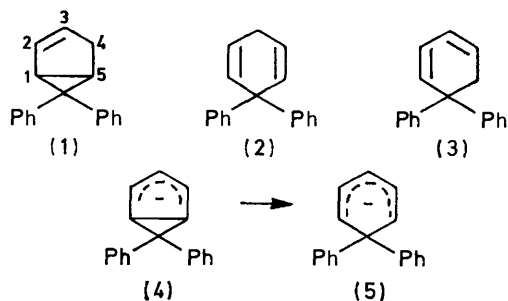


Base-catalysed Rearrangement and Hydrogen Isotope Exchange Reactions of Tricyclo[7.1.0.0^{2,7}]deca-2(7),3,5-triene (Cyclopropindene) and Related Compounds

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The rates of rearrangement and hydrogen isotope exchange of the title compound, catalysed by potassium *t*-butoxide in dimethyl sulphoxide or by potassium *t*-pentoxide in *t*-pentyl alcohol have been measured, and compared with the exchange rates for model hydrocarbons. It is tentatively suggested that the kinetic results taken together with the low stereoselectivity in the deprotonation step may be consistent with the participation of a tricyclodecatrienyl (homoindenyl) anion intermediate possessing a small degree of homoaromatic character. Exchange in benzylcyclopropane was only slightly faster than that in isobutylbenzene, indicative of the absence of substantial stabilisation of a benzylic carbanion by an α -cyclopropyl substituent.

In the course of investigations into the chemistry of cyclohexadienyl radicals, it was recently demonstrated that the dienes (2) and (3) could be obtained by the base-catalysed rearrangement of the diphenylbicyclohexene (1).¹ This isomerisation was effected in boiling



t-pentyl alcohol (Am^tOH), employing potassium *t*-pentoxide (Am^tOK) as the base. The reaction is essentially a carbanionic cyclopentenyl \rightarrow pentadienyl rearrangement [(4) \rightarrow (5)], in which the driving force is relief of strain in the bicyclic structure. The opening of a cyclopentenyl anion is expected to follow a disrotatory course,² and the constraint of the extra bonding to C-6 in the particular case of bicyclohexenyl anions such as (4) in no way inhibits this.

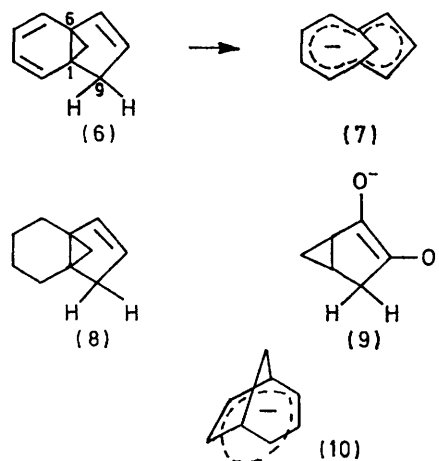
It seemed of interest to enquire whether, in the rearrangement of (1), two discrete carbanions are involved, or whether instead deprotonation and rearrangement might occur in concert. Two principal approaches to this problem were considered. In the first of these, the possibility of base-catalysed hydrogen isotope exchange in competition with the rearrange-

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‡ Inspection of models indicates that the five-membered ring in (1) is essentially planar, and therefore that no appreciable stereoselection in deprotonation is likely to arise simply from more favourable overlap with the π electrons of the double bond.

ment was explored. A preliminary experiment, in which (1) was recovered after *ca.* 35% rearrangement in Am^tOD and was subsequently examined by n.m.r. spectroscopy, revealed no evidence for the incorporation of deuterium (however see below).

The second approach depended on an investigation of stereoselection in deprotonation at C-4. It was considered that if pericyclic reorganisation occurs in concert with (and probably therefore gives assistance to) deprotonation there might be significant stereoelectronic control of the direction of deprotonation.‡ A precedent



for this exists in the stereochemical results on deprotonation of (6) to give the bridged 10π carbanion (7).³ This occurs by removal of the proton at C-9 *anti* to the

¹ D. J. Atkinson, M. J. Perkins, and P. Ward, *J. Chem. Soc. (C)*, 1971, 3240. See also S. W. Staley and J. P. Erdman, *J. Amer. Chem. Soc.*, 1970, **92**, 3832.

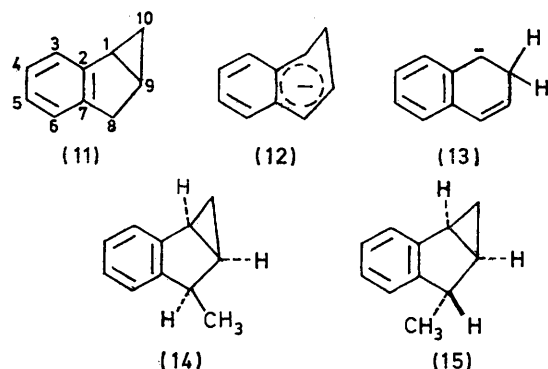
² (a) R. B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry,' Academic Press, New York, 1970; (b) M. J. Perkins and P. Ward, 'Mechanisms of Molecular Migrations,' ed. B. S. Thyagarajan, Wiley, New York, vol. IV, 1971.

³ P. Radlick and W. Rosen, *J. Amer. Chem. Soc.*, 1967, **89**, 5308.

cyclopropane ring, at a rate greater by a factor of 10^4 than deprotonation of (8) under comparable conditions. This rate enhancement provides compelling evidence for the occurrence of pericyclic reorganisation to the 10π aromatic anion in concert with deprotonation, and the 100% stereoselectivity in the deprotonation suggests the operation of powerful stereoelectronic control, reminiscent of that which operates in the solvolysis of cyclopropyl halides.^{2a,4}

Stereoelectronic control has also been postulated to account for the preferential (*ca.* 100 : 1) exchange of the *exo*-hydrogen in (9),^{5,*} although electronic factors were considered to be unimportant in a rationalisation of the slight stereoselectivity found in the protonation of the homoaromatic ion (10).⁶ Indeed, the direction of this depends on whether the proton is supplied by dimethyl sulphoxide (DMSO) or by methanol.

Because of the intimidating synthetic problems attendant on any attempt to probe the stereochemistry of the apparently irreversible deprotonation of (1), our attention was turned to the reaction of the tricyclo-[7.1.0.0^{2,7}]deca-2(7),3,5-triene (cyclopropindene) (11) with base. The base-catalysed isomerisation of this compound was found to give 1,2-dihydronaphthalene in essentially quantitative yield, both in DMSO-Bu^tOK,



and in Am^tOH-Am^tOK. The progress of the reactions could conveniently be monitored either by g.l.c. or by n.m.r. spectroscopy. No evidence was found for the formation of methylindenes, and base-catalysed dimerisation of the product⁷ was slow compared with the rearrangement. In [²H₆]DMSO the reaction occurs without detectable incorporation of deuterium into unrearranged starting material (by mass spectrometry), but in Am^tOD deuterium incorporation does compete with rearrangement, indicating the probable intermediacy of a discrete but short-lived bicyclic carbanion. It seemed possible that such a carbanion might properly be represented with some degree of homoaromatic delocalisation (12) quite distinct from the delocalisation in the cyclohexadienyl anion (13) to which it rearranges. To test

* More recently, however, a purely steric argument has been preferred for the stereoselectivity of this process (G. A. Russell, personal communication).

† This gross assumption finds a measure of support in the observation that the rearrangement rate does not decrease significantly as the reaction proceeds. Such a result is not unexpected if internal return is important.⁹

this possibility we have endeavoured to compare the rates of isomerisation and hydrogen isotope exchange in (11) with the rates of hydrogen isotope exchange in indane and tetralin. The possibility of stereoselection in the hydrogen exchange reaction of (11) has also been investigated, both by examining the stereochemistry of exchange in (11) itself, and by measuring the rates of exchange and rearrangement in the methyl derivatives (14) and (15).

Compounds (14) and (15) were prepared by cyclopropanation of 3-methylindene, the latter having been obtained by dehydration of 3-methylindan-1-ol over boric acid. The isomeric methyl derivatives (14) and (15) were separated by preparative g.l.c., and the major product was shown to have the *exo*-structure (15), on the basis of a negligible coupling constant between 8- and 9-H.⁸ For the minor (*endo*) isomer $J_{8,9}$ was 6.5 Hz.

The base-catalysed rearrangement of these methyl derivatives paralleled that of (11) itself. The product was an equilibrium mixture of 1-methyl- and 4-methyl-1,2-dihydronaphthalene. In Am^tOD-Am^tOK, both methyl derivatives of (11) incorporated deuterium in competition with their rearrangement. Epimerisation at C-8 was, however, slight, consistent with pronounced ion-pairing effects. Rearrangement of all three hydrocarbons in both [²H₆]DMSO-KOBu^t and Am^tOD-Am^tOK exhibited excellent pseudo-first-order kinetics, and the results are summarised in Table 1. Deuterium exchange in the alcoholic solvent was monitored mass spectrometrically after *ca.* 25% reaction, and was found to have occurred to a comparable extent in each of the three compounds (Table 2). Evidently the rate of exchange is greater than the rate of rearrangement. A simple analysis neglecting any primary isotope effect on the rearrangement of the deuteriated tricyclocarbenes[†] leads to a ratio $k_{\text{exch.}} : k_{\text{rearr.}}$ of *ca.* 2–3 for all three compounds. In view of this, the parallel (Table 1) between the rate ratios for rearrangement in the two solvent systems is not surprising.

Comparison of exchange and rearrangement in the isomers (14) and (15), suggests that a small preference for *exo*-proton abstraction may exist, although this effect is clearly several orders of magnitude smaller than that found in deprotonation of (6).

An *exo*-selectivity was also found in the exchange reaction of the unsubstituted compound (11). Recovery of unchanged (11) after exposure to Am^tOK-Am^tOD, and examination by n.m.r. spectroscopy confirmed that partial exchange had occurred at C-8, and revealed that it was predominantly the *exo*-proton which had

⁴ S. J. Cristol, R. M. Sequeira, and C. H. DePuy, *J. Amer. Chem. Soc.*, 1965, **87**, 4007.

⁵ G. A. Russell, J. J. McDonnell, P. R. Whittle, R. S. Givens, and R. G. Keske, *J. Amer. Chem. Soc.*, 1971, **93**, 1452.

⁶ J. M. Brown and E. N. Cain, *J. Amer. Chem. Soc.*, 1970, **92**, 3821.

⁷ L. G. Wideman, *J. Org. Chem.*, 1970, **35**, 1698.

⁸ J. D. Graham and M. T. Rogers, *J. Amer. Chem. Soc.*, 1962, **84**, 2249.

⁹ (a) J. E. Hoffmann, A. Schriesheim, and R. E. Nichols, *Tetrahedron Letters*, 1965, 1745; (b) D. J. Cram, 'Fundamentals of Carbanion Chemistry,' Academic Press, New York, 1965, p. 28.

been replaced. Nevertheless, prolonged exposure to these conditions and examination of unrearranged (11) after *ca.* 90% rearrangement using combined g.l.c.-m.s. revealed substantial incorporation of a second deuterium atom, and partial incorporation of a third (Table 2, expt. 2). The unexpected exchange of a third hydrogen

cyclohexene and cyclopentene by De Boer *et al.*,¹⁰ though we prefer an interpretation of these differences in terms of the increased strain imposed in the case of the five-membered ring on formation of the benzylic (or allylic) carbanion (*I* strain).¹¹ Extension of this argument would lead to the prediction that proton

TABLE 1
Rates ^a of rearrangement of (11) and its 4-*endo*- (14) and 4-*exo*- (15) methyl derivatives in Bu^tOK-DMSO and Am^tOK-Am^tOH

Compound	DMSO ^{b,c}				Am ^t OH ^{e,f}			
	Expt. no.	Temp. (°C)	10 ⁴ k/s ⁻¹	k _{rel.} ^d	Expt. no.	Temp. (°C)	10 ⁴ k/s ⁻¹	k _{rel.}
(11)	1	33.4	2.8	15	5	145.0	1.74	
				(A)	6	180.0	53.7	
(15)	2	33.4	0.18	1.0	7	165.0	13.5	10.8
				(B)	8	165.0	1.25	1.00
(14)	4	60.0	11.5		9	165.0	4.68	3.73

^a Pseudo-first-order rate constant (*ca.* ±5% in DMSO, ±1% in Am^tOH; each figure represents a mean of at least four experiments). ^b 0.88M in Bu^tOK (expts. 1 and 2) or 0.79M (expts. 3 and 4). ^c Followed by n.m.r. integration of the product vinyl proton(s) against the aromatic protons as internal standard. ^d Column (A): relative rates at 33.4°; column (B): relative rates at 60.0°. ^e 1.307M in Am^tOK (expts. 5-9). ^f Followed by g.l.c.

TABLE 2
Deuterium exchange rates for (11) and its 4-*endo*- (14) and 4-*exo*- (15) methyl derivatives in Am^tOK-Am^tOD ^a

Expt. no.	Compound	Unchanged ^b starting material (%)	Deuterium analysis (%) ^c					10 ⁴ k _{exch.} /s ⁻¹ ^d	k _{exch.} /k _{rearr.}
			² H ₀	² H ₁	² H ₂	² H ₃	² H ₄		
1	(11)	73.5	49.6	44.2	6.2	0.0	0.0	3.7	2.3
2	(11)	15.5	13.7	41.5	40.2	4.6	0.0	1.5 ^e	
3	(14)	73.5	52	N.d.				1.2	2.1
4	(15)	78.0	65	N.d.				0.28	1.7

^a 0.85M in Am^tOK for expts. 1 and 2 and at 165.0°; 1.1M for expts. 3 and 4 and at 160.0° ^b G.l.c. analysis of the quenched sample. ^c Analysis by coupled g.l.c.-m.s. at low eV for expts. 1 and 2; approximate values by n.m.r. integration for expts. 3 and 4. ^d Approximate pseudo-first-order rate constant ($-\log[{}^2\text{H}_0] = k_{\text{exch.}}t$) calculated from the single analysis. ^e Figure unreliable since solvent contains *ca.* 10% protium.

may involve the benzylic cyclopropane position, although a benzylic ion at this site would be highly distorted.

TABLE 3

Observed pseudo-first-order rate constants (s⁻¹) for deuterium exchange of aralkanes in [²H₆]DMSO-Bu^tOK and Am^tOD-Am^tOK

Compound	10 ⁴ k in [² H ₆]DMSO ^{a,b}	10 ⁵ k in Am ^t OD ^d
Indane	0.57 ± 0.4	2.25 ± 0.2
Tetralin	5.5 ± 0.3	N.d.
(16)	13.3 ± 0.6	N.d.
Benzylcyclopropane	27.5 ± 1.5	14.5 ± 1.0
n-Butylbenzene	2.54 ± 0.1	2.8 ± 0.15
Isobutylbenzene	0.65 ± 0.04	N.d.
Rearrangement of (11)	27 ± 1.5 ^e	10.2 ± 0.1

^a 0.728M-Bu^tOK at 43.0 ± 0.05°. ^b Simultaneous exchange technique used (see Experimental section). ^c k_{obs} For rearrangement of (11) in the same reaction medium at the same temperature. ^d 1.10M-Am^tOK at 160.0°.

The rates of exchange of protium for deuterium in tetralin and indane are given in Table 3. The exchange rate for indane is appreciably smaller than that for tetralin, and this parallels the results obtained with

¹⁰ S. B. Tjan, H. Steinberg, and T. J. de Boer, *Rec. Trav. chim.*, 1969, **88**, 680, 690.

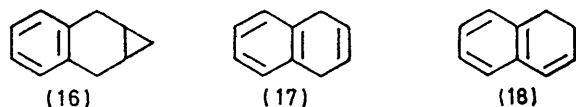
abstraction from (11) should be even slower than that from indane under comparable conditions. The experimental result is clearly contrary to this. In Am^tOD at 160°, *rearrangement* of (11) occurs more rapidly than does exchange in indane by a factor of *ca.* 9 (per benzylic hydrogen). As exchange in (11) is faster than rearrangement by a factor of *ca.* 2, and in addition a stereoselectivity factor dictates that this exchange rate refers predominantly to only the *exo*-proton at C-8, it seems probably that the rate of exchange of the *exo*-proton in (11) is greater than that of exchange of one proton in indane by a factor of at least 30 at this temperature. As both benzylic hydrogen atoms in (11) appear to be similarly orientated with respect to the adjacent π-system, there remain only two plausible interpretations of this high reactivity. These are stabilisation of the incipient carbanion either by the cyclopropyl group, or by homoaromatic electron delocalisation [development of homoiindenyl anion character (12)].

When this work was initiated, little was known concerning the effect of a cyclopropyl substituent on the ease

¹¹ E. L. Eliel, 'Stereochemistry of Carbon Compounds,' McGraw-Hill, New York, 1962, p. 265.

of formation of a carbanion.* Therefore a series of model studies was undertaken in which base-catalysed exchange of benzylic hydrogen in a series of aralkanes was examined. The results of this work, which have been set out in a preliminary communication,¹⁴ are summarised in Table 3. It seems clear that cyclopropyl substitution can facilitate carbanion formulation, but that the effect is a small one. This effect may stem in part from a weak conformation-dependent conjugative effect,¹⁵ and in part from an electronegativity effect resulting from the hybridisation in a bond to a cyclopropane ring.¹⁶ The results obtained were inadequate to determine the relative importance of these effects. A complete set of results in both base systems has not been obtained. Nevertheless, where comparison is possible a reasonable parallel exists, except that the spread of rate constants is magnified at the lower temperatures required for experiments in $[^2\text{H}_6]\text{DMSO}$.

The comparison of tricycloundecatriene (16) and tetralin was at first considered to afford a particularly appropriate reference for comparison of indane and tricyclodecatriene. However, in view of the small rate differences involved, conformational factors may be very important, in particular the orientation of the benzylic C-H bonds in (16) with respect to both the



π system and the cyclopropane ring. Examination of (16) after partial exchange by n.m.r. spectroscopy suggested some stereoselectivity in the exchange of benzylic hydrogen in this compound. However, because of a probable boat-boat interconversion of the cyclohexene ring (*cf.* the conformation of 1,4-cyclohexadienes¹⁷ and 9,10-dihydroanthracenes¹⁸) and its unknown equilibrium constant it has not yet been established which hydrogen is preferentially exchanged.

Theoretical analyses¹⁹ of stabilisation to be expected in cyclopropylcarbinyl anions give conflicting results. Destabilisation has been predicted by Miller,^{19a} whilst Danen,^{19b} using the INDO approximation, has con-

* In earlier work showing some evidence for stabilisation of a carbanion centre by cyclopropyl substitution, opening of the three-membered ring occurred.¹² Thus kinetic evidence for stabilisation of the anionic centre may in that case have been due to concerted rupture of the cyclopropane ring. However the fact that base-catalysed exchange in ethylcyclopropane occurs fastest at the unsubstituted cyclopropane positions suggests that any stabilisation of an adjacent carbanion by a cyclopropyl substituent must be small.¹³

¹² J. A. Landgrebe and J. D. Shoemaker, *J. Amer. Chem. Soc.*, 1967, **89**, 4465. See also E. Dunkelblum and S. Brenner, *Tetrahedron Letters*, 1973, 669.

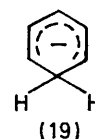
¹³ A. I. Shatenshtein, E. A. Yakovleva, M. I. Rikhter, M. Lukina, M. Yu, and B. A. Kazanskii, *Izvest. Akad. Nauk S.S.S.R. Otdel. Khim. Nauk*, 1959, 1805; A. I. Shatenshtein, *Adv. Phys. Org. Chem.*, 1963, **1**, 176.

¹⁴ M. J. Perkins and P. Ward, *Chem. Comm.*, 1971, 1134.

¹⁵ (a) W. A. Bennett, *J. Chem. Educ.*, 1967, **44**, 17; (b) M. Charton, 'The Chemistry of Alkenes,' ed. J. Zabicky, Interscience, New York, 1970, vol. 2, ch. 10; (c) M. E. H. Howden and J. D. Roberts, *Tetrahedron Supplement*, 1963, **2**, 403; (d) R. J. Piccolini and S. Winstein, *ibid.*, p. 423.

cluded that there might be some stabilising interaction, but if so that is likely to be small and not significantly dependent on the hybridisation of the carbanion centre or of the conformation of the molecule.

Returning to the question of hydrogen exchange in (11), the 30-fold rate enhancement compared with indane in the reactions at 160° seems too large to be explained simply in terms of cyclopropyl conjugation, particularly in view of the *I* strain argument that a rate reduction might have been expected. This leaves the possibility of weak homoaromatic stabilisation in the developing carbanion, although clearly the effect is very small compared with that in, for instance, (6). As with (6) it is possible that our results are explicable in terms of a single carbanion. This could have either a bicyclic or a cyclohexadienyl structure. However such an interpretation requires the assumption of extensive internal return effects in ion-pair intermediates (see below), and is less attractive than one involving the bicyclohexenyl \rightarrow cyclohexadienyl carbanion rearrangement already outlined. Nevertheless it should be appreciated that, although hydrogen exchange in the dienes (17) and (18) is very much more rapid than that in the thermodynamically less stable (11), the cyclohexadienyl anion initially formed from the rearrangement of the tricyclodecatrienes must be a different isomer from that involved in the base-catalysed hydrogen exchange of dihydronaphthalenes. Furthermore, whilst the kinetic barrier to protonation of a hypothetical single carbanion intermediate to give a bicyclic product may normally be much higher than that for protonation to give diene, this may not be so when the precursor of the anion is bicyclic. It is conceivable that reversion to bicyclic product might be preferred until the initially-formed ion pair and its solvation shell have together relaxed to an equilibrium situation. In this context, however, it must be noted that spectroscopic evidence suggests that the unsub-



stituted cyclohexadienyl anion (C_6H_7^-) is best represented as (19) with negligible homoaromatic delocalisation.²⁰

One interesting piece of evidence, which may be

¹⁶ A. Streitwieser, G. R. Ziegler, P. C. Mowery, A. Lewis, and R. G. Lawler, *J. Amer. Chem. Soc.*, 1968, **90**, 1357.

¹⁷ *E.g.*, O. L. Chapman and P. Fitton, *J. Amer. Chem. Soc.*, 1963, **85**, 41; H. Oberhammer and S. H. Bauer, *ibid.*, 1969, **91**, 10; D. J. Atkinson and M. J. Perkins, *Tetrahedron Letters*, 1969, 2335; but see also *e.g.*, G. Dallinga and L. H. Toneman, *J. Mol. Struct.*, 1967, **1**, 117; J. Loane and R. C. Lord, *J. Mol. Spectroscopy*, 1971, **39**, 340.

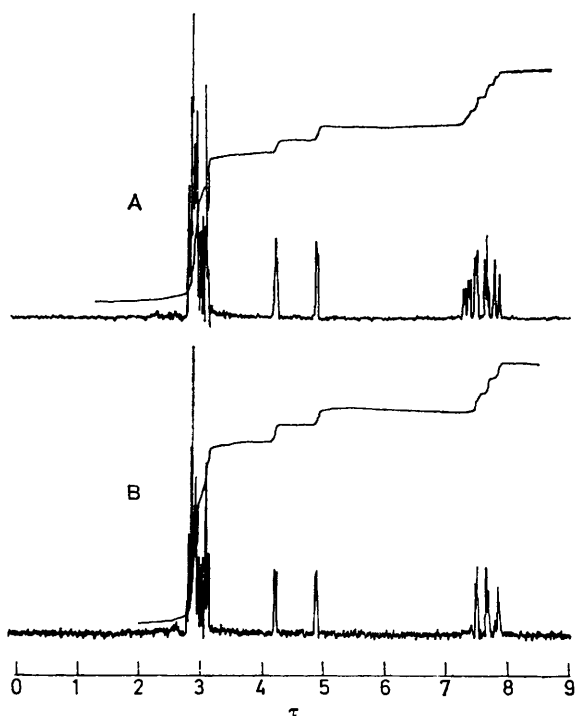
¹⁸ W. G. Ferrier and J. Iball, *Chem. and Ind.*, 1954, 1296; P. W. Rabideau and J. W. Paschal, *J. Amer. Chem. Soc.*, 1972, **94**, 5801.

¹⁹ (a) I. J. Miller, *Austral. J. Chem.*, 1970, **23**, 29; (b) W. C. Danen, *J. Amer. Chem. Soc.*, 1972, **94**, 4835.

²⁰ H. Kloosterziel and J. A. A. van Drunen, *Rec. Trav. chim.*, 1970, **89**, 368.

construed as supporting homoaromaticity in an initially-formed tricyclodecatrienyli anion, derives from observations on the rate of rearrangement of 6,6-diphenylcyclohexadiene in Am^tOH . This is a considerably easier process than the corresponding tricyclodecatriene rearrangement. Extrapolation of data for the latter system to the temperature (102.5°) at which the former was studied, suggested a rate ratio 1.1×10^2 .

Although the earlier n.m.r. data²¹ had appeared to indicate that the rearrangement of diphenylbicyclohexene in Am^tOD occurred without incorporation of deuterium in unchanged starting material, an examination by 220 MHz n.m.r. spectroscopy of material recovered after 85% conversion to product has since

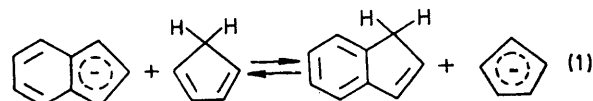


220 MHz ^1H N.M.R. spectra of 6,6-diphenylbicyclohexene (A) before, and (B) after partial base-catalysed rearrangement in Am^tOD

revealed that deuterium exchange and rearrangement proceed at approximately equal rates. Furthermore it was clear from this experiment that exchange is, within the limits of experimental detection, exclusively of the *exo*-allylic hydrogen (Figure). This presumably results from steric shielding of the *endo*-hydrogen by the *endo*-6-phenyl substituent. Using this exchange: rearrangement rate ratio together with the corresponding one for

* See ref. 8b, p. 19. The comparison is apparently based on the results of R. E. Dessy, W. Kitching, T. Psurras, R. Salinger, and T. Chivers (*J. Amer. Chem. Soc.*, 1966, **88**, 460), who studied the equilibration of R_2Hg and R_2Mg in tetrahydrofuran. It is also possible to infer from the results of olefin benzylation experiments that the acidities of toluene and propene are of the same order of magnitude (R. M. Schramm and G. E. Langlois, *J. Amer. Chem. Soc.*, 1960, **82**, 4912). All these references suggest that toluene is in fact a slightly stronger acid than propene, which lends weight to the suggestion advanced here that the bicyclohexenyl anions generated from (1) and (11) may enjoy some degree of homoaromatic stabilisation.

tricyclodecatriene (1·9), and assuming that the latter is not markedly temperature dependent, the rate ratio for rearrangement of the two compounds at 102.5° (1.1×10^2) leads to a rate ratio for exchange of *ca.* 60. With the additional assumptions that the transition state for deprotonation is carbanion-like, and that the transmission coefficients for the two exchange reactions are comparable, this rate factor represents a difference in ΔG^\ddagger of *ca.* 3 kcal mol⁻¹ at 102.5° . Now ΔG for reaction (1) may be calculated from relevant $\text{p}K_a$



data²² for indene and cyclopentadiene to be *ca.* 4.8 kcal mol⁻¹ (at 25°). In contrast, toluene and propene have been estimated to have very similar acidities.*

In view of the observed parallel between the present results and the acidities of cyclopentadiene and indene, and the fact that (1) and (11) are more acidic than comparison with appropriate model compounds would predict, it is tempting to conclude that deprotonation of (1) and (11) may indeed lead initially to carbanions possessing some degree of homoaromatic stabilisation (homocyclopentadienyl and homoindenyl respectively). This proposal must, however, be viewed with caution. For example, compounds (1) and (11) differ in that the double bond between C-2 and C-3 in (1) and C-2 and C-7 in (11) must be shorter in (1). Therefore changes in conformational strain on generating carbanions from the two molecules may contribute to the rate differences between them, although it would not account for the unexpectedly high exchange rates.

An additional problem concerns the variations in relative acidities of different substrates with environment.²³ These can cover several orders of magnitude, such that the comparisons made in the foregoing discussion merit re-evaluation under strictly comparable experimental conditions. The solvent-dependence of the products of base-catalysed rearrangement of (1)¹ is probably a manifestation of the re-ordering of hydrocarbon acidities in different solvents. In Am^tOH the bicyclohexenyl carbanion undergoes electrocyclic ring-opening to the dienyl anion (5), but in DMSO formation of the highly delocalised anion (19), which can be stabilised in DMSO by dispersion forces,^{23a} is favoured.

Two additional aspects of this work are deserving of comment. First, it seemed of interest to extend the model studies to measurements on the rate of base-catalysed isomerisation²⁴ of allylbenzene to the more

²¹ D. J. Atkinson, M. J. Perkins, and P. Ward, *J. Chem. Soc. (C)*, 1971, 3274.

²² R. E. Dessy, Y. O. Kuzumi, and A. Chen, *J. Amer. Chem. Soc.*, 1962, **84**, 2899; A. Streitwieser, J. I. Brauman, J. H. Hammons, and A. H. Pudjaatmaka, *ibid.*, 1965, **87**, 384.

²³ *E.g.* (a) C. D. Ritchie, in 'Solute-Solvent Interactions,' eds. J. F. Coetzee and C. D. Ritchie, Dekker, New York, 1969, p. 219; (b) A. I. Shatenshtein and I. O. Shapiro, *Theor. and Exp. Chem.*, 1969, **5**, 37.

²⁴ The mechanism of the analogous rearrangement of 3-phenylbut-1-ene has been discussed by D. J. Cram, ref. 8b, p. 207; D. J. Cram and R. T. Uyeda, *J. Amer. Chem. Soc.*, 1964, **86**, 5466.

stable β -methylstyrene. In the $[^2\text{H}_6]\text{DMSO}$ system this rearrangement was immeasurably fast, but in Am^tOD , it occurred at a measurable rate at room temperature. Extrapolation from measurements at 25.1 and 40.0° gives an estimated rate constant at 160° of $7(\pm 2) \text{ s}^{-1}$ which is faster than exchange in benzylcyclopropane by a factor of *ca.* 5×10^4 . Clearly a developing carbanion is stabilised to a considerably greater extent by an adjacent vinyl group than by cyclopropyl.* This is in contrast to the situation which obtains with the corresponding carbonium ions, where cyclopropyl stabilisation may exceed vinyl stabilisation,^{15b,25} and free radicals where cyclopropyl stabilisation is also thought to be very substantial.^{15b,19,26}

Finally, further reference must be made to ion-pairing phenomena in this work. Internal return in base-catalysed exchange reactions in $[^2\text{H}_6]\text{DMSO}$ ⁹ and in Bu^tOD ²⁷ (little detailed information is available on the use of Am^tOH as solvent) are extensively documented. However both types of systems have been widely used to compare rates of hydrogen exchange in weakly acidic molecules, and the relative reactivities obtained show good agreement with data obtained using, for example, caesium cyclohexylamide in cyclohexylamine, where exchange rates are believed to reflect actual rates of deprotonation of the molecules being studied.²⁸ This leads to the conclusion that the extent of any internal return phenomena involving initially-formed solvated ion pairs must be comparable for similar molecules. The general parallel between results in the two solvent systems employed in the present study, for which ion-pairing effects are very different, lends support to this argument. The one notable exception is found in the rate of rearrangement of (11) (and its methyl derivatives) in $[^2\text{H}_6]\text{DMSO}$. This is greater than exchange in indane by a factor of more than 100. However, as exchange in this system involves removal of D^+ from the low equilibrium concentration of Bu^tOD or from the relatively non-acidic $[^2\text{H}_6]\text{DMSO}$, it is perhaps not surprising that rearrangement of the carbanion should be much faster than exchange with solvent, and that this would be reflected in a relatively high rate of rearrangement when comparison is made with a reference reaction involving hydrogen isotope exchange. The alternative possibility that deprotonation and rearrangement are concerted in DMSO cannot be excluded from the available data, but seems unlikely in view of the relatively small rate enhancement. In addition, a more significant difference between the rate of rearrangement of the epimeric methyl derivatives (14) and (15) might have been expected (although see ref. 6). Rearrange-

ment of an intermediate carbanion without hydrogen exchange finds close analogies in examples of β -elimination reactions which proceed by an *E1cB* mechanism but do so without exchange.²⁹

EXPERIMENTAL

¹H N.m.r. spectra were recorded on a 60 MHz Perkin-Elmer R10 spectrometer. 100 and 220 MHz spectra were recorded by P.C.M.U., Harwell. Mass spectra were also recorded by P.C.M.U.; those used for deuterium analyses were run at the low electron impact energy of 12–15 eV when little or no fragmentation was discernible.³⁰ Data for kinetic measurements were obtained by n.m.r. integration or by g.l.c. analysis using a Perkin-Elmer F-11 gas chromatograph fitted with a flame ionisation detector. Unless otherwise stated, all hydrocarbon mixtures were analysed on Apiezon L columns (5 or 15%). Preparative g.l.c. was carried out using a Pye series 105 chromatograph fitted with a 23% APL column.

DMSO was dried over calcium hydride and distilled under reduced pressure onto molecular sieves (4 Å) activated by baking in a vacuum oven at 110°. Indane, tetralin, n-butylbenzene, and isobutylbenzene were dried by boiling under reflux with sodium metal, then distilling at atmospheric pressure, and collecting a centre-cut. All hydrocarbons were stored over molecular sieves. $[^2\text{H}_6]\text{DMSO}$ (Prochem; 99.5%) was used as supplied and assumed to be dry. Am^tOH was dried over calcium hydride and distilled.

To prepare Am^tOD , Am^tOH (109 ml), n-pentane (100 ml), and deuterium oxide (10 ml) were shaken together for several minutes, then the aqueous layer was removed, and discarded. Repetition of this procedure six times gave a pentane solution of Am^tOH *ca.* 90% deuteriated at oxygen (i.r.). The solution was dried (Na_2SO_4 , then CaH_2) and distilled through a packed column. The fraction with b.p. 101–102° (94 ml) was pure (g.l.c.) and contained 91% Am^tOD (n.m.r. integration).

Solutions of Bu^tOK in DMSO were prepared under an atmosphere of dry nitrogen.³¹ Clear, colourless solutions were obtained by using freshly sublimed butoxide. Solutions of Am^tOK in Am^tOH were prepared by dissolving clean potassium in the warm solvent under dry nitrogen. Its concentration was determined by titration against standard acid. All base solutions were stored and transferred under dry nitrogen.

Preparation of Hydrocarbons.—(a) *Tricyclo[7.1.0.0^{2,7}]-deca-2(7),3,5-triene* (11). This was prepared in 10% yield by Simmons–Smith cyclopropanation of indene.³² The product, isolated by preparative g.l.c. (130°), contained a trace of indene (<0.1% by g.l.c.) but no other detectable impurities (g.l.c., n.m.r.).

(b) *Benzylcyclopropane*. This was prepared by cyclopropanation of allylbenzene.³³ The product was separated from unchanged allylbenzene in 18% yield by fractional distillation under reduced pressure through a spinning-band

* Parallel results have recently been obtained for exchange in a series of ketones RCH_2COPh where $\text{R} = \text{Pr}^i$, cyclo-Pr, and vinyl (M. J. Perkins, N. P. Y. Siew, and P. Ward, unpublished observations).

²⁵ B. A. Howell and J. G. Jewett, *J. Amer. Chem. Soc.*, 1971, **93**, 798.

²⁶ J. C. Martin and J. W. Timberlake, *J. Amer. Chem. Soc.*, 1970, **92**, 978.

²⁷ W. D. Kolmeyer and D. J. Cram, *J. Amer. Chem. Soc.*, 1968, **90**, 1779.

²⁸ A. Streitwieser and H. K. Koch, *J. Amer. Chem. Soc.*, 1964, **86**, 404.

²⁹ F. G. Bordwell, *Accounts Chem. Res.*, 1972, **5**, 374.

³⁰ K. Biemann, 'Mass Spectrometry. Organic Chemical Applications,' McGraw-Hill, New York, 1962, p. 205.

³¹ A. Schriesheim and C. A. Rowe, *J. Amer. Chem. Soc.*, 1962, **84**, 3161.

³² A. L. Goodman and R. H. Eastman, *J. Amer. Chem. Soc.*, 1964, **86**, 908.

³³ E. C. Friedrich, *J. Org. Chem.*, 1969, **34**, 528.

column, b.p. 91—92° at 28 mmHg. It contained a trace of allylbenzene (<1%) but no other impurities were detected (g.l.c., n.m.r.).

(c) *1,4-Dihydronaphthalene*. Reduction of naphthalene with sodium in liquid ammonia gave 1,4-dihydronaphthalene (plates from methanol), m.p. 28—29° (lit.,³⁴ m.p. 24·7°) which was pure (g.l.c., n.m.r.) except for a trace of 1,2-dihydronaphthalene (<1%).

(d) *1,2-Dihydronaphthalene*. 1,4-Dihydronaphthalene (2·6 g) was added to a boiling solution of sodium ethoxide (from 4·5 g of clean sodium) in reagent grade ethanol (40 ml). After boiling for 2 h under reflux, the hot solution was poured onto ice and extracted with hexane. The hexane solution was washed thoroughly with water, dried (MgSO₄), and distilled under reduced pressure. The major product fraction (2·2 g, 85%), a liquid, b.p. 87° at 13 mmHg, was essentially pure 1,2-dihydronaphthalene (n.m.r.). No trace of 1,4-dihydronaphthalene was detectable (g.l.c.) but a small amount (<1%) of naphthalene was present.

(e) *exo- and endo-8-Methyltricyclo[7.1.0.0^{2,7}]deca-2(7),3,5-triene (14) and (15)*. 3-Methylindene was prepared by dehydration of 3-methylindanol³⁵ over boric acid,³⁶ Attempts to effect this dehydration over KHSO₄³⁵ gave low yields of hydrocarbon product (<20%) which contained an unidentified component (*ca.* 10%) in addition to the desired 3-methylindene. 3-Methylindanol (71·6 g, 0·49 mol) and boric acid (36 g, 0·58 mol) were ground together in a mortar and then transferred to a distillation flask. The apparatus was evacuated to 120 mmHg and the flask immersed in an oil-bath at 110°. After distillation of water had ceased (2·5 h) heating was continued for a further 1·2 h. The cooled mixture was stirred with pentane and all insoluble material removed by filtration. The filtrate was washed thoroughly with water, then dried (MgSO₄), and evaporated to leave a pale yellow oil (20·8 g). Distillation of this oil under reduced pressure, keeping the bath temperature below 140° gave a liquid (16·9 g, 28%), b.p. 74° at 12 mmHg. This product was pure by g.l.c. and n.m.r., $\tau(\text{CCl}_4)$ 2·5—3·0 (4H, m), 3·21 (1H, d, *J* 6 Hz), 3·56 (1H, d, *J* 6 Hz), 6·56 (1H, q, *J* 7 Hz), and 8·72 (3H, d, *J* 7 Hz). A zinc-copper couple was then prepared by the method of Shank and Shechter³⁷ from pure zinc powder (99·9 + %Zn; 56 g, 0·86 mol). The couple was transferred while still moist with dry ether to a flask containing dry ether (400 ml). The contents of the flask were stirred with a powerful mechanical stirrer and heated to reflux. Addition of iodine (*ca.* 100 mg) was followed by the dropwise addition of diiodomethane (158 g, 0·59 mol) in an equal volume of dry ether over 15 min. When this addition was half-completed, 3-methylindene (22·8 g, 0·175 mol) in an equal volume of ether was added over 5 min. Stirring and heating was continued for 40 h when g.l.c. analysis of a sample quenched into dilute acid showed no further decrease in the amount of starting material. The mixture was filtered through Celite and the filtrate and washings were shaken cautiously with ice-cold 5% aqueous HCl (much heat evolved). The yellow ethereal layer was then washed repeatedly with water until all zinc salts had been removed (6 times; testing with aqueous NaHCO₃), then with 1% sodium thiosulphate solution

(removing most of the colouration), and finally with water. After drying (MgSO₄) the ether was removed and the residue was distilled without fractionation under reduced pressure to give a liquid (14·8 g), b.p. 73—90° at 12 mmHg. Examination of this liquid by g.l.c. revealed the presence of unchanged 3-methylindene (55%), a product A (*ca.* 38%), and a product B (*ca.* 7%), in order of increasing retention times. A portion of the total product mixture was separated into its components by preparative g.l.c. to give a sample of A containing a small amount of B (5%) and a sample of B containing a small amount of A (10%). Both products exhibited closely similar mass spectra with strong parent ion peaks at *m/e* 144 (C₁₁H₁₂) in each case. The 100 MHz n.m.r. spectrum of A was consistent with its formulation as the *exo*-isomer (14),³⁸ $\tau(\text{CDCl}_3)$ 2·7—3·15 (4H, m), 6·95 (1H, q, *J* 7 Hz), 7·6—7·8 (1H, m), 8·34—8·6 (1H, m), 8·77 (3H, d, *J* 7 Hz), 9·0 (1H, t of d, *J* 8, 4·5 Hz), and 9·98 (1H, q, *J* 4·5 Hz). The assignment was confirmed by spin decoupling. The 100 MHz n.m.r. spectrum of B was consistent with its formulation as the *endo*-isomer (15), $\tau(\text{CHCl}_3)$ 2·7—3·12 (4H, m), 6·47 (1H, quintet, *J* 6·5 Hz), 7·6—7·84 (1H, m), 8·02—8·44 (1H, m), 8·70 (3H, d, *J* 6·5 Hz), 9·21 (1H, t of d, *J* 8, 4·3 Hz), and 9·97 (1H, quartet, *J* 4 Hz).

(f) *Tricyclo[8.1.0.0^{3,8}]undeca-3(8),4,6-triene (16)*. Diiodomethane (74 g, 0·276 mol) in an equal volume of dry ether was added dropwise over 30 min to a stirred suspension of a freshly prepared zinc-copper couple (from 25 g of zinc powder, 0·379 mol) and iodine (*ca.* 50 mg) in dry boiling ether (250 ml). When *ca.* one-tenth of the diiodomethane had been added, a solution of 1,4-dihydronaphthalene (18 g, 0·138 mol) in dry ether (30 ml) was added quickly over 3 min. The reaction mixture was boiled under reflux with stirring overnight, cooled, and filtered through Celite. The filtrate was washed with 1% aqueous HCl (120 ml) followed by 5% HCl (2 × 100 ml), water (3 × 100 ml), 1% sodium thiosulphate solution (20 ml), and finally water (2 × 100 ml). The ether solution was dried (MgSO₄) and distilled under reduced pressure to give a liquid (13·7 g), b.p. 94—101° at 10 mmHg. Examination of this liquid by g.l.c. showed that it contained 1,4-dihydronaphthalene (53%) and a product of longer retention time (47%). A portion of the mixture was separated by preparative g.l.c. into 1,4-dihydronaphthalene and *compound* (16), a crystalline solid, m.p. 31—32° (Found: C, 91·3; H, 8·05. C₁₁H₁₂ requires C, 91·6; H, 8·4%), which was pure by g.l.c. (<0·1% 1,4-dihydronaphthalene), $\tau(\text{CCl}_4)$ 3·0 (4H, s), 7·0 (4H, s), 8·6—9·0 (2H, m), and 9·5—10·1 (2H, m), *m/e* 144 (*M*⁺).³⁹

Rearrangement of Compounds (11), (14), and (15) in DMSO.—To a sample of compound (11), (14), or (15) (50 mg) in an n.m.r. tube was added a 0·85M solution of Bu^tOK in DMSO (9·3 ml) under dry nitrogen. The tube was sealed and its contents shaken to homogeneity, and then the progress of the reaction was observed by n.m.r. at 33·4°. When the unrearranged starting material could just be detected, the contents of the tube were quenched into water under nitrogen and the hydrocarbons extracted into pentane. The pentane extract was washed thoroughly

³⁸ The *exo*-isomer has previously been isolated from the products of u.v. irradiation of 1-methyl-1,2-dihydronaphthalene, H. Kleinhuis, R. L. C. Wijting, and E. Havinga, *Tetrahedron Letters*, 1971, 255; H. Heimgartner, L. Ulrich, H.-J. Hansen, and H. Schmid, *Helv. Chim. Acta*, 1971, 54, 2313.

³⁹ This compound has recently been reported: E. C. Friedrich and R. L. Holmstead, *J. Org. Chem.*, 1972, 37, 2546.

³⁴ W. Hüchel and J. Wolfering, *Annalen*, 1965, 686, 34.

³⁵ H. Cristol and F. Plenat, *Bull. Soc. chim. France*, 1962, 1325.

³⁶ W. Brandenburg and A. Galat, *J. Amer. Chem. Soc.*, 1950, 72, 3275.

³⁷ R. S. Shank and H. Schechter, *J. Org. Chem.*, 1959, 24, 1825.

with water (5 times), dried (MgSO_4), and then the solvent was evaporated leaving an oil which was examined by n.m.r. and g.l.c.

(a) (11) After 4 h the product exhibited an n.m.r. spectrum identical with that of authentic 1,2-dihydronaphthalene. G.l.c. analysis revealed a small quantity of unchanged starting material (3%) but no other products.

(b) (14) After 41 h the product exhibited an n.m.r. spectrum identical with that of an authentic mixture of 4-methyl-1,2-dihydronaphthalene and 1-methyl-1,2-dihydronaphthalene prepared by exposure of 1-methyl-1,4-dihydronaphthalene⁴⁰ to the above reaction conditions for 10 min. G.l.c. analysis confirmed the presence of 4-methyl-1,2-dihydronaphthalene (90%), and 1-methyl-1,2-dihydronaphthalene (8%), and revealed a trace of unchanged starting material (2%).

(c) (15) After 41 h the reaction mixture contained 4-methyl-1,2-dihydronaphthalene (86.5%), 1-methyl-1,2-dihydronaphthalene (6.5%), and unchanged starting material (7%).

Rearrangement of Compounds (11), (14), and (15) in Am^tOH .—Mixtures of one of the tricyclodecatrienes (60 mg) and 1.3M solution of Am^tOK in Am^tOH (4.0 ml) were sealed in tubes under nitrogen. Each tube was immersed in a thermostatically-controlled oil-bath at the temperatures and for the periods given in Table 4. Their contents were then cooled, quenched into water, and the mixtures were extracted with pentane. The pentane extracts were washed thoroughly with water, dried (MgSO_4), and evaporated to leave oils which were examined by g.l.c. and n.m.r.

TABLE 4

Products of rearrangement of compounds (11), (14), and (15) in Am^tOH — Am^tOK

Tricyclo-decatriene	$T/^\circ\text{C}$ (t/h)	Starting material	Products
(11)	145 (41.5)	10%	1,2-Dihydronaphthalene, 90%
(14)	165 (72)	<1%	4-Methyl-1,2-dihydronaphthalene, 81.5% 1-Methyl-1,2-dihydronaphthalene, 17.5%
(15)	165 (72)	4%	4-Methyl-1,2-dihydronaphthalene, 79% 1-methyl-1,2-dihydronaphthalene, 17%

Kinetics of Rearrangement of Tricyclodecatrienes.—(a) *In DMSO.* The rearrangements in solutions of Bu^tOK in DMSO were followed in n.m.r. tubes at 33.4° [(11) and (15)], or at $60 \pm 0.1^\circ$ [(14) and (15)], by n.m.r. integration of suitable peaks. In the case of (11), plots of $-\log_{10}(1 - 2[\int \text{vinyl}/\int \text{aromatic}])$ against time gave reasonably good straight lines from the slopes of which pseudo-first-order rate constants could be estimated with an accuracy of ca. $\pm 5\%$ (see Table 1). In the case of (14) and (15), the higher yield product (4-methyl-1,2-dihydronaphthalene; 92%) contains one vinyl proton, whereas the lower yield product (1-methyl-1,2-dihydronaphthalene; 8%) contains two vinyl protons. Therefore $-\log_{10}(1 - 3.72[\int \text{vinyl}/\int \text{aromatic}])$ (where $3.72 = 4 \times 0.92 + 2 \times 0.08$) was plotted against time.

(b) *In Am^tOH .* Each kinetic run comprised at least four reactions carried out in sealed tubes, as described in the product study, for different times spanning a range 0—ca. 3 half-lives. The products, isolated by quenching into water and extraction with pentane, were analysed by

g.l.c. First-order rate constants (Table 1) were estimated with an error of ca. $\pm 1\%$ from the slopes of excellent straight line plots of $-\log_{10} A/A_0$ against time, where A is the integrated peak corresponding to unchanged starting material and A_0 is the total integral of all peaks.

The Partial Rearrangement of Compounds (11), (14), and (15) in $[\text{}^2\text{H}_6]\text{DMSO}$ and in Am^tOD .—(a) *In $[\text{}^2\text{H}_6]\text{DMSO}$.* Each derivative (50 mg) was treated in an n.m.r. tube under dry nitrogen with a 0.83M solution of Bu^tOK in DMSO (0.3 ml). The progress of the reaction [at 33.4° for (11), or 59.8° for (14) and (15)] was followed by n.m.r. integration of the decaying high field quartet at τ ca. 10. After ca. 55—65% rearrangement, the contents of each tube were quenched into D_2O and the hydrocarbons isolated as before. The results of analysis by g.l.c. and by coupled g.l.c.—m.s. are given in Table 5. None of the tricyclodecatriene derivatives incorporated deuterium within the limit of experimental error.

TABLE 5

Deuterium incorporation in compounds (11), (14), and (15) during rearrangement in $[\text{}^2\text{H}_6]\text{DMSO}$ — Bu^tOK

Compound	Unrearranged starting material (%)	Observed peak height ^a at $M + 1$	Calculated peak height ^a at $M + 1$ due to natural isotopes ^b
(11)	45	130 0.12 ± 0.01	0.109
(14)	39	144 0.13 ± 0.01	0.121
(15)	37	144 0.13 ± 0.01	0.121

^a Relative to a peak of M of height 1.000. ^b From ref. 40.

(b) *In Am^tOD .* Reactions were carried out in sealed tubes as described previously and the results are given in Table 2. Examination of the products by n.m.r. showed that deuterium exchange had occurred almost exclusively at C-8 as expected.

(i) (14). The n.m.r. spectrum of the total products obtained from a reaction taken to 26% rearrangement (by g.l.c.) exhibited all the lines due to starting material together with a singlet at τ 8.70 {methyl group of $[\text{}^2\text{H}]$ - (14)} and a singlet at τ 8.05 (methyl group of $[\text{}^1,1,2,2,3\text{}^2\text{H}_5]$ -4-methyl-1,2-dihydronaphthalene).

(ii) (15). The n.m.r. spectrum of the total products obtained from a reaction taken to 22% rearrangement (by g.l.c.) exhibited all the lines due to starting material together with two singlets assigned to the methyl groups of $[\text{}^2\text{H}]$ - (15) and $[\text{}^1,1,2,2,3\text{}^2\text{H}_5]$ -4-methyl-1,2-dihydronaphthalene. The extent of incorporation of deuterium at C-8 in each case was estimated by integration of the multiplet at τ 6.47 (14) or 6.95 (15) due to the methine proton at C-8 in unexchanged starting material.

(iii) (11). The multiplet assigned to the benzylic protons at C-8 in the n.m.r. spectrum of (11) appears as an AB quartet (J 18 Hz) centred at τ 7.0, in which the low-field components are identified as being due to the *exo* proton by a further splitting (ca. 6 Hz) with 9-H. After 27% rearrangement in Am^tOD at 160° , this low-field group of lines was much decreased in intensity, whilst the high-field doublet was largely replaced by a broad singlet at τ ca. 7.15. These observations may be interpreted in terms of a marked preference for exchange of the *exo*-proton in (11).

Kinetics of Base-catalysed Deuterium Exchange of Alkanes in $[\text{}^2\text{H}_6]\text{DMSO}$ and in Am^tOD .—(a) *In $[\text{}^2\text{H}_6]\text{DMSO}$.*

⁴⁰ P. W. Rabideau and R. G. Harvey, *Tetrahedron Letters*, 1970, 4139.

Two flasks, one containing a solution of resublimed Bu^tOK (0.815 g) made up to 10.0 ml in [²H₆]DMSO under nitrogen, and the other containing a mixture of equal parts by volume of benzylcyclopropane, isobutylbenzene, n-butylbenzene, indane, tetralin, and tricyclo[8,1.0.0^{3,8}]undeca-3(8),4,6-triene (16) under nitrogen were sealed with rubber serum caps and clamped in a water-bath at 43.0 ± 0.05°. After allowing 15 min for thermal equilibration, a sample of the hydrocarbon mixture (1.2 ml) was injected into the base solution at *t* 0 and the resulting mixture swirled to homogeneity. Samples (0.6 ml) were withdrawn at measured intervals and quenched into water under nitrogen. The hydrocarbon mixture from each quenching was extracted into pentane and the extract washed three times with water. After drying (MgSO₄) each pentane extract was concentrated to a small volume (*ca.* 0.3 ml) by evaporation under reduced pressure. The hydrocarbon mixtures from 15 quenched samples were analysed by coupled g.l.c.-m.s. at low electron impact energy. It was suspected that some isotopic fractionation might occur on the g.l.c. column and therefore spectra were recorded at two positions, one on each side of the g.l.c. peak and disposed symmetrically about its apex. Tetralin, indane, and compound (16) exchanged a maximum of four hydrogens, whilst the other aralkanes exchanged a maximum of two hydrogens under the experimental conditions.

Treatment of data. The fraction of molecules containing no deuterium atoms [²H₀] in the material corresponding to each g.l.c. peak was calculated from the peak heights at *m/e* = *M*, *M* + 1, *M* + 2, *etc.* after correcting for natural isotopic abundance.⁴¹ An average value of [²H₀] from measurements made on both sides of each g.l.c. peak was taken. For each compound, plots of -log₁₀ [²H₀] against time gave reasonably good straight lines from whose slopes the values of *k*_{exch.} shown in Table 3 were estimated within error limits of *ca.* ±5%. A kinetic run to measure the rate of rearrangement of compound (11) in the same base solution and at the same temperature as in the above experiment was carried out.

(b) *In* Am^tOD. Five sealed-tube exchange reactions were carried out for each aralkane (indane, benzylcyclopropane, and n-butylbenzene) as follows. A sample of the hydrocarbon (20 μl) was added to the solution of Am^tOK in Am^tOD (1.10M, 1.0 ml) under dry nitrogen. After sealing, the tube was immersed in an oil-bath at 160.0 ± 0.1°. After a desired time (determined from preliminary exchanged experiments followed by n.m.r.) the tube was withdrawn, cooled quickly, and its contents quenched into water. The residue from a pentane extract

of the quench was analysed by mass spectrometry at low electron impact energy, recording two spectra, and averaging the two estimates of [²H₀] obtained. Values of the observed first-order rate constants for exchange of the three aralkanes are given in Table 3 together with the observed first-order rate constant for rearrangement of compound (11) in the same reaction medium and at the same temperature obtained by g.l.c. analysis of the products of five sealed tube reactions.

The Partial Rearrangement of 6,6-Diphenylbicyclohexene (1) in Am^tOD.—6,6-Diphenylbicyclohexene⁴² (1.0 g) was added to a 1.03M solution of Am^tOK in Am^tOD under nitrogen and the resulting solution was heated under reflux. The progress of the rearrangement was followed by g.l.c. (5% FFAP; 200°) and the reaction was stopped by cooling and adding D₂O (10 ml) when 14.4% of the bicyclohexene remained unconverted (to an equilibrium mixture of partially deuteriated 5,5-diphenylcyclohexa-1,3-diene and 3,3-diphenylcyclohexa-1,4-diene). The mixture was poured into water and extracted twice with a 1 : 1 pentane-ether mixture. The combined extracts were washed thoroughly with water, dried (MgSO₄), and the solvent evaporated to leave a pale yellow oil (0.974 g). The oil (0.974 g), maleic anhydride (0.25 g), and *p*-xylene were heated at 145–150° for 3 h. On addition of benzene to the cooled *p*-xylene solution, crystals of the Diels-Alder adduct of the conjugated diene separated, these were discarded. Benzene was removed from the filtrate by evaporation and *p*-xylene was removed from the residue under high vacuum at room temperature. The residual oil was chromatographed on a layer of silver nitrate-impregnated silica gel and elution with a 1 : 1 benzene-light petroleum (b.p. 60–80°) gave 6,6-diphenylbicyclohexene (67 mg; colourless needles; m.p. 78–79°) and 3,3-diphenylcyclohexa-1,4-diene (435 mg). Figure A shows the n.m.r. spectrum at 220 MHz of normal 6,6-diphenylbicyclohex-2-ene, and Figure B shows the spectrum of the sample of 6,6-diphenylbicyclohex-2-ene recovered from the above experiment. From the integral it can be estimated that *ca.* 85% of the *exo*-hydrogen at C-4 has exchanged for deuterium, but deuterium has not been incorporated to a measurable extent elsewhere in the molecule.

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⁴¹ J. H. Beynon, 'Mass Spectrometry and its Applications to Organic Chemistry,' Elsevier, Amsterdam, 1960.

⁴² H. E. Zimmerman, D. S. Crumrine, D. Döpp, and P. S. Huyffer, *J. Amer. Chem. Soc.*, 1969, **91**, 434.