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## Reactivity and Mechanism of the Reactions Involving Carbonyl Ylide Intermediate

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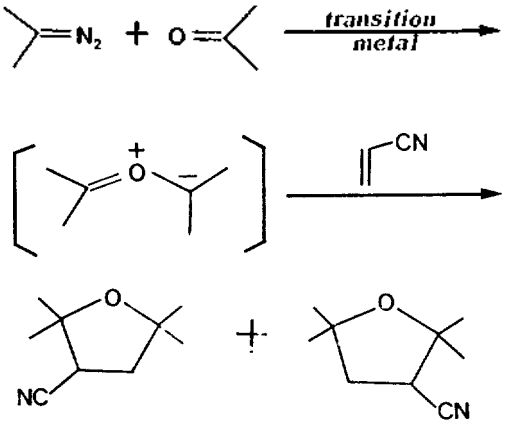
The stereoselective reactions of highly substituted oxygen heterocycles, especially tetrahydrofuran complex and tetrahydropyran derivatives, have attracted considerable attention in recent years.[1] Conceptually tetrahydrofuran formation seems to be proceeded by the 1,3-dipolar cycloaddition of carbonyl ylides with π-bonds.[2] The carbonyl ylides are generated usually by the methods of thermolysis or photolysis of epoxides possessing electron-withdrawing substituents,[3] the thermal extrusion of nitrogen from 1,3,4-oxadiazolines,[4] and the loss of carbon dioxide from 1,3-dioxolan-4-ones.[5] One of the simplest routes for the generation of carbonyl ylides involves the addition of a carbene or carbenoid onto the oxygen atom of a carbonyl group. This can be readily achieved by the transition metal catalyzed decomposition of a diazo ketone in the presence of a carbonyl group (Scheme 1).

In recent years, a widespread application of carbonyl ylides to new synthetic transformation has occurred.[2] This research has been stimulated the chemists' interest in the use of carbenes and carbenoids as reactive intermediates for the generation of other types of ylides.[6] Even though many studies have been reported for the intermediates of carbonyl ylides in the reactions of carbenes with a carbonyl oxygens,[7] the reactions are limited to the discussion of the transition metal catalyzed decomposition of a diazo compounds in the presence of a carbonyl group.




**Scheme 1**

In this paper we report the reactivity and mechanism of the reactions involving carbonyl ylide intermediate from the photolytic kinetic results of non-catalytic decompositions of diazomethane and diphenyldiazomethane in the presence of a carbonyl group.

## Experimentals

**General Photolysis Conditions.** Diazomethane was generated by Aldrich MNNG Diazald apparatus as follows.[8] 1 mmol of 1-methyl-3-nitro-1-nitrosoguanidine (MNNG) is placed in the inside tube of the Diazald kit through its screw-cap opening along with 0.5 mL of water of dissipate any heat generated. 3 mL of diethyl ether is placed in the outside tube and the two parts are assembled with a butyl "O"-ring and held with a pinch-type clamp. The lower part is immersed in a liquid nitrogen bath and about 0.6 mL of 5 N sodium hydroxide is injected dropwise, very slowly to prevent frothing through the silicone rubber septum *via* a syringe with a narrow-gauge needle to prevent leakage around the shank. The flask was then filled to the mark with the appropriate solvent. The diazomethane was transferred to a 10 mm×10 mm×150 mm pyrex tubes which were degassed by three freeze-pump-thaw cycles. The samples were irradiated with a 450 W high pressure Hanovia mercury arc lamp filtered through a uranium glass absorption sleeve (λ>340 nm) for 6-10 hours which time the signal at 2160 $cm^{-1}$ corresponding to the diazo compound had disappeared fully. Ylides were determined by the following method. After removal of solvent, the residue was placed in a 2 mL volumetric flask, 5 mg of internal standard compound (fluorinated1-1,4-dioxane and trifluorinated dioxolanes) was added and the mixture was diluted to the mark with the reaction solvent. Analysis by gas chromatography was performed using columns of a 530 μM×25 M 50% phenylmethyl silicone capillary and a 320 μM×30 M. Supelcowax 10 capillary by setting oven temperature programmed at 70-180℃ with an initial time of 5 min, a ramp rate of 5℃/min and a final time of 15 min. Analytical samples were obtained by preparative gas chromatography at 125℃.

**Rate Measurements.** The photolytic reactions were carried out in a two-legged glass vessel (leg capacity *ca.* 1 mL each) which was connected to a 1 mm quartz UV cell and a tap for introducing reaction solutions and for degassing of nitrogen.

The solution of etherated diazomethane or diphenyldiazomethane was introduced to the quartz UV cell and fluorinated acetones or acetophenone was pipetted into separate legs of the reaction vessel and were degassed.

The solutions were equilibrated at desired temperature before being thoroughly mixed and transferred to the UV cell which was then placed in the cell holder of the spectrometer. The appearance of the coloured species in the reaction mixture was measured by the increase in optical density at suitable intervals on UV/vis spectrophotometer. The initial

**Table 1.** Rate Constants and Activation Parameters for the Reactions of Ylide with Fluorinated Acetones and Acetophenone in Etherated Methylene

| Reaction | Temp. (K) | $k_2$ ($L \cdot mol^{-1} \cdot sec^{-1}$) | $E_a$ ($kcal \cdot mol^{-1}$) | $\Delta H^{\ddagger}$ ($kcal \cdot mol^{-1}$) |
|---|---|---|---|---|
| $:CH_2+$ | 77.0 | $2.90\times10^{-11}$ | | |
| $CH_3COCH_2F$ | 183 | $3.20\times10^{-4}$ | 4.3 | 3.9 |
| | 203 | $12.5\times10^{-4}$ | | |
| $:CH_2+$ | 77.0 | $1.87\times10^{-11}$ | | |
| $CH_3COCF_3$ | 183 | $2.84\times10^{-4}$ | 4.2 | 3.9 |
| | 203 | $3.96\times10^{-4}$ | | |
| $:CH_2+$ | 77.0 | $20.5\times10^{-8}$ | | |
| $CH_3COC_6H_5$ | 183 | $31.0\times10^{-3}$ | 3.2 | 2.8 |
| | 203 | $96.8\times10^{-3}$ | | |

**Table 2.** Rate Constants and Activation Parameters for the Reaction of Ylide with Various Ketones in Etherated Diphenylcarbene

| Reaction | Temp. (K) | $k_2$ ($10^3$ $L \cdot mol^{-1} \cdot sec^{-1}$) | $E_a$ ($kcal \cdot mol^{-1}$) | $\Delta H^{\ddagger}$ ($kcal \cdot mol^{-1}$) |
|---|---|---|---|---|
| $:C(C_6H_5)_2+$ | 298 | 6.42 | | |
| $CH_3COCF_3$ | 303 | 7.42 | 4.1 | 3.5 |
| | 308 | 8.02 | | |
| $:C(C_6H_5)_2+$ | 298 | 6.69 | | |
| $CH_3COCH_3$ | 303 | 7.14 | 2.0 | 1.4 |
| | 308 | 7.46 | | |
| $:C(C_6H_5)_2+$ | 298 | 3.34 | | |
| $CH_3COCH_2C_6H_4F$ | 303 | 4.16 | 7.6 | 7.0 |
| (*p*) | 308 | 5.07 | | |
| $:C(C_6H_5)_2+$ | 298 | 4.18 | | |
| $CH_3COCH_2C_6H_4F$ | 303 | 4.90 | 5.9 | 5.3 |
| (*m*) | 308 | 5.77 | | |

concentration of diazo compound was $2\times10^{-4}$ M and the reactions were carried out under the condition of pseudo-first order reaction so that the concentration of diazo compound was very small comparing with the concentration of ketone.

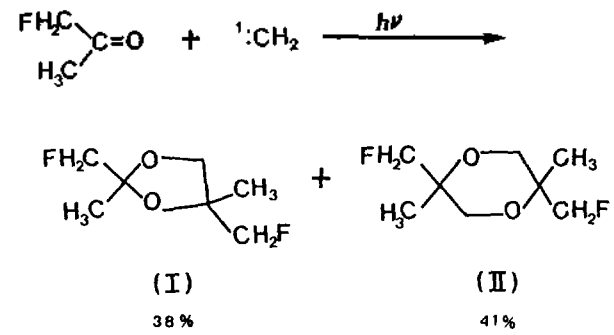
A quantitative analyses of the time dependence of the 278 nm (1-fluoroacetone), 287 nm (1,1,1-trifluoroacetone) and 278 nm (acetophenone) peaks show a good linearity to the first-order rate law. The reaction of ylide with ketone was found to conform the following rate law given by Eq. (1).

$$\frac{-d[\text{Ylids}]}{dt} = k_{obs}\,[\text{Ylide}] \qquad (1)$$

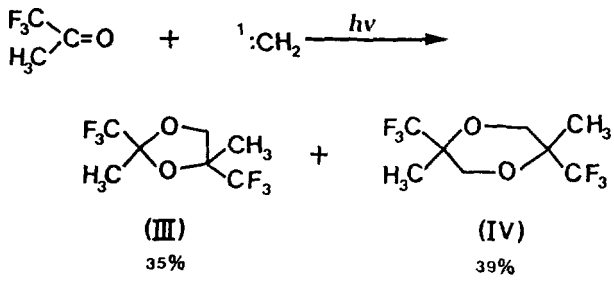
The concentration of ketone was kept always at least one hundred fold greater than [Ylide]. The reactions were carried out at constant light intensity to avoid complication. The first-order behavior was observed with Eq. (2).

$$k_{obs} = k_0 + k_2\,[R_2CO] \qquad (2)$$

Where $k_0$ is the rate constant when the concentration of ketone is zero and $[R_2CO]$ is the concentration of ketone. The $k_0$ showed nearly constant for the reactions in this study. The measured second-order rate constants and reaction conditions are shown in Tables 1 and 2.




**Scheme 2**



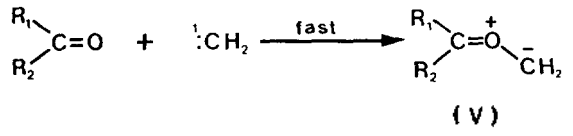

**Scheme 3**

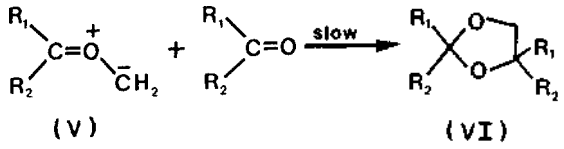
## Results and Discussion

The second-order rate constants are shown to decrease in the order $CH_3COC_6H_5 > CH_3COCH_2F > CH_3COCF_3$ for the same reaction condition of ylide in Table 1. This seems to be caused by the structure of the ketones reacting with methylene. Presumably the basicity of carbonyl oxygen of $CH_3COCF_3$ will be lower than the basicities of $CH_3COCH_2F$ and $CH_3COC_6H_5$ since the electron density at the carbonyl oxygen of $CH_3COCF_3$ will be reduced drastically by the three fluorines compared with $CH_3COC_6H_5$ and $CH_3COC_6H_2F$. While in case of $CH_3COC_6H_5$, the electron density at carbonyl oxygen will be higher than $CH_3COCH_2F$ and $CH_3COCF_3$. A similar trend shows in the ylide reaction for diphenylcarbene as shown in Table 2.

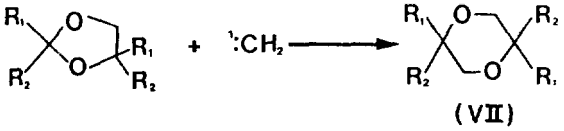
Generally the carbene is generated as singlet state in acetone.[9] But the singlet and triplet states of carbenes are often close enough in energy to be in thermal equilibrium. Even though the triplet state is generally favored in equilibrium, it is less reactive than singlet state in generating observable products.[10] In olefins, it is able to observe the properties of both singlet and triplet states for dicarbomethoxycarbene.[11] Thus, an alkene is a sufficiently effective trap to react with either singlet or triplet carbene befor equilibrium is established.

In this study, we have observed the prodcuts corresponding to the singlet state carbene from the product analysis. The reaction of 1-fluoroacetone with methylene gave the products of fluorinated 1,3-dioxolane (I) (38% yield) and fluorinated 1,4-dioxane (II) (41% yield) as the result of the reaction corresponding to the singlet carbene as shown in

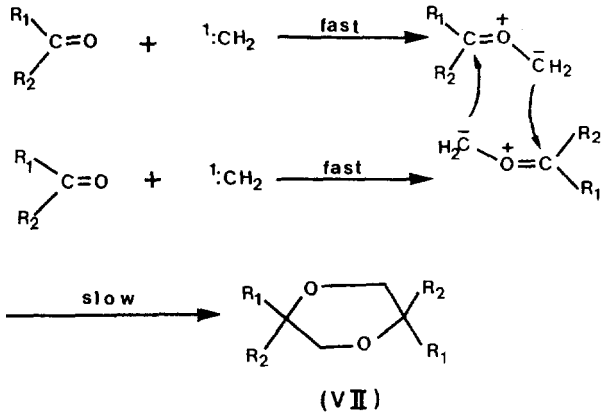



**Scheme 4**




**Scheme 5**




**Scheme 6**

Scheme 2.

The reaction of 1,1,1-trifluoroacetone with methylene gave the products of trifluoroinated 1,3-dixolane (III) (35% yield) and trifluorinated 1,4-dioxane (IV) (39% yield) as shown in Scheme 3.

Generation of the products (I) and (III) could be explained in quite conventional mechanism as follows. The singlet carbene forms ylide (V) which is captured intermolecularly by another molecule of ketone to give (VI) as shown in Scheme 4.

There are two possible interpretations for the formation of (II) and (IV) from (I) and (III) respectively. Compound (VI) presumably reacts with another singlet methylene to form (VII) because the ring strain energy of the dioxolane structure (VI) might be higher than the the dioxane structure (VII) (Scheme 5).

On the other hand it is also expected that dioxane product (VII) would be produced by the reaction of intermolecular ylide-ylide coupling as shown in Scheme 6.

If the reaction is proceeded through the intermolecular cyclization (Scheme 6), the activation energy could be lower than[12,13] that of the ring enlargement process (Scheme 5). The activation energies of 3.2-4.3 Kcal·mol$^{-1}$ for methylene and 2.0-7.6 Kcal·mol$^{-1}$ for diphenylcarbene show lower energy difference than that of 19.5 Kcal·mol$^{-1}$[14] for the singlet and triplet state of methylene. To confirm a possibility of the formation of dioxane product from a ring enlargement reaction of dioxolane with singlet methylene in previous condition, the reaction of VI (dioxolane) with singlet methylene has been proceeded, but the dioxane products (VII) have not observed. Therefore the cyclization is concluded to proceed *via* intermolecular ylide-ylide coupling mechanism as shown in Scheme 6.

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