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PHOTOLYSIS OF VINYL BROMIDES IN THE PRESENCE OF TETRABUTYLAMMONIUM AZIDE TRAPPING OF A VINYL CATION WITH AZIDE ION

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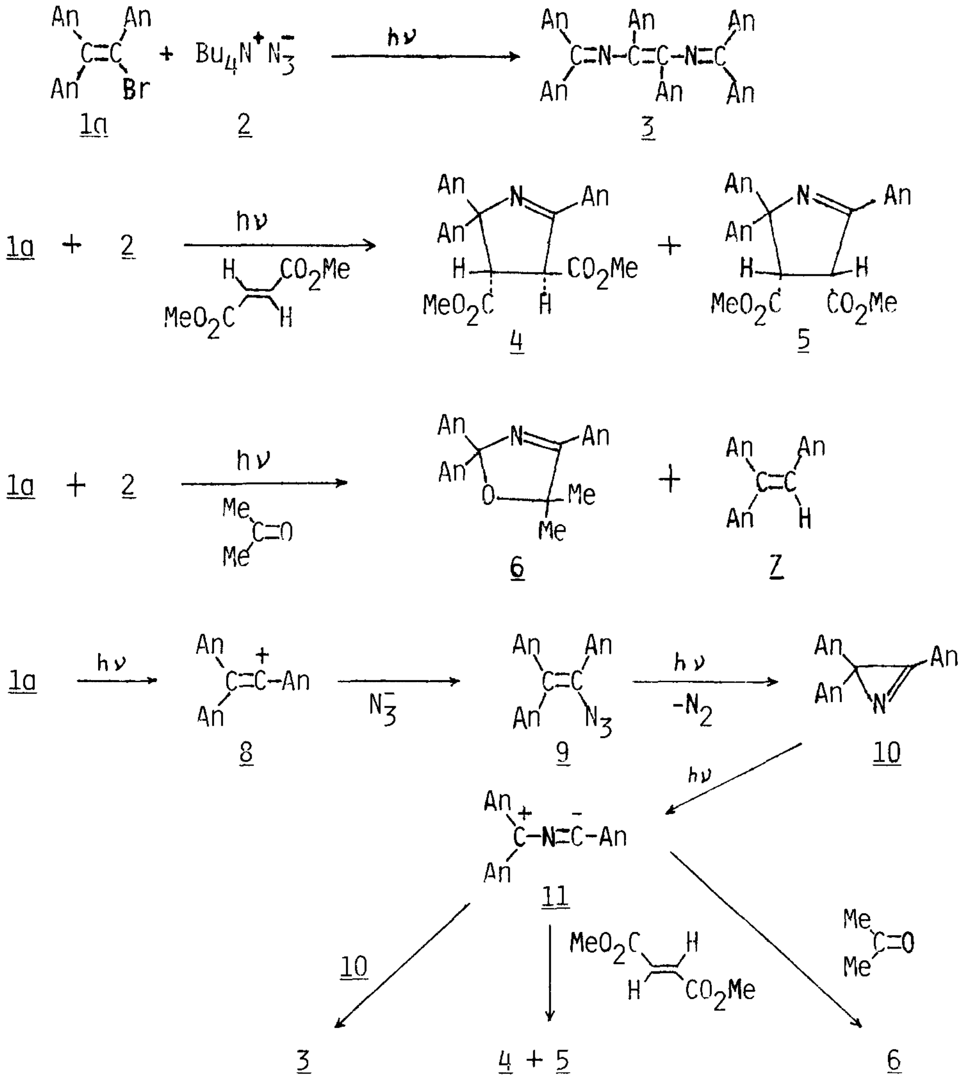
Abstract *Vinyl cations generated by the title photolysis gave vinyl azides by capture of an azide ion and their further photolyses resulted in the formation of cycloaddition-products via nitrile ylides derived from the corresponding azirines*

Recently it has been found that a vinyl cation intermediate is formed by photolysis of vinyl halides[1,2]. However, previous studies were carried out without the use of specific nucleophiles. If photo-induced vinyl cation intermediates could be trapped by some nucleophiles[3,4], it provides not only the direct evidence for the vinyl cation intermediates, but also a possibility for synthetic method of various vinyl derivatives. In this communication we wish to describe the reactions of aryl-substituted vinyl bromides with azide ion and present evidence for direct trapping of vinyl cation intermediates.

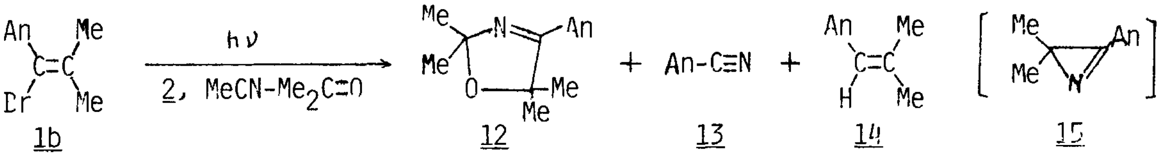
1,2,2-Tris(p-methoxyphenyl)vinyl bromide (1a)(1 mmol) was irradiated in acetonitrile (100 ml) in the presence of tetrabutylammonium azide (2)(2 mmol) through a Pyrex-filter with a 100-W high-pressure mercury lamp under nitrogen atmosphere at 5 °C for 1 h. After evaporation of the solvent the residue was extracted with ether. The ether solution was washed with water to remove the ammonium salt and dried over anhydrous sodium sulfate. After evaporation of the solvent the residue crystallized. Recrystallization from ethanol-benzene afforded orange crystals, mp 219-221 °C. It was assigned to 1,1,3,4,6,6-hexakis(p-methoxyphenyl)-2,5-diazahexa-1,3,5-triene (3)(42%) on the basis of the spectral data, elemental analysis, and chemical behavior[5].

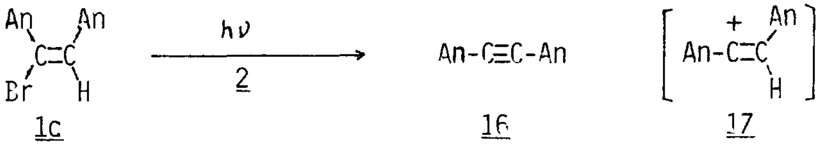
Since it is known that 2,5-diazahexa-1,3,5-triene derivatives are formed by photolysis of corresponding azirines[6,7], the sole formation of 3 is best explained in terms of a reactive intermediate, 1,2,2-tris(p-methoxyphenyl)-vinyl cation (8). Photolysis of 1a gives the vinyl cation 8, which further reacts with azide ion to give a vinyl azide 9 which affords an azirine 10 with loss of nitrogen. Further photolysis of 10 gives rise to 3 via a nitrile ylide 11. It is well known that nitrile ylides can be generated by photolysis of azirines[8] and that they undergo cycloaddition with dipolarophiles such as dimethyl fumarate[9] and acetone[10]. In order to confirm this sequence reactions of 1a with 2 in the presence of dimethyl fumarate or acetone were performed

On irradiation of 1a (1 mmol) with 2 (2 mmol) in the presence of dimethyl fumarate (4 mmol), there are obtained trans- and cis-3,4-bis(methoxycarbonyl)-2,5,5-tris(p-methoxyphenyl)-1-pyrrolines (4 and 5)[5,11] in 76 and 14% yields, respectively. Irradiation of 1a (1 mmol) with 2 (2 mmol) in acetone (100 ml) under similar conditions gave 5,5-dimethyl-2,2,4-tris(p-methoxyphenyl)-3-oxazoline (6)[5] and 1,1,2-tris(p-methoxyphenyl)ethylene (7)[12] in 90 and 5% yields, respectively. These results provide further evidence for the formation of the azirine 10 and the vinyl azide 9 via the vinyl cation 8.



Similarly irradiation of 1-bromo-1-p-methoxyphenyl-2-methylpropene (1b) with 2 in the mixed solvent of acetonitrile (90 ml) and acetone (20 ml)13) gave cycloaddition product, oxazoline 12, in 15% yield, together with 1-p-methoxyphenyl-2-methylpropene (14)(7%)12) and p-methoxyphenylbenzonitrile (13)(18%) However, irradiation of E-1,2-bis(p-methoxyphenyl)vinyl bromide (1c) in acetonitrile under conditions similar to the case of 1a gave 1,2-bis-(p-methoxyphenyl)acetylene (16) in 62% yield Loss of the proton from the reactive intermediate, vinyl cation 17, might occur more easily than a nucleophilic attack of azide ion on vinyl cation 17 14)





In conclusion, it is demonstrated that stable vinyl cation intermediates can be formed by photolysis of vinyl bromides, and that these intermediates provide the one-pot synthesis of heterocyclic compound when reacted with an azide ion Further study is in progress to explore the scope of the photolysis of vinyl halides with various nucleophiles for synthetic use

Referenes and Notes

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2) S A McNeely and P J Kropp, *J Am Chem Soc* , 98, 4319(1976)
3) It is well recognized that in kinetic study solvolysis of vinyl derivatives showed common ion effect, and Z Rappoport and Y Apeloig isolated vinyl chloride from acetolysis of vinyl bromides in the presence of excess tetraethylammonium chloride *J Am Chem Soc* , 97, 821 (1975)
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5) 3 NMR(δ,$CDCl_3$) 3 73(s,6H), 3 82(s,12H), and 6 50-7 62(m,24H), UV λ_{max}(log ε) 278 nm(4 55) and 413(3 68), MS(m/e) 718(M^+), Found C,76 50, H,5 95, N,3 63%, Calcd for $C_{46}H_{42}N_2O_4$ C,76 86, H,5 89, N,3 90% Acid hydrolysis of 3 gave 2-amino-2-(4-methoxyphenyl)-4'-methoxyacetophenone and 4,4'-dimethoxybenzophenone 4 NMR(δ,$CDCl_3$) 3 52(s,3H), 3 55(s,3H), 3 68(s,3H), 3 76(s,3H) 3 79(s,3H), 4 30(s,1H), 4 55(s,1H), and 6 54-7 95(m,12H),UV λ_{max}(log ε) 272 nm (4 42), IR ν 1734 cm^{-1}(C=O), MS(m/e) 503(M^+) 5 NMR(δ,$CDCl_3$) 3 33(s,3H), 3 57(s,3H), 3 72(s,3H), 3 83(s,3H), 3 85(s,3H), 4 38(d,1H,J=6 6Hz), 4 98(d, 1H,J=6 6Hz), and 6 60-8 01(m,12H), The cis adduct 5 isomerized to its trans isomer 4 on standing[9] 6 NMR(δ,CCl_4) 1 50(s,6H), 3 61(s,6H), 3 67(s,3H), and 6 52-7 84(m,12H), UV λ_{max}(log ε) 275 nm(4 32), Found C,74 57, H,6 54, N,3 17%, Calcd for $C_{26}H_{27}NO_4$ C,74 80, H,6 52, N,3 36% 12 NMR(δ,CCl_4) 1 40(s,6H), 1 50(s,6H), 3 77(s,3H), and 6 64-7 23(m,4H), MS(m/e) 233(M^+)

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11) Dimethyl fumarate was partially isomerized to dimethyl maleate during the reaction Photoaddition of azirines with dimethyl fumarate and dimethyl maleate proceeds stereospecifically to give trans adduct and cis adduct, respectively[9]

12) This compound might be formed by the hydrogen abstraction of a vinyl radical which is derived from the homolytic fission of the carbon-halogen bond of the starting vinyl halide

13) The irradiation was carried out under conditions similar to the case of 1a without a Pyrex filter Irradiation with a Pyrex filter in acetone for 11 h resulted in the recovery of the starting material 1b

14) It is known that in solvolysis a vinyl cation loses the proton on the β-position more easily than it is attacked by the solvent For example , see Z Rappoport and M Atidia, J C S Perkin II, **1972**, 2316

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