Gas chromatographic labelling is practicable only for systems with enough exchangeable atoms capable to take part in the isotopic exchange, that is, if they are in sufficiently loose bonds. Such is the case of hydrogens bonded to highly electronegative atoms with free electron pair (oxygen, sulphur, nitrogen) or even hydrogens bonded to carbon exhibiting under some structural conditions acidic behaviour. The products obtained on columns with diglycerol are shown in Figure 5. Compounds of the type acetyl acetone, aceto-acetic ester etc. with keto-enol tautomerism containing hydrogens loosened on both sides are deuterized on this column while the hydrogens of mono-oxo systems like acetone, methylethylketone etc. cannot be exchanged.

If one adds 10 % KOH as catalyst to a column with polyethylene glycol also the mono-oxo systems will deuterize. The hydrogens of nitromethane which can be only partly exchanged without catalyst deuterize to almost 100 % in the presence of the latter (Fig. 5).

The activation energy of H-D isotopic exchange can be evaluated from the gas chromatograph temperature dependence of the deuterium concentration in the deuterized product. In the case of e.g. cyclo-hexanone it is 8 kcal/mol.

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Some possibilities in hot synthesis of radio-halogen labelled organic compounds

Received on 8th March 1967

The stabilization processes of the energetic ^{38}Cl were studied in binary mixtures of carbontetrachloride with aliphatic alcohols and aromatic compounds as well in both liquid and solid states over a wide range of relative concentrations.

The irradiations were performed in the 2.5 MW VVR-S type reactor using a pneumatic tube for short time irradiations. Mixtures in solid state were irradiated at liquid nitrogen temperature.

The organic radiolabelled products were separated and identified by gaschromatographic technique. The inorganic activity was adsorbed on potassium ferrocyanide. Tricresyl phosphate was used as stationary phase. The assembly comprised two detectors. A Catharometer was used for measuring the chlorinated hydrocarbon retention time. The activities of the labelled compounds were measured by Geiger counter method and automatic recorder.

In CCl_4-ROH system, in addition to the formation of labelled CCl_4 in macroconcentration, that of a substantial amount of labelled alkylchloride ($R^{38}Cl$) with the same alkyl radical as that of the starting alcohol can be observed already at low ROH concentrations. Other chlorinated hydrocarbons are formed at a much lower yield. For illustration we have listed in Table 1. the labelled yield for each monochlorine derivate from irradiated CCl_4-ROH system at 0.5 mol fraction alcohol concentration.

It is apparent from the table that the main product out of the labelled monochlorine derivates is the alkylchloride with the same alkyl radical as that of the starting alcohol. In the solid phase the main product yield is 2-3 times higher as compared with that obtained from the liquid phase.

For CCl_4-C_6H_6 and CCl_4-C_6H_5Cl systems the labelled chlorobenzene and isomeric dichlorobenzene yields are listed in Table II. For the benzene mixture the chlorobenzene yield is again about twice as high in the solid as in the liquid phase. This difference in yield cannot be observed for the chlorobenzene mixture. The reason for this is that the labelled chlorobenzene is formed in the two systems by quite different reaction mechanisms. For CCl_4-C_6H_5Cl the labelled product is not obtained in a carrier free form, though its specific activity may be still rather high, since even for 0.05 mole fraction chlorobenzene concentration the labelled yield contains 17 % of the total activity produced.

TABLE I. Yields of labelled monochlorine derivates from irradiated liquid and solid CCl_4-ROH mixtures ($N_{ROH} = 0.5$ mole fraction).

ROH		$R^{38}Cl$			
		$RCH_3{}^{28}Cl$	$RC_2H_5{}^{38}Cl$	Rn-$C_3H_7{}^{38}Cl$	Ri-$C_3H_7{}^{38}Cl$
		per cent of total activity			
CH_3OH	Liquid	4.32	—	—	—
	Solid (glassy)	8.83	—	—	—
C_2H_5OH	Liquid	0.96	2.37	—	—
	Solid (glassy)	0.67	7.95	—	—
n-C_3H_7OH	Liquid	0.69	0.49	2.92	—
	Solid (glassy)	0.44	0.32	10.30	—
i-C_3H_7OH	Liquid	1.91	—	—	2.10
	Solid (glassy)	0.94	—	—	4.47

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.

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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.