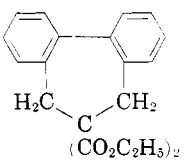
Communications TO THE EDITOR

Optical Activity in a Biphenyl Which has only A 2,2′-Three-carbon-atom Bridge

Sir:

While substituted biphenyls having 2,2′-three-atom bridges *as well as* large 6,6′-substituents have been resolved,[1] attempts to resolve 2,2′-bridged biphenyls devoid of 6,6′-substituents have been unsuccessful.[1,2,3]

We wish to report the preparation of optically active 6,6-dicarbethoxydibenzo[*a*,*c*]-1,3-cycloheptadiene, I, and the observation that this optically active substance has the 249 mμ band in its ultraviolet absorption spectrum as has biphenyl.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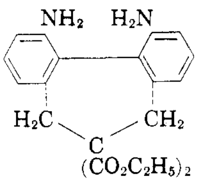
II

This band is generally assigned to inter-ring conjugation and, heretofore, interpreted as necessitating coplanarity of the two aromatic rings.[4] The extension of this interpretation to the spectrum of I would preclude enantiomorphism even though Fisher-Taylor-Hirschfelder models indicate a nonplanar configuration for the molecule.

Optically active (+) 6,6′-dinitrodiphenic acid[5] was converted *via* conventional reactions into (−) 1,11 - diamino - 6,6 - dicarbethoxydibenzo[*a*,*c*] - 1,3-cycloheptadiene (II), m.p. 111–113°; $[\alpha]^{32.5}$ −25.4° (l = 1, c, 1.062 g. in 95% ethanol). *Anal.* Calc'd for $C_{21}H_{24}N_2O_4$: C, 68.45; H, 6.57; N, 7.60. Found: C, 68.33; H, 6.42; N, 7.60. Then 2 g. of diamine II with 1.3 g. of powdered cuprous oxide was added to 67 ml. of 50% aqueous hypophosphorous acid and cooled to −15°. With vigorous stirring, a solution of 1.1 g. of sodium nitrite dissolved in 5 ml. of water was slowly added and the temperature was maintained at −15°. After two hours the reaction mixture was warmed to about 5° and extracted with cyclohexane. After washing with dil. sodium hydroxide, the dried solution was chromatographed on an alumina column and developed with cyclohexane containing 2% ethanol. The colorless eluate was evaporated under a vacuum to leave 0.8 g. of colorless I, m.p. 64–66°. *Anal.* Calc'd for $C_{21}H_{22}O_4$: C, 74.53; H, 6.57. Found: C, 74.51; H, 6.57. This, on being dissolved in cyclohexane gave an active solution; $\alpha_D^{32.5}$ +0.18°, $[\alpha]_D^{32.5}$ +2.25°, which became inactive after about five hours at this temperature. The ultraviolet and infrared absorption spectra of I obtained from the optically active cyclohexane solution were identical with those obtained from authentic racemic I (m.p. 64–66°) prepared from diphenic acid.

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[3] 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.*, 2708 (1955).

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[5] A. W. Ingersoll and J. R. Little, *J. Am. Chem. Soc.*, **56**, 2123 (1934).

8-Isotestosterone

Sir:

We have recently described[1] the synthesis of 8-isoprogesterone, a stereoisomer of the natural hormone which still retained appreciable biological activity. Inversion of configuration at C-8 carries with it a major conformational change since either ring B or ring C must now assume a boat conformation and it has also been found that striking rotatory dispersion changes[2] are associated with this stereochemical alteration. In view of the great current interest in androgen analogs[3] we would like to report the synthesis of 8-isotestosterone (VI) and its preliminary biological examination.

The eleven-step synthesis of Δ^{16}-8α-allopregnen-3β-ol-20-one acetate (I) from diosgenin has already been recorded.[1] Beckmann rearrangement[4] of its oxime with *p*-acetamidobenzenesulfonyl chloride in pyridine solution followed by hydrolysis yielded 8α-androstan-3β-ol-17-one (II), m.p. 151–153°,

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[2] C. Djerassi, R. Riniker, and B. Riniker, *J. Am. Chem. Soc.*, **78**, November (1956).

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