Secondary Deuterium Kinetic Isotope Effects in the Solvolysis of 4-t-Butylcyclohexyl and Bicyclo[3.2.1]octan-3-yl Toluene-*p*-sulphonates. New Results using 50% Aqueous Ethanol, Acetic Acid, and 97% Aqueous Hexafluoropropan-2-ol

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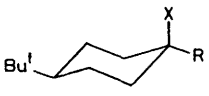
Secondary α-deuterium kinetic isotope effects for the solvolysis of *cis*- and *trans*-4-t-butylcyclohexyl toluene-*p*-sulphonates in 50% aqueous ethanol (1.200 ∓ 0.007 and 1.16 ∓ 0.01 respectively, 44.8°), acetic acid (1.172 ∓ 0.004 and 1.13 ∓ 0.01 respectively, 79.6°), and 97% aqueous hexafluoropropan-2-ol (1.232 ∓ 0.013, 40.0° and 1.175 ∓ 0.010, 56.2°, respectively) and for the solvolysis of *endo*- and *exo*-bicyclo[3.2.1]octan-3-yl toluene-*p*-sulphonates in 97% aqueous hexafluoropropan-2-ol (1.246 ∓ 0.009 and 1.234 ∓ 0.004 respectively, 25.2°) have been measured. Mechanisms for these reactions which involve ion-pair intermediates are proposed. Even in 97% aqueous hexafluoropropan-2-ol, intimate ion-pairs from *trans*-4-t-butylcyclohexyl toluene-*p*-sulphonate undergo further reaction more rapidly than internal return. The other three compounds investigated in this highly ionizing solvent of low nucleophilicity are believed to react, as anticipated, through reversibly formed intimate ion-pairs.

THE rates of acetolysis of *cis*- and *trans*-4-t-butylcyclohexyl toluene-*p*-sulphonates (tosylates) (1a) and (2a) were reported by Winstein and Holness,[1] and the products of solvolysis of these and other 4-t-butylcyclohexyl arenesulphonates have been investigated by Whiting [2] and his colleagues. Although the detailed product analyses provide important information about the rearrangement and product-determining steps, a fuller account of the whole solvolysis process has been facilitated by the technique of secondary deuterium kinetic isotope effect (k.i.e.) measurements. For the t-butylcyclohexane system so far, there have been published results only for the bromobenzene-*p*-sulphonates (brosylates) (1b) and (2b) in 50% aqueous ethanol (50E).[3]

Particularly interesting aspects of these results are that the α-k.i.e. for *trans*-brosylates (2b), 1.172 (35°), is distinctly lower than the value for the *cis*-diastereoisomers (1b), 1.202 (35°), and that both are lower than the maximum value currently expected for a secondary alkyl arenesulphonate undergoing solvolysis without nucleophilic assistance, *ca.* 1.23 (25°).[4] Related to these kinetic results, we believe, is the information that the ratio of inverted to retained substitution at the unrearranged position is consistently higher for the *trans*-4-t-butylcyclohexyl arenesulphonates than for the *cis*-stereoisomers (typically 46—107 compared with 10—19 respectively for acetolysis [2]).

It is desirable, when interpreting experimental results in terms of mechanistic detail for a given reactant, that rates and product analyses refer, as far as is practicable, to the same solvolytic conditions. If different carbocyclic systems are to be compared, it is essential that, as far as possible, the same leaving groups and solvolytic conditions be used.

In order to obtain α-k.i.e. results for compounds which have already been investigated by product analysis, and to be able to compare our results [5,6] for the solvolysis of bicyclo[3.2.1]octan-3-yl tosylates (3a,b) and (4a,b) with this other extensively investigated modified cyclohexyl system, we have measured the α-k.i.e. for the solvolysis of 4-t-butylcyclohexyl tosylates (1a,c) and (2a,c) in buffered acetic acid (AcOH) and 50E. We also present α-k.i.e. results for (1a,c), (2a,c), (3a,b), and (4a,b) in the highly ionizing, weakly nucleophilic medium, 97% aqueous hexafluoropropan-2-ol (97HFIP).[7,8] Only after the completion of our project did the first published report of other α-k.i.e. measurements in this solvent appear, results obtained for cyclopentyl brosylate by Shiner and his associates.[9]

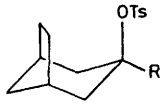


(1)

a: X = *p*-$CH_3C_6H_4SO_3$. R = H
b: X = *p*-$BrC_6H_4SO_3$. R = ^1H or ^2H
c: X = *p*-$CH_3C_6H_4SO_3$. R = ^2H

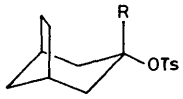
(2)

a: X = *p*-$CH_3C_6H_4SO_3$. R = H
b: X = *p*-$BrC_6H_4SO_3$. R = ^1H or ^2H
c: X = *p*-$CH_3C_6H_4SO_3$. R = ^2H
d: X = OH. R = ^1H or ^2H



(3)

a; R = ^1H
b; R = ^2H



(4)

a; R = ^1H
b; R = ^2H

RESULTS

Compounds (1a,c), (2a,c), (3a,b), and (4a,b) were all made by literature methods.[1,2,5,6] The deuterium incorporation of the trimethylsilyl ethers of the alcohol (2d) was measured by g.l.c.–mass spectrometry. The result (97% $^2H_1$) was corroborated by integrated ^1H n.m.r. spectroscopy on the tosylates (1a,c) ⩽3% ^1H at C(1). The deuterium content (>98% $^2H_1$) of (3b) and (4b) has already been reported.[6] No correction for incomplete deuteriation has been applied to the isotope effects which are shown in Table 1.

The results for (1a,c) and (2a,c) in 50E (1.200 and 1.16 respectively, 44.8°) are in good agreement with the values for the corresponding brosylates [3] (1.202 and 1.172 for *cis*-

and *trans*-isomers, 35°). The acetolysis result for the *cis*-compound (1.172, 79.6°) is comparable with, but slightly lower than, results reported earlier for the acetolysis of cyclohexyl tosylate (1.22,[10] 50.0° and 1.19,[11] 75.4°); the result for the *trans*-isomer (1.13, 79.6°) is distinctly lower. When the known temperature effect [4] is taken into account, it is seen that the change from the weakly ionizing, modestly nucleophilic acetic acid [8] to the strongly ionizing, strongly nucleophilic 50% aqueous ethanol [8] has no significant effect upon the α-k.i.e. of either (1a,c) or (2a,c).

In 97HFIP, the result for (1a,c) is 1.232 (40.0°) which, that this remains so even in 97HFIP. We know of no independent evidence that 97HFIP induces bimolecular substitution in solvolyses. But the observation [2] that the ratio of inversion to retention in the unrearranged substitution product from (2a) in other solvents is consistently higher than for (1a) appears to support this view. Several arguments, however, convince us that this is not correct. If the lower α-k.i.e. of (2a,c) is due to some S_N2 incursion, a change in solvent would cause different rate effects for (1a) and (2a) since solvents with

TABLE 1

Rates and secondary kinetic isotope effects for the solvolysis of (1a,c), (2a,c), (3a,b), and (4a,b) [a]

	AcOH [b]		50E [c]		97 HFIP [d]	
Compound	$10^5k^H/s^{-1}$	α-^{2}H-k.i.e.	$10^5k^H/s^{-1}$	α-^{2}H-k.i.e.	$10^5k^H/s^{-1}$	α-^{2}H-k.i.e.
(1a,c)	20.1 ∓ 1.3 [e] (79.6°)	1.172 ∓ 0.004 [f] (79.6°)	20.6 ∓ 0.4 (44.8°)	1.200 ∓ 0.007 (44.8°)	18.1 ∓ 0.8 [g] (40.0°)	1.232 ∓ 0.013 [f] (40.0°)
(2a,c)	7.92 ∓ 0.3 (79.6°)	1.13 ∓ 0.01 (79.6°)	4.55 ∓ 0.08 (44.8°)	1.16 ∓ 0.01 (44.8°)	45.3 ∓ 0.9 [i] (56.2°)	1.175 ∓ 0.010 (56.2°)
(3a,b)	63.4 ∓ 0.6 [h] (60.6°)	1.169 ∓ 0.008 [h] (60.6°)	49.1 ∓ 0.6 [f] (24.8°)	1.214 ∓ 0.007 [f] (24.8°)	282 ∓ 1 [e] (25.2°)	1.246 ∓ 0.009 25.2°
(4a,b)	14.4 ∓ 0.2 [h] (70.6°)	1.163 ∓ 0.008 [h] (70.6°)	4.26 ∓ 0.08 [f] (36.0°)	1.198 ∓ 0.008 [f] (36.0°)	11.0 ∓ 0.1 (25.2°)	1.234 ∓ 0.004 (25.2°)

[a] Rate constants are means of six values and isotope effects are means of six ratios unless otherwise indicated. Errors are standard errors. [b] Contains 0.15M-potassium acetate. [c] Aqueous 50% ethanol by volume containing 3.5×10^{-3}M-borax. [d] Aqueous 97% hexafluoropropan-2-ol by weight. [e] Mean of four values. [f] Mean of five values. [g] Mean of three values. [h] Ref. 6. [i] At 40 °C. $k^H = 3.98$ (∓0.2) $\times 10^{-5}$ s^{-1} (mean of four values).

on the basis of other experimental results,[4,12,13] is about the upper limit for S_N1 reactions. Remarkably, however, even in 97HFIP, the result for the *trans*-isomer (2a,c) is only 1.175 (56.2°): this is a surprisingly low α-k.i.e. for a secondary alkyl arenesulphonate in a solvent which, it has been postulated,[8,9,12,13] should cause all simple secondary alkyl arenesulphonates to react by the limiting extreme S_N1 mechanism. The ratio of the α-k.i.e. results for (1a,c) and (2a,c), therefore, remains constant at *ca.* 1.03—1.04 through AcOH, 50E, and 97HFIP. [The temperature difference between the reactions of (1a,c) and those of (2a,c) in 97HFIP is not large enough to be significant.]

We reported α-k.i.e. results earlier for the solvolysis of (3a,b) and (4a,b) in a range of solvents.[6] In all but the most nucleophilic, most weakly ionizing medium (98% aqueous ethanol), the results were uniformly high: 1.19—1.20 (25°) in formic and acetic acids, 50 and 80% aqueous ethanol, and 97% aqueous 2,2,2-trifluoroethanol (97TFE). The values are lower, however, than the limiting value of *ca.* 1.23, and were ascribed to a principal solvolytic mechanism which involves rate-determining ionization. The expectation was that 97HFIP would facilitate ionization but not subsequent nucleophilic capture of the intimate ion-pair or β-proton abstraction, consequently further reaction of the intimate ion-pair should become rate determining and the α-k.i.e. for both compounds would increase to the limiting value of *ca.* 1.23 (25°). The present results (Table 1) for (3a,b) and (4a,b) (1.246 and 1.234 respectively, 25.2 °C) are in accord with this earlier prediction.

DISCUSSION

Two plausible explanations of the anomalously low α-k.i.e. result for (2a,c) in 97HFIP originate in Schleyer's expositions of solvolysis mechanisms.[8,14,15] One is that covalent (2a,c) are solvolysed with a higher proportion of solvent-induced S_N2 mechanism than are (1a,c) and unequal ionizing and nucleophilic properties should cause different proportions of S_N1 and S_N2 for the two substrates. As can be seen from Table 2, the rate ratio for (1a) : (2a) in ethanol, acetic acid, formic acid, and 97HFIP, solvents which represent a wide range in nucleophilic and ionizing properties, are rather similar at 40 °C. And, if reaction of (2a) in the strongly nucleophilic ethanol includes a significant S_N2 contribution, the addition of ethoxide should enhance the rate and introduce an appreciable second-order term into the

TABLE 2

Rate constants and rate ratios for solvolysis of 4-t-butylcyclohexyl toluene-*p*-suphonates (1a) and (2a) at 40 °C

	$10^5k/s^{-1}$		Ratio
Solvent	(1a)	(2a)	k(1a)/k(2a)
C_2H_5OH [a]	0.120	0.0278	4.3
CH_3CO_2H [a]	0.122	0.0348	3.5
HCO_2H [a]	88.1	23.3	3.8
97HFIP [b]	18.1	3.98	4.5

[a] Results extrapolated from literature values [1] at other temperatures. [b] This work.

rate law. This was not found.[1] The product analyses, however, constitute the most compelling reason for rejecting the bimolecular substitution mechanism as the sole or principal cause of the lower α-k.i.e. for (2a,c).

It is known that a completely unimolecular solvolysis reaction [2-adamantyl 2,2,2-trifluoroethanesulphonate (tresylate) in 97TFE [13] or tosylate in trifluoroacetic acid [12]] has an α-k.i.e. of *ca.* 1.23 (25 °C) and that such reactions of the adamantyl system are overwhelmingly substitutions (S_N1).[16] Correspondingly, the α-k.i.e. for a clean S_N2 reaction of a secondary alkyl sulphonate ester is expected to be *ca.* 1.0.[4,17] But the major product from ethanolysis and acetolysis of (2a) [as

for (1a)] is 4-t-butylcyclohexene, and unrearranged substitution represents <20% of the overall reaction. Consequently, a reduction in the α-k.i.e. for the *overall* reaction from a hypothetical limiting value of *ca.* 1.23 to, for example, 1.17 in aqueous ethanol cannot be accommodated simply by varying the relative proportions of S_N1 and S_N2 mechanisms within only 20% of the total reaction.

The other explanation due to Schleyer for α-k.i.e. being less than the maximal value of *ca.* 1.23 (25 °C) is steric in origin. Although Shiner has argued that the structure of the alkyl group has little effect upon an α-k.i.e.,[4] Schleyer has claimed that buttressing of the α-C–H by bulky alkyl groups can depress the α-k.i.e.[15] Low results for pinacolyl brosylate (1.153; 97TFE; 25 °C)[18] and 1-(1-adamantyl)ethyl brosylate (1.107; 97TFE; 25 °C) have been ascribed to this effect.[15] Without wishing at the present to comment upon the general validity of this argument, we cannot accept it as significant in the solvolysis of (2a). In the molecular vicinity of the reaction site, (2a) is simply a cyclohexane derivative. There is less molecular congestion in (2a) than in either (3a), (4a), or 2-adamantyl tosylate none of which show reduced α-k.i.e.s in 97HFIP [(3a) and (4a)] or other highly ionizing solvents (2-adamantyl tosylate).

The explanation which we prefer has its basis in the extended ion-pair mechanism for solvolysis which has been developed over the years for example by Winstein,[19] Shiner,[18,20] Sneen,[21] and others.[5,6,16,22] On the basis of presently available evidence, we believe that the cause of the surprisingly low α-k.i.e. for (2a) in 97HFIP is its unusually low ratio of internal return to further reaction, and because this ratio is consistently lower for (2a) than for (1a), (3a), and (4a) in all the solvents that we have used, the α-k.i.e. for (2a,c) is consistently lower than the values for (1a), (3a), and (4a) in these solvents as well.

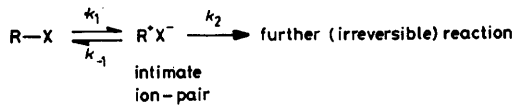
It is well known that secondary alkyl arenesulphonates undergo some extent of internal return during solvolysis.[23–26] It has been detected by an isotope scrambling study for *trans*-4-t-butylcyclohexyl tosylate in acetic acid[25] and, for *cis*-4-t-butylcyclohexyl tosylate, by isolation of the *trans*-tosylate after interrupting the incomplete solvolysis in acetic acid and in aqueous acetone.[23] And it has also been established by product analysis that internal return occurs in deamination reactions with both inversion and retention of configuration.[27]

The effect of different extents of internal return upon the α-k.i.e. of *cis*- and *trans*-4-t-butylcyclohexyl tosylates is estimable on the basis of current theory.[13,19,28,29] For the abbreviated general ion-pair solvolysis mechanism shown in the Scheme, the solvolytic kinetic isotope effect, $k.i.e._t$, is given by equation (1) where $k.i.e._i$ and p.i.e.

$$k.i.e._t = k.i.e._i \times p.i.e. = \frac{k_1^H}{k_1^D} \times \frac{k_2^H}{k_2^D} \cdot \frac{(k_{-1}^D + k_2^D)}{(k_{-1}^H + k_2^H)} \quad (1)$$

are the ionization and the partitioning[29,30] isotope effects respectively.

When $k_{-1} > k_2$ (substantial internal return) p.i.e. $\sim (k_2^H/k_2^D)(k_{-1}^D/k_{-1}^H)$ and if the composite rate constant k_2 is predominantly for ion-pair separation or alkene formation (as opposed to solvent capture of the intimate ion-pair), then p.i.e. >1.[29] This is because there will be more extensive covalence between leaving group and



SCHEME

nascent carbonium ion at the transition state for ion-pair formation (return) than at the transition state for ion-pair separation or β-proton abstraction.[9] For such a mechanism, relationship (2) applies where K^H/K^D

$$k.i.e._t \sim \frac{k_1^H}{k_1^D} \times \frac{k_2^H}{k_2^D} \cdot \frac{k_{-1}^D}{k_{-1}^H} = \frac{K^H}{K^D} \times \frac{k_2^H}{k_2^D} \quad (2)$$

is the *equilibrium isotope effect* for the pre-equilibrium between covalent starting material and intimate ion-pairs.

Solvolyses of 2-adamantyl tosylate[12] and tresylate[13] in all common solvents, and the few other previously reported reactions of secondary alkyl arenesulphonates in such highly ionizing solvents as trifluoroacetic acid are accommodated by this mechanism and correspond to the limiting α-k.i.e. of *ca.* 1.23 (25 °C).[4,12,13] The present results for (1a,c), (3a,b), and (4a,b) in 97HFIP also fit this mechanism.

On the other hand, if $k_2 > k_{-1}$ (little or no internal return) and k_2 again comprises β-proton abstraction or ion-pair separation (rather than nucleophilic capture), then from equation (1) p.i.e. ~ 1 and $k.i.e._t \sim k.i.e._i = k_1^H/k_1^D$. We have already ascribed this mechanism to the reactions of (3a,b) and (4a,b) in solvents less ionizing than 97HFIP.[6]

The present α-k.i.e. result for *trans*-4-t-butylcyclohexyl tosylate even in 97HFIP is compatible with such a mechanism. In other words, not even 97HFIP causes the transition state for ionization (internal return) of (2a) to become significantly lower in free energy than the activated complexes for ion-pair separation or β-proton abstraction.

Shiner[9] has recently pointed out that rate-determining solvent capture of the intimate ion-pair in a substitution reaction would also give rise to an α-k.i.e. which is less than the limiting maximum (1.23; 25 °C). This is because the activated complex associated with this mechanism includes partial covalent bonding between the incoming nucleophile and the electron-deficient carbonium ion of the intimate ion-pair. In the Scheme, this corresponds to $k_{-1} > k_2$ with k_2 being predominantly for solvent capture of the intimate ion-pair as opposed to ion-pair separation or β-elimination. Such a mechanism would lead to substitution with inversion of configuration and, indeed, (2a) shows a higher ratio of

inversion to retention than (1a) as mentioned above. Although this mechanistic possibility must in general be considered, it can be ruled out in the present case by the product analysis. It represents, of course, Sneen's solvolytic S_N2 mechanism [21] which has been severely and, in some cases unjustifiably, criticised,[31] and is vulnerable to the evidence brought against the conventional S_N2 involvement (see above): unrearranged substitution is such a small proportion of the overall reaction (<20% in acetic acid and aqueous ethanol).

Each of compounds (3) and (4) has only two principal conformations, the six-membered ring in chair and boat forms, because the bicyclic system is sufficiently rigid that twist forms of the six-membered ring are inaccessible.[5,32] Compound (3a) reacts principally, perhaps exclusively, through its ground-state conformation with an axial tosylate group whereas the evidence suggests that (4) reacts mainly through its less stable conformation with the tosylate leaving group in a *quasi*-axial position on the boat-shaped six-membered ring.[5,6]

Analogously, (1a—c) react through their chair forms and (2a—c) react mainly through twist forms.[2,3] Consequently, the slowness of ionization of (2a), even in 97HFIP, may be due not so much to the low partial rate factor for ionization of some appropriate twist conformer, as to its exceedingly low concentration.[1,2] And the proportion of this unstable conformer may be largely unaffected by the nature of the solvent.

A satisfying corollary of this interpretation of an unexpected result is that we are provided with an acceptable reason for the consistently higher inversion : retention ratio of unarranged substitution products for (2a) compared with (1a). If compound (2a) undergoes only little internal return in any solvent, it has the very high inversion : retention associated with nucleophilic capture of first-formed intimate ion-pairs. Compound (1a) on the other hand, in the more ionizing less nucleophilic solvents, undergoes extensive internal return. When this occurs with inversion of configuration [23] to give the more stable less reactive *trans*-isomer, *subsequent* ionization and solvent capture of the new intimate ion-pair leads to substitution with *overall* retention of configuration. Furthermore, as the proportion of the reaction which proceeds through solvent-separated ion-pairs increases, the stereospecificity of substitution may be expected to decrease. This is because the cation of a solvent-separated ion-pair should be better able than the cation of an intimate ion-pair to react with solvent from both sides. It would be interesting to know what the stereochemical result is for the unrearranged substitution in the very highly ionizing non-nucleophilic solvents.

EXPERIMENTAL

The preparation and characterization of (3a,b) and (4a,b) have already been described.[6]

Hexafluoropropan-2-ol was dried over molecular sieves and fractionally distilled from barium oxide.[33] 97HFIP was 3 parts water + 97 parts hexafluoropropan-2-ol by weight. Water was distilled from potassium permanganate solution. The preparation of other solvolysis media, the solvolytic procedures, and details of our kinetics methods have already been described.[5,6,30,34]

4-t-Butylcyclohexanols (Emanuel) were separated by alumina chromatography (light petroleum–ethyl acetate) and purified by sublimation (80° at 4 Torr). Each was shown by g.l.c. to be uncontaminated with its diastereoisomer (<0.7%): *cis*-isomer, m.p. 78—78.5° (lit.,[1] 80.5—81.5°); *trans*-isomer, m.p. 76—77° (lit.,[1] 80—81°).

4-t-Butylcyclohexyl toluene-*p*-sulphonates were made from the corresponding alcohols by the Tipson [35] method and were recrystallized at low temperature from light petroleum; *cis*-isomer (1a), m.p. 74.5—75° (lit.,[1] 79—80°); $\bar{\nu}_{max.}(CCl_4)$ 2 950, 2 870, 1 370, 1 190, 1 175, 912, 870, and 675 cm^{-1}; $\tau(CCl_4)$ 2.3 and 2.6 (4 H, ABq, *J ca.* 8 Hz), 5.34 (1 H, m), 7.57 (3 H, s), 7.7—9.3 (9 H, m), and 9.15 (9 H, s); *trans*-isomer (2a), m.p. 88—89° (lit.,[1] 89.4—90°); $\bar{\nu}_{max.}(CCl_4)$ 2 950, 2 865, 1 370, 1 190, 1 180, 950, 850, and 670 cm^{-1}; $\tau(CCl_4)$ 2.35 and 2.8 (4 H, ABq, *J ca.* 8 Hz), 5.5—6.0 (1 H, m), 7.60 (3 H, s), 7.7—9.3 (9 H, m), and 9.19 (9 H, s).

1-Deuterio-4-t-butylcyclohexanols were made by reduction of 4-t-butylcyclohexanone with sodium borodeuteride in ethanol under reflux for 48 h. The 1 : 3 mixture of *cis*- and *trans*-isomers was separated and the isomers were purified as described above for the perprotio-analogues: *cis*-isomer, m.p. 78—78.5°; *trans*-isomer, m.p. 76—77°. Mass spectral analysis of the trimethylsilyl ether of the *trans*-isomer showed 96.7% deuterium incorporation.

The deuteriated tosylates (1c) and (2c) were made and purified as described above for the perprotio-analogues: *cis*-isomer (1c), m.p. 73.5—74.5°; $\bar{\nu}_{max.}(CCl_4)$ 2 950, 2 870, 1 368, 1 195, 1 175, 910, and 672 cm^{-1}; $\tau(CCl_4)$ 2.31 and 2.73 (4 H, ABq, *J* 8.2 Hz), 7.59 (3 H, s), 7.9—9.1 (9 H, m), and 9.17 (9 H, s); no signal was detected at τ *ca.* 5.3 even at high sensitivity using a concentrated solution; *trans*-isomer (2c), m.p. 87—88°; $\bar{\nu}_{max.}(CCl_4)$ 2 955, 2 865, 1 370, 1 190, 1 180, 1 055, 940, 930, 920, 850, and 670 cm^{-1}.

Analytical g.l.c. was done on a Perkin-Elmer F11 gas chromatograph fitted with an inlet splitter, using a 50 ft SCOT Carbowax 20M column at 160° with nitrogen (20 lb in^{-2}) as carrier gas. The n.m.r. spectra (60 MHz) and i.r. spectra were recorded on Perkin-Elmer–Hitachi R24 and Perkin-Elmer 457 instruments respectively. Mass spectrometry was done by P.C.M.U., Harwell.

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