

Preparation of 2-D-, 3-D- and 4-D-phenol

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In connection with our microwave investigations of phenol, all the monodeuterio-phenols with deuterium at the ring atoms were prepared, and their purity established by PMR and IR-spectroscopy.

2-D, 3-D AND 4-D-PHENOL.

It was mentioned by Hall *et al.* ⁽¹⁾ that the deuteriophenols could be obtained by a reaction between the corresponding bromophenols and butyllithium, followed by heavy acetic acid, but no experimental details were given.

We have been able to reproduce their results under conditions to be described below. Also the purity of the samples has been established.

Butyllithium in ether was prepared and titrated according to the prescriptions of Organic Reactions ⁽²⁾. The solution was found to contain 0.92 mole/liter of butyllithium.

The bromophenols were purum samples. They were used without further purification.

A 250 ml three-neck flask with reflux condenser and a magnetic stirrer was heated over a free flame and flushed with dry nitrogen. 4 grammes of bromophenol (0.023 moles) dissolved in 50 ml of ether was dried over molecular sieves and placed in the flask. This was followed by 50 ml of the solution of butyllithium (0.046 moles) added during 5 minutes. After varying reaction-conditions to be found in Table 1, 2.5 grammes of D₂O was added while cooling the flask. After 15 minutes of stirring the phenol was extracted from the ether with 50 ml 1 N NaOH solution. After acidification to pH 5 the phenol was again extracted by three times 25 ml ether. After drying over CaCl₂ the ether was removed and the phenol distilled on the vacuum line. The constant pressure fraction distilling at *ca.* 0.5 mm Hg at room temperature was collected. The yields are also found in Table 1.

TESTS OF PURITY.

IR spectra of the deuteriated phenols in CS₂ were compared with spectra of the parent bromophenols. No bromophenol was found in any of the samples.

In all the spectra a line at 1075 cm⁻¹ could be used to give crude estimates of the contents of ordinary phenol. Table 1 also contains the purities thus estimated.

The spectrum of 2-D-phenol contained a line at 750 cm⁻¹ often found in ortho-substituted benzenederivatives.

The PMR-spectrum of 4-D-phenol showed the well-known structure of a para-substituted compound.

TABLE 1.

	2-D-phenol	3-D-phenol	4-D-phenol
Reaction time <i>h</i>	1	2	2
Reaction temp. °C	25	35	35
Estimated purity %	>97	>80	>90
Yield grammes (%)	1.84 (84)	0.86 (39)	0.98 (44)

A detailed analysis of the PMR spectra is planned.

The microwave spectra have been assigned ⁽³⁾ for all the monodeuteriated phenols, and have been found to be consistent with the structures assumed for these compounds.

We therefore conclude that the above syntheses are satisfactory with respect to the isotopic purity of the samples.

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REFERENCES

1. HALL, G. E., LIBBY, E. H. and JAMES, E. L. — *J. Org. Chem.*, **28** : 311 (1963).
2. JONES, R. G. and GILMAN, H. — *Organic Reactions*, VI, 352 (1952).
3. PEDERSEN, T., LARSEN, N. W. and NYGAARD, L. — *J. Mol. Structure*, in press.

Application of the microwave discharge modification of the Wilzbach technique for the tritium labelling of some organics of biological interest

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The modification of the Wilzbach technique using microwave discharge ⁽¹⁾ has been routinely used in our laboratory for rapid tritium labellings. The applicability of the method and the effects of some of the reaction parameters were studied and published previously ⁽²⁾. The main advantage of the method is its simplicity and rapidity and the low extent of decomposition of the compound to be labelled during the reaction. Specific activities obtained, however, are not high enough for some investigations.