A Novel Isotopic Hydrogen Labelling Procedure for Certain Cycloalkenes

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WE report a simple general labelling procedure for many of the cycloalkenes, using the addition–elimination reaction of hydrogen halides (HX) in the presence of isotopic water. Up to 80°, DX (or TX) adds to the cycloalkene; however, at approximately 110°, elimination of HX occurs leaving a deuterated (or tritiated) species. DCl was used in the present experiments (Table, showing a representative number of olefins), although DBr is probably even faster.[1] A methyl

TABLE

Exchange of cycloalkenes with deuterium chloride[a]

Run No.	Compound	% Approach to equilibrium isotope incorp.	Run No.	Compound	% Approach to equilibrium isotope incorp.
1	Cyclopentene	59·8[f]	9	1-t-Butylcyclohexene[c]	18·0
2	1-Methylcyclopentene	69·0[f]	10	4-t-Butylcyclohexene[d]	16·8
3	Cyclopentadiene	35·4	11	1-Phenylcyclohexene	9·0
4	1-Methylcyclohexene	57·0	12	Cycloheptatriene[f]	3·9
5	3-Methylcyclohexene	19·8	13	Cycloheptene[f]	25·0
6	4-Methylcyclohexene	18·8	14	1-Methylcycloheptene[e,f]	46·4
7	1,2-Dimethylcyclohexene	53·8	15	Cyclo-octene	19·8
8	1-Isopropylcyclohexene[b]	39·6	16	Cyclo-octa-1,5-diene	51·6

[a] DCl used for all reactions except runs 7, 9—11 ($DCl/SnCl_4$); all reactions performed for 48 hr. at 130° except runs 1—3, 12, 15, and 16 (24 hr.).

[b] 10% Cyclohexene formed with $DCl/SnCl_4$.

[c] 0·2% Cyclohexene formed.

[d] 3·7% 4-t-Butylcyclohexene isomerises to 1- and 3-t-butylcyclohexenes.

[e] 26·7% Cycloheptene formed.

[f] Deuteration under heterogeneous conditions (refs. 2 and 3); cyclopentene (2·5); 1-methylcyclopentene (6·0); cycloheptene (17·0); 1-methylcycloheptene (6·7); cycloheptatriene (0·4); cyclo-octene (23·3).

group adjacent to a double bond accelerates reaction whereas a small degree (~2%) of double-bond shift may be observed in 3- and 4-methylcyclohexenes. With isopropylcyclohexene, competing degradative elimination (10% under some conditions) occurs,[4] whereas with norbornene, limonene, α-pinene, and *p*-mentha-1,5-diene theoretical equilibrium is readily achieved although the final poduct is a mixture of at least four isomers in each case. Straight-chain alkenes readily exchange under these conditions yielding isomeric mixtures which in many instances can be separated by preparative gas chromatography.

The present technique is satisfactory for labelling with tritium at low-to-medium specific activities; however, care should be exercised in extrapolation to high specific activities with cyclohexene derivatives because of the possiblity of initiating a competing radiation-induced disproportionation reaction.

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