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SYNTHESES OF STABLE CARBONYL YLIDES BY INTRAMOLECULAR CARBENIC REACTION

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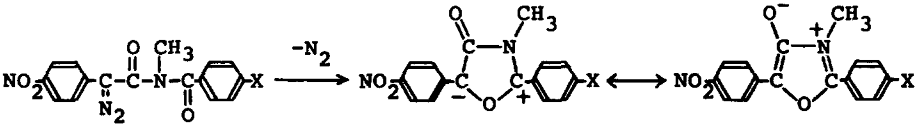
An intermediacy of carbonyl ylides was reported in the thermolysis of epoxides[1] with electron-withdrawing groups, 1,3,4-oxadiazolines,[2] and in the reaction of carbene with carbonyl.[3] This communication deals with the first finding of synthesis of stable carbonyl ylides (II) having novel type of mesoionic structure (III) by the intramolecular carbene-carbonyl reaction.

The diazocompounds (Ia,b,c) were prepared by the ordinary diazo-transfer reaction[4] of corresponding imides with p-toluenesulfonyl azide in pyridine solution at 0°C using triethylamine.[5] In the typical reaction, diazocompound (Ia) (0.32 g, 1.0 mmol) was decomposed in absolute benzene (20 ml) at 80°C under nitrogen atmosphere in the presence of Cu(acac)$_2$. After nitrogen evolution was ceased (for about an hour), red crystals were precipitated. Filtration followed by washing with hot benzene (5 ml) gave red crystalline analytically pure 2-phenyl-5-(p-nitrophenyl)-anhydro-4-hydroxy-1,3-oxazolium hydroxide (IIa)[6] which was stable in crystalline state in air for several weeks: mp 187-189°C, 85 %. Other diazocompounds (Ib and Ic) gave similar results to give the corresponding mesoionic oxazolones (IIb and IIc). The yields and melting points of II are shown in Table 1. The formation of II may reasonably be explained by the intramolecular attack of carbene generated by the decomposition of I on carbonyl oxygen.



a X=H
b X=OCH_3
c X=Br

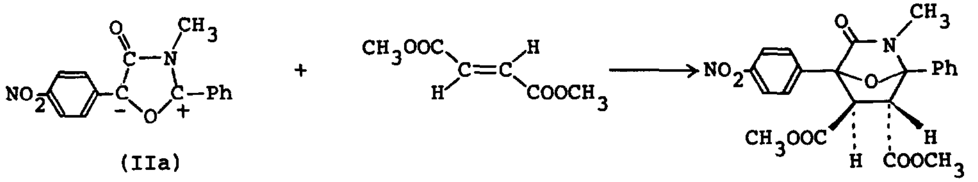
(I) (II) (III)

Table 1. Melting Points, Yields and Spectral Properties of II

II	mp (°C)	yield (%)	IR (KBr) C=O (cm^{-1})	UV (benzene) nm (ε)	NMR ($CDCl_3$) $N-CH_3$ (δ)
IIa	187-189	85	1672	475 (21,000)	3.77
IIb	188-190	88	1670	482 (30,000)	3.72
IIc	192-193	54	1660	485 (24,000)	3.74

The stability of the carbonyl ylides (II) may be attributed to the contribution of mesoionic structure (III) which is isoelectronic structure of münchnons.[7] We call this new mesoionic system as iso-münchnon.

In accordance with the anticipated reactivity of II as a type of carbonyl ylide toward dipolarophiles, reaction of IIa with dimethyl fumarate in benzene at 80°C gave a cycloadduct (IV) in a few minutes in quantitative yield, mp 166-168°C. Nmr($CDCl_3$); δ 8.4-7.2 (m, 9H), 4.01 (d, 1H, methine-H, J=4.0 Hz), 3.66 (d, 1H, methine-H, J=4.0 Hz), 3.66 (s, 3H, OCH_3), 3.40 (s, 3H, OCH_3), 2.66 (s, 3H, NCH_3). Ir(KBr); 1730 (C=O), 1520 and 1348 cm^{-1} (NO_2).



(IIa)

(IV)

The small coupling constants of the methine protons would indicate that two methoxycarbonyl groups are trans to each other, and that the cycloaddition takes place stereospecifically.

References and Footnotes

1) A.Robert and B.Moisan, Chem.Commun., 337 (1972), and references cited therein.
2) R.Rajagopalan and B.G.Advani, Tetrahedron Lett., 2689 (1967); W.Hoffman and H.J.Luthardt, Chem.Ber., 101, 3861 (1968).
3) K.Ueda, T.Ibata, and M.Takebayashi, Bull.Chem.Soc.Japan, 45, 2779 (1972); S.Bien and A.Gillon, Tetrahedron Lett., 3037 (1974), and references therein.
4) M.Regitz, Angew.Chem.Intern.Edn., 6, 733 (1967).
5) Melting points and yields of diazoimides: Ia; 120-125°C (65%), Ib; 111-113°C (60%), Ic; 131-132°C (40%).
6) Satisfactory elemental analyses were obtained for all new compounds.
7) R.Huisgen, H.Gotthardt, and H.O.Bayer, Angew.Chem., 76, 185 (1964).