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OPTICAL STABILITY OF A NINE-MEMBERED RING BRIDGED BIPHENYL[1]

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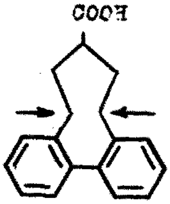
THE stereochemistry of 1,2,3,4-dibenzcyclonona-1,3-diene-7-carboxylic acid (I) is of considerable interest for several reasons. As revealed by a study of Dreiding models, interconversion of the enantiomeric forms requires that the molecule assume a transition state conformation in which two hydrogens situated on C5 and C9 (arrows) suffer a maximum in non-bonded interaction; cogwheeling is precluded by the presence of the bridge. The effect of such interactions in rigid bicyclic structures has been a subject of recent concern.[2] In addition, extensive spectroscopic investigations



I

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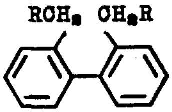
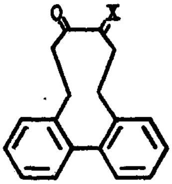
into the relation between conjugation and conformation of 2,2'-bridged biphenyls[3] make it desirable to compare the U.V. spectrum of a simple nine-membered ring compound, e.g. I, with the well-known spectra of eight-, seven- and six- ring analogs.

Previous attempts at preparation of an appropriate compound have failed.[4] We now report the synthesis of I.



II a, $R{=}COOH$; b, $R{=}CH_2COOH$
c, $R{=}CH_2COOCH_3$; d, $R{=}CH_2OH$
e, $R{=}CH_2Br$; f, $R{=}CH_2CN$
g, $R{=}CH_3$



III a, X=O
b, $X{=}N_2$

Arndt - Eistert double chain-extension of IIa (m.p. 152-153°,[5] also obtained in a polymorphic form, m.p. 174-175° [Found: C, 70.84; H, 5.33; neut. eq., 142. $C_{16}H_{14}O_4$ requires: C, 71.10; H, 5.22; neut. eq., 135]) gave IIb, m.p. 160-161° [Found: C, 72.53; H, 6.20; neut. eq., 157. $C_{18}H_{18}O_4$ requires: C, 72.46; H, 6.08; neut. eq., 149]; methyl ester (IIc), polymorphic forms, m.p. 61-62° and 74.5-75.5° [Found: 73.52; H, 6.79. $C_{20}H_{22}O_4$ requires: C, 73.60; H, 6.79]. For large scale runs, IIb was most

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[2] L. de Vries and S. Winstein, J.Amer.Chem.Soc. 82, 5363 (1960); S. Winstein and R.L. Hansen, Ibid. 82, 6206 (1960); L. de Vries and P.R. Ryason, J.Org.Chem. 26, 621 (1961).

[3] G.H. Beaven, D.M. Hall, M.S. Lesslie and E.E. Turner, J.Chem.Soc. 854 (1952) et seq.

[4] G.H. Beaven, G.R. Bird, D.M. Hall, E.A. Johnson, J.E. Ladbury, M.S. Lesslie and E.E. Turner, J.Chem.Soc. 2709 (1955).

[5] J. Kenner and E.G. Turner, J.Chem.Soc. 2101 (1911); R. Weitzenböck, Monatsh. 34, 193 (1913).

conveniently prepared from IIa by $LiAlH_4$ reduction of the ethyl ester to IId, m.p. 88-89° [Found: C, 79.11; H, 7.32. $C_{16}H_{18}O_2$ requires: C, 79.31; H, 7.49], conversion to IIe, m.p. 48-49.5° [Found: C, 52.11; H, 4.19; Br, 43.37. $C_{16}H_{16}Br_2$ requires: C, 52.20; H, 4.38; Br, 43.42], with PBr_3 in benzene, conversion to IIf, m.p. 51-52° [Found: C, 82.97; H, 6.19; N, 10.59. $C_{18}H_{16}N_2$ requires: C, 83.04; H, 6.20; N, 10.76], with NaCN, and acid hydrolysis of IIf. Reductive ring closure of IIc with sodium in xylene yielded crude acyloin, oxidation of which with bismuth oxide gave IIIa, (25% overall yield from IIc) m.p. 202-203° [Found: C, 81.60; H, 6.09; mol. wt., 248. $C_{18}H_{16}O_2$ requires: C, 81.79; H, 6.10; mol. wt., 264]; quinoxaline derivative, m.p. 151-152° [Found: C, 85.78; H, 5.93; N, 8.71; mol. wt., 319. $C_{24}H_{20}N_2$ requires: C, 85.68; H, 5.99; N, 8.33; mol. wt., 336]. Treatment of the *p*-toluensulfonylhydrazone of IIIa with base gave diazoketone IIIb.

The photochemical Wolff rearrangement has been useful in ring contractions of classical[6] and of medium membered[7] rings. In the present case, IIIb was rearranged both thermally and photochemically (mercury source) (65%) to I, m.p. 137-138.5° [Found: C, 81.01; H, 6.68; mol. wt., 258. $C_{18}H_{18}O_2$ requires: C, 81.17; H, 6.81; mol. wt., 266]; *p*-toluide, m.p. 184-185° [Found: C, 84.69; H, 7.34; N, 4.19; mol. wt., 347. $C_{25}H_{25}NO$ requires: C, 84.47; H, 7.09; N, 3.94; mol. wt., 355]. The acid was optically activated by a second order asymmetric transformation[8] *via* the quinidine salt in

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[6] L. Horner and E. Spietschka, *Chem.Ber.* **88**, 934 (1955); T.H. Colby, Ph.D. Dissertation, Univ.of Washington, 1957; W. Kirmse, *Angew. Chem.* **69**, 106 (1957); W. Kirmse, L. Horner and K. Muth, *Chem.Ber.* **91**, 430 (1958); M.P. Cava, R.L. Litle and D.R. Napier, *J.Amer.Chem. Soc.* **80**, 2257 (1958); J. Meinwald and P.G. Gassman, *Ibid.* **82**, 2857 (1960); *Idem*, *Ibid.* **82**, 5445 (1960); J. Meinwald and E.G. Miller, *Tetrahedron Letters* No. 7, 253 (1961).

[7] L. Friedman, A. Rosegay and R.L. Litle, private communication.

[8] M.M. Harris in W. Klyne and P.B.D. de la Mare, *Progress in Stereochemistry* Vol. 2, p. 158. Academic Press, New York (1958).

acetone; the liberated acid had $[\alpha]_D^{28}$ - 48° (c 1.0, benzene) and racemized in o-xylene according to the expression $k_1 = 10^{12.5}e^{-24.0/RT}$ ($t_{0.5}^{50.0}$ 53 min). The optical stability of the molecule, which is chiefly the outcome of directed interaction between non-bonded hydrogens, is comparable to that of the corresponding seven-[9] and eight-[10] membered ring bridged biphenyls whose resistance to racemization is to a greater (and compensating) extent accounted for in terms of angle strain. A more quantitative discussion is reserved for the detailed paper.

In relation to the lower ring homologs, the biphenyl conjugation band of I [shoulder at 231 mμ (3.74)] has suffered a pronounced drop in extinction and a hypsochromic shift. The spectrum of I is markedly similar to that[11] of the open-chain analog IIg, including the long wave length features. Clearly, the angle of torsion in I has been significantly increased. The present work also firmly supports the view[12] that the assignment[13] of the 281 m band in phenyldihydrothebaine as a "diphenyl band" is in error.

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[9] D.C. Iffland and H. Siegel, J.Amer.Chem.Soc. 80, 1947 (1958).

[10] L.V. Dvorken, R.B. Smyth and K. Mislow, J.Amer.Chem.Soc. 80, 486 (1958).

[11] P.M. Everitt, D.M. Hall and E.E. Turner, J.Chem.Soc. 2286 (1956).

[12] D.M. Hall and F. Minhaj, J.Chem.Soc. 4584 (1957); cf. R. Robinson, Nature,Lond. 160, 815 (1947).

[13] E.A. Braude and W.F. Forbes, J.Chem.Soc. 3776 (1955).