

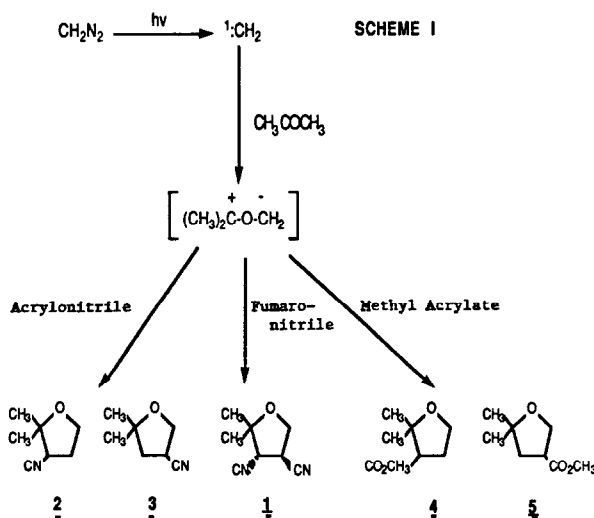
CARBONYL YLIDE FORMATION IN THE REACTION OF METHYLENE WITH ACETONE

Nicholas J. Turro* and Yuan Cha
 Department of Chemistry, Columbia University
 New York, New York 10027

SUMMARY: Photolysis of diazomethane in acetone yields a carbonyl ylide as an intermediate.

The reaction of carbene with nitriles¹ and ketones² to form the corresponding ylides has received considerable attention. In nitrile solvent, methylene (CH₂) has been found to react with the nitrile to form nitrile ylide, which is detectable by spectroscopy and product analysis.³ The formation of carbonyl ylide from methylene reaction with ketone has been proposed as an intermediate in the reaction with acetone⁴ and formaldehyde,⁵ respectively. We now report the results of an ylide trapping experiment which provides additional insight into the CH₂-ketone reaction, and is consistent with a carbonyl ylide formation mechanism.

A typical experimental procedure using fumaronitrile as dipolarophile is as follows: a solution of acetone (10 ml) containing ca. 0.03 M diazomethane (diazirine could not be used as a methylene precursor because of strong competing absorption⁶ of acetone as solvent below 330 nm) was cooled to -78°C, and fumaronitrile (ca. 0.05 M) was added at -78°C (in order to reduce the rate of thermal addition of diazomethane to the electron deficient olefins).⁷ The solution was irradiated for 30 min. with an Oriel 1000 W Xe-Hg lamp at -78°C (λ > 350 nm, Corning 0-52). The solvent was evaporated under reduced pressure after the photolysis, and the products isolated from the photolysis of diazomethane in acetone in the presence of fumaronitrile, acrylonitrile, and methyl acrylate are shown in Scheme I.



That cycloaddition occurs, indicates that the carbonyl ylide is formed in the photolysis of diazomethane in acetone solution. This ylide is presumably produced by electrophilic attack of singlet CH_2 onto the lone-pair electrons of the oxygen atom in acetone. The ratio of the two regioisomers (2:3 or 4:5) derived from the carbonyl ylide cycloaddition with an unsymmetrical dipolarophile (e.g., acrylonitrile and methyl acrylate), is ca. 2:1. Frontier molecular orbital theory correctly rationalizes the regioselectivity of most 1,3-dipolar cycloadditions.⁸ When carbonyl ylides are used as 1,3-dipoles, the dipole highest occupied (HOMO) and the dipolarophile lowest unoccupied (LUMO) orbital interaction stabilizes the transition state. The favored cycloadduct is that formed by the union of the atoms with the largest coefficients in the dipole HOMO and the dipolarophile LUMO. An electron-deficient olefin has the largest coefficient on the unsubstituted carbon in the LUMO. That the reaction of this carbonyl ylide with an unsymmetrical dipolarophile yields the two regioisomers in a ratio of ca. 2:1, indicates that in the HOMO of the carbonyl ylide, the electron density at unsubstituted carbon is greater than that at the disubstituted carbon atom.

EXPERIMENTAL: The reaction of fumaronitrile yields one major product (ca. 62%) on the basis of VPC analysis. The reaction mixture was purified by VPC (5% SE-30) to give trans-2,2'-dimethyl-3,4-dicyanotetrahydrofuran 1 as a white solid. IR (CCl_4) 2980, 2250, 1390, 1380, 1080 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3 , 200 MHz) δ 4.26 (dd, $J=9.3$ and 8.25 , 1H), 4.07 (dd, $J=9.3$ and 6.7 , 1H), 3.46 (ddd, $J=8.07$, 8.25 and 6.7 , 1H), 3.10 (d, $J=8.07$, 1H), 1.46 (s, 3H), 1.40 (s, 3H); m/e 150 (M^+), 135, 120, 72, 43; Anal. (high resolution MS) Calcd. for $\text{C}_8\text{H}_{10}\text{N}_2\text{O}$ 150.0791; Found 150.0789. When acrylonitrile as the quencher, 2 and 3 were obtained in 54% yield on the basis of VPC analysis. IR (CCl_4 , mixture of the two compounds) 2980, 2253, 2247, 1385, 1370, 1055; $^1\text{H-NMR}$ (CDCl_3 , 200 MHz) for 2: δ 4.0 (m, 2H), 2.78 (dd, $J=15$, 1H), 2.38 (m, 2H), 1.37 (s, 6H); for 3: δ 4.0 (m, 2H), 31.6 (m, 1H) 2.1 (m, 2H), 1.40 (s, 6H); m/e 125 (M^+) 110; Anal. Calcd. for $\text{C}_7\text{H}_{11}\text{NO}$: C, 67.17; H, 8.86; N, 11.19; Found: C, 66.69, H, 8.97; N, 11.43. When methyl acrylate as the quencher, 4 and 5 were obtained in 48% yield. IR (CCl_4 , mixture of the two compounds) 2980, 1738, 1380, 1370, 1175, 1059; $^1\text{H-NMR}$ for 4: δ 4.0 (m, 2H), 3.69 (s, 3H), 2.78 (dd, $J=15$, 1H), 2.4 (m, 1H), 2.15 (m, 1H), 1.38 (s, 3H), 1.10 (s, 3H); for 5: δ 3.9 (m, 2H), 3.69 (s, 3H), 3.2 (M, 1H), 2.03 (m, 2H), 1.29 (s, 3H), 1.21 (s, 3H); m/e 158 (M^+), 143, 127; Anal. (high resolution MS) Calcd. for $\text{C}_8\text{H}_{14}\text{O}_3$ 158.0939; Found 158.0944.

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