

## Unsaturated Macrocyclic Compounds. Part LXXXVIII.<sup>1</sup> Monodehydro-[24]annulene

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The partial catalytic hydrogenation of 1,7,13,19-tetrahydro[24]annulene to [24]annulene is shown to give monodehydro[24]annulene as a by-product.

A NUMBER of annulenes have been obtained by the partial catalytic hydrogenation of dehydroannulenes.<sup>2</sup> For instance, 1,7,13-tridehydro[18]annulene and 1,7,13,19-tetrahydro[24]annulene have been hydrogenated to [18]annulene and [24]annulene, respectively.<sup>3</sup> Surprisingly, in these cases involving the hydrogenation of polydehydroannulenes, we could not isolate a dehydroannulene containing fewer acetylenic bonds than the starting material, even when a deficit of hydrogen was used. It has now been found that in the catalytic hydrogenation of 1,7,13,19-tetrahydro[24]annulene [*e.g.* (1)] to [24]annulene [*e.g.* (2)], monodehydro[24]annulene [*e.g.* (3)] is formed as a by-product.

The hydrogenation of 1,7,13,19-tetrahydro[24]-

annulene<sup>4</sup> was carried out essentially as described previously,<sup>3</sup> except that a 10% palladium-calcium carbonate catalyst was used instead of a Lindlar catalyst. The reaction was terminated when 6.5 mol. equiv. of hydrogen had been absorbed, and the resulting material was chromatographed on alumina coated with 1% silver nitrate.<sup>5</sup> This adsorbent proved to be superior to the previously employed alumina,<sup>3</sup> and the product could be smoothly separated into [24]annulene (12%), monodehydro[24]annulene (1.2%), and unchanged tetrahydro[24]annulene (28%).

The new substance crystallized as red-violet needles. A monodehydro[24]annulene structure was indicated by the mass spectrum, which showed the empirical formula

<sup>3</sup> F. Sondheimer, R. Wolovsky, and Y. Amiel, *J. Amer. Chem. Soc.*, 1962, **84**, 274.

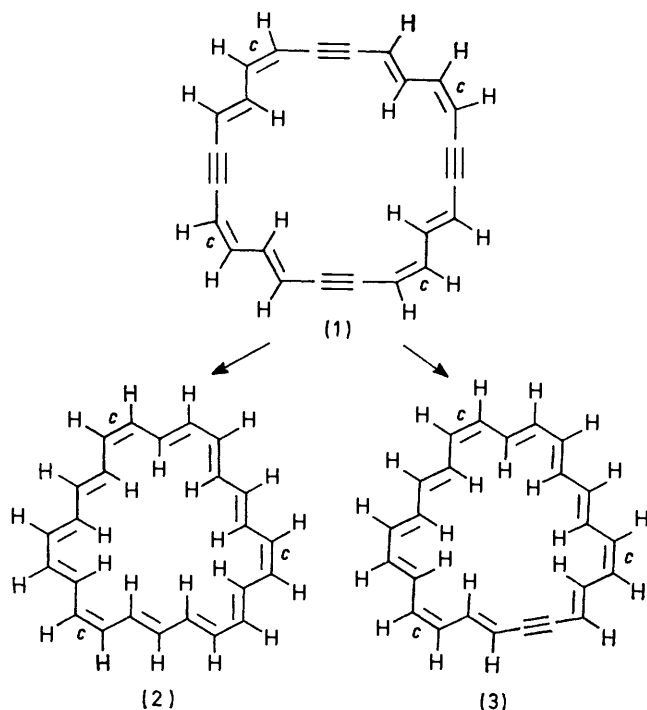
<sup>4</sup> F. Sondheimer and R. Wolovsky, *J. Amer. Chem. Soc.*, 1962, **84**, 260.

<sup>5</sup> See R. Wolovsky, *J. Amer. Chem. Soc.*, 1965, **87**, 3638.

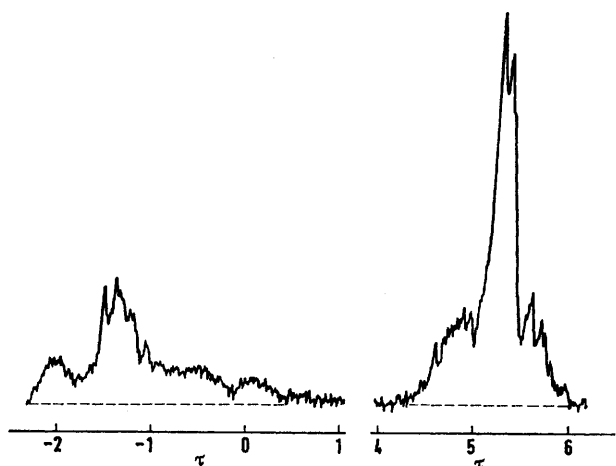
<sup>1</sup> A. B. Holmes, and F. Sondheimer, *Chem. Comm.*, 1971, 1434 is considered to be Part LXXXVII.

<sup>2</sup> For a review, see F. Sondheimer, *Proc. Roy. Soc.*, 1967, **297**, A, 173.

to be  $C_{24}H_{22}$ . The i.r. spectrum, which exhibited a weak acetylenic band at  $2175\text{ cm}^{-1}$ , was consistent with this



formulation. The electronic spectrum (in benzene) showed a shoulder at  $356\text{ nm}$  ( $\epsilon\ 135,000$ ) and a maximum at  $370\text{ nm}$  ( $156,000$ ), with absorption beyond  $600\text{ nm}$ . This



N.m.r. spectrum (100 MHz) of monodehydro[24]annulene (*e.g.* (3)) in  $[^2\text{H}_8]$ tetrahydrofuran at  $-80^\circ$ , obtained by use of a time-averaging computer (internal standard  $\text{Me}_4\text{Si}$ )

spectrum is similar to that of [24]annulene [main maxima (in benzene) at  $360\text{ nm}$  ( $\epsilon\ 183,000$ ) and  $375\text{ nm}$  ( $195,000$ )],<sup>3</sup> the small hypsochromic shift and reduced

<sup>6</sup> See F. Sondheimer, D. A. Ben-Efraim, and Y. Gaoni, *J. Amer. Chem. Soc.*, 1961, **83**, 1682.

<sup>7</sup> I. C. Calder and F. Sondheimer, *Chem. Comm.*, 1966, 904.

intensity of the dehydro-compound being expected for the introduction of an acetylenic bond.<sup>6</sup>

The n.m.r. spectrum of monodehydro[24]annulene at  $-80^\circ$  (Figure) consisted of complex multiplets at  $\tau\ -2.4\text{--}0.4$  and  $4.3\text{--}6.0$  (the room temperature spectrum was similar, but was less well resolved). The integrated areas of the low- and high-field bands were in the ratio *ca.* 8 : 14. The integration shows the bands to be due to the inner and outer protons, respectively, and indicates a 'tri-cis' structure, such as (3). The relative positions of the two bands are similar to those of [24]annulene (inner protons,  $\tau\ -2.9\text{--}1.2$ ; outer protons,  $4.8\text{--}5.8$ ).<sup>7</sup> They clearly demonstrate the existence of a paramagnetic ring current, as expected of a 24 out-of-plane  $\pi$ -electron system.<sup>8</sup>

#### EXPERIMENTAL

*Preparation of 1% Silver Nitrate-coated Alumina.*—A solution of silver nitrate (5 g) in distilled water (500 ml) was added to alumina (500 g; Woelm neutral, activity I) in a round-bottomed flask, and the mixture was shaken. The water was then evaporated off under reduced pressure (water pump) on a boiling-water bath. The residue was then heated under reduced pressure for a further 3 h.

*Monodehydro[24]annulene and [24]Annulene.*—A solution of crystalline 1,7,13,19-tetrahydro[24]annulene<sup>4</sup> (250 mg) in benzene (150 ml) was stirred vigorously in hydrogen over 10% palladium-calcium carbonate (500 mg; Fluka; previously saturated with hydrogen) at  $24^\circ$  and 758 mmHg. The reaction was terminated when 130 ml (6.5 mol. equiv.) of hydrogen had been absorbed (*ca.* 10 min). The catalyst was filtered off and washed and the filtrate was evaporated under reduced pressure in a water-bath at *ca.*  $40^\circ$ . The residue was dissolved in ether (5 ml) and chromatographed on a column of 1% silver nitrate-coated alumina (180 g), prepared with ether. Three separate coloured bands (I, II, and III) were observed to move down the column. Band I, eluted with ether, was unchanged tetrahydro[24]annulene (71 mg, 28%). Band II, also eluted with ether, was monodehydro[24]annulene (3.0 mg, 1.2%; determined spectroscopically). Band III, eluted with ether and ether-benzene (1 : 1), was [24]annulene (30 mg, 12%; determined spectroscopically).

The experiment was carried out four times, and the combined monodehydro[24]annulene fractions were evaporated under reduced pressure. Crystallization from ether-pentane gave the pure *monodehydro-compound* (7 mg) as red-violet needles, which decomposed on attempted m.p. determination (Found:  $M^+$ , 310.1719.  $C_{24}H_{22}$  requires  $M$ , 310.1721);  $\lambda_{\text{max}}$  (benzene), see Discussion;  $\lambda_{\text{max}}$  (ether) 344sh and 354 nm;  $\nu_{\text{max}}$  (KBr) 2175w and 1000s  $\text{cm}^{-1}$ ; n.m.r. spectrum, see Discussion and Figure.

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<sup>8</sup> J. A. Pople and K. G. Untch, *J. Amer. Chem. Soc.*, 1966, **88**, 4811; F. Baer, H. Kuhn, and W. Regel, *Z. Naturforsch.*, 1967, **22a**, 103; H. C. Longuet-Higgins, in 'Aromaticity,' *Chem. Soc. Special Publ.*, 1967, No. 21, p. 109.