Concerning the Stability of Cyclopropylcarbinyl Anions

By M. J. PERKINS* and P. WARD

(*Department of Chemistry, King's College, Strand, London* WC2R 2LS)

Summary Rate data for base-catalysed hydrogen exchange in benzylcyclopropane and related compounds suggest that cyclopropyl exerts only a weak stabilising effect on an adjacent carbanion.

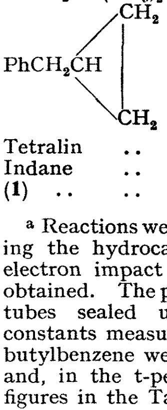
DESPITE an extensive literature on the stability of cyclopropylcarbinyl cations[1] and radicals,[1,2] little seems to be known about the corresponding anions. In the cation series, cyclopropyl stabilisation may be greater than that due to a vinyl group,[3] and it is common practice to equate, in a qualitative sense, the effects of vinyl and cyclopropyl substitution.

A cyclopropyl group might be expected to stabilise an adjacent anionic centre by virtue of its relatively low-lying lowest vacant MO (conjugative stabilisation). In addition, the relatively high *s*-character of the bond from a cyclopropyl substituent should effectively raise its electronegativity (non-conjugative stabilisation). We have located only one literature report in which carbanion stabilisation by cyclopropyl has been inferred from a quantitative (kinetic) study.[4] In that work cyclopropylcarbinyl → allylcarbinyl rearrangement accompanied carbanion formation, and the results did not rigorously exclude the possibility that the observed rate enhancement might have originated in a concerted bond cleavage. It therefore seemed important to acquire further information on the stability of cyclopropyl-substituted carbanions, and, in addition, to compare the effect of a cyclopropyl substituent with that of vinyl.

Base-catalysed exchange of benzylic hydrogen in benzylcyclopropane occurs without rearrangement,[5] and we have now compared the rate of this exchange and that of exchange in (**1**),† with the rates of exchange in several model compounds. The results, obtained using two different solvent systems, are summarised in the Table.

TABLE

Relative rates of hydrogen exchange in alkylbenzenes per benzylic hydrogen atom[a]

Hydrocarbon	Base system $0{\cdot}728$M-Bu^{t}OK in$(CD_3)_2SO$ at $43{\cdot}0°$	 $1{\cdot}10$M-Am^{t}OK in O-deuterio-Am^{t}OH at $160°$[b]
$PhCH_2CH_2CH_2CH_3$	1·00	1·00
$PhCH_2CH(CH_3)_2$ ..	0·26	n.d.
 ..	11·0	5·2
Tetralin	1·1	n.d.
Indane	0·11	0·40
(**1**)	2·6	n.d.

[a] Reactions were followed by quenching at intervals and analysing the hydrocarbons by mass spectrometry, employing low electron impact energies. Good pseudo-first-order plots were obtained. The pentanol experiments were carried out in pressure tubes sealed under nitrogen. The pseudo-first-order rate constants measured for the reaction n-butylbenzene → [$^2H_1$]-n-butylbenzene were: in the $(CD_3)_2SO$ system $1{\cdot}52 \times 10^{-2}$ min^{-1}, and, in the t-pentyl alcohol system $1{\cdot}68 \times 10^{-3}$ min^{-1}. The figures in the Table represent mean values from several determinations. Individual measurements were normally within ±10% of these mean values.

[b] n.d. = not determined.

Kinetic measurements of hydrogen exchange in both systems are undoubtedly complicated by ion-pairing phenomena and internal return,[6] and they therefore do not determine true kinetic acidities. However, the complications are quite different in the two solvents employed, and as there are no major discrepancies between the two sets of figures (where these have been determined), we consider that these do provide a valid indication of relative carbanion stability.[7] Furthermore, in view of the highly developed carbanion character at the transition state,[8] the exchange rates should be fairly sensitive to carbanion stability. Therefore the results suggest that the stabilising effects of cyclopropyl substitution, whilst clearly discernible in the acyclic system, are quite small.

The comparison of rates of exchange for tetralin and (**1**) does not substantially add to this conclusion. The experiments were included to attempt to distinguish between conjugative (conformation dependent) and non-conjugative

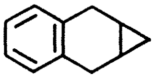
---

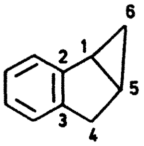
† M.p. 31—33°, prepared by cyclopropanation of 1,4-dihydronaphthalene.

effects of cyclopropyl. But the rate ratios are so small that these effects cannot confidently be separated from the effects of small conformational energy differences between the molecules. The relatively slow exchange rate found for indane may probably be associated with the increase in ring strain required to generate a planar benzylic carbanion. However, other interpretations have been advanced to account for a similar rate reduction noted for deprotonation of cyclopentene when compared with cyclohexene.[9]

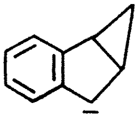
We have also found that isomerisation of allylbenzene to β-methylstyrene is immeasurably fast in the (CD$_3$)$_2$SO system, and that the rate for the same reaction in the *O*-deuterio-t-pentyl alcohol system exceeds that of hydrogen exchange in benzylcyclopropane by *ca.* 5×10^4. This figure was obtained by extrapolation to 160° from rate data obtained between 25° and 45°, and must be regarded as no more than a crude approximation. Nevertheless, we conclude that cyclopropyl is very much less effective than a double bond in stabilising an adjacent carbanion.

Finally, we note that, in the t-pentyl alcohol system, exchange in (**2**), which competes with base-catalysed isomerisation to 1,2-dihydronaphthalene, is about seventeen times faster than exchange in indane. The possibility of weak homoaromatic stabilisation in the ion (**3**) will be discussed in the full paper.‡


(1)



(2)


(3)

(*Received, July 12th,* 1971; *Com.* 1185.)

‡ A referee has drawn our attention to a report by Shatenshtein ***et al.*** (see A. I. Shatenshtein *Adv. Phys. Org. Chem.*, **1963**, **1**, 176) that only the cyclopropyl hydrogens of ethylcyclopropane are exchanged on exposure to KND$_2$/ND$_3$ at 120°. Clearly any effect of cyclopropyl stabilisation is much smaller than the effect of high *s*-character in the cyclopropyl-hydrogen bonds. It is noteworthy in this context that the most acidic protons in (**2**) are those at C-4, rather than the benzylic cyclopropyl hydrogen at C-1. Presumably geometrical constraints prevent effective conjugation between a carbanion lone pair at C-1 and the aromatic π-system.

[1] *e.g.* M. Charton in "The Chemistry of Alkenes," Vol 2, ed. J. Zabicky, Interscience, New York, 1970, p. 511.

[2] J. C. Martin and J. W. Timberlake, *J. Amer. Chem. Soc.*, 1970, **92**, 978.

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

[4] J. A. Landgrebe and J. D. Shoemaker, *J. Amer. Chem. Soc.*, 1967, **89**, 4465.

[5] A. F. Maercker and J. D. Roberts, *J. Amer. Chem. Soc.*, 1966, **88**, 1742.

[6] D. J. Cram, "Fundamentals of Carbanion Chemistry", Academic Press, New York, 1965, p. 28; A. Streitwieser and H. K. Koch, *J. Amer. Chem. Soc.*, 1964, **86**, 404; J. N. Roitman and D. J. Cram, *ibid.*, 1971, **93**, 2231, and earlier papers.

[7] *Cf.* the discussion by J. M. Brown and J. L. Occolowitz, *J. Chem. Soc.* (*B*), 1968, 411.

[8] J. R. Jones, *Chem. Comm.*, 1967, 710; but see F. G. Bordwell and W. J. Boyle, *J. Amer. Chem. Soc.*, 1971, **93**, 512.

[9] S. B. Tjan, H. Steinberg, and T. J. de Boer, *Rec. Trav. chim.*, 1969, **88**, 680, 690; J. M. Brown in "Organic Reaction Mechanisms 1969", eds. B. Capon and C. W. Rees, Interscience, London, 1970, p. 140.