TABLE II. Yields of labelled chlorine derivates from irradiated liquid and solid CCl_4-Ar mixtures ($N_{AR} = 0.5$ mole fraction).

Aromatic compound			Ar-^{38}Cl			
			$RC_6H_5{}^{38}Cl$	R_o-$ClC_6H_4{}^{38}Cl$	R_m $ClC_6H_4{}^{38}Cl$	R_p-$ClC_6H_4{}^{38}Cl$
			per cent of total activity			
C_6H_6	Liquid		10	less than 0.5		
	Solid (glassy)		18	less than 0.5		
C_6H_5Cl	Liquid		33	5	3	5
	Solid	Cryst.	9	2	3	6
		Glassy	11	8	4	8

Disubstituted derivates in measurable quantities are obtained from CCl_4-chlorobenzene mixtures only. Incidentally it is of interest to note that labelled dichlorobenzene yields are appreciably higher in the glassy than in the crystalline solid phase.

I. KISS, K. BEREI and L. VASÁROS
Central Research Institute for Physics, Budapest

Synthesis of Hexadeuteriocyclopentadiene

Received on 11th April 1967

The few references in the literature to the deuteration of cyclopentadiene have been evaluated. The Grignard reagent (1) can only be used for the preparation of the monodeuterio compound. McBee (2) reported a 25 % yield of cyclopentadiene on dechlorinating hexachlorocyclopentadiene with zinc in ethanol. This method was inconvenient since a large quantity of *O*-deuterio ethanol would be needed for the preparation of the deuterated compound. Besides, several trial runs gave only tetrachlorocyclopentadiene. Dehalogenation with zinc in deuterium oxide or deuterium oxide in dioxane (3) gave only a tarry gum from which no monomeric cyclopentadiene could be isolated. Other known methods of introducing deuterium into organic molecules such as catalytic exchange with deuterium oxide on platinum (4), or dehalogenation of hexachlorocyclopentadiene with zinc and *O*-deuterio ethanoic acid (5), likewise, gave none of the desired compound.

TABLE 1. Summary of Experimental Results [a].

Run	Temp. °C	Time hr	Yield % (monomer)	Mole % D							Atom % D
				d_6	d_5	d_4	d_3	d_2	d_1	d_0	
1 [b]	160	24	13	48.0	6.8	0.9	0.0	0.0	0.6	43.7	54.4
2 [c]	160	24	66.6	51.6	18.6	8.2	4.2	4.1	4.9	8.3	76.9
3	160	2	70.0	40.3	19.0	10.3	8.0	7.0	6.9	8.4	70.5
4 [d]	160	2	86.5	43.7	20.4	9.6	6.9	6.0	6.0	7.4	73.6
5	100	24	81.6	31.8	18.0	11.3	10.2	8.9	8.9	10.9	64.9
6	160	96	10.0	69.9	20.0	4.1	1.7	1.5	1.5	1.7	90.9
7	160	24	75	66.8	19.5	2.6	3.8	2.5	2.4	2.6	87.9

[a] The same molar quantities were used in all runs.

[b] Dicyclopentadiene was exchanged instead of monomer.

[c] Two exchanges were made, the first one with 0.69 mole of D_2O and the second one with 2.06 moles.

[d] Furnace preheated to 160° C.

The most promising method of deuterating cyclopentadiene appeared to be the base catalyzed exchange reaction described by Kursanov and Parnes (6). The source of deuterium was deuterium oxide in dioxane solution. They observed a statistical introduction of deuterium at all positions in the molecule. Since the catalyst employed was N,N'-dimethylpyridonimine, which is not readily available, and since no details of the possibility of preparing cyclopentadiene deuterated in excess of 90 % was mentioned, attempts to increase the deuterium content by using another base as catalyst were made. A 40 % yield of cyclopentadiene with a deuterium content of only 34.2 atom % was obtained when the cyclopentadiene was exchanged with a sixfold excess of deuterium oxide in dioxane in presence of sodium carbonate under the same experimental conditions as those mentioned by Kursanov. Another 10 % of the product, analyzing only 17.8 atom % D, was isolated when the non-volatile fraction was cracked at 250° C. These results show that exchange occurs only in the monomer and that no exchange occurs in the dimer. In order to increase the rate of exchange, and, at the same time, to keep the cyclopentadiene as monomer, a temperature of at least 160° C is needed. The polymer obtained from this reaction was cracked to the monomer at 250° C. The results obtained in a series of experiments are shown in Table 1.

The exchange of technical grade dicyclopentadiene (run 1) provides further indications that the reaction occurs only with the monomeric form of cyclopentadiene. A large quantity of undeuterated compound was observed since most of the trimer or higher polymers, also present in the dimer, were not all depolymerized to the monomer at 160° C. The same result was obtained whenever the polymer was not cracked back to the monomer before a second exchange was done (run 2). The highest deuterium content was observed when the time of heating was extended to 4 days (run 6), but the yield of the monomer was very low; only a white gummy polymer, melting at 259-262° C, was obtained. A reaction time of 2 hours at 160° C (run 4) or 24 hr at 100° C (run 5) gave very good yields of product, but the introduction of deuterium was not optimal. The best result was obtained by heating the mixture for 24 hr at 160° C (run 7). The yield of monomer being very good, a second exchange can easily be done in order to increase the deuterium content of the cyclopentadiene.

All exchange reactions were done on 0.045 mole of cyclopentadiene, freshly prepared from its dimer (except for run 1), and 2.75 moles of D_2O 99.7 atom % D, in the presence of 0.3 g of sodium carbonate. The reaction was carried out in a sealed glass tube, 35 cm in length and 3 cm in diameter, placed in a heated rocking furnace (7). When the reaction was over, the tube was cooled in ice water and then opened. Practically no monomeric cyclopentadiene was obtained on distillation on a vacuum manifold. The polymeric cyclopentadiene was therefore extracted with ether and the solvent was removed under reduced pressure. The flask containing the low pressure residue was connected to a bent glass tube, to which was attached in series, a Stock trap in an acetone-dry ice bath and a Drierite tube. The liquid was heated up to 260° C or 2 hr in a bath of Wood's metal. The volatile product was redistilled on the vacuum line at constant vapor pressure. A larger quantity of normal cyclopentadiene was obtained whenever the polymer was cracked at 350° C. This fraction came from the cracking of higher polymeric material which was not converted to the monomeric form of cyclopentadiene during the exchange reaction.

R. N. Renaud and J. C. Stephens

Division of Pure Chemistry, National Research Council of Canada,
Ottawa, Canada

REFERENCES

1. Mironov, V. A., Sobolev, E. V. and Elizarova, A. N. — *Dokl. Akad. Nauk. SSSR*, **143** : 112 (1962).
2. McBee, E. T., Meyers, R. K. and Baranauckas, C. F. — *J. Am. Chem. Soc.*, **77** : 86 (1955).
3. Leitch, L. C. — Patent No. 564, 064 (Sept. 30, 1958).
4. Leitch, L. C. — *Can. J. Chem.*, **32** : 813 (1954).
5. Schissler, D. O., Thompson, S. O. and Turkevich, J. — *Disc. Farad. Soc.*, **10** : 46 (1951).
6. Kursanov, D. N. and Parnes, Z. N. — *Proc. Acad. Sci. USSR*, **106-111** : 385 (1956).
7. Fraser, R. R. and Renaud, R. N. — *J. Am. Chem. Soc.*, **88** : 4 365 (1966).

The synthesis and chromatographic behavior of D-mannitol-1-^{14}C-1-PO_4, D-mannitol-1-$^{32}PO_4$ and ^{32}PPA*

Received on 10 July 1967

In the course of an investigation dealing with the utilization of D-mannitol and inorganic phosphate by *Absidia glauca* it was found necessary to confirm the existence and establish the identity of the 1-Phosphate ester of this polyol. This paper describes the synthesis of radioactive mannitol-1-phosphate labeled with carbon-14 and phosphorus-32 by a modification of the procedure of Seegmiller and Horecker (1951) for the synthesis of glucose-6-phosphate. In addition we document the paper and gel chromatographic behavior on Sephadex G-15 of the products and ^{32}PPA prepared by the method of Bell (1948) for the synthesis of polyphosphoric acid.

Polyphosphoric Acid. Orthophosphoric acid (100 ml, 85 %) was cautiously added with stirring in the cold to 200 g of reagent grade P_2O_5. After the bulk of the P_2O_5 had dissolved, the stirred mixture was heated for 3 hours on a steam bath, allowed to cool and the heavy syrup of polyphosphoric acid (PPA) transferred to a dry bottle for storage. Titration equivalent of the material was 112 % ortho. ^{32}PPA was prepared as described by adding 8 mC of carrier-free $H_3{}^{32}PO_4$ (Cambridge Nuclear Corp., Cambridge, Mass.) to the 85 % ortho phosphoric acid.

D-mannitol-1-$^{32}PO_4$. D-mannitol (5.0 g) was added to 150 g of ^{32}PPA followed by 10 ml of deionized water. The reaction was stirred at 25° C for 10 hours and then terminated by the addition of 300 ml of water. Sodium

---

* Phosphorus-32 labeled Polyphosphoric Acid.