# Bis-(*p*-3,5-dioxo-1,2,4-triazolin-4-ylphenyl)methane: A Highly Reactive Bifunctional Enophile

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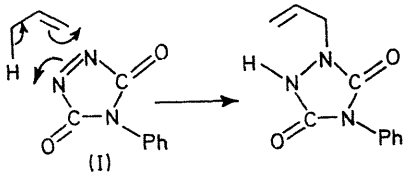
*Summary* Bis-(*p*-3,5-dioxo-1,2,4-triazolin-4-ylphenyl)methane has been synthesised for the first time as a moderately stable bifunctional reagent capable of very rapidly crosslinking allylic olefin-units, and rubber, in solution.

4-PHENYL-1,2,4-TRIAZOLINE-3,5-DIONE (I)[1–3] is an extremely active dienophile[1,2] and enophile.[3] In the latter capacity (exemplified below) this compound and its analogues are of considerable interest in applied synthetic chemistry, and we have become concerned with their potentialities in the chemical modification of olefinic polymers. A bifunctional counterpart of (I), for example, might be used for the rapid cross-linking of olefinic rubbers at low temperatures.

We therefore report a synthesis of the title compound (III) (see Scheme).

A solution of bis-(4-isocyanatophenyl)methane† (0·1 mol) was added to a stirred, cooled solution of ethyl carbazate (0·2 mol) in benzene, to give fine crystals of the adduct which were filtered off after the mixture had been stirred overnight (step 1). The dried adduct was added to 4N-aqueous KOH (100 ml) and EtOH (100 ml), and the mixture was stirred on a steam-bath for 2 h (*cf.* ref. 4), and filtered into an excess of 5% aqueous acetic acid (step 2) to precipitate compound (II) (31·0 g); its i.r. spectrum (Nujol) was practically coincident with that of authentic 4-phenyl-1,2,4-triazolidine-3,5-dione.[4]



(I)

Several methods for the final oxidation step (3) were investigated[2,5] but the most satisfactory was that with fuming nitric acid.[6] To a vigorously stirred and chilled

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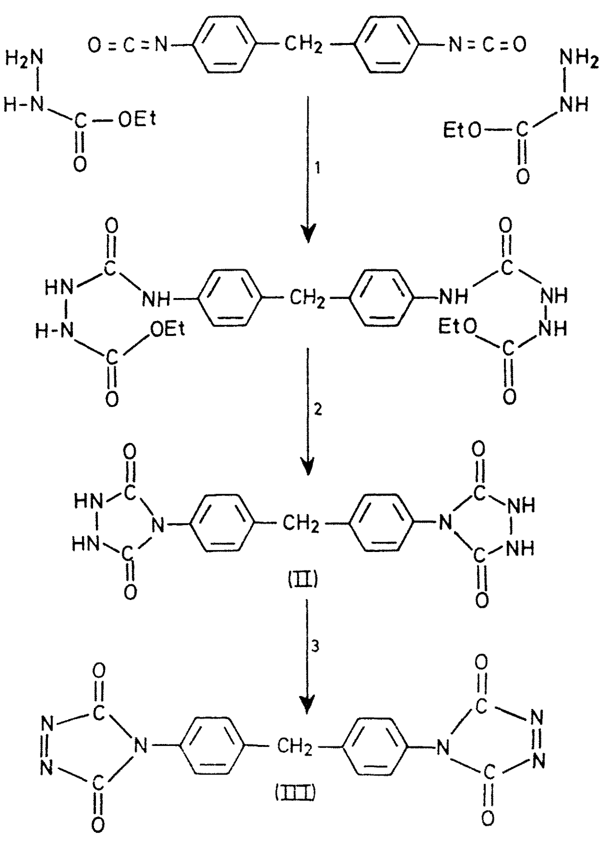
† Marketed under trade-name DESMODUR R by Bayer.



SCHEME

(−10 °C) suspension of dry (II) (0·005 mol) in dichloromethane (40 ml) was added fuming nitric acid (1·0 ml) dropwise during 10 min. The clear red solution was washed briefly with ice–water (200 ml), dried [cold; over anhydrous $Na_2SO_4$ (15 g); 2 h], and evaporated to dryness below room temperature. The red residue was then taken up in ethyl acetate (15 ml) and filtered into light petroleum (b.p. 30—40°; 150 ml) whereupon (III) was precipitated (68%) as a carmine-red crystalline powder [$\lambda_{max}$ 548 nm ($\epsilon$ 328) compares with data for other *mono*functional triazolinediones:[5] $\lambda_{max}$ 538—546 nm, $\epsilon$ (1 chromophore per molecule) 150—211]. Samples prepared by this method were stable in the dark for some weeks; made by other methods (III) has only a transient existence. Unfortunately it is not sufficiently volatile for vacuum sublimation purification (*cf.* ref. 5).

When a dilute solution of (III) in benzene was added to a slight excess of various allylic olefins (e.g., *trans*-but-2-ene, 2-methylpent-2-ene, dihydromyrcene, and geraniol) the colour was discharged in a few seconds and relatively polar bis-ene-adducts were quickly precipitated as pastes which crystallized with difficulty. Addition of a solution of (III) (0·001 M in benzene) to a solution of Natural Rubber (2%; benzene) resulted in instant gelation due to cross-linking, while a rubber film dipped into the solution underwent rapid surface hardening. Because of its extremely high reactivity, however, compound (III) cannot be successfully used for the uniform crosslinking of dry unextended rubber. Red particles of (III) became neatly encapsulated, presumably within micro-sheaths of highly vulcanized polymer, on attempts to compound the material with rubber on a laboratory mill.

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