Diazepines: a Novel Ring Contraction[1]

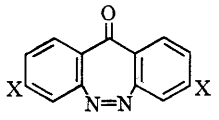
By R. J. DUBOIS and F. D. POPP*

(*Department of Chemistry, Clarkson College of Technology, Potsdam, New York* 13676)

WE have previously described the preparation of the 3,8-dihalogenobenzo[*c,f*][1,2]diazepin-11-one (I) system.[2] In a study of the chemistry of this system we have subjected it to a modified Wittig reaction,[3] with compounds of the type (II) and sodium hydride in dioxan, to yield products of the type (III).[4]

When reaction was attempted with (I; X = Cl), ethyl 4-(diethoxyphosphinyl)crotonate (II; R = $CH{=}CHCO_2Et$), and sodium hydride in dioxan the expected product (III) was not obtained; a compound, containing only twelve carbon atoms and lacking any carbonyl absorption in the i.r., was the only product isolated. On the basis of i.r., n.m.r., and elemental analysis this compound appeared to be 3,8-dichlorobenzo[*c*]cinnoline (IV).

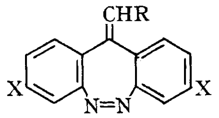
The structure of this product was proved, by independent synthesis, to be (IV). Cyclization of 4,4′-dichloro-2,2′-dinitrobiphenyl[5] with lithium aluminium hydride gave the cinnoline (IV), m.p. 256°.[6] This synthetic material was identical in all respects with that obtained by reaction of (I) as indicated above.



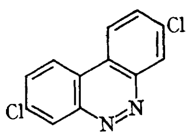
(I)

$(EtO)_2P(:O)CH_2R$

(II)



(III)



(IV)

Sodium hydride in dioxan, sodium hydride in dioxan with (II; R = CO_2Et, CN, $CONR_2$, or COPh), and sodium hydride and triethyl phosphite in dioxan did not bring about this conversion. Compound (I) could, however, be converted into (IV), although in poorer yield, by treatment with sodium hydride in dimethyl sulphoxide.

(*Received, April 2nd*, 1968; *Com.* 408.)

---

[1] Diazepines, for previous parts in the series, see R. J. Dubois, J. Hagymassy, A. C. Noble, and F. D. Popp, *J. Heterocyclic Chem.*, 1966, **3**, 377.

[2] A. Catala and F. D. Popp, *J. Heterocyclic Chem.*, 1964, **1**, 178.

[3] W. S. Wadsworth and W. D. Emmons, *J. Amer. Chem. Soc.*, 1961, **83**, 1733.

[4] A. C. Noble, R. J. Dubois, and F. D. Popp, unpublished observations.

[5] N. Kornblum and D. L. Kendall, *J. Amer. Chem. Soc.*, 1952, **74**, 5782.

[6] Reported m.p. 259°, K. E. Calderbank and R. J. W. LeFevre, *J. Chem. Soc.*, 1951, 649.