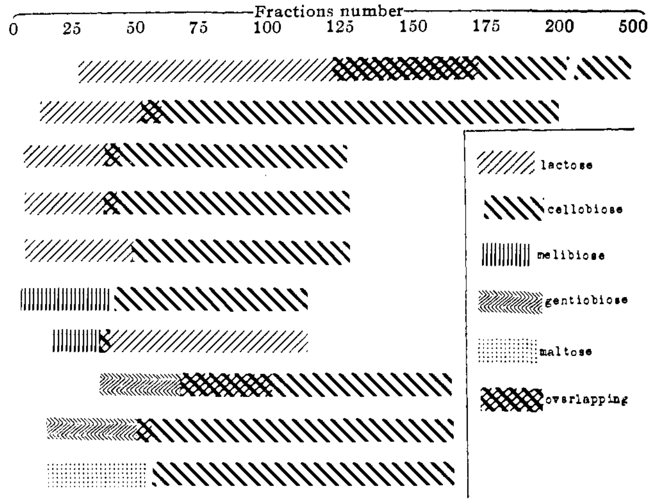
CHART I, SEPARATION OF DISACCHARIDES ON A THERMOCOLUMN



Disaccharides used,	g.	Temp., °C.	Disaccharides recovered,[a] g.
Cellobiose Lactose	0.20 .20	22 ± 2	... 0.17
Cellobiose Lactose	.20 .20	49 ± 3	.16 .17
Cellobiose Lactose	.20 .20	68 ± 3	.15 .15
Cellobiose Lactose	.20 .10	68 ± 3	.15 .08
Cellobiose Lactose	.10 .20	68 ± 3	.08 .17
Cellobiose Melibiose	.10 .10	68 ± 3	.08 .08
Lactose Melibiose	.10 .10	49 ± 3	.07 .08
Cellobiose Gentiobiose	.10 .10	49 ± 3	... .07
Cellobiose Gentiobiose	.10 .10	68 ± 3	.08 .07
Cellobiose Maltose	.10 .10	68 ± 3	.08 .08

[a] The discrepancy between the amount of each disaccharide used and that recovered is due to the loss during spot-checking, concentration, precipitation and drying, as well as to overlapping.

thermoregulator is placed inside this tube. A small window in the asbestos tape permits observation of the thermometer.

Preparation of the Thermocolumn.—The thermocolumn, 20 by 420 mm., is prepared from a mixture of charcoal and Celite (1:1) according to Whistler and Durso.[4] After washing with water, the column is heated to the temperature at which the chromatographic separation is to be carried out. The thermocolumn then is washed with 4 l. of 3% aqueous ethanol. Fractions are collected automatically.

Separation of Sugars.—A pair of disaccharides, dissolved in a small amount of 3% aqueous ethanol was transferred onto the top of the column. As the solution moved into the column, about 5 ml. of 3% aqueous ethanol was added at the top of the column. This was repeated three times. Then the column was eluted continuously with 3% aqueous ethanol by gravity. Each fraction collected was about 20 ml. at 50° (23 ml. at 70°). Each fifth fraction was spot-checked by paper chromatography using *n*-butyl alcohol–pyridine–water (6:4:3) as the solvent. The fractions containing the same sugar were combined, concentrated, and dried in the usual manner. The recovered sugars were weighed and spot-checked again, separately.

Results.—A series of five pairs of disaccharides, lactose and cellobiose, melibiose and lactose, melibiose and cellobiose, gentiobiose and cellobiose, and maltose and cellobiose was selected for chromatographic separation in the thermocolumn. The amount of the sugar in each pair being separated, the temperature used for the chromatography, and the results are shown in Chart I. The procedure described above was used for the separation of each of the pairs of the disaccharides.

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[4] R. L. Whistler and D. F. Durso, THIS JOURNAL, **72**, 677 (1950).

COMMUNICATIONS TO THE EDITOR

CYCLIC POLYOLEFINS. XXXVIII. POSITION ISOMERS OF DISUBSTITUTED CYCLOÖCTATETRAENES

Sir:

We wish to report separation of the four possible position isomers of diphenylcycloöctatetraene (1,2-, 1,3-, 1,4-, 1,5-) and the identification of each.

The reaction of phenyllithium with cyclooctatetraene has been reported previously to form phenylcycloöctatetraene.[1] Phenyllithium and phenylcycloöctatetraene have been found to react in a similar manner, forming a mixture of hydrocarbons containing the diphenylcycloöctatetraenes. After a preliminary short-path distillation under reduced pressure to separate most of the phenylcycloöctatetraene as a low-boiling fraction, and a high-boiling residue, the fraction of intermediate boiling point was subjected to countercurrent distribution in a 200-tube automatic instrument[2] in which the volume of each phase is 10 ml. The first distribution employed as solvents (in the following ratios) cyclohexane (166 ml.)–ethanol (100 ml.) and water (20 ml.) containing silver nitrate (13.1 g.). Hydrocarbons less soluble in the aqueous alcoholic silver nitrate phase ($K \sim 6.5$)[3] than the diphenylcycloöctatetraenes, and the remaining phenylcycloöctatetraene ($K \sim 0.17$), which was more soluble in that phase, were readily separated. After 658 fundamental transfers, the upper phase was removed by single withdrawal

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[1] A. C. Cope and M. R. Kinter, THIS JOURNAL, **73**, 3424 (1951).

[2] Manufactured by the H. O. Post Scientific Instrument Co., based on the design described by L. C. Craig, W. Hausmann, E. H. Ahrens, Jr., and E. J. Harfenist, *Anal. Chem.*, **23**, 1236 (1951).

[3] The partition ratio K is defined as the concentration of the material in the upper phase (in this case principally cyclohexane) divided by the concentration in the lower phase.

until all of the diphenylcyclooötatetraene fractions had been removed from the instrument (a total of 1300 transfers). From this distribution, 1,2-diphenylcycloöctatetraene (I), $K \sim 0.77$, and 1,3-diphenylcycloöctatetraene (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 methylcyclohexane-nitromethane, into pure 1,4-diphenylcycloöctatetraene (III), $K \sim 1.23$ and 1,5-diphenylcycloöctatetraene (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-diphenylcycloöctatetraene, which theoretically are possible, unless the double and single bonds in the cycloöctatetraene 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*) diphenylcycloöctanes 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-diphenylcycloöctanes,[5] while IV yielded both 1,5-diphenylcycloöctanes,[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-diphenylcycloöctane was isolated, which was identical with an authentic sample synthesized as follows. Phenyllithium was added to cycloöctane-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-diphenylcycloöcta-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-diphenylcycloöctanes, 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 phenylcycloöctatetraene,[8] also can be employed to prepare polyphenyl substituted cycloöctatetraenes. 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-diphenylcycloöctatetraenes III and IV have been isolated as crystalline solids, and more complete separation of the mixture by countercurrent distribution is in process.

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(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.

(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 PHENANTHRO[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

$$g^{(0)} = \frac{\alpha^2\beta^2}{6}\sum_{i>k=1}^{6}\frac{\mathbf{R}_{ik}\cdot(\mathbf{n}_i \times \mathbf{n}_k)}{R_{ik}{}^3}\left[\mathbf{n}_i\cdot\mathbf{n}_k - 3\,\frac{(\mathbf{n}_i\cdot\mathbf{R}_{ik})(\mathbf{n}_k\cdot\mathbf{R}_{ik})}{R_{ik}{}^2}\right] \qquad (2)$$

$$\mathbf{R}_{ik} = \mathbf{R}_k - \mathbf{R}_i \qquad (3)$$

For benzene, the mean polarizability, α, and the anisotropy ratio, β, are 9.89×10^{-24} cc. and −0.58 respectively. $\mathbf{R}_i$ is the position vector of the center of the i-th benzenoid ring and $\mathbf{n}_i$ 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, $\mathbf{n}$, 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

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(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).