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CATALYTIC TRITIATION AND ^{3}H NMR SPECTROSCOPY OF SELECTED IMIDAZOLES AND EPOXIDES

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SUMMARY

A number of imidazoles and epoxides, important for the study of the mechanisms of epoxy resin cure, have been tritiated by one-step catalytic procedures. Tritium nuclear magnetic resonance spectroscopy has been employed to determine the positions and extent of labeling in these compounds and the observed pattern of labeling is discussed.

INTRODUCTION

The last decade has witnessed a tremendous increase in the development of applications of epoxy resins in both traditional and newly expanding areas, such as coatings, adhesives, electronics and high-performance composites(1). This growing interest in applications and requirements of

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high quality and performance has provoked a new wave of fundamental research into resin synthesis, curing systems, properties of cured products, methods for their characterisation and the mechanisms of epoxy resin cure. The customary methods of following the kinetics of these reactions, for example, differential scanning calorimetry(2) or Fourier-transform infra-red spectroscopy(3) have certain limitations. Thus the calorimetric method measures heat flow and overall enthalpy change and cannot identify the intermediates formed whilst the infra-red method can only be applied in instances where clear spectral changes are observed. Consequently there is a need for a more generally applicable method and it is in this connection that the possibility of using substrates labelled with tritium is attractive, particularly as techniques such as radio-high performance liquid chromatography enable the ready separation of such intermediates. The problem of having to prepare a suitably labelled substrate has been greatly reduced by the development of a variety of one-step catalytic procedures(4) which allow tritium to be readily incorporated into many organic compounds. The emergence of ^{3}H nmr spectroscopy(5) as a routine analytical technique capable of providing the pattern of labeling in a non-destructive manner is a further important development. These aspects are illustrated in the present paper where the one-step catalytic tritiation and ^{3}H nmr spectroscopy of some 15 imidazoles and epoxides are studied. Imidazoles are amongst the most widely used of epoxy curing agents, producing resins with good high temperature properties whilst the epoxides chosen are good models for the cure reaction.

EXPERIMENTAL

The reaction conditions for the catalytic tritiation of some 15 imidazoles and epoxides are summarised in Table 1. With the exception of imidazole itself which was tritiated by a base-catalysed hydrogen isotope exchange mechanism all the others were labelled using a heterogeneous procedure, pre-reduced platinum oxide being the catalyst. This was prepared by mixing 100 mg of catalyst with distilled water (100 ml) followed by the slow addition of sodium borohydride (400 mg). The mixture was heated at 70°C for 2 hrs to complete the reduction. After cooling the solution was decanted off and the catalyst washed several times with water.

For the heterogeneous platinum catalysed procedure a small amount of the compound (20-100 mg) was placed in a thick-walled tube together with the tritiated water (3-10 μl; 50Ci ml^{-1}) and pre-reduced catalyst (10-100 mg). If the compound was a solid melting above the temperature used for labeling a small amount of dioxan (100-200 μl) was added. At this stage the tube was cooled in liquid nitrogen, evacuated and sealed. It was then heated at 85-165°C for between 12-48 hours at the end of which time the tube was allowed to cool, opened, the contents removed and washed with methanol (5 ml) to which had been added a small amount of decolourising charcoal. The solution was filtered and purification achieved using preparative thin layer chromatography.

The specific activity of the tritiated product was determined by dissolving a known amount of the compound in a small volume (50-100 μl) of a suitable solvent such as dimethyl sulphoxide and counting some 5 μl's using a Beckman LS 1800 scintillation counter.

For the nmr determination the labelled compound was dissolved in 50-100 μl of a deuteriated solvent such as CD_3SOCD_3 containing a trace of tetramethylsilane (TMS). The solution was loaded by syringe into 3mm diameter combination tubes (Wilmad, SK 1374 A) which were then sealed and mounted in Teflon spacers inside standard 5mm nmr tubes and the latter capped. The ^{3}H nmr spectra were obtained (usually with ^{1}H noise decoupling) at 25°C with a Bruker WH 90 pulse spectrometer operating at 96 MHz (90 MHz for ^{1}H) and with quadrature detection. The flip angle was usually 30°, the repetition interval 1.6s and, depending upon the amount of radioactivity present, between 10^2 and 3.5×10^4 transients were acquired. The data were stored in 4K channels and Fourier transformed to provide spectral display widths of up to 13 ppm. Referencing was to a ghost reference generated from the ^{1}H resonance frequency of the internal standard (measured at 90 MHz) by multiplying by the Larmor ratio 1.06663974.

TABLE 1

Experimental conditions used for tritiating the imidazoles and epoxides together with the specific activities obtained

Compound	**Weight (mg)**	**HTO (µl)**	**PtO$_2$ (mg)**	**Temp (°C)**	**Time (hrs)**	**Specific activity (mCi/mmol)**
Imidazole	20	5	–	85	48	130
1-Methylimidazole	30	5	10	165	27	31
2-Phenylimidazole	20	3	20	150	48	30
2-Methylimidazole	50	5	30	130	29	80
1,2-Dimethylimidazole	50	3	20	165	27	53
1-Benzyl,2-methylimidazole	50	3	20	165	40	60
2-Ethyl,4-methylimidazole	20	8	20	140	20	46
2-(p-Dimethylaminophenyl)-4,5-dimethylimidazole[#]	50	3	20	100	24	9
1,3-Dibenzyl-2-methyl-imidazolium bromide[‡]	100	10	50	140	24	87
1-Dodecyl-2-methyl-3-benzylimidazolium chloride[‡]	20	5	20	110	12	21
Phenylglycidyl ether	100	10	100	165	27	49
Diglycidyl ether of bisphenol A	50	3	30	150	24	12
1,2-Epoxy decane	50	3	50	120	36	10
Styrene oxide	50	3	30	120	48	18
t-Butylglycidyl ether	30	3	30	120	30	9

[#] plus 100 µl dioxan

[‡] plus 200 µl dioxan

TABLE 2

^3H n.m.r. results for the tritiated imidazoles

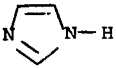
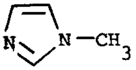
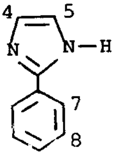
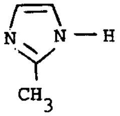
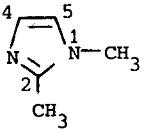
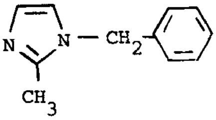
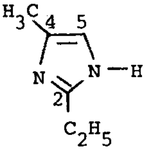
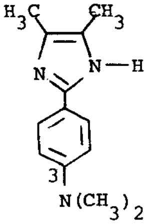
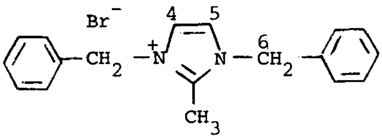
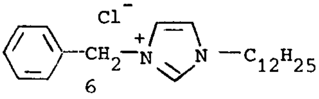
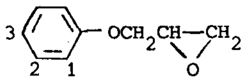
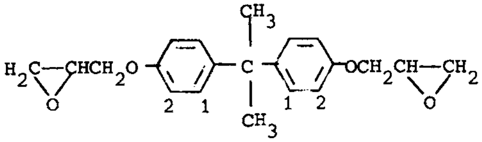
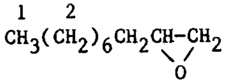
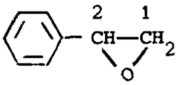
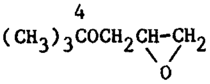
	Compound	**Structure**	**^3H Distribution (relative %)**	
1.	Imidazole		C-2(H)	100
2.	1-Methylimidazole		C-2(H)	65
			N-1 (CH_3)	35
3.	2-Phenylimidazole		C-4,5(H)	88
			C-7(H)	4
			C-8(H)	8
4.	2-Methylimidazole		C-2(CH_3)	38
			C-4,5(H)	62
5.	1,2-Dimethylimidazole		N-1(CH_3)	10
			C-2(CH_3)	60
			C-4(H)	15
			C-5(H)	15
6.	1-Benzyl,2-methylimidazole		C-2(CH_3)	7
			C-4,5(H)	93
7.	2-Ethyl,4-methylimidazole		C-2(C_2H_5)	56
			C-4(CH_3)	36
			C-5(H)	8
8.	2-(p-Dimethylaminophenyl)-4,5-dimethylimidazole		N-3(CH_3)	100
9.	1,3-Dibenzyl-2-methylimidazolium bromide		C-2(CH_3)	2
			C-4,5(H)	18
			C-6(Ar)	80
10.	1-Dodecyl-2-methyl-3-benzylimidazolium chloride		C-6(Ar)	100

TABLE 3

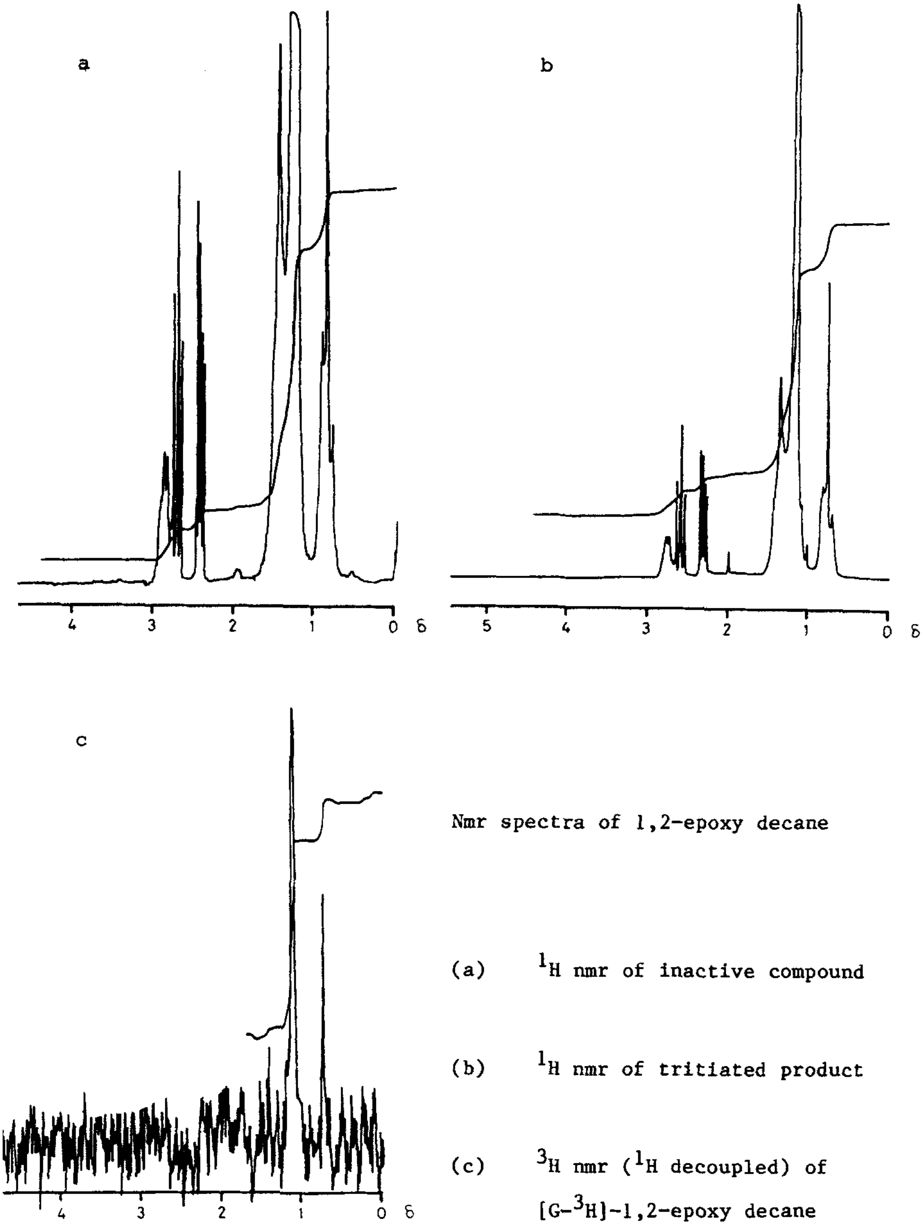
^{3}H n.m.r. results for the tritiated epoxides

	Compound	**Structure**	**^{3}H Distribution (relative %)**	
1.	Phenylglycidyl ether		C-2(H) C-3(H)	37.5 62.5
2.	Diglycidyl ether of bisphenol A		C-1(H) C-2(H)	67 33
3.	1,2-Epoxy decane	 $\overset{1}{CH_3}(\overset{2}{CH_2})_6CH_2\underset{\diagdown O \diagup}{CH{-}CH_2}$	C-1(H) C-2(H)	9 91
4.	Styrene oxide		C-2(Ar)	100
5.	t-Butylglycidyl ether	 $\overset{4}{(CH_3)_3}COCH_2\underset{\diagdown O \diagup}{CH{-}CH_2}$	C-4(CH$_3$)	100

RESULTS AND DISCUSSION

Table 1 shows that satisfactory levels of incorporation of tritium were achieved in all cases, with that for imidazole, which was prepared by a base-catalysed hydrogen exchange procedure, being particularly good. For the remaining nine imidazoles tritiated by the platinum-catalysed heterogeneous exchange procedure the specific activities are all within a factor of ten of one another. Nevertheless there are some interesting features to the tritium distribution (Table 2). Even in the presence of pre-reduced PtO_2 it is still possible for the base-catalysed hydrogen isotope exchange procedure to operate and this may be partly responsible for the observed tritium distribution in 1-methylimidazole, with 65% of the label located at the C-2(H) position. All the other imidazoles (as distinct from the imidazolium salts) have the C-2 position substituted - with either CH_3 or C_2H_5 groups these remain amongst the most favoured sites of exchange (compounds 7, 5, 4 and 6 in that order). However, in contrast there is little incorporation into a phenyl group substituted at C-2 but when the ring contains a dimethylamino group specific tritiation occurs in the N-methyl groups. For the two imidazolium salts exchange into the aromatic rings is favoured; in the case of compound 10, exclusively.

The specific activities obtained by this labeling procedure for the tritiation of the epoxides (Table 1) are in general lower than for the imidazoles. The ^{3}H nmr results (Table 3) show that for compounds 1, 2 and 4 the labeling is confined to the aromatic positions. For compounds 3 and 5, for which the lowest specific activities were obtained, the labeling is surprisingly specific. The epoxides, contrary to the imidazoles, showed signs of undergoing decomposition during the catalytic procedure, probably because of attack by water on the epoxide ring at the high temperatures employed.



Nmr spectra of 1,2-epoxy decane

(a) ^1H nmr of inactive compound

(b) ^1H nmr of tritiated product

(c) ^3H nmr (^1H decoupled) of [G-^3H]-1,2-epoxy decane and/or temperature. Nevertheless for the application in mind the specific activities were more than adequate. Details of the kinetics of the reaction between the model epoxides and the imidazoles will be the subject of a separate publication.

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