Tetrahedron Letters No. 17, pp. 755-757, 1962. Pergamon Press Ltd. Printed in Great Britain.

THE REACTION OF BICYCLO[2.2.1]HEPTADIENE WITH AMYLSODIUM

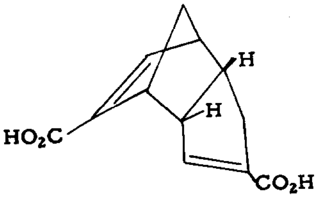
A NOVEL CLEAVAGE REACTION

R.A. Finnegan and R.S. McNees

Department of Chemistry, The Ohio State University, Columbus 10, Ohio

(Received 11 June 1962)

WHEN a pentane suspension of amylsodium was allowed to react for 5 hr at room temperature with an equimolar amount of bicyclo[2.2.1]heptadiene (I) and the reaction mixture forced onto an excess of solid CO_2, a crystalline acid (II) could be isolated in good yield. This acid, λ_{max}^{EtOH} 222 mμ, ν_{max}^{KBr} 1675 cm^{-1} (α, β-unsaturated acid), provided microanalytical data in close agreement with those calculated for the empirical formula $C_6H_6O_2$ while its high melting point (204-205°, sublimes) (sealed capillary, corrected) suggested that it was at least dibasic, $C_{12}H_{12}O_4$. The relationship of this molecular formula to those of the starting materials, which was at first puzzling, became clear when II was recognized as a known dimer of cyclopentadienecarboxylic acid.



II

Structure II was assigned by Peters[1] to Thiele's acid,[2] the main product obtained when cyclopentadienyl Grignard reagent[1a] or the corre-

---

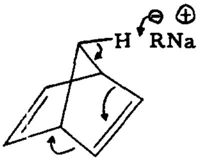
[1] D. Peters, J. Chem. Soc. a 1761 (1959); b 1832 (1960); c 1042 (1961).

[2] J. Thiele, Ber. 34, 68 (1901).

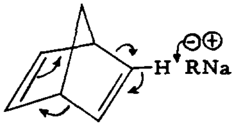
sponding sodium[1c,3] or potassium[2] reagent is carbonated and the resultant carboxylate salt acidified. An authentic sample of II prepared from cyclopentadienylmagnesium bromide proved to be indistinguishable (mixed m.p. undepressed, infrared and ultraviolet spectra) from the acid obtained from I. In addition, the dimethyl esters,[1a] m.p. 84-84.5° (uncorrected), of each acid were shown to be identical by the usual criteria.

That the production of cyclopentadiene from I during the reaction with amylsodium is accompanied by the formation of acetylene, as in the thermal decomposition of I,[4,5] was readily demonstrated. Hydrolysis of the solid residue remaining after an aliquot of the reaction mixture was evaporated to dryness under reduced pressure afforded a gas which was identified as a mixture of acetylene and cyclopentadiene by gas chromatographic methods.

The results reported here may be contrasted with those previously reported by Wittig[6] on the reaction of I with ethereal butyllithium. In the latter reaction, addition of the metal alkyl to the diene was the predominant reaction pathway and while a low yield of hydrogen abstraction resulted, no cleavage products were observed. The cleavage reaction is visualized as being initiated by hydrogen abstraction[7] either at C-7 (as in A) or at C-2 (as in B).



A



B

---

[3] K. Ziegler, H. Froitzheim-Kuhlhorn and K. Hafner, Chem. Ber. 89, 434 (1956).

[4] W.G. Woods, J. Org. Chem. 23, 110 (1958).

[5] J.H. Birley and J.P. Chesick, J. Phys. Chem. 66, 568 (1962).

[6] G. Wittig and E. Hahn, Angew. Chem. 72, 781 (1960).

[7] Hydrogen abstraction and cleavage are pictured as concerted merely for convenience. Stepwise changes may also, of course, be written.

While the data at hand do not distinguish between these two possibilities, process B appears more likely by analogy to the work of Wittig[6] and in view of the demonstrated facile exchange of a vinyl hydrogen in the corresponding monoölefin bicyclo[2.2.1]heptene under similar conditions.[8]

Finally it should be noted that the difference in behavior between the sodium and the lithium alkyls toward diene I is an illustration of a very general reactivity relationship, i.e. when a substrate offers the possibilities both of addition and abstraction reactions, the lithium reagent will tend to add preferentially, while the sodium reagent will tend to abstract hydrogen preferentially.

Acknowledgement - This research was supported by grants from the Research Corporation and from the Petroleum Research Fund of the American Chemical Society. Grateful acknowledgement is made to the donors of these funds.

---

[8] R.A. Finnegan and R.S. McNees, Chem. & Ind. 1450 (1961).