

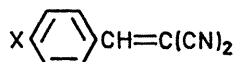
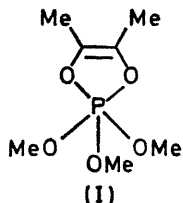
## Synthesis of 2-Acetyl-3-aryl-1,1-dicyano-2-methyl-cyclopropanes

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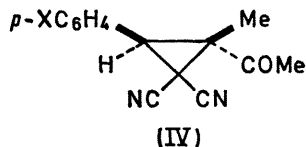
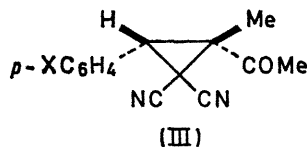
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**Summary** The initial betaines formed from a trimethoxy-1,3,2-dioxaphospholen and benzylidene-malononitriles cyclize with expulsion of trimethyl phosphate to form cyclopropanes.

THE 2,2,2-trimethoxy-1,3,2-dioxaphospholen (I) is a very useful reagent in organic synthesis.<sup>1</sup> We now report a new reaction which gives substituted cyclopropanes.



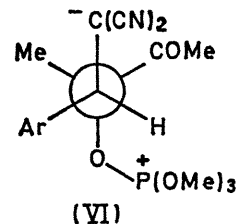
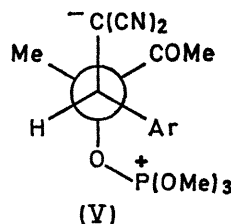
(IIa) X = H  
 (IIb) X = NO<sub>2</sub>  
 (IIc) X = MeO



When (I) was heated in methylene chloride for 20 h with benzylidene-malononitriles, the dicyano-cyclopropanes, *cis*- and *trans*-(III), were isolated. The assignment of structures (III) and (IV) was made from the n.m.r. spectrum: the magnetic anisotropy of the aromatic nucleus shifts the C-methyl signal of the cyclopropane (IV) upfield relative to the absorption of the C-methyl group of the isomer (III), while the reverse takes place for the methyl absorption of

the Me-CO group. (IIIa) and (IVa), isomer ratio 67:33, 83% yield; (IIIa), m.p. 104°, n.m.r. (CDCl<sub>3</sub>) δ 7.5 (m, 5H), 3.16 (s, 1H), 2.22 (s, 3H), 1.88 (s, 3H); (IVa) [mixed with (IIIa)], δ 7.5 (m, 5H), 3.82 (s, 1H), 2.43 (s, 3H), 1.53 (s, 3H); (IIIb) and (IVb), isomer ratio 75:25, 89% yield: (IIIb), m.p. 129°, n.m.r. (CDCl<sub>3</sub>) δ 7.5-8 (q, 4H), 3.40 (s, 1H), 2.44 (s, 3H) 2.00 (s, 3H); (IVb) [mixed with (IIIb)], δ 7.5-8 (q, 4H), 4.01 (s, 1H), 2.58 (s, 3H), 1.67 (s, 3H); (IIIc), (20% yield) only one isomer, probably (IIIc), m.p. 140-142°, δ 7.5-8 (q, 4H), 3.78 (s, 3H), 3.11 (s, 1H), 2.25 (s, 3H), 1.84 (s, 3H). All compounds had satisfactory analyses for the suggested structures.

We suggest that the mechanism of the reaction involves the intermediates (V) and (VI), where the stabilized carbanion displaces the trimethyl phosphate. The cyclopropane (III) is the major product of the reaction. This observation is consistent with the view that the rate of formation of the betaine (V) is greater than that of the betaine (VI), which is more sterically hindered. The yields of cyclopropanes depend very much on the electronic density on the electrophilic carbon of the olefin. This reaction failed with ethyl benzyldenecyanoacetate and with 2-cyano-3-methyl- and 2-cyano-3-phenyl-cinnamonitrile.



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