The Reaction of Picryl Azide with Olefins

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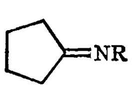
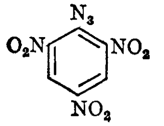
THE preparation of cyanogen azide has been announced recently; this azide reacts rapidly at room temperature with olefins to form either aziridines or Schiff bases (*e.g.*, I; R = CN), the latter being readily hydrolysed to the corresponding ketones.[1] The azide decomposes violently, is only safely handled in solution, "and great care should be taken in any work with this compound."



(I)



(II)

We have been examining the reactions of picryl azide (II), and have observed that, although it decomposes when heated in inert solvents to form 4,6-dinitrobenzofuroxan,[2] it reacts readily at room temperature with a variety of olefins to form either aziridines or Schiff bases. No dihydropyrazoles have been isolated. The rate of reaction of picryl azide with olefins has been followed spectroscopically and by measuring the nitrogen evolved. For some deactivated olefins, *e.g.*, $\alpha\beta$-unsaturated ketones, the rate is so slow that it cannot be distinguished from the spontaneous decomposition of picryl azide. A selection of second-order rate constants (determined by gas evolution) is given in the Table (solvent: ethyl benzoate).

Norbornylene, dicyclopentadiene, and α-pinene yield light-sensitive aziridines; simple olefins, such as cyclopentene, give Schiff bases (I; R = picryl). For preparative purposes chloroform appears to be the best solvent and reaction times vary from a few minutes (norborylene, dihydropyran) to 4 days (cyclohexene). Mild acid hydrolysis of the Schiff bases affords picramide and the corresponding ketone. Similar reactions have been observed with 4-azido-3,5-dinitropyridine and 1,3,5-triazidotrinitrobenzene.[3]

Olefin	Temp. (°c)	k (l. mole^{-1} sec.$^{-1}$)
Dicyclopentadiene ..	22·5	$3{\cdot}2 \times 10^{-3}$
Cyclo-octene	22·0	$1{\cdot}0 \times 10^{-5}$
Indene..	30·2	$7{\cdot}0 \times 10^{-6}$
α-Pinene	25·0	$5{\cdot}6 \times 10^{-6}$
Cyclohexene	22·0	$6{\cdot}2 \times 10^{-7}$
β-Pinene	25·0	$2{\cdot}8 \times 10^{-7}$

Picryl azide forms a solid charge-transfer complex with bis-8-hydroxyquinolinatocopper(II). The crystal structure of the adduct has been determined[4] and in this solid the azide group is not linear, the angle at the central nitrogen atom being 168·3° with a standard deviation of 1·8°. Huisgen[5] has suggested that azides react with olefins by a synchronous mechanism which requires bending of the azide group; the energy needed to bend this group is thought to be small.[6]

Picryl azide has been prepared from picryl chloride and sodium azide.[2] We have prepared it in quantity by nitration of either *o*- or *p*-nitroazidobenzene. Both picryl azide and triazidotrinitrobenzene seem to be far safer to handle than cyanogen azide.

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[4] A. S. Bailey and K. C. Prout, *J.*, in the press.
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