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# Carbonyl Ylide from
# 3-Chloro-3-p-nitrophenylcarbene and Acetone

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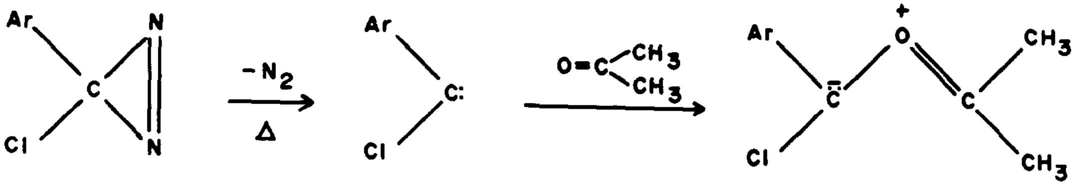
Summary: 3-chloro-3-p-nitrophenylcarbene readily reacts with acetone to form carbonyl ylide which undergoes 1,3 cycloaddition with dipolarophiles.

Recent years have witnessed extensive investigations into the chemistry of carbonyl ylide both from the theoretical and synthetic standpoints.[1] These authors have developed the formation of carbonyl ylide through the carbene-carbonyl reaction and reported the 1,3-dipolar cycloaddition with ethylenic and acetylenic compounds.

Since diazirines are precursors for carbenes[2] we propose to generate carbonyl ylide from the thermolysis or photolysis of diazirine in the presence of acetone. We wish to report evidence for the capture of chlorocarbene by acetone to form a carbonyl ylide. The 1,3-dipolar-cycloadditions of the carbonyl ylide to dipolarophile are also reported.

3-chloro-3-p-nitrophenyldiazirine, 1, was prepared in 25% yield by Graham[3] oxidation of p-nitrobenzamidine hydrochloride with freshly prepared aqueous sodium hypochlorite in DMSO. The UV and IR spectra of 1 agreed with literature descriptions.[4]

Thermal decomposition of 1 in the presence of acetone and dimethyl acetylene dicarboxylate (DMADC) gave dimethyl-2-hydroxy-5,5-dimethyl-2-(p-nitrophenyl)-2,5-dihydrofuran-3,4-dicarboxylate, 5, in 30% yield, together with minor unidentified products. The structure of 5 was characterized[5] on the basis of NMR and IR spectra. The presence of the hydroxyl group was confirmed by the singlet signal at δ 3.82 ppm and an absorption at 3480 $cm^{-1}$ in the IR spectrum. The formation of 5 can be explained via the intermediacy of a carbonyl ylide, 3, which is generated by the carbene-carbonyl reaction as described in scheme.



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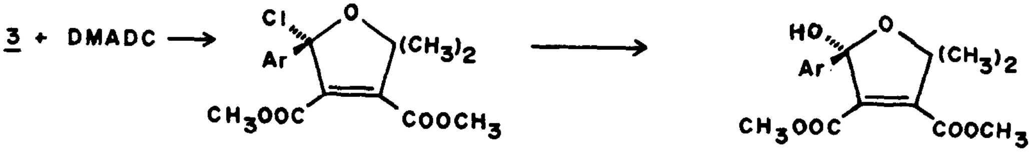
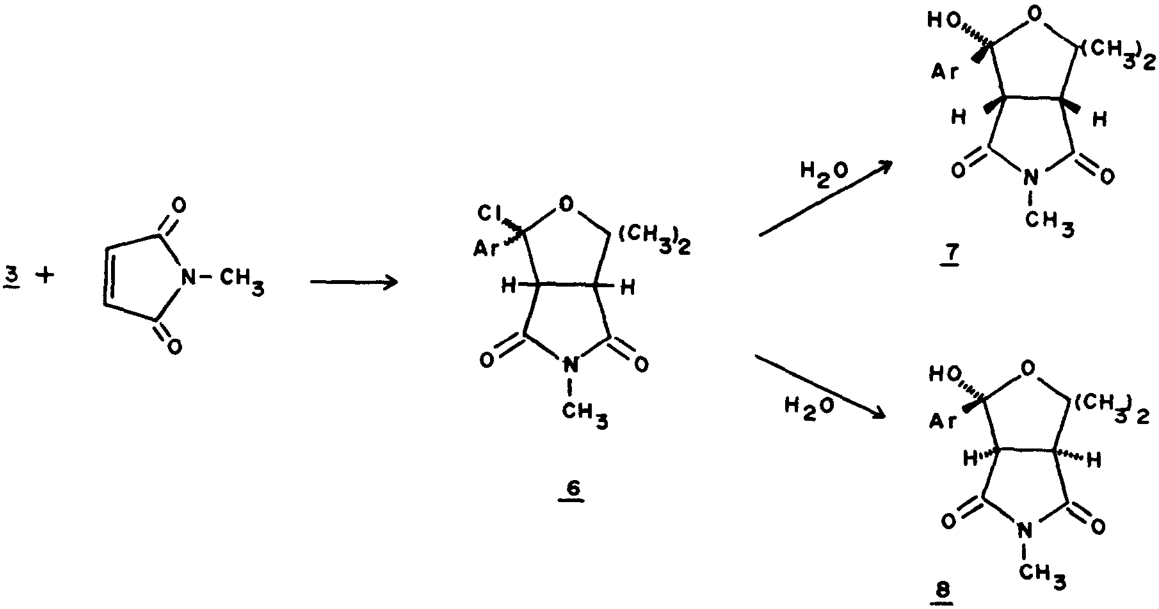


4 5

Isolation of the 1,3-dipolar cycloadduct, 4, arising from 3 and DMADC was unsuccessful, despite detailed inspection of the reaction mixture by means of column chromatography. Apparently 4 was hydrolyzed during silica gel column chromatography because of its high reactivity.



6 7 8

Similar results were obtained when 1 was thermolized in the presence of acetone and an ethylenic dipolariphile, N-methylmaleimide to yield cycloadduct, 6. The products are a mixture of stereoisomers of 2-hydroxy-5,5-dimethyl-2-(p-nitrophenyl)-tetrahydrofuran-N-methyl-3,4-dicarboximide (7 and 8) in 37 and 8% yields, respectively. Characterization of the stereoisomers of 6 is unknown since 6 cannot be isolated; however, their stereochemistry may be inferred to by examining 7 and 8. Product 7 has been assigned tentatively as the OH-endo- product on the basis of a small chemical shift difference between the two methine proton signals (δ3.34 and 3.63) in contrast with the OH-exo-isomer, 8 (δ3.72 and 4.79). Isolation of 8 in pure state has been unsuccessful thus far.

Irradiation of 1 at 4K produced no detectable ESR signal; this confirms the production of a singlet species. Photolysis of 1 at 25°C in the presence of acetone and DMADC yielded 5. It is likely that the singlet carbene is involved in both the thermolysis and photolysis experiments. Laser photolysis[6] of 1 in the presence of acetone gave rise to a transient ($\lambda_{max}$ = 590 nm and $\tau \sim 500$ ns in acetone). The quenching rate constants ($k_q$ in $M^{-1}s^{-1}$) at 304K for the reaction of the carbonyl ylide with a variety of substrates are as follows: diethyl fumarate, $6.4 \times 10^8$; tetramethyl ethylene, $2.9 \times 10^6$: oxygen, $7 \times 10^7$; methanol, $5.5 \times 10^6$ and DMADC, $1.5 \times 10^8$. The laser photolysis confirmed DMADC to be an efficient dipolarophile for 1,3-cycloaddition.

General procedure for thermal decomposition of 1 in the presence of acetone and dipolarophiles: a toluene solution (50 ml) of the diazirine (1 mmol), acetone (100 mmol) and dipolarophile (2 mmol) was heated at 80°C under a nitrogen atmosphere. After the evolution of $N_2$ ceased ( 5 hours), the reaction products were separated by silica gel column chromatography.

5: mp 134.0-134.5°C; yield 30%; NMR($CDCl_3$)δ1.65 (s, $CH_3$), 1.69 (s, $CH_3$), 3.67 (s, $OCH_3$), 3.82 (s, OH), 3.87 (s, $OCH_3$), 7.70 and 8.17 (ABq, Ar); IR(KBr disk) 3480 (OH), 1730 (ester C=O), 1520 and 1350 $cm^{-1}$ ($NO_2$). Anal. Obsd: C, 54.44; H, 4.86; N, 3.93%. Calcd for $C_{16}H_{17}O_8N$: C, 54.70; H, 4.88; N, 3.99%.

7: mp 173.0-175.0°C; yield 37%; NMR($CDCl_3$)δ1.61 (s, $CH_3$), 1.66 (s, $CH_3$), 2.93 (s, OH), 3.04 (s, N-$CH_3$), 3.34 (d, CH, J=10.0 Hz), 3.63 (d, CH, J=10.0 Hz), 7.87 and 8.22 (ABq, Ar); IR(KBr disk) 3400 (OH), 1690 (C=0), 1525 and 1355 $cm^{-1}$ ($NO_2$). Anal. Obsd: C, 56.22; H, 5.00; N, 8.88%. Calcd for $C_{15}H_{16}O_6N_2$: C, 56.22; H, 5.00; N, 8.75%.

8: NMR spectrum was measured in a mixture with 7. NMR($CDCl_3$)$\delta$1.35 (s, $CH_3$), 1.39 (s, $CH_3$), 2.87 (s, OH), 3.02 (s, N-$CH_3$), 3.72 (d, CH, J=5.1 Hz), 4.79 (d, CH, J=5.1 Hz), 8.35 (s, Ar).

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## References and Notes:

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5. All new compounds show satisfactory elemental analysis.
6. D. Griller, M.T.H. Liu and J.C. Scaiano, unpublished results. Laser photolysis of 3-chloro-3-phenyldiazirine in the presence of acetone also gave rise to a transient at 450 nm but the intensity of absorption is much weaker than that observed for 1.

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