Tungsten Hexachloride-catalyzed Decomposition of Diazo Compounds. A Novel Oxazole Synthesis

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Synopsis. Benzoylphenyldiazomethane and diazoacetophenone react with several nitriles in the presence of WCl_6 catalyst to produce 2-substituted 4,5-diphenyloxazoles (**1a—d**) and 2-methyl-5-phenyloxazole (**2**) in good yields. The remarkable catalysis is ascribed to the good affinity of tungsten with carbenes. The catalytic decomposition of diphenyldiazomethane yields diphenylcarbenium ion, which is transformed into triarylmethanes in aromatic solvents.

Lewis acid-catalyzed decomposition of diazo compounds gives intermediary carbene complexes, which are often too much reactive for synthetic applications.[1] The requisite selectivity should be attained by proper choice of the metal salt catalyst in which the central metal atom has good affinity with carbenes and therefore stabilizing the intermediate carbene complex. Among them tungsten salt seems to be a candidate since low valent tungstens give very stable carbene complexes.[2] On this account we have investigated the catalytic activity of tungsten hexachloride in the thermal decomposition of diazo compounds.

Decomposition of Diazo Ketones in Nitriles. When benzoylphenyldiazomethane was treated with tungsten hexachloride suspended in benzonitrile at room temperature, immediate decomposition occurred. Work-up gave 2,4,5-triphenyloxazole (**1a**). Similarly upon the catalytic decomposition in several nitriles the diazo ketone afforded oxazoles **1b—d** in good to moderate yields. Diazoacetophenone was also converted into 2-methyl-5-phenyloxazole (**2**).

a: R=Ph; d: R=Me
c; R=Et; d: R=CH₂=CH
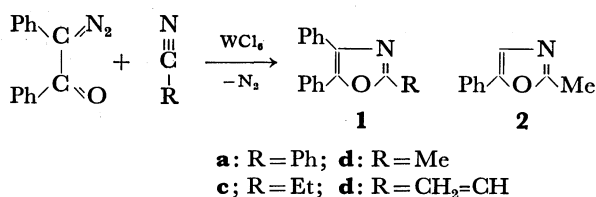
The results are in sharp contrast to the thermal, photochemical or copper(II)-catalyzed decomposition which give only negligible yields of oxazoles.[3] The remarkable catalysis by WCl_6 can be attributed to the Lewis acidity of the salt[4] coupled with its good affinity with carbenes.[2,5] The dual character would probably account for the assumption that both α-keto carbenes and nitriles are assembled together within the ligand sphere of W(VI) and are cyclocoupled effectively. Another noteworthy facet is the formation of 2-vinyl-4,5-diphenyloxazole (**1d**) in the reaction of benzoylphenyldiazomethane with acrylonitrile, where none of the cyclopropanation product has been detected. This suggests the electrophilic nature of carbenic center.[6] These observations are in accord with the following mechanistic postulation.[7]
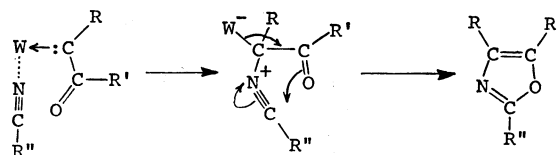
Decomposition of Diphenyldiazomethane. Tungsten hexachloride catalyzes the decomposition of diphenyldiazomethane (**3**) in another way. *N*-Benzhydrylacetamide was produced in the reaction with acetonitrile. When **3** was treated with WCl_6 dissolved in *N,N*-dimethylformamide (DMF), immediate decomposition was again observed and a light green solution was obtained which upon hydrolysis gave benzhydrol and upon methanolysis benzhydryl methyl ether (see Experimental). Deuterium oxide quenching of this solution resulted in no deuterated benzhydrol. Obviously the aliphatic proton of diphenylcarbenium ion intermediate originates from the catalyst, but the proton source could not be eliminated in spite of repeated sublimations.[8] The catalytic decomposition of **3** in aromatic solvents (benzene, toluene, and anisole) gave Friedel-Crafts type products, triarylmethanes (Ph_3CH, 58%; $Ph_2CHC_6H_4Me$, 47%; $Ph_2CHC_6H_4$-*p*-OMe, 76% respectively).

Experimental

All the temperatures were uncorrected. The IR spectra were obtained on a Shimadzu spectrometer 27-G, mass spectra on a Hitachi RMU-6L, and PMR spectra on JEOL JNM-PMX 60, JEOL C-60-H, or Varian EM-360 spectrometer. Unless otherwise stated, commercial tungsten hexachloride was sublimed once (160 °C/0.2 Torr). All the experiments were performed under a nitrogen atmosphere and at room temperature.

Triphenyloxazole (1a). A solution of benzoylphenyldiazomethane (0.11 g, 0.50 mmol) in benzonitrile (3 ml) was added to a suspension of WCl_6 (0.20 g, 0.49 mmol) in the same solvent (2 ml). Nitrogen evolution immediately occurred and after 5 min the solution turned to light brown, then to dark blue after 2 h. After the addition of water the reaction mixture was extracted (AcOEt), dried (Na_2SO_4), and concentrated *in vacuo*. Preparative TLC (alumina, benzene, R_f 0.6—0.8) afforded **2a** (80 mg, 66%). Mp 113—115 °C (lit,[9] 114—115 °C); IR (Nujol): 3050; 1602, 1595, 1555, 1490, 1450, 968, 770, 694, cm⁻¹; MS: *m/e* 297 (M⁺); PMR (CCl_4): δ 7.2—8.1 (m, Ph). Byproducts were diphenylethanedione (**4**) (13 mg, 12%) and 2-chloro-1,2-diphenylethanone (**5**) (21 mg, 18%).

2-Methyl-4,5-diphenyloxazole (1b):[9] 65% yield; bp 80—90 °C (bath temp)/0.1 Torr; IR (neat): 3060, 2940, 1602, 1585, 1500, 1443, 1270, 1226, 1051, 1020, 967, 767, 699 cm⁻¹; MS: *m/e* 235 (M⁺); PMR (CCl_4): δ 2.50 (s, 3H, Me), 7.1—7.6 (m, 10H, Ph).

2-Ethyl-4,5-diphenyloxazole (1a):[9] 45% yield; bp 110—125 °C (bath temp)/0.3 Torr; IR (neat): 3060, 1603, 1570, 1500, 1450, 1211, 1060, 1024, 965, 761, 692 cm^{-1}; MS: m/e 249 (M$^+$); PMR (CCl$_4$): δ 1.43 (t, $J=9$ Hz, 3H, Me), 2.85 (q, $J=9$ Hz, 2H, CH$_2$), 7.0—8.1 (m, 10H, Ph). 4 was a by-product (7%).

4,5-Diphenyl-2-vinyloxazole (1d):[10] 50% yield; bp 150—168 °C (bath temp)/0.2 Torr; IR (neat): 1600, 1530, 1180, 1070, 1029, 980, 760, 695 cm^{-1}; MS: m/e 247 (M$^+$); PMR (CCl$_4$): δ 5.3—6.9 (m, 3H, CH=CH$_2$), 7.0—8.2 (m, 10H, Ph). By-products were 4 (19%), 5 (13%) and 2-hydroxy-1,2-diphenylethanone (15%).

2-Methyl-5-phenyloxazole (2): 66% yield; mp 56—58 °C (lit,[11] 58 °C); IR (Nujol): 1580, 1560, 1215, 1132, 1060, 940, 839, 830, 764, 698, 676 cm^{-1}; MS: m/e 159 (M$^+$); PMR (CCl$_4$): δ 2.48 (s, 3H, Me), 7.1—7.8 (m, 6H, aromatic protons). 2-Chloro-1-phenylethanone (41%) was also obtained.

Decomposition of 3 in Acetonitrile. A solution of 3 (97 mg, 0.50 mmol) in acetonitrile (1 ml) was added to a suspension of WCl$_6$ (0.20 g, 1.5 mmol) in the same solvent (5 ml). After 10 h the reaction mixture was worked up. Preparative TLC (silica gel, benzene) afforded N-benzhydrylacetamide[12] (R_f 0.3—0.4, 38 mg, 32%) along with 9,10-diphenylphenanthrene[13] (R_f 0.9—0.95, 57 mg, 64%).

Decomposition of 3 in DMF. A solution of 3 (97 mg, 0.50 mmol) in DMF (1 ml) was added to a solution of WCl$_6$ (0.20 g, 0.50 mmol) in DMF (5 ml). After 1 h the reaction mixture was quenched (H$_2$O) and extracted (ether). Preparative TLC (silica gel, benzene, R_f 0.2—0.3) of the crude product afforded benzhydrol (63 mg, 77%) along with tetraphenylethylene (R_f 0.8—0.9, 13 mg, 9%). Quenching with methanol afforded benzhydryl methyl ether in 60% yield.[14]

Decomposition of 3 in Anisole. A solution of 3 (0.10 g, 0.53 mmol) in anisole (1 ml) was added to a brown solution of WCl$_6$ (0.20 g, 0.51 mmol) in anisole (5 ml). After 5 h the reaction mixture was quenched with water and extracted with ether. The organic layer was dried (Na$_2$SO$_4$), concentrated *in vacuo*, and the residue was purified by preparative TLC (silica gel, benzene, R_f 0.8—0.9, 0.10 g, 76%). Mp 61—62 °C (lit,[15] 61 °C); IR (Nujol): 1610, 1510, 1250, 1030, 700 cm^{-1}; MS: m/e 274 (M$^+$); PMR (CCl$_4$): δ 3.73 (s, 3H, OMe), 5.47 (s, 1H, CH), 6.6—7.1 (ABq, 4H, C$_6$H$_4$-OMe), 7.0—7.5 (m, 10H, Ph).

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1) W. Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York (1971), p. 85. See also R. Noyori, *Tetrahedron Lett.*, **1973**, 1691.

2) C. P. Casey and T. J. Burkhardt, *J. Am. Chem. Soc.*, **95**, 5833 (1973) and references cited therein.

3) In these reactions Wolff rearrangement predominates over the dipolar cycloaddition. R. Huisgen, G. Binsch, and L. Ghosez, *Chem. Ber.*, **97**, 2628 (1964). A preliminary results of the present note have been published in K. Kitatani, T. Hiyama, and H. Nozaki, *Tetrahedron Lett.*, **1974**, 1531.

4) In order to check the contribution of Lewis acidity to the catalysis, benzoylphenyldiazomethane was treated with such halides as ZnCl$_2$, SnCl$_4$, TiCl$_4$, and AlCl$_3$ in acetonitrile. The major product was 2-chloro-1,2-diphenylethanone (5) in each case (ZnCl$_2$, 33%; SnCl$_4$, 22%; TiCl$_4$, 48%; AlCl$_3$, 41%), although the desired product 1b was obtained as follows: ZnCl$_2$, 12%; SnCl$_4$, 6%; TiCl$_4$, 16%; AlCl$_3$, 8%.

5) T.-L. Ho, *Chem. Rev.*, **75**, 1 (1975).

6) In contrast, thermal reaction of electron-deficient diazo compounds (*e.g.* 10-diazoanthrone) with acrylonitrile affords cyanocyclopropanes. N. Filipescu and J. W. Pavlik, *J. Chem. Soc., C*, **1970**, 1851.

7) The intermediacy of 5 is readily excluded because it does not react with acetonitrile even in the presence of WCl$_6$ at room temperature.

8) The addition of deuterium oxide prior to the reaction resulted in the formation of the products derived from diphenyldeuteriomethyl cation. In the reaction of benzoylphenyldiazomethane with acetonitrile, however, the presence of water in the reaction mixture strongly depressed the oxazole formation (17% yield).

9) M. Lora-Tamayo, R. Madronero, and H. Leiprand, *Chem. Ber.*, **97**, 2230 (1964).

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12) H. L. Wheeler, *Am. Chem. J.*, **26**, 345 (1901).

13) W. A. Mosher, F. W. Steffgen, and P. T. Lansbury, *J. Org. Chem.*, **26**, 670 (1961).

14) The nature of the reactive species responsible for these products is still obscure. A possible explanation might involve diphenylcarbenium ion (protonated carbene) probably complexed with tungsten.

15) A. Bistrzycki and C. Herbst, *Ber.*, **35**, 3133 (1902).