Double 1,3-Cycloadditions of Sydnones. Synthesis of 9,10-Diazatetracyclo[6,3,0,$0^{4,11}$,$0^{5,9}$]undecanes[1]

By P. M. WEINTRAUB

(*Hess and Clark, Division of Richardson-Merrell, Ashland, Ohio* 44805)

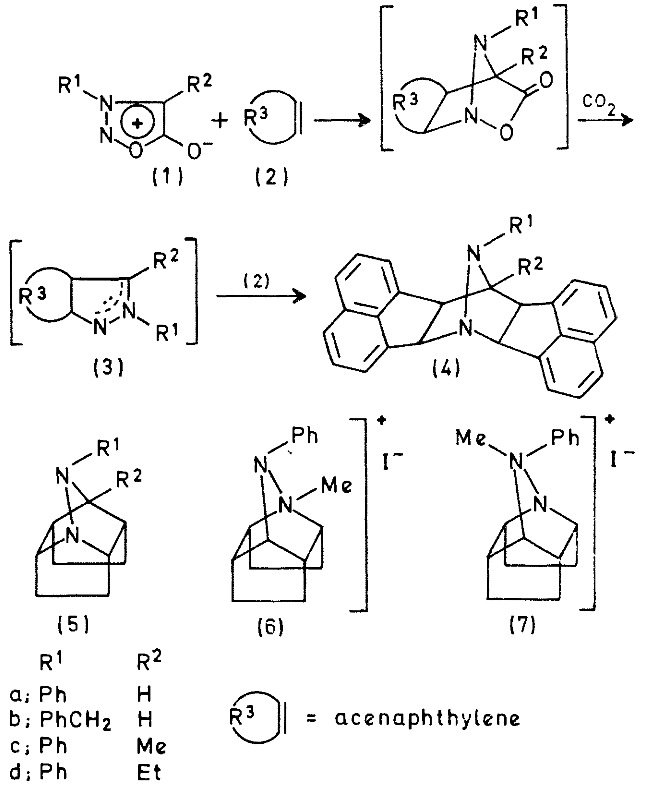
Summary Reaction of sydnones with *cis,cis*-cyclo-octa-1,5-diene gives the novel 9,10-diazatetracyclo[6,3,0,$0^{4,11}$,$0^{5,9}$]undecane ring system.

SYDNONES are known to undergo 1,3-cycloadditions to olefins[2] and acetylenes[2] with concomitant loss of carbon dioxide to give 2-pyrazolidines and pyrazoles, respectively. One of the interesting examples of this addition is the reaction of 3-phenylsydnone (**1**; R^1 = Ph, R^2 = H) with acenaphthylene (**2**) to give dimer (**4**) as a minor product.[3] Consequently, the reaction of intermediate (**3**) (R^1 = 1,8-naphthyl) with more (**2**) must be competitive with the electronic reorientation to give the corresponding pyrazolidine. We have used this reaction to prepare the novel diazatetracycloundecanes (**5**).

Thus, heating (**1**; R^1 = Ph, R^2 = H) with cyclo-octa-1,5-diene at 150° gave a crystalline, acid-soluble adduct, m.p. 81—82° (44%), which formed a monohydrochloride, m.p. 214—216° (decomp.) and a monopicrate, m.p. 198—200°. Elemental analysis of the adduct was in accord with the formula $C_{15}H_{18}N_2$: a 1 : 1 adduct with loss of carbon dioxide. The ^1H n.m.r. spectrum showed no vinyl protons: it had peaks at δ ($CDCl_3$) 1·55—192 (m, 8H), 2·09—2·52 (m, 2H), 3·27—3·62 (pair of t, 2H) 4·42 (t, 1H, *J* 4 Hz), 6·35—7·43 (m, 5H), in accord with structure (**5a**).

Similarly, 3-benzylsydnone (**1**; R^1 = $PhCH_2$, R^2 = H) gave (**5b**), b.p. 141°/0·1 mm (22%), hydrochloride, m.p. 237—238°, picrate, m.p. 146—147°. A hydrocarbon substituent at C-4 of the sydnone seemed to facilitate the reaction. Thus, (**1**; R^1 = Ph, R^2 = Me) gave (**5c**) (62%) as a viscous liquid, picrate, m.p. 175—177°, while (**1**; R^1 = Ph, R^2 = Et) gave (**5d**) as a white solid, m.p. 85—89° (64%). No isolable products were obtained from 4-chloro- or 4-nitro-3-phenylsydnones.

(**5a**) gave two isomeric methiodides (**6**), m.p. 233—234°, (25·2%), ($CDCl_3$) 1·83—2·60 (m, 8H), 3·00—3·46, 3·41 (m and s, 5H), 4·25—4·45 (m, 0·6H), 4·58 (t, 2H, *J* 4 Hz), 7·54 (s with additional splittings, 5H) and (**7**), double m.p. 120—121°, 227—231°, (38·7%), δ ($CDCl_3$) 1·60—2·30 (m, 8·5H), 2·30—2·72 (m, 1·5H) 3.18—3·75 (broad partially resolved t, 2H), 3·87 (s, 3H), 4·28—4·63 (broad d, 1H), 6·33 (t, 1H, *J* 4 Hz), 7·50—7·70 (m, 3H), 7·88—8·53 (m, 2H),



in a ratio of 2 : 3, respectively. The structural assignments are based on the downfield chemical shift[4] of the C-11 methine proton of **(6)** (δ 6·33) compared with **(5a)** (δ 4·42) and **(7)** (δ 4·58).

(*Received, May 4th*, 1970; *Com.* 671.)

---

[1] For the previous paper in this series see P. M. Weintraub and R. E. Bambury, *Tetrahedron Letters*, 1969, 579.

[2] See R. Huisgen, *Bull. Soc. chim. France*, 1965, 3431; R. Huisgen, *Angew. Chem. Internat. Edn.*, 1963, **2**, 565; R. Huisgen, *ibid.*, 1963, **2**, 563; R. Huisgen and H. Gotthardt, *Chem. Ber.*, 1968, **101**, 1059.

[3] H. Gotthardt and R. Huisgen, *Chem. Ber.*, 1968, **101**, 552; R. Huisgen, R. Grashey, H. Gotthardt, and R. Schmidt, *Angew. Chem. Internat. Edn.*, 1962, **1**, 49.

[4] J. B. Davis, *Chem. and Ind.*, 1968, 1094.