

## Preparation of Hexadeuteriocyclopentadiene by Deuterioxide-catalyzed Hydrogen Exchange in Hexamethylphosphoric triamide Solution

Received September 28th, 1970

Several methods have been proposed for the preparation of cyclopentadiene- $d_6$ , but none of them appears to be satisfactory. Reductive cleavage of ferrocene- $d_{10}$  with alkali metal in liquid  $\text{NH}_3$ , followed by hydrolysis with  $\text{D}_2\text{O}$  <sup>(1)</sup>, is very cumbersome and gives very low yields. Reductive dechlorination of hexachlorocyclopentadiene with zinc and  $\text{D}_2\text{O}$  <sup>(2)</sup> has proved to be ineffective <sup>(3)</sup>. The most promising method appears to be the base-catalyzed exchange reaction described by Kursanov and Parnes <sup>(4)</sup>: Renaud and Stephens <sup>(3)</sup> obtained fairly good results by heating at 160° C cyclopentadiene,  $\text{D}_2\text{O}$  and  $\text{Na}_2\text{CO}_3$  in a sealed glass tube. However the exchange times are rather lengthy (24 h); furthermore cyclopentadiene is recovered as a polymer, which needs to be cracked in order to get back the monomeric cyclopentadiene.

As the exchange implies the cyclopentadiene anion as intermediate <sup>(4)</sup>, we have tried to find out a solvent able to enhance the reactivity of bases <sup>(5)</sup> and at the same time unable to exchange its hydrogens with  $\text{D}_2\text{O}$ . We have found that cyclopentadiene exchanges very easily and under very mild conditions with  $\text{D}_2\text{O}$  in the presence of NaOD on using hexamethylphosphoric-triamide (HMP) as solvent. In a typical experiment, 0.36 mole of cyclopentadiene (freshly prepared from its dimer), 3.3 mole of  $\text{D}_2\text{O}$  (Merck, deuterium content 99,75 %) and 0.018 mole of NaOD are added to 250 ml of HMP (dried over CaO and vacuum distilled). The mixture is kept at room temperature for 1 h 30' under intermittent stirring; then it is distilled, under nitrogen at normal pressure, through a small-diameter column, 80 cm long, filled with glass helices. Cyclopentadiene distils with a small amount of water at 37° C and is collected in an acetone-dry ice bath (yield 75-80 %).

After five successive exchanges (maintaining constant cyclopentadiene :  $\text{D}_2\text{O}$  : NaOD ratios) we have obtained about 0.10 mole (~8 ml) of cyclopentadiene- $d_6$ ; its Raman spectrum in the regions of CH and CD stretchings is shown in the figure. The deuterium content of the product obtained in this way is evaluated to be 99 %, both from the intensity decrease of CH lines in the Raman spectrum and from NMR measurements.

Other experiments have been carried out in order to ascertain the time required for the attainment of the exchange equilibrium. After exchange time of 16 h, 4 h, 1 h 20' and 40' at room temperature, there are no remarkable

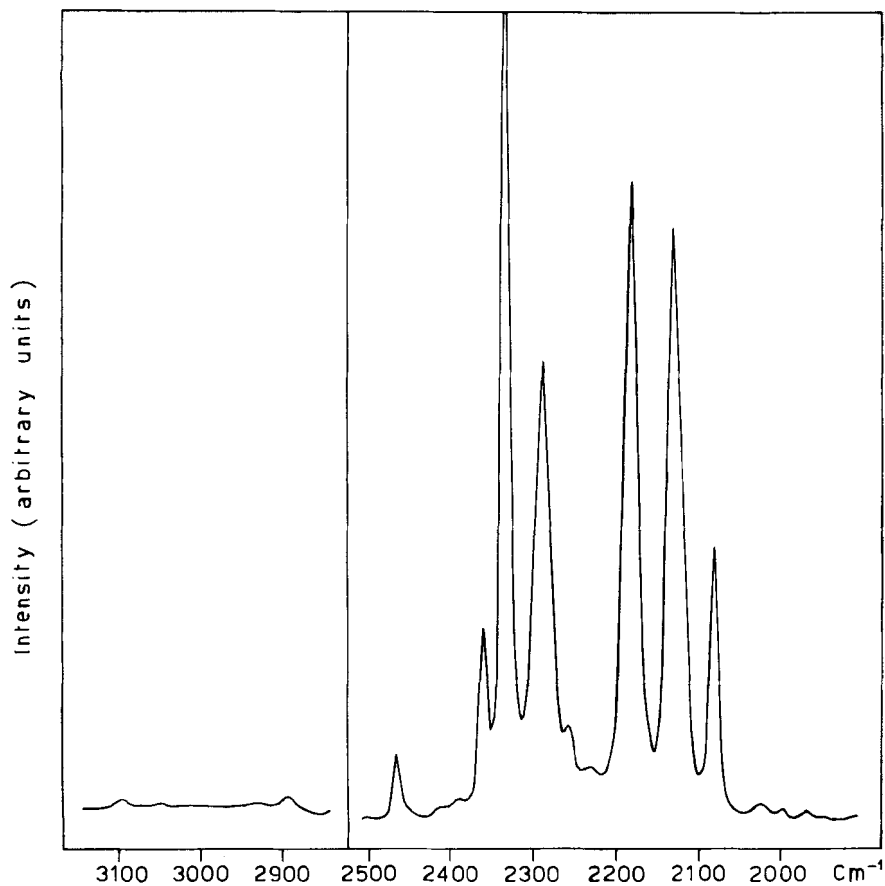


FIG. 1. Raman spectrum of cyclopentadiene- $d_6$ . Cary Spectrophotometer with Hg- $e$  excitation and 10 ml cell.  $T = -25^\circ \text{C}$ .

differences in the intensity ratios of CH and CD Raman lines; therefore the equilibrium between hydrogen and deuterium is reached in a very short time.

We thank Prof. F. Montanari for helpful suggestions.

ENZO GALLINELLA and PAOLO MIRONE

Istituto di Chimica fisica, Università di Modena, Modena

Istituto Chimico "G. Ciamician, Università" di Bologna, Bologna (Italy)

#### REFERENCES

1. TRIFAN, D. S. and NICHOLAS, S. — *J. Am. Chem. Soc.*, **79** : 2746 (1957);  
FRITZ, H. P. and SCHÄFER, L. — *Chem. Ber.*, **97** : 1829 (1964).
2. N. R. C. — Canada, British Patent No. 822, 617 (Oct. 28, 1959).
3. RENAUD, R. N. and STEPHENS, J. C. — *J. Labelled Compounds*, **3** : 416 (1967).
4. KURSANOV, D. N. and PARNES, Z. N. — *Doklady Akad. Nauk SSSR*, **109** : 315 (1956).
5. PARKER, A. J. — *Chem. Rev.*, **69** : 1 (1969).