

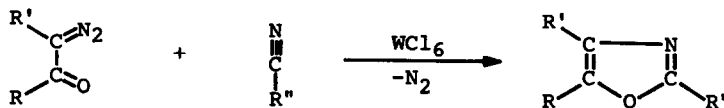
A NOVEL OXAZOLE SYNTHESIS UTILIZING TUNGSTEN(VI) CATALYZED
DECOMPOSITION OF α -DIAZO CARBONYL COMPOUNDS IN NITRILES

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The behaviour of diazo compounds upon metal-catalyzed decomposition is clearly distinguished from that in usual thermolysis and photolysis.¹ Whereas the catalysis of transition metals of lower oxidation state, i.e. M(0), M(I), M(II) species,² is well documented, the one of as high as hexa-valent metals is not known. This communication describes the unprecedented catalysis of Lewis acids in the title reaction.



A solution of azibenzil (0.50 mmol) in benzonitrile (3 ml) was added to WCl_6 ³ (0.50 mmol) suspended⁴ in benzonitrile (2 ml) at room temperature. Nitrogen evolution immediately occurred and after five minutes the solution turned to light brown, then to dark-blue after 2 hr, to yield 2,4,5-triphenyl-oxazole as the major product (66%)⁵ by usual work-up. In contrast, only negligible yields of oxazoles are recorded in the copper(II) catalyzed decomposition.⁶ Other reactions of azibenzil, diazoacetophenone, and methyl diazoacetate with nitriles gave following results: [R, R', R'', reaction time (hr), yield of oxazole^{7a}]: [Ph, Ph, Me, 14, 65%^{7b}]; [Ph, Ph, Et, 44, 45%]; [Ph, Ph, $\text{CH}_2=\text{CH}$ -, 12, 50%^{7c}]; [Ph, H, Me, 2, 57%^{7d}]; [OMe, H, Me, 0.25, 20%]. Noteworthy is the formation of 2-vinyl-4,5-diphenyloxazole in the reaction of azibenzil with acrylonitrile, none of the cyclopropanation product being detected.

In order to check the contribution of Lewis acidity⁸ to the catalysis, azibenzil was treated with such halides as SnCl_4 , TiCl_4 and AlCl_3 in aceto-

nitrile. The major product was desyl chloride in each case (SnCl_4 : 22%; TiCl_4 : 48%; AlCl_3 : 41%), although the desired product, 2-methyl-4,5-diphenyloxazole, was obtained as follows: SnCl_4 , 6%; TiCl_4 , 16%; AlCl_3 , 8%. The remarkable catalysis of WCl_6 is attributable to the good affinity of the metal with carbenes.⁹

Further studies are in progress to extend the potential of this tungsten(VI) catalyzed decomposition reaction of diazo compounds.

References and Footnotes

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4. Dissolution of a small portion of WCl_6 was evidenced by grey coloration of the solution.
5. Mp $113-115^\circ$ (lit., $114-115^\circ$: M. Lora-Tamayo, R. Madroñero, and H. Leiprand, Chem. Ber., **97**, 2230 (1964)); ms: m/e 297 (M^+). Identified by comparison with the authentic ir spectrum in Sadtler Standard Spectra, Grating 8666K. By-products were benzil (12%) and desyl chloride (18%).
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7. (a) Isolated yield unless specified. All the products were identified spectrometrically. (b) Estimated by nmr. (c) By-products were benzil (19%), desyl chloride (13%) and benzoin (15%). (d) Accompanied by phenacyl chloride (41%).
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