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Alkyl *N*-Phenylcarbamoylazoformates: A Novel Class of Unsymmetrical Azodicarbonyl Enophiles of Moderate Reactivity

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Summary The enophilic behaviour of examples of the title compounds is described.

In order to meet specific technical demands in the chemical modification of natural rubber we have been seeking novel reagents whose reactivity in pericyclic 'ene' additions to allylic olefins is intermediate between that displayed by azodicarboxylate esters[1] and the cyclic triazolinediones.[2] In this regard the behaviour of monothiobenzil[3] as an enophile[4] was recently reported.

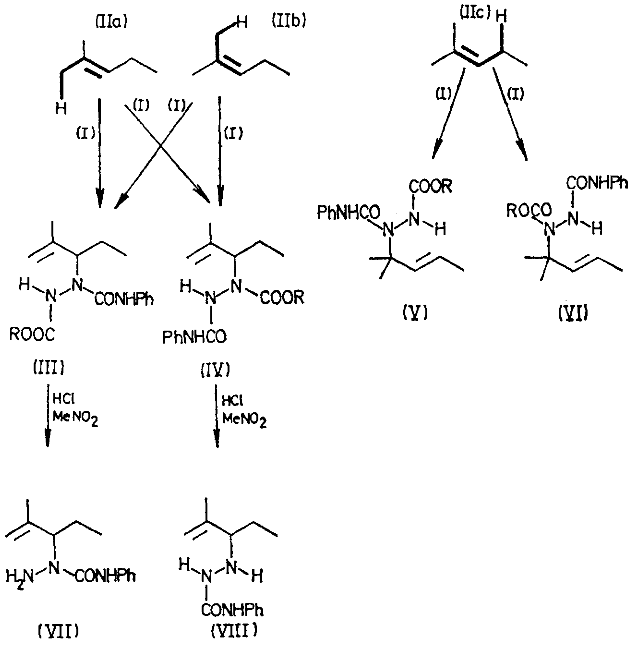
We here discuss the enophilic reactivity of some new open-chain azodicarbonyl compounds (I), typified by ethyl *N*-phenylcarbamoylazoformate (Ia). Compound (Ia) is

$$\mathrm{PhNHC(O)N{=}NCO_2R}$$

(Ia) $R = Et$
(Ib) $R = Bu^t$

prepared in consistently high yields (>90%) by the oxidation in dichloromethane of 4-phenyl-1-ethoxycarbonyl semicarbazide[5] with equimolar quantities of *N*-bromosuccinimide and pyridine at room temperature, washing the mixture with water and aqueous K_2CO_3, and removing the solvent. It crystallizes from light petroleum (60—80°)-benzene (1:1) as a stable orange solid, m.p. 83—84°, ν_{max} 3420, 3300, 1779, and 1730 cm^{-1}; λ_{max} (ϵ) (CH_2Cl_2) 234 (10,360), 326 (3780), and 405sh (<100) nm. Compound (Ib) obtained similarly, is spectrally almost the same, and has m.p. 89°.

Addition of compounds (I) to 2-methylpent-2-ene (II), an olefin presenting three distinct 'ene' systems as indicated in the emphasized bonds in (IIa) (IIb), and (IIc), can theoretically give rise to four 'ene' adducts (III)—(VI)



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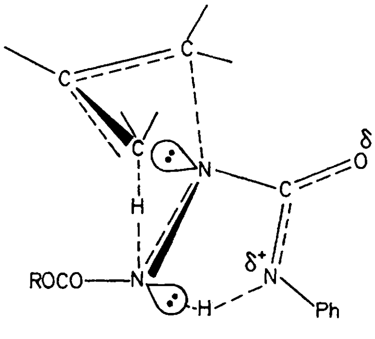
(Scheme). When (Ia) was dissolved in a 25-fold molar excess of (II) for 20 h at 25°, and the excess of (II) removed, the residue [mass spectra and elemental analysis satisfactory for 100% formation of a (Ia)–(II) 1 : 1 adduct] gave an n.m.r. spectrum fully interpretable in terms of 88% of compounds (III) + (IV) (R = Et) and 12% of compounds (V) + (VI) (R = Et). Similarly, (Ib) gave an adduct mixture which broadly analysed as 93% of (III) + (IV) (R = $\mathrm{Bu^t}$) and 7% of (V) + (VI) (R = $\mathrm{Bu^t}$). To determine the principal orientation of the *enophile* the total product from (Ib) was treated with hydrogen chloride in nitromethane to remove t-butoxycarbonyl groups.[6] This provided in high yield the hydrochloride of (VII) (n.m.r. and supporting analyses correct) not detectably contaminated with other isomers, *e.g.* (VIII). Thus it is proven that (I) and 'ene' systems (IIa) and/or (IIb) are principally chosen in this reaction, and (ii) the enophile orientation principally used is that giving rise to (III).

Studies of the reactions of (Ia) with other allylic olefins lead to the general finding that only those alkenyl groups specifically demanded by an 'ene' addition course appear in the corresponding semicarbazide adducts. The kinetics of such additions, monitored by reference to the 326 nm band of (Ia), are first order both in [olefin] and [(Ia)] for a variety of solvents whose medium effects are found to be small [k(ethanol)/k(cyclohexane) $\leqslant$ 5]. Typically, the first-order half-life in 3M-2-methylpent-2-ene (CH_2Cl_2) at 25° for (Ia) is 65 min, and for (Ib) is 280 min. The second-order rate constants (10^5 l mol^{-1} s^{-1}) for the reactions of (Ia), in benzene, at 65°, with several olefins are: hex-1-ene, 12; 2-methylpent-1-ene, 53; 2-methylpent-2-ene, 108; squalene (per olefin unit) 95; natural rubber (per olefin unit) 83; and 2,3-dimethylbut-2-ene, 8·7. Note that the general increase in reactivity with increased flanking of the ethylenic bond by alkyl groups (*cf.* results for ethyl azodicarboxylate[1]) is sharply reversed at the trialkylethylene–tetraalkylethylene transition. In the case of 2-methylpent-2-ene our activation data (benzene solvent) of $\Delta H^{\ddagger}$ *ca.* 15 kcal mol^{-1} and $\Delta S^{\ddagger}$ *ca.* −28 cal K^{-1} mol^{-1} further reflect tightly ordered bimolecular transition states offering energetically satisfactory pathways for the pericyclic processes of 'ene' addition.

Remarkably, (Ia) is roughly 40 times as reactive in representative additions to allylic olefins as the symmetrical open-chain azo-dicarbonyl enophile *trans*-ethylazodicarboxylate. This fact seems to run counter to a simple electronic prediction based on the likely effects of the corresponding acyl groups on the π-electron densities of the azo-systems. We believe, therefore, either that (Ia) could have a *cis*-configuration about its azo-linkage (a point now being investigated§) or that the transition states for *trans*-(Ia) reactions benefit from a special form of internal hydrogen bonding which could assist a charge flow towards the H-seeking nitrogen atom.



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§ Reports (G. O. Schenck, H. R. Kopp, B. Kim, and E. Koerner von Gustorf, *Z. Naturforsch*, 1965, B, **20**, 637; E. Koerner von Gustorf, D. V. White, B. Kim, D. Hess and J. Leitich, *J. Org. Chem.*, 1970, **35**, 1155) that photochemically generated *cis*-azodicarboxylate esters are considerably more reactive than the conventional *trans*-isomers in various cycloadditions have prompted us to examine whether (Ia) could have a natural *cis*-configuration about the azo-bond, which seems conceivable if the synthetic precursor 4-phenyl-1-ethoxycarbonyl semicarbazide happens to adopt an internally hydrogen bonded *cisoid* conformation in solution whilst being oxidized by *N*-bromosuccinimide. However, our evidence for a *cis*-configuration based on spectral examination is not decisive, and an *X*-ray molecular structure determination is currently in progress.

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