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DEUTERO[18]ANNULENE*

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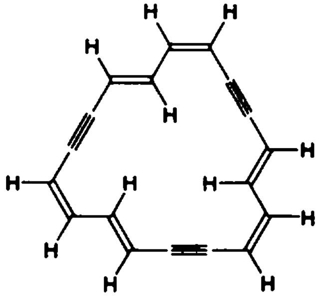
Abstract—Partial catalytic deuteration of 1,7,13-tridehydro[18]annulene (**1**) led to deutero[18]annulene, consisting mainly of [18]annulene-d_6 (**3**). It was shown that the recovered **1** contained some deuterium. The integrated areas of the outer:inner proton bands in the NMR spectrum of the deutero[18]annulene was found to be ca. 2:1, as in [18]annulene (**2**) itself. An explanation for this phenomenon is given, taking into account the conformational mobility of **2**. Catalytic deuteration of **1**, **2** and deutero[18]annulene gave deuterocyclooctadecanes, extensive hydrogen-deuterium exchange having occurred in each case.

THE synthesis of [18]annulene (**2**) by partial catalytic hydrogenation of 1,7,13-tridehydro[18]annulene (**1**) has been described previously.[1, 2] We now report the results obtained by substituting deuterium for hydrogen in this reduction. If no hydrogen-deuterium exchange occurs, the reaction was expected to lead to a 1,2,7,8,13-14-hexadeutero[18]annulene (*eg*. **3a**), a compound of considerable interest.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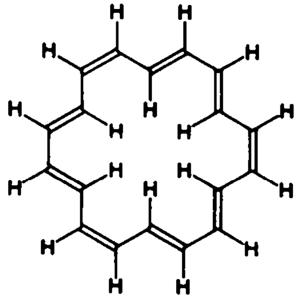
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1,7,13-Tridehydro[18]annulene (isomer I, **1**)[2, 3] in benzene was stirred in deuterium over a 10% palladium-calcium carbonate catalyst until ca. 6 molar equivalents had

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been absorbed.[*] Chromatography on alumina impregnated with silver nitrate then gave crystalline deutero[18]annulene in ca. 20 % yield, as well as ca. 7 % of recovered tridehydro[18]annulene.

Mass spectral analysis[4] of the deuterated [18]annulene showed that it consisted mainly (ca. 46 %) of [18]annulene-d_6, as well as lesser amounts of other deutero[18]-annulenes (see Table 1 and Fig 1). The average number of deuterium atoms per molecule was found to be 5·5. The product (average molecular formula, $C_{18}H_{12\cdot5}D_{5\cdot5}$) contains ca. 0·5 hydrogen atom per molecule more than the starting material **1** ($C_{18}H_{12}$), and it was suspected that a source of the hydrogen was **1**. This indeed proved to be the case, since mass spectral examination of the recovered tridehydro-[18]annulene (Table 2) showed that an average of 0·4 deuterium atom per molecule has been incorporated. Another possible source of hydrogen is the benzene used as solvent, in view of the known hydrogen-deuterium exchange in benzene over palladium and platinum catalysts.[5]

TABLE 1. DISTRIBUTION OF DEUTERO[18]ANNULENES FROM DEUTERATION OF TRIDEHYDRO[18]ANNULENE (1)
(AEI MS9 spectrometer, 20 eV)

M/e	237	238	239	240	241	241
No. of D per molecule	3	4	5	6	7	8
Rel. peak intensity	94	302	766	1000	350	124
Percentage	3·6	11·2	28·0	46·1	8·0	3·0

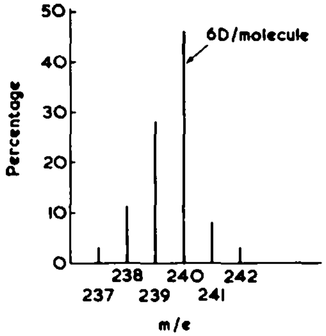

FIG. 1 Distribution of deutero[18]annulenes from deuteration of tridehydro[18] annulene (MS9, 20 eV).

TABLE 2. DISTRIBUTION OF DEUTEROTRIDEHYDRO[18]ANNULENES RECOVERED FROM DEUTERATION OF TRIDEHYDRO[18]ANNULENE (1)
(AEI MS9 spectrometer, 8 eV)

M/e	228	229	230	231	232	233
No. of D per molecule	0	1	2	3	4	5
Rel. peak intensity	1000	227	44	32	70	24
Percentage	88·2	2·4	0·5	2·2	5·7	1·1

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[*] This excess was used, since it has been found in the partial catalytic hydrogenation of **1** that the optimum yield of [18]annulene is obtained when 5–6 molar equivalents of hydrogen are absorbed (Ref 1).

The ultraviolet spectrum of the deutero[18]annulene showed no significant difference from that of the undeuterated substance, as already reported by Blattmann *et al.*[6] for samples supplied by us.

The NMR spectrum of the deutero[18]annulene at −60° exhibited low and high field bands at the same positions (within experimental error*) as the undeuterated material,[8] but these bands were not as well defined (Fig 2). This lack of definition is presumably due to the H-D coupling in the deuterated compound, as well as the fact that it is actually a mixture of different deutero[18]annulenes. The same correspondence of the inner and outer proton signals was observed in the NMR spectra determined at −30° and 0°, as well as of the coalesced peaks at 110°.[8]

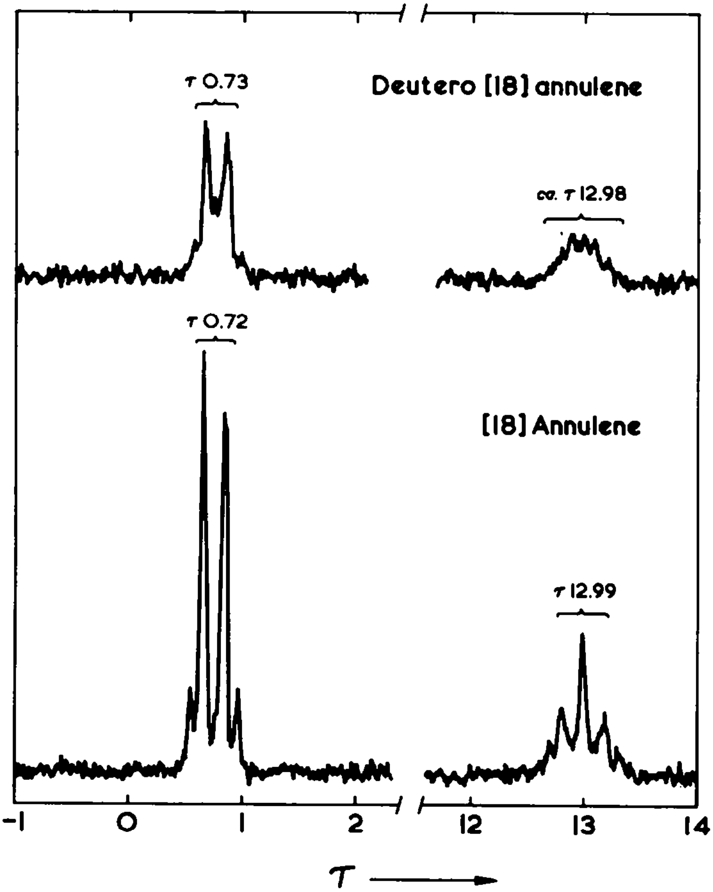

FIG. 2 NMR spectra at −60° of deutero[18]annulene and [18]annulene, measured in tetrahydrofuran-d_8 at 60 MHz.

The integrated areas of the outer : inner proton bands in the NMR spectrum of the deuterated[18]annulene was found to be ca. 2:1 [experimental values, 2·0:1 (−60°,

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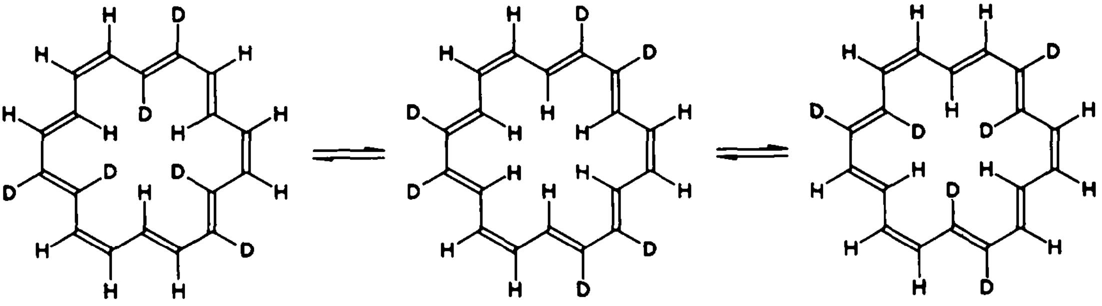
* Although deuterium isotope effects on chemical shifts are known, they are usually less than 1 Hz for deuterated *cis*- and *trans*- olefinic systems (see Ref 7).

60 MHz), 2·3 : 1 (−60°, 100 MHz), 2·1 : 1 (−30°, 100 MHz)]. This appears surprising at first sight since the outer : inner proton ratio is 3 : 1 in the 1,2,7,8,13,14-hexadeutero-[18]annulene **3a**, expected to be formed from **1** by over-all *trans* addition of deuterium to the acetylenic bonds. However, the observed ratio is easily explicable, taking into account the conformational mobility of [18]annulene.[8, 9] The [18]annulene-d_6 is presumably an equilibrium mixture of the three structures **3a**, **3b**, and **3c**, the outer : inner proton ratios being 9 : 3, 6 : 6 and 9 : 3, respectively. The average outer : inner proton ratio is therefore 24 : 12, or 2 : 1, in agreement with the experimental result. By application of the same type of argument, the outer : inner proton ratio in the NMR spectra of the other deutero[18]annulenes should also be 2 : 1.



3a **3b** **3c**

In view of the above-described hydrogen-deuterium exchange in tridehydro[18]-annulene and [18]annulene, it appeared of interest to investigate the extent of this exchange in the course of their catalytic deuteration to deuterated cyclooctadecanes. Tridehydro[18]annulene (**1**), [18]annulene (**2**), and the deutero[18]annulene in ethyl acetate were separately stirred in deuterium over a platinum catalyst until uptake ceased. The resulting crystalline deuterocyclooctadecanes were then subjected to mass spectral analysis[4] (Tables 3–5, Figs 3–5). As expected,[10] very extensive hydrogen-deuterium exchange* had occurred in all three cases, as indicated by the fact that the

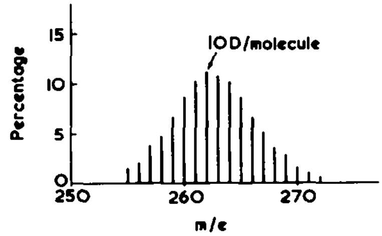


FIG. 3 Distribution of deuterocyclooctadecanes from deuteration of tridehydro[18]annulene (MS9, 70 eV)

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* The source of hydrogen in these cases is presumably ethyl acetate. Deuterium exchange and solvent participation have also been found to occur in the catalytic deuteration of systems related to tridehydro-[18]annulene and [18]annulene (R. Wolovsky and R. B. Woodward, unpublished results).

Table 3. Distribution of deuterocyclooctadecanes from deuteration of tridehydro[18]annulene (1)
(AEI MS9 spectrometer, 70eV)

M/e	255	256	257	258	259	260	261	262	263	264	265	266	267	268	269	270	271	272
No. of D per molecule	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Rel. peak intensity	69	106	170	250	343	458	550	600	600	567	489	396	301	217	159	102	67	45
Percentage	1·5	2·1	3·3	4·8	6·6	8·8	10·3	11·1	10·9	10·3	8·6	6·8	5·1	3·6	2·7	1·6	1·1	0·7

Table 4. Distribution of deuterocyclooctadecanes from deuteration of [18]annulene (2)
(AEI MS9 spectrometer, 70 eV)

M/e	255	256	257	258	259	260	261	262	263	264	265	266	267	268	269	270	271	272
No. of D per molecule	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Rel. peak intensity	23	57	110	203	311	425	541	600	600	540	440	336	230	147	103	54	34	21
Percentage	0·6	1·3	2·5	4·7	7·1	9·3	11·8	12·8	12·5	11·0	8·7	6·5	4·3	2·7	1·9	0·9	0·6	0·4

Table 5. Distribution of deuterocyclooctadecanes from deuteration of deutero[18]annulene
(AEI MS12 spectrometer, 70 eV)

M/e	259	260	261	262	263	264	265	266	267	268	269	270	271	272
No. of D per molecule	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Rel. peak intensity	8·4	16·8	26·9	44·8	67·4	89·8	102	100	92·1	72·5	47·7	29·9	17·8	9·7
Percentage	1·4	2·6	4·0	6·7	9·9	13·0	14·3	13·7	12·4	9·4	5·9	3·6	2·1	1·1

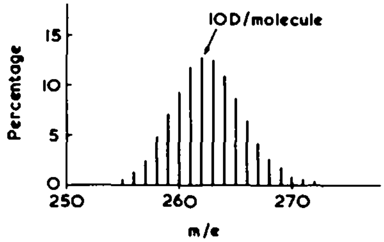

FIG. 4 Distribution of deuterocyclooctadecanes from deuteration of [18]annulene (MS9, 70 eV).

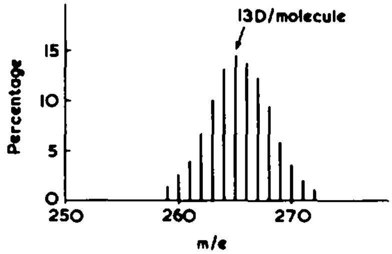

FIG. 5 Distribution of deuterocyclooctadecanes from deuteration of deutero[18]annulene (MS12, 70 eV).

average number of deuterium atoms per molecule present (10·7, 10·5, and 12·4 respectively) was far less than the theoretical number (24, 18, and 24, respectively). It is interesting that the results obtained in the deuteration of 1 ($C_{18}H_{12}$) and 2 ($C_{18}H_{18}$) are very similar to each other. In a blank experiment, undeuterated cyclooctadecane in ethyl acetate was stirred in deuterium over a platinum catalyst for several hours, but no appreciable exchange was observed.

The possibility was considered that 1 might be converted exclusively to [18]-annulene-d_6 (3) by deuteration in the presence of tris(triphenylphosphine)chlororhodium(I), since it has been shown that this catalyst causes no hydrogen-deuterium exchange.[11] However, in preliminary experiments, it was found that 1 in benzene was recovered unchanged on shaking in hydrogen over this catalyst, and no trace of [18]annulene could be isolated.

EXPERIMENTAL

General procedures. Mass spectral analyses were performed with an AEI MS9 or MS12 spectrometer at 8, 20 or 70 eV. The samples were introduced directly on the probe, with the ion chamber at 120–140°. Distributions of deutero compounds were calculated from the average relative peak intensities of three determinations at slightly different multiplier settings. NMR spectra were recorded in THF-d_8 with a Varian A60 or HA100 spectrometer (TMS used as internal standard). EtOAc was dried over anhydrous $CaSO_4$ and distilled. Benzene was washed 5 times with an equal volume each of conc H_2SO_4, H_2O, Na_2CO_3aq, and was then dried and distilled. Light petroleum refers to the fraction b.p. 40–60°.

Deutero[18]*annulene.* A mixture of 10% Pd-$CaCO_3$ (100 mg) and benzene (5 ml) was stirred in D_2 for 30 min, and a soln of 1 (31 mg)[2, 3] in benzene (1·5 ml) was then added from a side-arm. The mixture was stirred vigorously in D_2 until 18 ml of D_2 (ca. 6 molar equiv) had been absorbed, in 6·3 min. The catalyst was removed by filtration, and the filtrate was percolated through a short column of Al_2O_3 (Woelm, neutral, activity I). The resulting soln was concentrated to small volume, and chromatographed on Al_2O_3 (50 g; Woelm, neutral) impregnated with 10% of $AgNO_3$ (made up with light petroleum). Elution with light petroleum and crystallization from this solvent gave starting material (2·1 mg, 7%). Elution with light petroleum-ether (9 : 1) led to a yellow soln, which had no characteristic UV spectrum. Finally, elution with light petroleum-ether (3 : 1 to 1 : 1) and crystallization from CH_2Cl_2-light petroleum afforded deutero-[18]annulene (6·1 mg, 19%) as red-brown crystals, homogeneous by TLC (Merck Kieselgel GF_{254} impregnated with 10% of $AgNO_3$).

Deuterocyclooctadecanes. PtO_2 (5 mg) in EtOAc (5 ml) was stirred in D_2 for 1 hr, and a soln of 1, 2, or deutero[18]annulene (3 mg) in benzene (5 ml) was added. The mixture in each case was stirred vigorously in D_2 until uptake ceased (< 30 min). Filtration, evaporation under reduced pressure and crystallization from EtOAc-MeOH in each case yielded deuterocyclooctadecane (ca. 1 mg) as fluffy colourless crystals. Under the same conditions, but using H_2 instead of D_2, 1 yielded cyclooctadecane (m.p. 71·5–72·5°; lit[12] m.p. 71–72°), free of any cycloalkenes as shown by mass spectrometry.

Equilibration of cyclooctadecane. PtO_2 (5 mg) in EtOAc (5 ml) was stirred in D_2 for 1 hr. A soln of cyclooctadecane (3 mg) in benzene (5 ml) was then added, and the mixture was stirred in D_2 for 2 hr. The recovered cyclooctadecane contained no deuterium, as shown by mass spectrometry.

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