

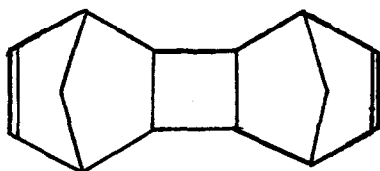
DIMERIZATION OF BICYCLOHEPTADIENE BY METAL CARBONYLS

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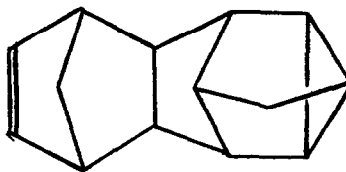
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REACTION of [2:2:1]-bicycloheptadiene with iron pentacarbonyl, di-iron nonacarbonyl, tri-iron dodecacarbonyl or dicobalt octacarbonyl gives similar mixtures of metal-free products from which we have isolated in a pure state five ketones¹ and four dimeric hydrocarbons (two more dimers are produced by nickel tetracarbonyl¹). From chemical and spectroscopic evidence we formulate the dimer melting at 68.5-69° (20% yield) as the endo-trans-endo isomer of structure (I) (nickel carbonyl yields the exo-trans-exo isomer,¹ m.p. 92-93°). One liquid dimer (8% yield), containing a bicycloheptene and a nortricyclene unit, has structure (II); another liquid dimer (1% yield) may be the other stereoisomer of II, although other possibilities are not excluded. But probably the most remarkable product is the highest-melting dimer (m.p. 163-164°, yield 4%), easily separated because it is the first



I



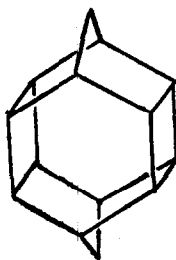
II

¹ C.W. Bird, R.C. Cookson and J. Hudec, Chem. & Ind. 20 (1960); R.C. Cookson, R.R. Hill and J. Hudec, Ibid. 589 (1961).

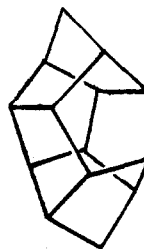
to be eluted from a column of silica gel.²

This dimer (Found: C, 91.11; H, 8.70; M.W. in freezing benzene, 179. $C_{14}H_{16}$ requires: C, 91.25; H, 8.75; M.W., 184) is saturated by the usual chemical tests and is almost transparent down to 200 m μ . The infra-red spectrum, which is relatively simple, has no band where cis double bonds usually absorb and also lacks the bands at 3100 and 800-815 cm^{-1} usually characteristic of nortricyclenes. The stability to strong acid makes the presence of a nortricyclene group even more unlikely, and the possibility of a hydrogen atom on a cyclopropane ring in the molecule is eliminated by the absence of proton resonance at fields higher than 8.3 τ . In fact the proton resonance spectrum (kindly measured by Dr. L. Pratt) consists of only two unresolved peaks at 7.62 and 8.245 τ , in the ratio of 3:1, corresponding to tertiary and secondary protons.

Neglecting structure involving extensive and improbable rearrangements, we must consider two possible formulations of the saturated dimer: two molecules of the monomer might unite face to face to give III, or at right angles to one another to give IV. The dimer was quite unchanged by passage



III



IV

² This dimer has also been made by Dr. Lemal and Mr. Shim, whom we thank for their courtesy in agreeing to this simultaneous publication of results.

through a silica tube at 500° with a contact time of 30 sec. This stability to heat, and the lack of splitting in the resonance signal from the tertiary protons under high resolution, while not entirely excluding III, do argue strongly in favour of IV.

The dimer (IV) is formed, with the other products, when bicycloheptadiene is boiled with iron pentacarbonyl in light, but it is also formed (in about the same yield) with di-iron nonacarbonyl at room temperature in the dark. The ability of light to induce this reaction with iron pentacarbonyl may, then, depend merely on its well known promotion of loss of carbon monoxide to give the more reactive monacarbonyl.³

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³ J. Dewar and H.O. Jones, Proc. Roy. Soc. A **79**, 66 (1906).