

Addition Reactions of Cyclopentadienylidene: Synthesis of Spiro[2,4]heptadienes

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PHOTOLYSIS of diazocyclopentadiene in hydrocarbons¹ and ether² affords C-H insertion products of (presumed) intermediate, cyclopentadienylidene (I). Addition of (I) to olefins has not been reported,



though the reaction is known in the case of the dibenzo-derivative, fluorenylidene.³

Irradiation (Hanovia, 450 watt, high pressure mercury lamp, pyrex filter, 5 hr.) of dilute (0.1—0.2 M) solutions of diazocyclopentadiene⁴ in pure tetramethyl-, trimethyl-, t-butyl-, and n-butyl-ethylene afforded spiro[2,4]heptadienes (IIa, b, c, and d), respectively. Yields and physical properties

¹ W. Kirmse, L. Horner and H. Hoffman, *Annalen*, 1958, **614**, 19.

² J. E. Basinski, Ph.D. Thesis, Yale University, 1961.

³ M. Jones, Jr. and K. R. Rettig, *J. Amer. Chem. Soc.*, 1965, **87**, 4013, 4015; and references therein.

⁴ T. Weil and M. Cais, *J. Org. Chem.*, 1963, **28**, 2472.

are summarized in the Table. Products were isolated by vacuum distillation of the tarry residue remaining after removal of olefin. Purification of

(IIb, IIc) is the deshielding of cyclopropyl relative to alkyl protons, an effect which has already been noted.⁶

TABLE

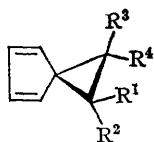
Compound	b.p./Torr. (m.p.)	n.m.r. ^a	u.v. ($\epsilon \times 10^{-3}$) ^b	Yield, %
IIa	(57—58°)	6.38—6.07 M (4.0); 1.38 S (11.0)	237 (9.5) 273 (1.8)	35
IIb	56—59°/15	6.45—5.95 M (4.0); 2.18—1.86 Q, $J = 7$, (0.96); 1.33 S, 1.33—1.24 D (9.3) ^c	234 (14.0) 262 (3.9)	33
IIc	65—66°/18	6.48—6.21 M (2.9); 5.94—5.76 M (1.0); 2.17—1.50 M (3.3); 0.95 S (9.5)	228 (9.4) 258 (3.1)	46
IIId	71—76°/14	6.51—5.77 M (4.0); 2.17—0.69 M (12.0)	228 (5.6) 257 (2.5)	30

^a Chemical shifts in p.p.m. downfield from internal Me₄Si. S = singlet, D = doublet, Q = quarter, M = multiplet. Numbers in parentheses give signal areas.

^b Solvent pentane.

^c One line of the R² doublet falls under the six-proton singlet due to R³ and R⁴. Total integral area for methyl protons is satisfactory.

(IIa) was effected by sublimation; (IIb, c, and d) were purified by preparative v.p.c.⁵



(II) a; R¹=R²=R³=R⁴=Me
 b; R¹=H, R²=R³=R⁴=Me
 c; R¹=R²=R³=H; R⁴=Bu^t
 d; R¹=R²=R³=H; R⁴=Bu^t
 e; R¹=R²=R³=R⁴=H

Structure is assigned on the basis of satisfactory elemental analyses and spectral properties. N.m.r. data are essentially definitive. Thus, all products exhibited a four-proton multiplet in the vinyl region, assigned to the cyclopentadienyl protons. No other vinylic or allylic protons could be observed. An interesting feature of these spectra

The ultraviolet spectrum of spiro[2,4]heptadiene, (IIe), prepared from sodium cyclopentadienide and ethylene bromide,⁷ has been discussed by Wilcox⁸ and Chirdoglu.⁹ Compound (IIe) exhibits maxima at 223 and 257 m μ . Both authors indicate that the long-wavelength band suggests conjugation between the cyclopropyl and cyclopentadienyl units. [The geometry in (II) is optimal for such conjugation.] The compounds reported here exhibit similar spectra. It is of considerable interest, to note the bathochromic shifts, of both maxima attending successive alkylation of the cyclopropyl ring.

Detailed studies of the selectivity of (I) and the spectral properties of (II) are in progress.

(Received, November 22nd, 1965; Com. 729.)

⁵ Minor products, presumably resulting from insertion reactions¹ are also observed, but have not yet been characterized.

⁶ K. Bangert and V. Boekelheide, *Tetrahedron Letters*, 1963, 1119.

⁷ R. Ya. Levina, N. N. Mezentsova, and O. V. Lebedev, *Zhur. obshchei, Khim.*, 1955, 25, 1097.

⁸ C. F. Wilcox, Jr. and R. R. Craig, *J. Amer. Chem. Soc.*, 1961, 83, 4258.

⁹ G. Chirdoglu and B. Tursch, *Bull. Soc. chim. belg.*, 1957, 66, 600.