

Behavior of Carbonyl Ylide Generated
from 3-Chloro-3-(p-nitrophenyl)diazirine and Acetone.
1,3-Dipolar Cycloaddition to Benzaldehyde and Epoxide Formation

Toshikazu IBATA,* Jiro TOYODA, and Michael T. H. LIU[†]

Institute of Chemistry, College of General Education, Osaka University,
Toyonaka, Osaka 560

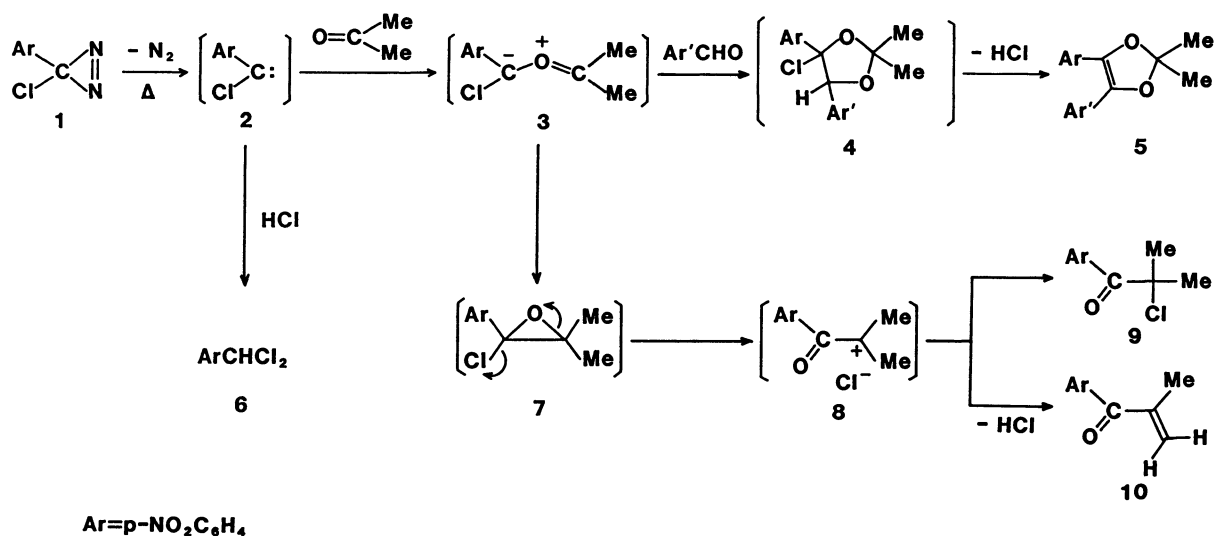
[†] Department of Chemistry, University of Prince Edward Island,
Charlottetown, P. E. I., Canada, C1A 4P3

A carbonyl ylide generated from 3-chloro-3-(p-nitrophenyl)diazirine and acetone either 1,3-dipolar cycloadds to benzaldehydes to afford 2,2-dimethyl-4-aryl-5-(p-nitrophenyl)-dioxole or intramolecularly cyclizes to give 2-chloro-2-methyl-3-(p-nitrophenyl)-3-propanone and 2-methyl-3-(p-nitrophenyl)-1-propene-3-one as final products.

The chemistry of carbonyl ylide has attracted the interests of organic chemists from theoretical and synthetic perspectives.¹⁾ However, only a few investigations have been reported on the formation and 1,3-dipolar cycloaddition of chlorine-substituted carbonyl ylide.²⁻⁴⁾ The previous papers of this series dealt with the 1,3-dipolar cycloaddition of the carbonyl ylide (3) generated from the reactions of 3-chloro-3-(p-nitrophenyl)diazirine (1) and acetone toward ethylenic and acetylenic dipolarophiles.⁵⁾ In this paper, we wish to report the reactions of the chlorine-substituted carbonyl ylide (3) with carbonyl compounds such as meta and para-substituted benzaldehydes.

Thermal decomposition of 3-chloro-3-(p-nitrophenyl)diazirine (1) in the presence of excess acetone and two molar amount of p-nitrobenzaldehyde (in benzene solution, at 80 °C, under 3.0-3.5 atm of N₂ atmosphere, for 24 h), gave 2,2-dimethyl-4,5-di(p-nitrophenyl)dioxole (5a) in 53% yield, [red crystals with yellowish green fluorescence (λ_{max} 440 nm, λ_{max}^f 530 nm in benzene); mp 198-

201 °C; IR(KBr) 1626 (C=C), 1509, and 1340 cm^{-1} (NO_2); $^1\text{H-NMR}(\text{CDCl}_3)$ δ 1.62 (s, 6H, 2 CH_3), 7.57, 7.79 ppm (ABq, 8H, arom-H); $^{13}\text{C-NMR}(\text{CDCl}_3)$ δ 25.64, 114.28, 124.00, 126.87, 134.87, 135.42, and 147.34 ppm],⁶⁾ together with p-nitrobenzal chloride (6) and 2-chloro-2-methyl-3-(p-nitrophenyl)-3-propanone (9).



Scheme 1 .

The formation of the dioxole (5a) can be explained by the 1,3-dipolar cycloaddition of p-nitrobenzaldehyde with the carbonyl ylide intermediate (3), produced via carbene-carbonyl reaction⁷⁾ of chloro-(p-nitrophenyl)carbene (2) with acetone, to give 1,3-dipolar cycloadduct (4a).³⁾ The dioxole (5a) may be formed through the subsequent elimination of hydrogen chloride from 4a. Failure of the isolation of 4a in spite of the careful inspections of the reaction products with medium pressure liquid chromatography on silica gel indicates the fast hydrogen chloride elimination from 4a.

The formation of p-nitrobenzal chloride (6) is elucidated by the reaction of chloro-(p-nitrophenyl)carbene (2) with hydrogen chloride according to the following experimental results. The diazirine (1) does not give 6 upon storage in a benzene solution saturated with hydrogen chloride gas at 25 °C for 3 h. On the contrary 6 was obtained in quantitative yield when the above solution was kept at 80 °C in which thermal decomposition of 1 occurs to give the chlorocarbene (2) and N_2 .

The formation of α -chloroketone (9) can be interpreted by the electrocyclization^{4,8)} of the carbonyl ylide (3) to give 2-chloro-3,3-dimethyl-2-(p-nitrophenyl)oxirane (7), followed by the simultaneous or stepwise process of epoxide ring opening at C₃-O bond and bond breaking at C₂-Cl to give a carbocation ion pair intermediate (8), which yields 9 by the recombination⁴⁾ as shown in Scheme 1.

Table 1. Yields of the Reaction Products 5, 6, 9, and 10

Run	Ar'CHO	Yield/%			
		<u>5</u>	<u>6</u>	<u>9</u>	<u>10</u>
a	p-NO ₂ C ₆ H ₄ CHO	53	19	4	-
b	m-NO ₂ C ₆ H ₄ CHO	46	18	5	-
c	p-CNC ₆ H ₄ CHO	30	23	7	5
d	p-ClC ₆ H ₄ CHO	16	25	15	13
e	p-CH ₃ C ₆ H ₄ CHO	1	27	5	21
f	p-CH ₃ OC ₆ H ₄ CHO	-	23	4	14
g	none	-	4	22	15

All the reactions listed in the Table were carried out heating (80 °C, 3 h) a benzene solution (40 ml) of diazirine (1 mmol) and substituted benzaldehyde (2 mmol). The yields of the products were based on the isolated amount of the products on silica gel column chromatography using hexane-benzene as an eluent.

Other substituted benzaldehydes, such as m-nitro-, p-cyano-, p-chloro-, p-methyl, and p-methoxybenzaldehydes also gave the corresponding dioxoles (5), p-nitrobenzal chloride (6), α -chloroketone (9), and 2-methyl-3-(p-nitrophenyl)-1-propene-3-one (10)⁹⁾ along with p-nitrobenzaldehyde¹⁰⁾ as shown in Table 1.⁶⁾ Treatment of α -chloroketone (9) with bases, such as triethylamine, 1,4-diazabicyclo[2.2.2]octane, and sodium hydride in benzene solution at 80 °C recovered 9 without formation of 10. Therefore, formation of the vinyl ketone (10) is also explained by the intermediacy of the carbocation ion pair (8). Decomposition of 1 in the absence of benzaldehydes, yielded only 6, 9, and 10 (Table 1, run g)

together with 28% yield of p-nitrobenzaldehyde.¹⁰⁾

Electron-releasing substituents on benzaldehydes decrease the yields of dioxoles (5); especially p-tolualdehyde and p-anisaldehyde gave only a trace or no dioxole (Table 1, runs e and f). These are attributed to the decrease in dipolarophilicity of benzaldehydes. This indicates that the 1,3-dipolar cycloaddition proceeds through the carbonyl ylide-HOMO controlled process.¹¹⁾ The total yields of 9 and 10 increase by the decrease in the dipolarophilicity of the benzaldehydes. Therefore, the 1,3-dipolar cycloaddition and the electrocyclization of the carbonyl ylide (3) are confirmed to proceed competitively in this reaction system (Scheme 1). The comparison of these results with the previous observations that the reaction of the carbonyl ylide (3) with electron-deficient ethylenic and acetylenic dipolarophiles gave no 9 and 10⁵⁾ indicates that those ethylenic and acetylenic dipolarophiles are much more reactive toward 3 than benzaldehydes not to compete with electrocyclization to afford the epoxide (7).

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