption $\times (10)^6$ = structural shift for hydrogen relative to water.

In view of the NMR results which are unambiguous, some of the chemical evidence regarding the structures of the enol esters must be recognized as misleading. Thus, *the enol esters in each case afford upon ozonolysis* $(-70°)$ *over 50% yield of cis-caronic acid* which fact, in itself, argues for the caradiene structure. The production of *cis*-caronic acid from a cycloheptatriene structure is unusual, but certainly within the realm of possibility.[4]

The NMR spectrum of Δ^2-4-methylcaren-5-one (III),[5] which is formed by methylation of sodioeucarvone, b.p. 70° (5 mm.), $n^{20}D$ 1.4809, λ_{max} 206, 300 mμ (log ϵ 3.71, 2.89); ν_{max} 1698, 1665, 1007 cm.$^{-1}$. Found: C, 80.34; H, 9.95, shows the absorption of two tertiary bridge hydrogens (at B) well resolved from the methyl hydrogen absorption

(2) All NMR spectra measured by Dr. J. N. Shoolery and staff of Varian Associates, Palo Alto, California on the commercial Varian instrument. We are grateful to Dr. Shoolery and also to Dr. H. S. Gutowsky for their interest in this problem.

(3) See L. H. Meyer, A. Saika and H. S. Gutowsky, ibid., 75, 4567 (1953).

(4) E. H. Farmer and C. K. Ingold, J. Chem. Soc., 117, 1362 (1920), have observed the formation of small amounts of caronic acid by oxidation of what is now known to be 4,4-dimethyl-3-carboxy-Δ^2-cyclopenten-1-one [N. J. Toivonen, Chem. Zentr., 98, II, 1248 (1927)].

(5) This structure has been established inter alia by ozonolysis to cis-caronic acid.