

THE REACTIVITY OF DIAZO KETONES VI<sup>1</sup>  
THE FORMATION OF DIOXAN DERIVATIVES BY  
THE REACTION OF PHENYL ACETYLDIAZOMETHANE  
OR METHYL BENZOYLDIAZOMETHANE WITH  
SULPHUR DIOXIDE IN ETHANOL

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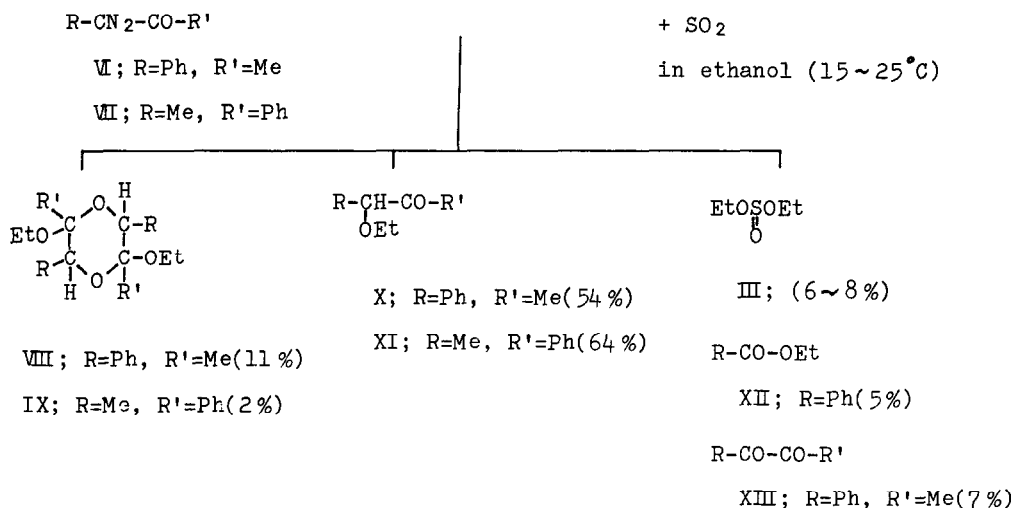
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In a preceding paper,<sup>2</sup> Tanaka, Nagai and Tokura have reported the reaction of azibenzil (I) with sulfur dioxide in ethanol to give 3,4,5-triphenyl pyrazole (II) together with diethyl sulphite (III), benzoin (IV) and ethyl benzoate (V).

The present authors now wish to report the novel reaction of phenyl acetyldiazomethane (VI) or methyl benzoyldiazomethane (VII) with sulphur dioxide in ethanol to give dioxan derivatives (VIII or IX), instead of the pyrazoles, together with diethyl sulphite (III), ethylbenzoate, (XII), and a diketone, (XIII), (Scheme I), where the pronounced substituent effect is observed. The reaction of VI or VII with sulphur dioxide gas in ethanol occurred readily. When sulphur dioxide gas was passed through the solution of VI or VII in ethanol at 15~25°C the color of the solution changed from orange to yellow gradually within two hours. After the reaction was finished, alcohol was removed from the reaction mixture under a reduced pressure. White crystals of VIII or IX crystallized from the residues were filtered. The filtrates were analyzed by a preparative gas chromatography, III, X, XI, XII and XIII

being separated. The identifications of these five products were carried out by the elemental analyses, comparisons of their infrared spectra and gas chromatographic retention times with those of the authentic samples.<sup>3</sup>

## Scheme I \*\*



\*\* The yields are in mole % based on the starting materials.

2,5-Diethoxy-2,5-dimethyl-3,6-diphenyl-1,4-dioxan, (VIII), mp 215~217°C, was identified by the following manners.

The NMR spectrum (CDCl<sub>3</sub>) showed the presence of two methyls (τ, 8.8, s, 6H), two methyls of ethoxy groups (τ, 8.75, t, 6H), two methylenes of ethoxy groups (τ, 6.55, q, 4H), two methines (τ, 5.2, s, 2H) and phenyl protons (τ, 2.35~2.85, m, 10H). The IR spectrum contained absorptions at  $\nu_{\text{Nujor}}$ , 1235, 1180, 1125 and 1060 cm<sup>-1</sup> (six membered cyclic diether). Mass; m/e, 311 (M<sup>+</sup>-OEt), 162 (Ph-CH=C(OEt)Me)<sup>+</sup>, 133 (162-Et). Found; C, 74.50; H, 8.03, Mol. M.W. 320. C<sub>22</sub>H<sub>28</sub>O<sub>4</sub> req. C, 74.13; H, 7.92, Mol. M.W. 356.

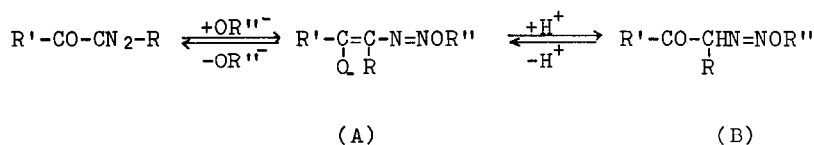
2,5-Diethoxy-2,5-diphenyl-3,6-dimethyl-1,4-dioxan, (IX), mp 96~97°C, was confirmed by IR, NMR and Mass spectra, and elemental analysis.

IR;  $\nu_{\text{Nujor}}$ , 1240, 1190, 1130 and 1090 cm<sup>-1</sup> (six membered cyclic diether). NMR (CDCl<sub>3</sub>); two methyls (τ, 8.8, d, 6H), two methyls of ethoxy groups (τ, 8.75

t, 6H), two methylenes of ethoxy groups ( $\tau$ , 6.65, q, 4H), two methines ( $\tau$ , 6.1, q, 2H) and phenyl protons ( $\tau$ , 2.30~2.85, m, 10H). Mass; m/e, 311 ( $M^+ - OEt$ ), 162 ( $Ph-CH=C(OEt)Me^+$ ), 133 (162-Et). Found; C, 73.84; H, 7.81.  $C_{22}H_{28}O_4$  req. C, 74.13; H, 7.92.

$\alpha$ -Diazo ketones are stable in alcohol and also in liquid sulphur dioxide.  $\alpha$ -Diazo ketones do not react with alcohol or sulphur dioxide without thermal or photochemical decomposition. So behavior of  $\alpha$ -diazo ketones in alcohol-sulphur dioxide system seems to be of considerable interest. It has been reported<sup>4</sup> that the interaction of alcohol with sulphur dioxide gives a very small amount of  $ROSO_2H$ . However, the formation of  $ROSO_2H$  seems to be ineffective in the present reaction, for HA type acids react<sup>5</sup> with diazo ketones ( $R_1-CN_2-CO-R_2$ ) to yield such products as  $R_1CAHCOR_2$  and  $R_1R_2CHCAO$ . In the previous communication<sup>2</sup>, it has been proposed that the reaction of I with sulphur dioxide in ethanol occurs by the interaction between the alcohol stabilized anion<sup>6</sup> with sulphur dioxide (Scheme II).

Scheme II



In the present reactions, it seems plausible that such mesomeric anion (A) and the protonated species (B)<sup>6</sup> are associated with the formation of cyclic diethers (VIII, IX) and  $\alpha$ -ketoethers (X, XI) (Scheme III).

Scheme III

