1,3-Dipolar Cycloadditions of Conjugated Nitrones to Carbon–Carbon Double Bonds

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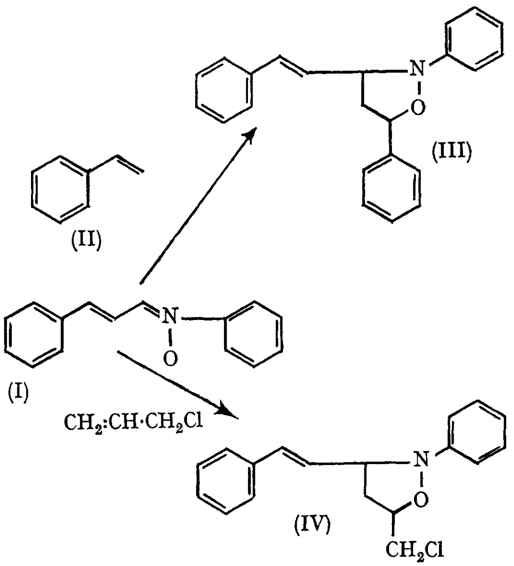
DIPOLAR cycloadditions of non-conjugated nitrones of both the aliphatic and aromatic series with multiple bonds,[1,2] and intramolecular nitrone–olefinic condensation have been reported,[1] but dipole cycloadditions of conjugated nitrones have not been effected. Aliphatic conjugated nitrones have not been isolated and undergo intramolecular cycloadditions. We report the 1,3-dipolar cycloaddition of some conjugated aryl nitrones to carbon–carbon double bonds.

α-Cinnamyl-*N*-phenylnitrone was prepared by the condensation of cinnamaldehyde and phenylhydroxylamine in quantitative yield as against the 20% yield reported by Utzinger *et al.*,[3] and β-2-furylvinyl-*N*-phenylnitrone, m.p. 1600, by the condensation of β-phenylacrolein with phenylhydroxylamine in quantitative yield. Its i.r. spectrum had bands at 877 (trans-CH=CH), and 1560 and 1625 cm.$^{-1}$ (C=C conjugated with C=N). The cycloaddition products prepared from these conjugated nitrones and conjugated alkenes and other unsaturated compounds are given in the Table. All the products are white, crystalline, compounds and were isolated as single major components. Structures (III) and (IV) for the cycloadducts of α-cinnamyl-*N*-phenylnitrone with

TABLE

Isoxazolidines cyclo-adducts

Conj. nitrone	Conj. alkene and other unsaturated compounds	M.p. of adduct	Yield % (pure)	Solvent reaction (period and temp.)	Solvent of crystallization
Cinnamylphenylnitrone	Styrene	115°	80	Dry benzene 36 hr. Reflux temp.	Light petroleum
,,	Allyl chloride	92°	65	Dry benzene 20 hr. Reflux temp.	Light petroleum
,,	Methacrylate	93°	61	Dry benzene 10 hr. Reflux temp.	Methanol
,,	Acrylonitrile	85°	66	Excess acrylonitrile, 2—3 days room temp.	Light petroleum
,,	Mesityl oxide	210°	45	Dry benzene 48 hr. Reflux temp.	Methanol
β-2-Furylvinyl-*N*-phenylnitrone	Styrene	85°	57	Dry methanol 30 hr. Reflux temp.	Light petroleum



styrene and allyl chloride, respectively, are assigned by elemental analysis, molecular weight, u.v. and i.r. spectra, and n.m.r. (60 Mc./sec., $CDCl_3$).

The n.m.r. spectrum of (III) in $CDCl_3$ showed the following signals in addition to the aromatic protons [(III), 3·34 (I*H*, s), 3·50 (I*H*, d), 4·91 (I*H* quart.), 5·25 (I*H* quartet, partially split), 7·40 τ (2*H* m); (IV) gave analogous signals].

The signals are analogous to the corresponding signals in isoxazolines,[4] the cycloaddition products of phenylacrylonitrile oxide with conjugated alkenes or $\alpha\beta$-unsaturated esters and amides. The structures (III) and (IV) thus assigned are analogous to the corresponding products reported for non-conjugated nitrones,[1] and the other adducts may be assumed to be of similar structure.

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