

### Base-Catalyzed Deuterium Exchange in Cycloheptatriene. Evidence for the Cycloheptatrienide Anion

Sir:

In response to the continuing, theoretically based assertion that the cycloheptatrienide anion should exist under experimentally accessible conditions and having failed in the approach with which Dauben and Rifi achieved such a brilliant success,<sup>1</sup> we looked to base-catalyzed exchange of deuterium in cycloheptatriene<sup>2</sup> to provide indirect support for the existence of the anion.

Deuterium exchange, determined from the mass spectral cracking pattern in the region  $m/e$  91 and above,<sup>3</sup> occurred extensively when cycloheptatriene (1 ml., 91.4%, kindness of Shell Chemical Co.) was heated for 12 hr. at 115° in 100 ml. of deuterated (> 96% by infrared) triethylcarbinol (prepared by shaking 50-ml. portions of triethylcarbinol 1 hr. each with six successive 5-ml. portions of 99.5% deuterium oxide containing a little potassium carbonate and dried by treating with excess sodium and decanting) containing 5 g. of reacted potassium metal (no exchange occurred on heating pure cycloheptatriene in 10% methanolic sodium methoxide for 24 hr. at 110°). The resulting sample A contained 90.8% deuterium distributed between octadeuterio- (55.9), heptadeuterio- (25.0), hexadeuterio- (13.2), and penta- and tetradeuterio- (5.9%) cycloheptatrienes (maleic anhydride adduct, m.p. 104.5–105.0°).<sup>4</sup>

Disclosure of both the stepwise and the random nature of the exchange appears when perdeuterated cycloheptatriene (sample B: 86.0% deuterium as D<sub>8</sub>: 31.9%, D<sub>7</sub>: 39.0%, D<sub>6</sub>: 20.4%, and D<sub>5</sub> and less: 8.7%), which shows only broad singlets in the n.m.r. at  $\tau = 3.54, 3.93, 4.77, \text{ and } 7.82$  p.p.m. (positions 3 and 4, 2 and 5, 1 and 6, and 7,7, respectively) is exchanged for 30, 60, and 180 min. in triethylcarbinol (2 ml.) containing reacted potassium (144 mg.) at 99.5°. While the three samples revealed a regular increase in protonated species, the relative areas of the four types of hydrogen remained equal throughout within the limits of experimental error. Exchange had occurred at the same rate at all four positions. A blank experiment in which cycloheptatriene-7,7- $d^2$  (*vide infra*) was heated 15 min. at 97° was negative.<sup>5</sup>

Elegantly suited to the further study of the exchange, 7,7-dideuteriocycloheptatriene cannot be obtained in structurally homogeneous form from the photolytic reaction of benzene and deuteriodiazomethane,<sup>6,7</sup> which actually leads to a product having significant, but variable amounts of deuterium in the vinyl positions. This photorearrangement *per se* was brought into focus by irradiating ( $\lambda > 300$  m $\mu$ ) 30  $\mu$ l. of 7-deuteriocycloheptatriene (from tropylium bromide and lithium aluminum deuteride in ether) and

(1) H. J. Dauben, Jr., and M. R. Rifi, *J. Am. Chem. Soc.*, **85**, 3041 (1963); *q.v.* for the bulk of references relevant to this problem.

(2) R. E. Davis and A. Tulinsky, *Tetrahedron Letters*, No. 19, 839 (1962).

(3) That hydrogen is lost randomly in the process generating parent minus one was confirmed in the mass spectrum of cycloheptatriene-7,7- $d^2$ . On this basis of calculation, excellent agreement with an analysis by low-voltage mass spectroscopy was obtained (kindness of Dr. J. L. Franklin, Humble Oil and Refining Co.).

(4) E. P. Kohler, M. Tishler, H. Potter, and H. T. Thompson, *J. Am. Chem. Soc.*, **61**, 1060 (1939).

(5) Apparently, the 1,5-transannular shift of A. P. ter Borg, H. Kloosterziel, and N. Van Meurs, *Proc. Chem. Soc.*, 359 (1962), does not intervene.

(6) W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **72**, 2305 (1950).

(7) Deuterated diazomethane was obtained by shaking decalin solutions of diazomethane with 20% potassium deuterioxide in deuterium oxide at 0° for 6–12 hr. and was analyzed directly by mass spectrography. Losses are substantial (15–30%). Exchange, being negligible at pH 7 or 11.6, is base-catalyzed.

10  $\mu$ l. of benzene in an n.m.r. tube in carbon tetrachloride solution and measuring relative areas of the four types of hydrogen periodically. After irradiation for 300 min., partial redistribution of the 7-deuteron had occurred, mainly to the adjacent position: (7,7) 0.51, (1,6) 0.35, (2,5) 0.05, (3,4) 0.09.<sup>8</sup>

Although the extent of the photorearrangement can be decreased by irradiating with filtered light of  $\lambda > 380$  m $\mu$  (Corning filter No. 3360), structurally homogeneous 7,7-dideuteriocycloheptatriene is better prepared by the decomposition of diazomethane in benzene catalyzed by copper sulfate.<sup>9</sup>

The random distribution of deuterium in cycloheptatriene exchanged in triethylcarbinol is occasioned by a rapid intramolecular base-catalyzed rearrangement which, being roughly 12 times faster than the exchange, prevents observations on the exchange step.

In dimethyl sulfoxide the relative rates are reversed, exchange becoming much faster than intramolecular rearrangement. A sample of 7,7-dideuteriocycloheptatriene (50  $\mu$ l.) in anhydrous dimethyl sulfoxide (10 ml.) and triethylcarbinol (1 ml.) containing potassium (79 mg.) was converted in 30 min. at 25° to a sample from which 0.312 deuteron had exchanged (mass spectroscopy) and in which 0.29 deuteron had disappeared from the 7,7-position (by n.m.r.). Similarly, perdeuterated cycloheptatriene (sample A) containing 0.17 proton each in the (3,4), (2,5), (1,6), and (7,7) positions had 0.02, 0.01, 0.04, and 0.41 in these positions after 30-min. exchange.<sup>10</sup>

The rate of exchange being essentially equal to the rate of appearance of the solvent hydrogen at the 7-position (predicted 6/7), the intermediacy of the sevenfold symmetrical cycloheptatrienide anion is a consistent hypothesis.

(8) This photorearrangement is structurally similar to that reported by O. L. Chapman and S. L. Smith, *J. Org. Chem.*, **27**, 2291 (1962).

(9) E. Müller, H. Fricke, and W. Rundel, *Z. Naturforsch.*, **15b**, 753 (1960); G. Wittig and K. Schwarzenbach, *Ann.*, **660**, 1 (1961).

(10) Cf. D. J. Cram, C. C. Kingsbury, and B. Rickborn, *J. Am. Chem. Soc.*, **81**, 5835 (1959).

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### Electrogenerative Hydrogenation

Sir:

Conventional chemical hydrogenation of unsaturated compounds is effected by contact of hydrogen and substrate with a suitable catalyst. For electrochemical hydrogenation,<sup>1</sup> external power is utilized to generate hydrogen which adds to the unsaturated molecule. We report here a new hydrogenation technique which may be described as *electrogenerative hydrogenation*. Hydrogen is placed on one side of an electrolyte barrier while an unsaturated compound is placed on the other side. The electrolyte phase is bounded by porous, electrolyte-impermeable, catalytic electrodes. Under operating conditions, hydrogen ions are formed at one electrode and conducted through the electrolyte while electrons are conducted through an external circuit containing a variable resistor and ammeter. Hydrogenation takes place at the counter catalytic electrode where unsaturate, hydrogen ions, and electrons are combined. Hydrogenation rate or potential may be

(1) (a) For a recent review see: D. Popp and H. P. Schultz, *Chem. Rev.*, **62**, 19 (1962); (b) see also P. S. Farrington and D. T. Sawyer, *J. Am. Chem. Soc.*, **78**, 5536 (1956).