VIII

IX   X

which showed absorption at τ 4.9 and 5.1 (1 H each) characteristic of the terminal methylene group. Final chemical confirmation of the structure of IX follows from its rearrangement,[5] on heating with methanolic hydrochloric acid, into the tetracyclic ketone X, m.p. 132–134° (*Anal.* Found: C, 79.53; H, 7.75), which had the typical cyclopentanone absorption at $\sim$1750 cm.$^{-1}$, while the n.m.r. spectrum showed the disappearance of vinylic absorption and the appearance of a characteristic methyl absorption at τ 9.0 (singlet, 3 H).[6]

(5) *Cf.* ref. 1a and J. F. Grove, T. P. C. Mulholland, J. MacMillan, and W. B. Turner, *J. Chem. Soc.*, 3049 (1960).

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The Direct Observation of a Norcaradiene–Cycloheptatriene Equilibrium

Sir:

Although the existence of simple norcaradiene derivatives has recently been demonstrated,[1] the question of the relationship between cycloheptatrienes and norcaradienes remained to be answered.[2,3] The presence of small equilibrium concentrations of norcaradienes has been invoked frequently to account for certain reactions of cycloheptatrienes, notably Diels–Alder additions, in which products derived from the norcaradiene structures usually are obtained.[4] Recent low-temperature n.m.r. studies of cycloheptatriene[5] and certain of its derivatives[6] uncovered no evidence for the presence of the corresponding norcaradienes.

We now wish to present evidence showing that the adduct of cyanotrifluoromethylcarbene to benzene is, at room temperature, a rapidly equilibrating mixture of

(1) E. Ciganek, *J. Am. Chem. Soc.*, **87**, 652 (1965).

(2) For a recent review of the cycloheptatriene–norcaradiene problem, see S. J. Rhoads in "Molecular Rearrangements," P. De Mayo Ed., Part 1, Interscience Publishers, Inc., New York, N. Y., 1963, pp. 700–703.

(3) In the special case of benzonorcaradiene, the inversion of the cyclopropane ring observed at elevated temperatures is believed to involve the corresponding *o*-quinonoid cycloheptatriene as an intermediate [E. Vogel, D. Wendisch, and W. R. Roth, *Angew. Chem.*, **76**, 432 (1964)].

(4) Other possible explanations are discussed by R. Huisgen and G. Juppe, *Chem. Ber.*, **94**, 2332 (1961), and in ref. 6.

(5) F. A. L. Anet, *J. Am. Chem. Soc.*, **86**, 458 (1964); F. R. Jensen and L. A. Smith, *ibid.*, **86**, 956 (1964).

(6) K. Conrow, M. E. H. Howden, and D. Davis, *J. Am. Chem. Soc.*, **85**, 1929 (1963).

7-cyano-7-trifluoromethylcycloheptatriene **(1)** and 7-cyano-7-trifluoromethylnorcaradiene **(2)**. Thermolysis of cyanotrifluoromethyldiazomethane[7] in benzene gave

1   2   3
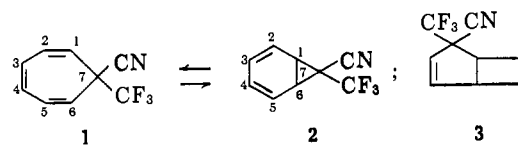
as the main product (77% yield) a colorless liquid,[8] b.p. 76° (7.5 mm.), $\lambda_{max}^{cyclohexane}$ 258 mμ (ϵ 3740) (unchanged between room temperature and $-100°$). The room temperature F^{19} n.m.r. spectrum in fluorotrichloromethane shows only one singlet at $+4125$ c.p.s. (relative to the solvent signal; 56.4 Mc.) with a width at half-height of 1.9 c.p.s.; the room temperature proton n.m.r. spectrum (same solvent) displays a complex multiplet at τ 3.2 to 3.8 (4 protons) and a doublet (separation 7 c.p.s.), split further, centered at τ 5.30 (2 protons). On lowering the temperature to *ca.* $-85°$, the singlet in the F^{19} n.m.r. spectrum broadens gradually; on further cooling, new signals of unequal intensities appear at $+4187$ and $+3760$ c.p.s. Similarly, the high-field doublet in the proton n.m.r. spectrum, on cooling, first broadens and then gives rise to two new signals, a doublet ($J = 7$ c.p.s.) centered at τ 4.60 and a fairly broad singlet (half-band width 12 c.p.s. at $-112°$), with no discernible fine structure, at τ 7.05. The areas of the τ 4.6 and 7.0 signals were in the ratio of *ca.* 80:20. The n.m.r. spectra thus show the presence of two species which are in rapid equilibrium at room temperature.[9] The major component is undoubtedly the cycloheptatriene **1** (only olefinic protons in the H^1 n.m.r. spectrum).[10] The low energy of activation for the equilibration excludes any structure but that of a valence tautomer for the minor component. The position of the τ 7.05 signal (assigned to protons 1 and 6 in structure **2**) is that expected for a norcaradiene,[1] but it is also compatible with the other valence tautomer, 4-cyano-4-trifluoromethylbicyclo[3.2.0]hepta-2,6-diene **(3)**. However, the known[11] high activation energy required for the conversion of the parent bicyclo[3.2.0]-hepta-2,6-diene to cycloheptatriene and the absence of any bicyclo[3.2.0]heptane derivatives in the hydrogenation products of the mixture of **1** and **2** (see below) strongly indicate that the second species is actually the norcaradiene **2**. The absence of a third signal in the low-temperature F^{19} n.m.r. spectrum shows that only one of the two possible isomers of **2** is present in detectable amounts.

Catalytic hydrogenation of the equilibrium mixture gave 7-cyano-7-trifluoromethylnorcarane (**4**; one isomer), 1-cyano-1-trifluoromethylcycloheptane **(5)**, and α-cyclohexyl-β,β,β-trifluoropropionitrile **(6)** in different ratios depending on the catalyst used. With rhodium,

(7) S. Proskow, to be published.

(8) All new compounds gave satisfactory elemental and molecular weight analyses.

(9) J. A. Pople, W. O. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp. 218–225.

(10) The major component **1** itself may be a rapidly equilibrating mixture of the two nonplanar 7-cyano-7-trifluoromethylcycloheptatrienes, as indicated by the observed broadening of the 4187 c.p.s. signal in the F^{19} n.m.r. spectrum on cooling to below $-112°$; the half-band width of the 3760 c.p.s. signal, assigned to **2** on the basis of its relative area, remained constant.

(11) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **12**, 186 (1961).

4   **5**   **6**
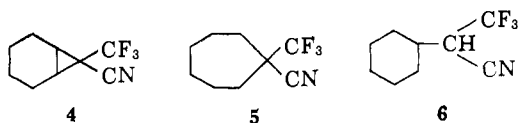
the ratio of **4:5:6** was 73:12:15, with platinum, 17:11:72. Both **4** and **6**, and probably part of **5**, are derived from the norcaradiene **2**; its apparent rate of hydrogenation thus is higher than that of the cycloheptatriene **1**. Isolation of **4** and **6** provides supporting evidence for the presence of the norcaradiene **2** in the equilibrium mixture although it constitutes no proof by itself since rearrangement of the cycloheptatriene **1** to the norcaradiene **2** could have taken place on the catalyst.[12,13]

(12) By comparison, hydrogenation of cycloheptatriene over rhodium gave only cycloheptane; less than 0.005% norcarane could have been detected. Catalytic hydrogenation of ethyl 7-cycloheptatrienecarboxylate, on the other hand, gave considerable amounts (up to 14%) of ethyl *exo*-7-norcaranecarboxylate in addition to ethyl cycloheptanecarboxylate and traces of ethyl cyclohexylacetate. The chemical shift of the protons on C-1 and C-6 in ethyl 7-cycloheptatrienecarboxylate (triplet at τ 4.63 in CFCl$_3$), however, is essentially the same as the corresponding shift in cycloheptatriene (τ 4.72 in CDCl$_3$); the equilibrium concentration of ethyl 7-norcaradienecarboxylate thus must be very small. Details will be described in a forthcoming publication.

(13) The adduct of bis(trifluoromethyl)carbene to benzene has recently been shown to have the cycloheptatriene structure: D. M. Gale, W. J. Middleton, and C. G. Krespan, *J. Am. Chem. Soc.*, **87**, 657 (1965).

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The Thermal Vapor-Phase Rearrangement of 1,5-Hexadien-3-ol. Preparation of 5-Hexenal[1]

Sir:

Berson and Jones[2] have recently reported the rearrangement of two pairs of epimeric 3-hydroxy-1,5-hexadienes in the bicyclo series to the corresponding δ,ε-unsaturated ketones according to the scheme
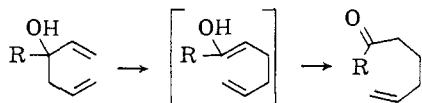
and have suggested the term "oxy-Cope rearrangement" for this transformation. These communications prompt us to report our studies on the parent compound, which is devoid of the complications inherent in a bicyclic system.

We were originally interested in a facile preparation of 1,3,5-hexatriene from 1,5-hexadien-3-ol (I), readily available *via* reaction of the allyl Grignard reagent and acrolein.[3]

Although it has been postulated[4] that the dehydration of any of the six isomeric hexadienols would give hexatriene, the only previously reported attempt[5] at vapor-phase dehydration of I resulted in resins.
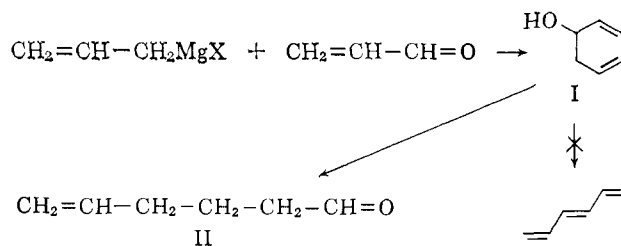
(1) From the M.S. Thesis of L. Levasseur, June 1964.
(2) J. A. Berson and M. Jones, Jr., *J. Am. Chem. Soc.*, **86**, 5017, 5019 (1964).
(3) L. W. Butz, E. W. Butz, and A. M. Gaddis, *J. Org. Chem.*, **5**, 171 (1940).
(4) J. M. Shackelford, W. A. Michalowicz, and L. H. Schwartzman, *ibid.*, **27**, 1631 (1962).
(5) O. Kiun-Houo, *Ann. Chim.*, **13**, 175 (1940).

$$CH_2=CH-CH_2MgX \ + \ CH_2=CH-CH=O \ \longrightarrow$$

I

$$CH_2=CH-CH_2-CH_2-CH_2-CH=O$$

II

When we passed the vapors of I through a 25-cm. column filled with 8–20 mesh alumina, maintained at 300° in a nitrogen atmosphere, we were able to detect minute traces of hexatriene in the product by means of its characteristic ultraviolet spectrum. Vapor phase chromatography indicated two main constituents in that fraction of the product boiling above 80°, one of which was shown to be surviving I. The second component, II, appeared to be an unsaturated aldehyde. When the dehydration attempt was repeated at 400°, none of I appeared to survive. Subsequent trials indicated that alumina was not necessary for the reaction[6]; indeed, a column packed with glass wool gave the same percentage of II in the higher boiling fraction and much less low boiling material. Under optimum conditions for the transformation of I → II (distillation of I through a 50-cm. column packed with 3-mm. Pyrex helices and maintained at 380°) 92%[7] of the product fraction boiling above 80° consisted of II. This corresponds to an over-all yield of 57% based on I.

The structure of the rearrangement product II is based on the following evidence. Molecular weight determinations and carbon–hydrogen analyses of the compound and its 2,4-dinitrophenylhydrazone were consistent with the formula $C_6H_{10}O$. The compound reduced Tollens' reagent and gave positive Schiff and Baeyer tests. The infrared spectrum exhibited a strong carbonyl band (in cm.$^{-1}$) at 1735, an aldehydic C–H band at 2700, and bands consistent with an isolated terminal vinyl group at 915, 995, 1300, 1420, 1650, and 3075. The ultraviolet spectrum consisted only of end absorption in the 220–230 mμ region, no further maxima in the region below 280 mμ, and only a small ill-defined peak (ε <10) at about 290 mμ. Further chemical structure proof seemed essential since our other physical constants[8] were not in sufficient agreement with the two reported preparations[9,10] of 5-hexenal. We were particularly concerned with the unambiguous determination of the linearity of the carbon chain and the position of unsaturation. Consequently, the compound was found to absorb 102% of the amount of hydrogen (over Pd–C) calculated for the saturation of one double bond, and the 2,4-dinitrophenylhydrazone derivative of the hydrogenation product showed no melting point depression on admixture with an authentic sample of the same derivative

(6) We initially experienced some difficulty with vapor phase chromatography of the hexadienol. Peaks due to formation of the rearrangement product appeared in the chromatograms of highly purified hexadienol if the injection port or column temperatures exceeded 200° and particularly if 10-ft. rather than 2-ft. columns were used.
(7) As ascertained by vapor phase chromatography and confirmed by quantitative 2,4-dinitrophenylhydrazone precipitation.
(8) B.p. 120–121°, lit.[9] b.p. 118–118.5°; $n^{20}D$ 1.395, lit.[9] $n^{20}D$ 1.4109; m.p. of 2,4-dinitrophenylhydrazone 101–101.5°, lit. 93–94°,[9] 96°.[10]
(9) M. S. Kharasch, J. Kuderna, and W. Nudenberg, *J. Org. Chem.*, **18**, 1225 (1953);
(10) R. R. Burford, F. R. Hewgill, and P. R. Jeffries, *J. Chem. Soc.*, 2937 (1957).