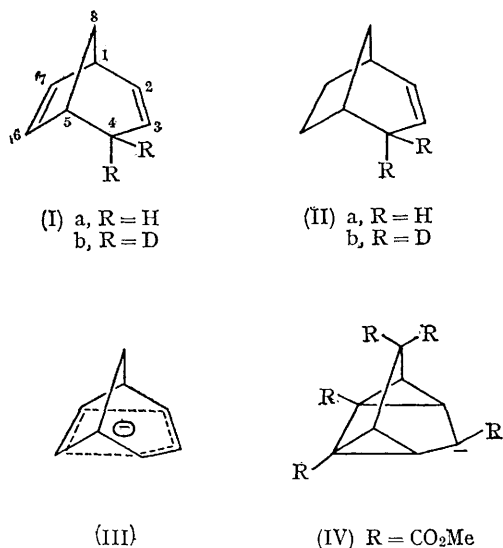


## A Non-Classical Carbanion

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STABILISATION of an allylic anion by intramolecular overlap of its  $\pi$ -system with an olefinic double bond is predictable on the basis of Hückel molecular orbital theory. Certainly several published results may be interpreted in accordance with this, notably the observation of Birch<sup>1</sup> that a 1,5-diene was isomerised in base very much faster than a mono-ene, and the reported<sup>2</sup> rapid base-catalysed isomerisation of cyclo-octa-1,5-diene to cyclo-octa-1,3-diene. We wish to report a definitive example of a large rate-enhancement in this type of system.



Preparation of [4,4-<sup>2</sup>H<sub>2</sub>]-bicyclo[3,2,1]-octa-2,6-diene (Ib) by a previously described method,<sup>3</sup> but using Ph<sub>3</sub>P=CD<sub>2</sub> gave a product with > 76% dideuteration (mass spectrometry). Reduction of (Ia) or (Ib) with benzenesulphonyl hydrazide in diglyme at 110° gave > 98% of bicyclo[3,2,1]-oct-2-ene [(IIb) was 81% dideuterated (mass spectrometry)], albeit at a rather irreproducible rate.

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† Samples of (Ia) and (IIa) used were purified both before and after reaction by vapour-phase chromatography (12-foot Castorwax, 115°). Parent-peak analysis of (I) was carried out at a nominal 8.5 ev. on an Atlas CH4; (II), at a nominal 9 ev.

<sup>1</sup> A. J. Birch, *J. Chem. Soc.*, 1947, 1642.

<sup>2</sup> D. Devaprabhakara, C. G. Gardenas, and P. D. Gardner, *J. Amer. Chem. Soc.*, 1963, **85**, 1553.

<sup>3</sup> C. Cupas, W. E. Watts, and P. von R. Schleyer, *Tetrahedron Letters*, 1964, 2503.

<sup>4</sup> D. J. Cram and R. T. Uyeda, *J. Amer. Chem. Soc.*, 1962, **84**, 4358.

Preliminary experiments on the rate of dedeuteriation of (Ib) and (IIb) in dimethyl sulphoxide (DMSO) (1.28N in potassium t-butoxide) revealed a major difference in rate; infrared examination of aliquots in the 3200—2000 cm.<sup>-1</sup> region suggested that the extent of reaction of (Ib) in three minutes at 30° was comparable with that of (IIb) in forty hours at 92°. In twelve hours at 30°, (Ib) was completely voided of deuterium.

In order to obtain more accurate data, further runs were carried out with (Ia) in diperdeuteromethyl sulphoxide (0.96N in potassium t-butoxide). (I) was recovered from the reaction aliquot and subjected to mass-spectrometric isotope analysis.†

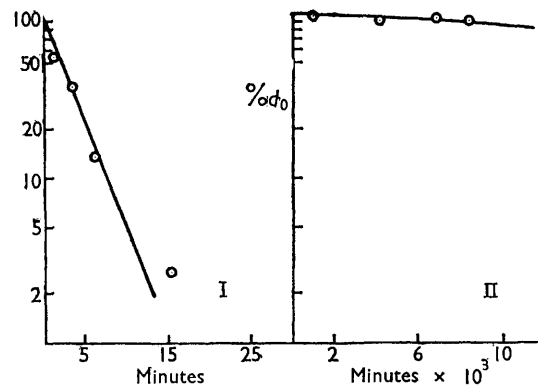


FIGURE 1

The results of four aliquots from two separate runs at 60.0° are shown in Figure 1, and permit estimation of a half-life of 2 minutes under these conditions. Exchange occurred exclusively in the 4-position as evidenced by infrared examination of aliquots (diminution of 2880 and 2820 cm.<sup>-1</sup> bands only, and new adsorption at 2100 cm.<sup>-1</sup>), and the much higher rate of deuterium incorporation in (Ia) compared to (Ib). After prolonged periods at 60°, appreciable di- and tri-deuterated products (but no higher incorporation) were produced from (Ia), suggesting that intramolecular isomerisation<sup>4</sup>

is important, but protonation of (III) at C-6 is not.

Reactions of (IIa) under identical conditions in nitrogen-filled, sealed tubes over protracted periods gave the data of Figure 1, which could be extrapolated to a half-life of forty days. Exchange had again occurred in the 4-position as evidenced by the diminution of the 2865 and 2835  $\text{cm}^{-1}$  bands relative to the 3035  $\text{cm}^{-1}$  band in an aliquot studied by infrared examination. A run with cyclohexene under the same conditions suggested that this incorporated deuterium about three times faster than (IIa).

The data show that (I) undergoes isotope exchange, at 60°,  $3 \times 10^4$  times faster than (II). For a pair of weakly acidic substrates of closely related structure in DMSO, where specific solvent interactions with the developing carbanion are

small, Brönsted's relationship<sup>5</sup> should be fairly well adhered to. Consequently, the rate enhancement in (I) reflects its enhanced acidity relative to (II). Part of the enhancement is undoubtedly due to a favourable field effect exerted by the double bond; for comparison, the vinyl hydrogens of norbornadiene exchange twenty times faster than those of norbornene in cyclohexylamine-cæsium cyclohexylamide.<sup>6</sup> We feel that the major part of the effect must be ascribed to the special stability of a 6  $\pi$ -electron system accorded to (III) by electron delocalisation. It is of interest that Prinzbach *et al.*<sup>7</sup> have recently suggested that the production of anomalous products in the protonation of (IV), might be explained by intermediacy of the analogue of (III).

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<sup>5</sup> J. N. Brönsted and K. J. Pedersen, *Z. phys. Chem.*, 1924, **108**, 185.

<sup>6</sup> A. Streitwieser, Jr., private communication, 10/6/1965.

<sup>7</sup> H. Prinzbach, W. Eberbach, and G. von Vek, *Angew. Chem. Internat. Edn.*, 1965, **4**, 436.