

Some examples of bromine insertion have also been observed. Photolysis of Ia ($R = \text{NO}$, $X = \text{H}$) in benzene containing excess CCl_3Br followed by oxidation of the product with chromium trioxide in acetone gave 18-bromoprednisone acetate (IIa, $X = \text{Br}$; 16%), m.p. 172–175° dec., $[\alpha]_D +179^\circ$, $\lambda_{\text{max}}^{\text{MeOH}}$ 239 m μ (ϵ 16,300). Similar photolysis and oxidation of 11 β -hydroxyandrost-1,4-diene-3,17-dione nitrite⁶ gave 18-bromoandrost-1,4-diene-3,11,17-trione (18%), m.p. 183–186° dec., $[\alpha]_D +212^\circ$, $\lambda_{\text{max}}^{\text{MeOH}}$ 239 m μ (ϵ 17,200).

The radical-exchange reaction has also been observed in the photolytic cleavage^{7,8} of cyclic nitrites. Thus, photolysis of cyclopentanol nitrite gave 5-bromopentanal and 5-iodopentanal in the presence of CCl_3Br and of iodine, respectively.^{9,10}

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(7) P. Kabasakalian and E. R. Townley, *J. Org. Chem.*, **27**, 2918 (1962).

(8) M. Akhtar and D. H. R. Barton, *J. Am. Chem. Soc.*, **86**, 1528 (1964).

(9) Infrared and nuclear magnetic resonance spectra and microanalytical data in accord with the structures assigned have been obtained for all new compounds.

(10) For the photolytic rearrangement of iodohydrins formed *in situ* see K. Heusler and J. Kalvoda, *Helv. Chim. Acta.*, **46**, 2732 (1963), and earlier papers there cited.

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The Absolute Configuration of Menthyl Arenesulfonates¹

Sir:

The ready availability of optically active sulfoxides by the Grignard synthesis^{2–4} has sparked new interest in the question of the absolute configuration of the precursor menthyl arenesulfonates. Andersen² assigned the (*S*)-configuration to the asymmetric sulfur in (–)-menthyl (–)-*p*-toluenesulfonate [(–)-I]⁵ by comparing the rotation of (–)-I with that of (–)-menthyl (–)-*p*-iodobenzenesulfonate [(–)-II]⁵ at the D-line; Herbrandson and Cusano⁶ had previously made a "tentative" assignment of the (*S*)-configuration to the asymmetric sulfur in (–)-II on the basis of kinetic and thermodynamic studies. Most recently, Andersen⁷ has reversed himself and has claimed the (*R*)-configuration for (–)-I and (–)-II. We now present unequivocal evidence which forces a choice between these two assignments.

Crystals of (–)-II are monoclinic with the space group $P2_1$ and a density of 1.53 g./cm.³. The cell constants are $a = 17.26 \text{ \AA}$., $b = 7.656 \text{ \AA}$., $c = 6.925 \text{ \AA}$., and $\gamma = 105.1^\circ$. This requires two molecules per unit cell. Three-dimensional intensity data were

(1) We gratefully acknowledge support by the National Science Foundation (grant GP-757) for the work conducted at New York University and by the Public Health Service (grant AM-5785) for the work conducted at the University of Chicago.

(2) K. K. Andersen, *Tetrahedron Letters*, No. 3, 93 (1962).

(3) K. Mislow, A. L. Ternay, Jr., and J. T. Melillo, *J. Am. Chem. Soc.*, **85**, 2329 (1963).

(4) C. J. M. Stirling, *J. Chem. Soc.*, 5741 (1963).

(5) The diastereomers of I and II prepared from (–)-menthol have opposite signs of rotation at the D-line; the prefixes of I and II refer to these signs.

(6) H. F. Herbrandson and C. M. Cusano, *J. Am. Chem. Soc.*, **83**, 2124 (1961).

(7) K. K. Andersen, *J. Org. Chem.*, **29**, 1953 (1964).

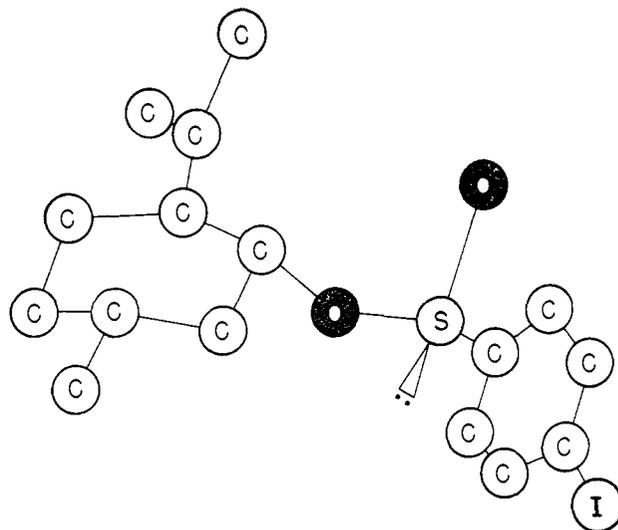


Figure 1.

collected with Mo $K\alpha$ radiation with Weissenberg geometry employing a scintillation counter for a detector. The 875 observed intensities were transformed to structure amplitudes without any correction for absorption. The structure was solved using the iodine as a heavy atom and refined with a full-matrix least-squares program.⁸

The final disagreement factor, R , was 11%. The structure is shown in Fig. 1. The standard deviations of the bond distances are quite large (0.04 \AA .); this is probably due to preferential absorption which was neglected in correcting the intensity data. The average for the benzene bond lengths is 1.38 \AA ., and for the carbon-carbon saturated bond lengths it is 1.53 \AA .

The absolute configuration around the sulfur atom can be determined in this structure because the absolute configuration of the (–)-menthyl group is known.⁹ As suggested by Mathieson,¹⁰ the absolute configuration around an atom can be determined by ordinary X-ray techniques if an internal known asymmetric reference center is present in the molecule.¹¹ In the present case our internal reference is the (–)-menthyl group. *Using the above method the absolute configuration about the sulfur atom in (–)-II is (S).*

The configurations of I and II were correlated as follows. Reaction of *p*-toluenesulfinyl chloride and (–)-menthol at -78° in ether-pyridine afforded a diastereomeric mixture of (–)-menthyl *p*-toluenesulfonates, $[\alpha]_D -38.5^\circ$ (Ia),¹² which was converted to *p*-tolyl butyl sulfoxide (IIIa), $[\alpha]_D -51^\circ$, by reaction with an excess of *n*-butylmagnesium bromide. Optically pure III, prepared from *n*-butylmagnesium bromide and diastereomerically pure (–)-I ($[\alpha]_D -206^\circ$), has $[\alpha]_D +187^\circ$. Therefore the ratio of enantiomers in IIIa is 36.4% (+)-III:63.6% (–)-III. This accurately reflects the ratio of diastereomers in precursor Ia (36.4% (–)-I:63.6% (+)-I), as shown by an ancillary experiment. A mixture ($[\alpha]_D -119^\circ$) of Ia (3.256 g.) and (–)-I (3.000 g.) was subjected to the Grignard

(8) The observed structure amplitudes and the final coordinates for the structure are available upon request from E. B. F.

(9) V. Prelog, *Helv. Chim. Acta*, **36**, 308 (1953).

(10) A. M. Mathieson, *Acta Cryst.*, **9**, 317 (1956).

(11) A pertinent example of this technique is the establishment of the absolute configuration at sulfur in (+)-methylcysteine sulfoxide (R. Hine and D. Rogers, *Chem. Ind. (London)*, 1428 (1956).

(12) Except for the *p*-toluenesulfonates, whose rotations were measured in nitrobenzene, all rotations refer to acetone solution.

reaction with *n*-butylmagnesium bromide. The product IIIb had $[\alpha]_D +63.2^\circ$ and thus was a mixture of 66.9% (+)-III:33.1% (-)-III, in perfect accord with the figures predicted from the composition of the precursor.

Reaction of *p*-iodobenzenesulfinyl chloride and (-)-menthol under identical conditions gave a diastereomeric mixture of (-)-menthyl *p*-iodobenzenesulfonates, $[\alpha]_D -20.9^\circ$ (IIa). From the rotations of the pure diastereomeric components⁶ the composition of IIa is 25.9% (-)-II:74.1% (+)-II.

In the synthesis of I and II, the (+) isomer is the more rapidly formed. Since steric factors unquestionably control the relative abundance of the diastereomeric product ratios, it follows that (-)-I and (-)-II have corresponding configurations. This conclusion is buttressed by the following observation. Reaction of 1-butanethiol and (-)-menthol at -78° gave a diastereomeric mixture of (-)-menthyl 1-butanethiols which afforded IIIc, $[\alpha]_D +99^\circ$, on treatment with *p*-tolylmagnesium bromide. Since the signs of IIIa and IIIc are opposite, it follows that the absolute configuration around sulfur in the predominant diastereomer leading to IIIa and IIIc must be the same. We shall discuss in a separate paper the relevance of the present findings to the resolution of the other discrepancy which we had earlier remarked upon.³

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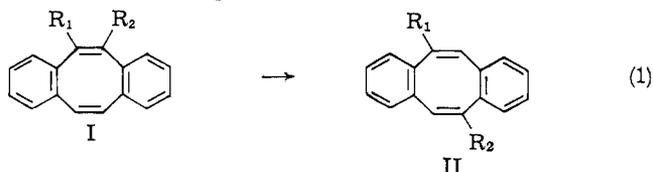
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Thermal and Photochemical Rearrangement of Substituted Dibenzo[*a,e*]cyclooctatetraenes

Sir:

5,6-Diphenyldibenzo[*a,e*]cyclooctatetraene (Ia) is available from the reaction of phenylacetylene with benzyne.¹ Heating this hydrocarbon to temperatures of 140 – 200° , either as the pure melt or as a solution in decalin or triglyme, leads to the remarkable rearrangement shown in eq. 1.²



a, $R_1 = R_2 = C_6H_5$; b, $R_1 = R_2 = p\text{-}CH_3C_6H_4$; c, $R_1 = R_2 = p\text{-}BrC_6H_4$; d, $R_1 = C_6H_5$; $R_2 = p\text{-}BrC_6H_4$; e, $R_1 = R_2 = CO_2CH_3$

Hydrocarbon IIa [λ_{max} 260 $m\mu$ (ϵ 34,700)] was formed in 96% yield. Hydrogenation (Pd-charcoal) furnished a tetrahydro derivative, m.p. 174 – 174.5° , the n.m.r. spectrum of which exhibited a ratio of aromatic:methine:methylene hydrogens equal to 18.2:2.0:3.9. Ozonization of IIa yielded *o*-benzoylbenzoic acid.

(1) M. Stiles, U. Burckhardt, and A. Haag, *J. Org. Chem.*, **27**, 4715 (1962).

(2) Satisfactory elemental analyses were obtained for all the compounds described. Melting points obtained were: Ib, 168 – 169° ; Ic, 222 – 222.5° ; Id, 197.5 – 198° ; Ie, 176.5 – 177° ; IIa, 183 – 184° ; IIb, 181 – 183° ; IIc, 204 – 204.5° ; IIId, 170 – 171° ; IIe, 187.5 – 188° .

The di-*p*-tolyl (Ib) and di-*p*-bromophenyl (Ic) compounds were prepared from benzenediazonium-2-carboxylate and the appropriately substituted phenylacetylene. Similar generation of benzyne in the presence of methyl propiolate yielded the 5,6-dicarbo-methoxy compound (Ie). An equimolar mixture of phenylacetylene and *p*-bromophenylacetylene reacted with benzyne to furnish the monobromo compound (Id) in addition to Ia and Ic. Treatment of either Ic or Id with butyllithium, followed by hydrolysis, succeeded in removing bromine to produce Ia in yields of 53% and 33%, respectively.

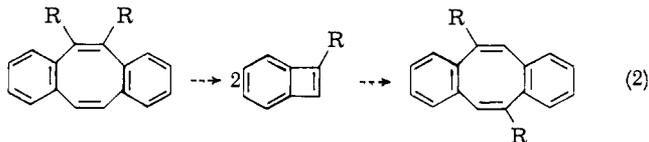
Each of the 5,6-disubstituted dibenzocyclooctatetraenes Ib–e underwent isomerization to the 5,11-isomer under conditions similar to those described for Ia. The yields of IIb–e were 93%, 87%, 95%, and 75%, respectively. Table I lists first-order rate constants and activation parameters for the rearrangement of Ia–d.

TABLE I
RATES OF REARRANGEMENT OF I TO II^a

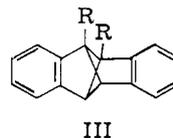
Compd.	Solvent (temp., °C.)	$10^4 k$, sec. ⁻¹	ΔH^\ddagger , kcal.	ΔS^\ddagger , e.u.
Ia	Decalin (164.5)	4.8	28.9	-13
	Triglyme (164.0)	4.6	29.1	-13
Ib	Decalin (164.9)	7.1	29.1	-12
Ic	Decalin (164.8)	5.3	31.7	-7
Id	Decalin (164.8)	4.9	30.1	-10

^a The reactions were followed by spectrometric determination of product appearance at λ_{max} . The rates were cleanly first order over the measured course of the reaction, which was one to three half-lives.

Isomerization of an equimolar mixture of Ia and Ic in triglyme at 195° produced a 99% yield of a mixture of IIa and IIc, with no contamination by IIId, as shown by thin-layer chromatography. Furthermore, the isomerization of Id yielded IIId which contained no detectable IIa or IIc. These two experiments eliminate an obvious possibility for the mechanism, a dissociation-recombination such as that of eq. 2.



A reaction path which would explain most simply the rearrangement of I to II includes the "twisted" intermediate III. The structure of III is such that reversion to the dibenzocyclooctatetraene structure could lead to either I or II. The feasibility of structure III as an intermediate may be argued from the results of Srinivasan,³ who reported that photolysis of *cis,cis*-1,5-cyclooctadiene yielded tricyclo[4.2.0.0^{2,6}]octane, which possesses the carbon skeleton central to III.



Photolysis of a solution of hydrocarbon Ia in methylcyclohexane (Hanovia lamp, Pyrex filter) at 0° produced a 36% yield of isomer IIa. The remainder was starting material, with no evidence for other isomers by thin-layer chromatography.

(3) R. Srinivasan, *J. Am. Chem. Soc.*, **85**, 819, 3048 (1963).