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THE REACTION OF CHLOROFORM AND SODIUM METHOXIDE WITH CYCLOOCTENE, 1,5-CYCLOOCTADIENE AND 1,3,6-CYCLOOCTATRIENE

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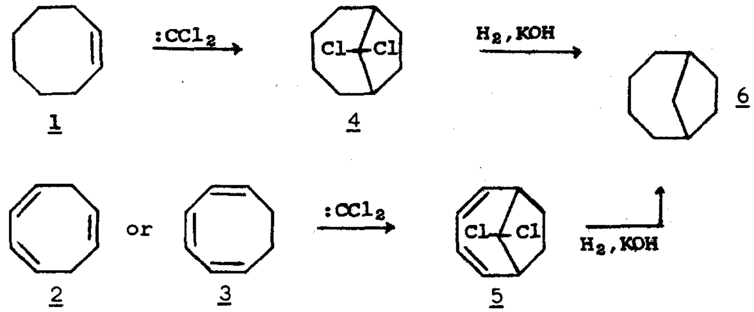
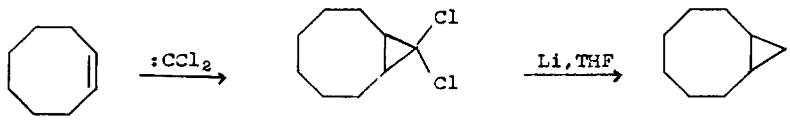
It was recently reported that dichlorocarbene, as generated from chloroform and sodium methoxide, adds to an excess of cyclooctene (1), 1,3,6-cyclooctatriene (2), and 1,3,5-cyclooctatriene (3), as well as assorted alkyl, cycloalkyl, aryl and alkoxy derivatives, to give products with the bicyclo[4.2.1]nonane skeleton.[1] Thus, the products from 1 and 2 (or 3) were claimed to be 4 and 5, respectively[1].



Sanne and Schlichting claimed that catalytic hydrogenation of 5 gave 4, and that hydrogenation of 4 or 5 in the presence of Raney Nickel and potassium hydroxide gave the saturated hydrocarbon bicyclo[4.2.1]nonane, 6.[1a,b] This unusual course of events is unprecedented in carbene chemistry,[2] and is difficult, if not impossible, to rationalize mechanistically, since all experience leads to the prediction that the products should have the bicyclo[6.1.0]nonane skeleton. Surprisingly, work that was published since the original report of Sanne and Schlicting on the same or related reactions carried no comments on these unusual reactions.[3-6] We have studied the reactions of 1, 2 and 1,5-cyclooctadiene (7) with chloroform and sodium methoxide, duplicating the conditions given by Sanne and Schlicting[1a] as closely as possible, and have concluded that their structure assignments are uniformly incorrect, as the products of these reactions do, in fact, have the bicyclo[6.1.0]nonane skeleton.

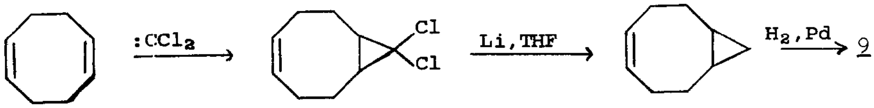
The product from cyclooctene (1) was homogeneous by g.l.c., and was saturated according to its n.m.r. spectrum. The physical constants, b.p. 89-90° (5.5 mm.), $n^{27}D$ 1.4983, agree roughly with those reported by Sanne and Schlicting for their adduct 4, b.p. 62-63° (0.3 mm.), $n^{25}D$ 1.5058.[1a] Dechlorination of our adduct with lithium in tetrahydrofuran[7] gave a product, b.p. 88-89° (68 mm.), $n^{24.5}D$ 1.4672, which was homogeneous by g.l.c., and whose physical data agree with those given by Cope and Woo[6] for bicyclo[6.1.0]nonane (9), b.p. 89°(66 mm.) $n^{25.5}D$ 1.4668. This material was identical in all respects (i.r., n.m.r. and g.l.c. retention time) with authentic bicyclo[6.1.0]nonane prepared separately (<u>vide</u> <u>infra</u>). The n.m.r. spectrum of <u>9</u> showed multiplets at 1.8-2.1, 0.58 and -0.30 p.p.m. with integrated areas in the ratio of approximately 12:3:1. The position of the high field resonance(τ 10.3) is that expected for one of the geminal cyclopropane hydrogens in structure <u>9</u>, and can not be rationalized on the basis of <u>6</u>. Thus, LaLonde and Tobias[8] report that the n.m.r. spectrum of norcarane shows a multiplet (1 proton) centered at τ 10.04 and another multiplet at τ 9.1 to 9.7. Boikess and Winstein[9] generalize a number of observations with the statement that "cyclopropane rings fused to other rings commonly show one methylene proton at τ above 10 and the other three at τ <u>ca</u>.9.3." Finally, Fieser and Sachs[5] report a resonance at τ 10.2 in the bis-methylene adduct of 1,5-cyclooctadiene. Thus, the adduct from cyclooctene and CCl_2 can safely be assigned the structure <u>8</u>.



<u>1</u> <u>8</u> <u>9</u>

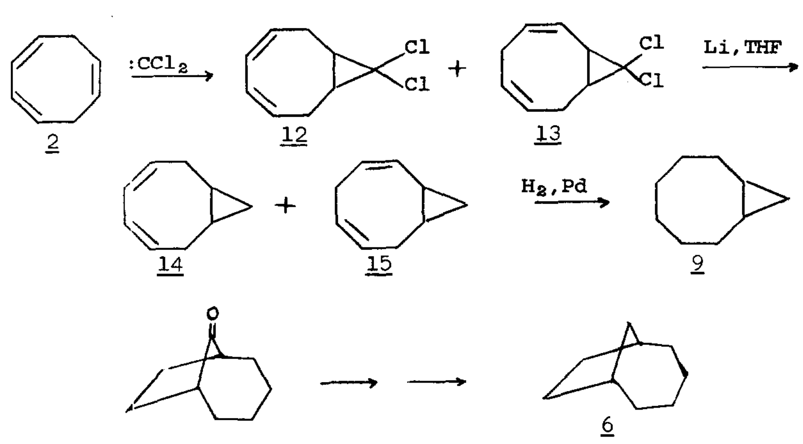
The adduct from 1,5-cyclooctadiene [<u>Anal</u>. Calc'd for $C_9H_{12}Cl_2$: C, 56.57; H, 6.28. Found C, 56.80; H, 6.38.]

was homogeneous by g.l.c., and had an n.m.r. spectrum with vinyl and saturated hydrogen in the ratio of 1:5 exactly. The physical properties of the adduct [b.p. 86-87° (2 mm.), $n^{25}D$ 1.5235] agree well with those reported for compounds assigned structure 10 without proof by Fray[3] [b.p. 111-114° (18 mm.), $n^{20}D$ 1.5243] and Farah and Gilbert[4] [b.p. 115-116° (12 mm.)]. Dechlorination[7] of our adduct gave a single compound, by g.l.c., b.p. 67° (22 mm.). Hydrogenation of the latter over palladium on charcoal (2.84 mmole) led to the uptake of 2.7 mmole of hydrogen, and the formation of 9 which was identical in all respects (i.r., n.m.r., g.l.c.) with the material derived above from cyclooctene. Thus the adduct and dechlorination product from 1,5-cyclooctadiene can be assigned structures 10 and 11, respectively.



7 10 11

The products from the reaction of 1,3,6-cyclooctatriene 2[10] and CCl_2 gave two overlapping peaks on g.l.c. analysis, with area ratios close to 1:1. The physical properties [b.p. 49-50° (0.5 mm.), $n^{25}D$ 1.5390] were close to those reported for the product of this reaction by Sanne and Schlicting[1a] [b.p. 45° (0.01 mm), $n^{25}D$ 1.5337]. The elemental analysis of our material was only fair [Anal. Calc'd. for $C_9H_{10}Cl_2$: C, 57.18; H, 5.29. Found: C, 55.07; H, 5.13]. The n.m.r. spectrum of the mixture showed vinyl and saturated hydrogens in the exact ratio of 2:3. The material reacted readily with N-phenylmaleimide to give in 17% yield an adduct, m.p. 239.5-240° (d) [Anal. Calc'd. for $C_{19}H_{17}Cl_2O_2N$: C, 63.00; H, 4.73; Cl, 18.93. Found: C, 62.88, H, 3.78; Cl, 19.47]. Dechlorination[7] of the mixture of products from the original CCl_2 addition gave material which showed four closely spaced peaks on g.l.c. analysis, and which had a complicated n.m.r. spectrum, clearly featuring a resonance above τ 10. Hydrogenation of this mixture led to the uptake of 1.3 moles of H_2 per mole of mixture (assuming composition C_9H_{12}), and formation of product which had two peaks on g.l.c. analysis in the ratio of 2.24:1. The larger of these peaks had the same retention time as 9 as obtained from 1 and 7, and was inseparable from these materials on simultaneous injection into the gas chromatograph. The n.m.r. spectrum of the hydrocarbon product obtained from the triene 2 was identical to that of 9 as obtained above, except for an additional sharp resonance at 1.5, and a weak multiplet centered at 0.80, p.p.m. Some of the original adduct from 2 was first hydrogenated and then dechlorinated to give a final hydrocarbon product showing one very strong peak on g.l.c. analysis, corresponding to 9, and only traces of other components. The n.m.r. spectrum of this sample was identical to that of 9 as obtained above. Thus, it appears that the two adducts derived from 2 and CCl_2 must be assigned structures 12 and 13, and that two of the dechlorination products are 14 and 15.



As final proof that there is no error in our structure assignments, authentic samples of bicyclo[4.2.1]nonane (6) and bicyclo[6.1.0]nonane (9) were prepared. The former was made by Wolff reduction[11] of the semicarbazone of the known bicyclo[4.2.1]nonane-9-one.[12] The semicarbazone, m.p. 204.5-205.5°, was heated in a sealed tube at 190-200° with sodium ethoxide and absolute ethanol. The product was isolated after extraction, washing and vacuum sublimation, and was a camphoraceous solid, m.p. 94-95° in a sealed capillary (reported[13] m.p. 95-96°) [*Anal*. Calcd. for C_9H_{16}: C, 87.01; H, 12.99. Found: C, 87.99; H, 12.46]. This hydrocarbon was separable on g.l.c. from the bicyclononane 9 prepared synthetically and from the olefin-dichlorocarbene adducts, and was not present even as a minor component in any of the hydrocarbon mixtures derived from the adducts. The n.m.r. spectrum of 6 shows a number of low-lying highly split multiplets in the region 0.9 to 2.6 p.p.m. with a sharp resonance at 1.45 p.p.m. and no resonance upfield from TMS. This hydrocarbon was compared directly with a sample provided by M. Hartmann, prepared by reduction of bicyclo[4.2.1]nonane-2-one,[13] and the two were found to be identical in all respects (m.p., g.l.c. retention time, i.r. and n.m.r. spectra). Hartmann reports that this hydrocarbon was also prepared by him from the 9-ketone, as well as from the 2- and 3-ketones in the bicyclo[4.2.1]nonane series.[14]

Bicyclo[6.1.0]nonane 9 was prepared by the Simmons-Smith reaction with cyclooctene, using the modification of LeGoff.[15]

Thus, the structure assignments made by Sanne and Schlicting[1] for the products of CCl_2 addition to 1 and 2 and, by implication, to the numerous other eight-ring olefin derivatives, must be discarded. Mechanistically, there is happily nothing unusual about these "carbene"[16] addition reactions which result in the expected cyclopropane derivatives.[2] Unhappily, other routes must be sought for the bicyclo[4.2.1]nonane derivatives whose synthesis originally led to this investigation.

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