Azulenes: a Synthesis Based on Intramolecular Carbene Addition

By Lawrence T. Scott

(*Department of Chemistry, University of California, Los Angeles, California* 90024)

Summary Copper(I) chloride-catalysed decomposition of the diazoketones derived from dihydrocinnamic acids produces bicyclo[5,3,0]decatrienones which have been converted into azulenes in two steps.

The diazoketone (**1a**),[1] prepared quantitatively from dihydrocinnamic acid, loses nitrogen rapidly when treated with copper(I) chloride in benzene under reflux to give the bicyclic trienone (**4a**) in 40—50% yield.† Steric constraints (Bredt's rule) presumably confine intramolecular addition of the ketocarbene derived from (**1a**) to the 1,2-position of the benzene ring. The unstable norcaradiene (**2a**) then opens to (**3a**) which isomerizes to the cross-conjugated trienone (**4a**) under the reaction conditions; no evidence could be found for the double-bond isomer of (**3a**) and (**4a**) previously reported[1] as the sole bicyclic product obtained (12% yield) by decomposing (**1a**) with copper metal in hot decalin. Interception of the intermediate ketocarbene by solvent (benzene) competes with the intramolecular reaction only to a small extent.

Aluminium hydride reduction[2] of (**4a**) followed by dehydration–dehydrogenation of the crude alcohol (**5a**) at *ca.*

---

† Consistent spectra and combustion analysis.

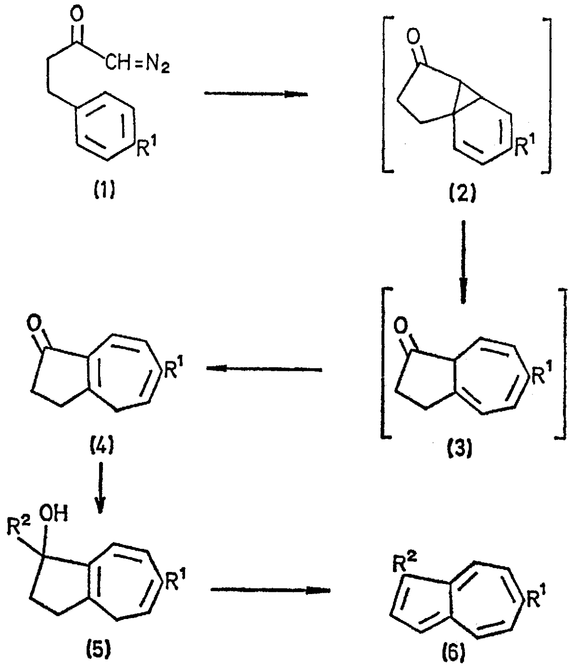
400° with 10% Pd/C in a flow system[3] affords the azulene (**6a**) in 20—40% yield. Dehydrogenations with sulphur were less satisfactory. Similarly, Grignard addition of MeMgCl to (**4a**) produces the teriary allylic alcohol (**5b**), which can be converted into 1-methylazulene (**6b**)[4] by the hot tube method described above or, with equal success, by heating (**5b**) in oleic acid with 10% Pd/C at 200° and distilling the product from the mixture.

Repetition of these steps starting from (**1c**) leads to the 6-substituted azulenes (**6c**)[4] and (**6d**)†. The intermediate (**3c**) can be identified in the n.m.r. spectrum of the crude cyclization product but rearranges to (**4c**)† on chromatography. Overall yields of substituted azulenes prepared by this route compare favourably with that for azulene itself. The previously unknown 1,6-dimethylazulene (**6d**) has λ_{max} (hexane) 595 nm (log ϵ 2·51), in good agreement with the value predicted by Plattner's empirical rules[5] (predicted 594 nm).

Creation of the bicyclic ring system of azulene with a high degree of unsaturation and versatile functionality in a single step from simple benzene derivatives makes this synthesis one of the most convenient available.[6,7] Intramolecular carbene additions to aromatic hydrocarbons[1,7,8] and ketocarbene additions to benzene[9] have only recently been observed.

Financial support by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the University of California, Los Angeles Research Committee, is acknowledged.

(*Received, 4th September* 1973; *Com.* 1247.)



	R^1	R^2
a	H	H
b	H	Me
c	Me	H
d	Me	Me

---

[1] A. Constantino, G. Linstrumelle, and S. Julia, *Bull. Soc. chim. France*, 1970, 907, 912.

[2] H. C. Brown and H. M. Hess, *J. Org. Chem.*, 1969, **34**, 2206.

[3] *Cf.* E. Kóvats, P. A. Plattner, and H. H. Günthard, *Helv. Chim. Acta*, 1954, **37**, 983.

[4] P. A. Plattner and E. Heilbronner, *Helv. Chim. Acta*, 1947, **30**, 910.

[5] P. A. Plattner, *Helv. Chim. Acta*, 1941, **24**, 283E; E. Heilbronner in 'Non-Benzenoid Aromatic Compounds,' ed. D. Ginsburg, Interscience, New York, 1959, pp. 171—276.

[6] W. Keller-Schierlein and E. Heilbronner in 'Non-Benzenoid Aromatic Compounds,' ed. D. Ginsburg, Interscience, New York, 1959, pp. 277—337.

[7] The transition metal-catalysed rearrangement of phenyl substituted bicyclobutanes to bicyclo[5,3,0]decatetraenes has been interpreted as proceeding also *via* intramolecular carbene addition to a benzene ring and constitutes the key step in another azulene synthesis reported recently by P. G. Gassman and T. Nakai, *J. Amer. Chem. Soc.*, 1971, **93**, 5897; *ibid.*, 1972, **94**, 2877; P. G. Gassman and W. J. Greenlee, *Synthetic Comm.*, 1972, **2**, 395.

[8] E. Vogel, A. Vogel, H. K. Kübbeler, and W. Sturm, *Angew. Chem. Internat. Edn.*, 1970, **9**, 514; E. Vogel and H. Reel, *J. Amer. Chem. Soc.*, 1972, **94**, 4388; L. N. Mander, personal communication; L. T. Scott, M. Baum, and C. H. Hartman, unpublished results

[9] L. T. Scott, Ph.D. Thesis, Harvard, 1970; K. van Buren and L. T. Scott, unpublished results.