Novel Cycloaddition Reactions of Isocyanides with Diphenylacetylene Using Transition-metal Complexes

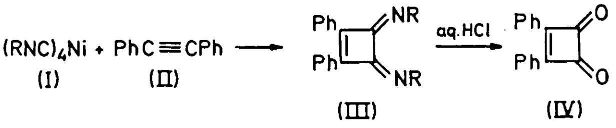
By YOSHIO SUZUKI* and TAKEO TAKIZAWA

(*Faculty of Pharmaceutical Sciences, University of Tokyo, Bunkyo-ku, Tokyo, Japan*)

Summary Reaction of tetrakis(aryl isocyanide)nickel complexes (Ia—c) with diphenylacetylene gave the diiminocyclobutenes (IIIa—c); on pyrolysis, the acetylene complex (Va) gave (IIIa) as sole product, while with (Vd) the major product was iminocyclopentadiene (VId).

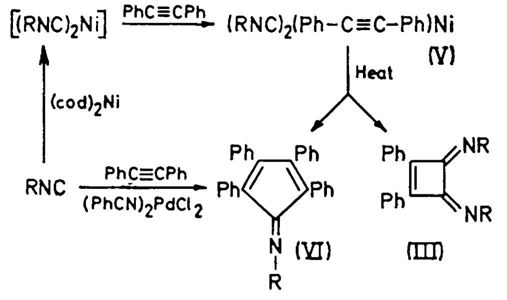
WE previously reported the cycloadditions of isocyanide to acetylenes substituted with electron-withdrawing groups to give tri-iminocyclopentene and pyrindine derivatives, whereas aryl and alkyl substituted acetylenes were unreactive, probably owing to the lower electron affinity of their triple bonds.[1] As the isocyano-group is isoelectronic with carbon monoxide and reactions of various metal carbonyls with carbon monoxide and reactions of various metal carbonyls with acetylenes are well known,[2] it was expected that the reactions of isocyanides with diphenylacetylene would give cyclized products *via* co-ordination to a transition metal.

An equimolar mixture of (Ia)[3] and diphenylacetylene (II) was refluxed in toluene for 1 h under nitrogen. Addition of n-hexane and chromatography of the filtrate yielded the yellow di-iminocyclobutene (IIIa), m.p. 205—206°, [30% based on (II)]. Its structure was established by elemental analysis, molecular weight determination, and its i.r., u.v., and n.m.r. spectra. Hydrolysis of (IIIa) with aqueous HCl gave diphenylcyclobutenedione (IV), identical with an authentic sample.[4] The tetrakis(aryl isocyanide)nickel complexes (Ib and c) reacted with acetylene (II) to give the di-imino-cyclobutenes (IIIb), m.p. 158—160° (90%) and (IIIc), m.p. 169—171° (22%). Under similar conditions, tetrakis-(t-butyl isocyanide)nickel[5] and tetrakis-(2,6-dimethylphenyl isocyanide)nickel were unreactive to (II).



a; R = 2,6-Me$_2$,4-BrC$_6$H$_2$ b; R = Ph c; R = p-MeO·C$_6$H$_4$

A mixed ligand complex of isocyanide and acetylene formed initially is possibly an important intermediate in the formation of (III). Bis(cyclo-octa-1,5-diene)nickel [(cod)$_2$-Ni] reacted readily with 2 mol. equiv. of the isocyanide in toluene at room temperature and subsequent addition of 1 mol. equiv. of (II) gave yellow microcrystals of (Va) [ν(N≡C) 2160 and 2100 cm^{-1}; ν(C≡C) 1830 cm^{-1}] whose i.r. spectrum is similar to that of the known complex (Ve).[6] Heating of complex (Va) at 80—100° in toluene gave di-iminocyclobutene (IIIa) (30%). However, pyrolysis of complex (Vd), prepared similarly, in toluene gave the cyclopentadiene (VId) as dark violet crystals, m.p. 190—191° (65%), together with a small amount of (IIId), m.p. 175—177°. The structure of (VId) was supported by elemental analyses and hydrolysis with aqueous HCl to tetracyclone, as well as its i.r., u.v., and n.m.r. spectral data.



a; R = 2,6-Me$_2$,4-BrC$_6$H$_2$ c; R = p-MeO·C$_6$H$_4$
d; R = 2,6-Me$_2$C$_6$H$_3$ e; R = Bu^t

Reaction of the isocyanides R–NC (R as in a, c, and d) with (II) in the presence of bis(benzonitrile)palladium chloride (molar ratio 1:2:1) gave the iminocyclopentadienes (VIa), m.p. 186—187° (VIc), m.p. 206—207°, and (VId) in 21, 10, and 14% yield, respectively, in addition to the known palladium complex of tetraphenylcyclobutadiene, $Pd_3Cl_3(Ph_4C_4)_2$,[7] (30—40% based on Pd).

(*Received*, 17*th April* 1972; *Com.* 653.)

---

[1] T. Takizawa, N. Obata, Y. Suzuki, and T. Yanagida, *Tetrahedron Letters*, 1969, 3407; Y. Suzuki, N. Obata, and T. Takizawa, *ibid.*, 1970, 2667.

[2] F. L. Bowden and A. B. P. Lever, *Organometallic Chem. Rev.*, 1968, **3**, 227.

[3] W. Hieber, *Z. Naturforsch.*, 1950, **5b**, 129; F. Klages and K. Moenkemeyer, *Chem. Ber.*, 1950, **83**, 501.

[4] A. T. Blomquist and E. A. LaLancette, *J. Amer. Chem. Soc.*, 1961, **83**, 1387.

[5] S. Otsuka, A. Nakamura, and Y. Tatsuno, *J. Amer. Chem. Soc.*, 1969, **91**, 6994.

[6] S. Otsuka, T. Yoshida, and Y. Tatsuno, *Chem. Comm.*, 1971, 67.

[7] R. Hüttel and H. J. Neugebauer, *Tetrahedron Letters*, 1964, 3541; P. M. Maitlis, D. Pollock, M. L. Games, and W. J. Pryde, *Canad. J. Chem.*, 1965, **43**, 470.