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FOUR C$_9$H$_{10}$ POLYCYCLIC OLEFINS

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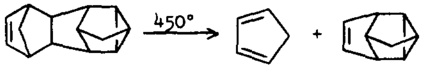
In view of the very marked interest in polycyclic olefins(1) and their photochemical,(2) thermal(3) and cationic(4) reactions, we would like to report the synthesis of four new C$_9$H$_{10}$ olefins: tetracyclo(3.2.1.1^{3,8}.0^{2,4})non-6-ene (I), bicyclo(4.2.1)nona-2,4,7-triene (II), and both exo- (IIIa) and endo- (IIIb) isomers of tricyclo(4.2.1.0^{2,5})nona-3,7-diene. Compounds (I), (II) and (IIIa) can be prepared in good yields by pyrolyzing the appropriate bicyclo(2.2.1)hepta-2,5-diene dimer (IV) or (V), eq 1 and 2. The reactions were carried out by passing bicycloheptadiene dimer through a heated Pyrex tube and gave the nonenes and cyclopentadiene in equal molar amounts. The diene (IIIa) rearranges to the triene (II) under the pyrolysis conditions and hence (II) is favored by longer reaction times or higher temperatures, 450 vs. 280°. At 350° and olefin residence time of 8 sec, the product ratio of (II) to (IIIa) was 4:1. Temperatures above 525° are less desirable for preparing (II) and



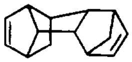
(IV) (I) (1)

(V) (II) exo isomer (IIIa) (2)

(IIIa) since further rearrangements occur giving allylbenzene and other by-products.

The dimerization of bicycloheptadiene to the requisite starting dimers has been described using Fe(0),(5) Ni(0)(6) or Co(0)(7,5c) catalysts or agents. Iron(0) gives the best yields of dimer (IV) whereas nickel(0) catalysts are best for preparing (V). Only the three _trans_ isomers of (V) are known(7) (i.e., the _exo-exo_, _endo-exo_, and _endo-endo_ isomers). The _endo-trans-exo_ isomer (or the _endo-trans-endo_) pyrolyzes more easily than the _exo-trans-exo_ and hence is much preferred as a starting material.

We have found that the bicycloheptadiene dimer "tentatively" assigned by Cookson and co-workers(6a) as (VI) is instead the _endo-trans-exo_



(VI)

isomer of (V). Their preparation involved using nickel carbonyl as the dimerizing agent. This reassignment of structure has further importance since a number of subsequent investigators(6a,5c) have followed Cookson's assignment in describing the dimers obtained by using various nickel and cobalt catalysts. We have prepared the dimer thought to be (VI) by the nickel carbonyl method and found its NMR spectrum to be identical with that of the _endo-trans-exo_ isomer of (V). Arnold and co-workers,(7) using a cobalt catalyst, prepared this same isomer and published its NMR spectrum, and we concur in this assginment both from our own NMR data and the chemistry associated with its pyrolysis. Also the infrared spectrum of this isomer when obtained by us has been found identical with Cookson's spectrum for compound (VI) in further confirmation of this reassignment.*

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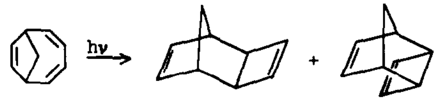
* This comparison was made by G. N. Schrauzer between our spectrum supplied to him and his particular spectrum which had earlier been compared and found identical with that of Cookson.(6b) G. N. Schrauzer, personal communication.

The following example illustrates the preparative method. A liquid comprised of 82.9% (IV) (two isomers) and 17.1% (V) (14.4% *exo-trans-exo* and 2.7% *endo-trans-exo*) was introduced at the rate of 9.8 g/hr with nitrogen as a carrier gas (22 ml/min) through a 17 cm long (13 ml volume) vertical Pyrex tube heated at 450°C and the product collected in a dry-ice cooled trap. With an average residence time of 8 sec in the hot tube, all of (V) and 77% of (IV) pyrolyzed. The product contained, on a mole basis, 50% cyclopentadiene, 37% (I), 11% (II) and 2% other nonenes. The cyclopentadiene was removed under reduced pressure in a rotary evaporator at 0-25° to prevent its dimerization, and the tetracyclononene (I) (bp 44°C/ 19 mm, N_D^{20} 1.5055) was separated by distillation through a spinning-band column. After purification by vpc (I) had a N_D^{20} 1.5050, D_4^{20} 1.007 g/ml, fp -35.0°. The diene (IIIa) was not isolated at 450°, but at 350° the ratio of (II) to (IIIa) was 4:1. Since (IIIa) has a boiling point close to (I), it was advantageous to eliminate (IIIa) by operating at 450° where it completely isomerized to (II).

Properties of the other olefins were for the triene (II), bp 81°/ 105 mm, N_D^{20} 1.5375, D_4^{20} 0.9706, fp -9.27°, and, for the diene (IIIa), bp 102°/105 mm N_D^{20} 1.5000, D_4^{20} 0.9647, fp -81.5°.

Ultraviolet irradiation of the triene (II) in acetone$^{(2d)}$ gave both the *exo*-(IIIa) and *endo*-(IIIb) tricyclononadienes as two of the major products, eq 3. These were separated by vpc with a 30% carbowax 20M on



(3)

(II) (IIIa) 13% (IIIb) 20%

Chromosorb P column at 158°. Having both isomers facilitated making the stereochemical assignments from their NMR spectra. Compound (IIIb) was a solid with mp of about 28°.

Mass spectra of the four new compounds established the MW of each as 118 which corresponds to a C_9H_{10} hydrocarbon.

Structural assignments consistent with NMR spectra were based on data taken at 60 and 100 MHz which included spin decoupling and determination of coupling constants. Some of the observed NMR parameters were as follows (tetramethylsilane as internal reference): The spectrum of (I) showed δ = 5.99 (triplet, 2 H), 2.54 (triplet, 2 H), 1.89 (multiplet, 1 H), 1.67 (multiplet, 1 H) 1.52 (triplet, 2 H) 1.20 (multiplet pair 2 H); that for (II), 6.05 and 5.87 (overlapping multiplets, 4 H), 5.17 (multiplet, 2 H), 3.08 (triplet, 2 H), 1.92 (4 multiplets, 1 H), 1.30 (doublet, 1 H); the spectrum of (IIIa), 6.18 (singlet, 2 H), 6.03 (triplet, 2 H), 2.35 (complex multiplet, 4 H), 1.55 (complex doublet, 1 H), 1.26 (complex doublet, 1 H); and the spectrum of (IIIb), 5.84 (singlet, 2 H), 5.76 (triplet, 2 H), 2.94 (doublet, 2 H), 2.54 (complex multiplet, 2 H), 1.85 (complex doublet, 1 H), 1.49 (complex doublet, 1 H). An AB quartet for the methylene bridge protons is observed up field in spectra for (II), (IIIa) and (IIIb).

A difference in the coupling constant, J, between the two non-equivalent allylic protons was used as one means of distinguishing between the exo and endo isomers of (III). This coupling constant was $\leq$ 1 Hz for the isomer assigned the exo structure (IIIa) and 3.5 Hz for the endo isomer (IIIb). Models indicate that the dihedral angle between these two allylic protons is about 75° in (IIIa) and 40° in (IIIb). The Karplus relationship(8) would then predict that J should be about 1 Hz for the exo and about 5 Hz for the endo isomer. The above assignments are thus consistent with these predictions.

The IR spectrum of (I) has a strong absorption band at 12.24 microns as expected for a nortricyclene structure,(9) and (II) shows a band at 257 mμ (ϵ_{max}, 4740) due to the conjugated diene.

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