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THE FORMATIONS OF CYCLOADDUCTS BY THE REACTIONS OF AZIBENZIL WITH SULFUR DIOXIDE

Toshikazu Nagai, Masanobu Tanaka and Niichiro Tokura
Department of Applied Chemistry, Faculty of Engineering,
Osaka University, Suita, Osaka, Japan.

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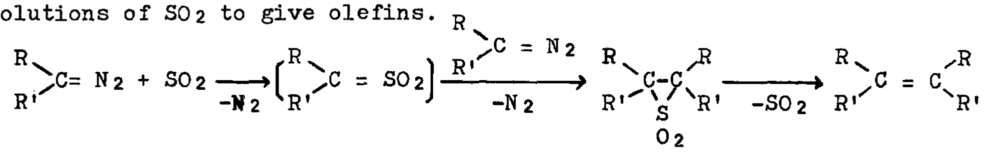
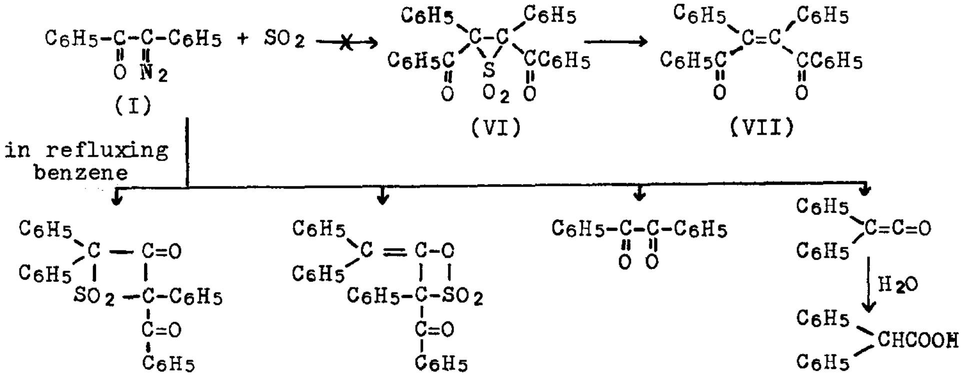
It has been reported[1] that the reactions of diazoalkanes with sulfur dioxide below ordinary temperature form stable or transient episulfones, followed by the evolutions of SO_2 to give olefins.



We now wish to report the reaction of azibenzil (I) with sulfur dioxide to give interesting four membered cyclic sulfones (II and III) together with IV and V, instead of the episulfone (VI) or olefin (VII).

The formations of II and III should indicate that the Wolff rearrangement partially occurred to give diphenyl ketene which underwent cycloaddition to the keto-sulfene formed. The present result might present the first observation of the cycloaddition of sulfene to ketene.



(II) 44 %* , (III) 7 % , (IV) 23 % , (V) 23 %

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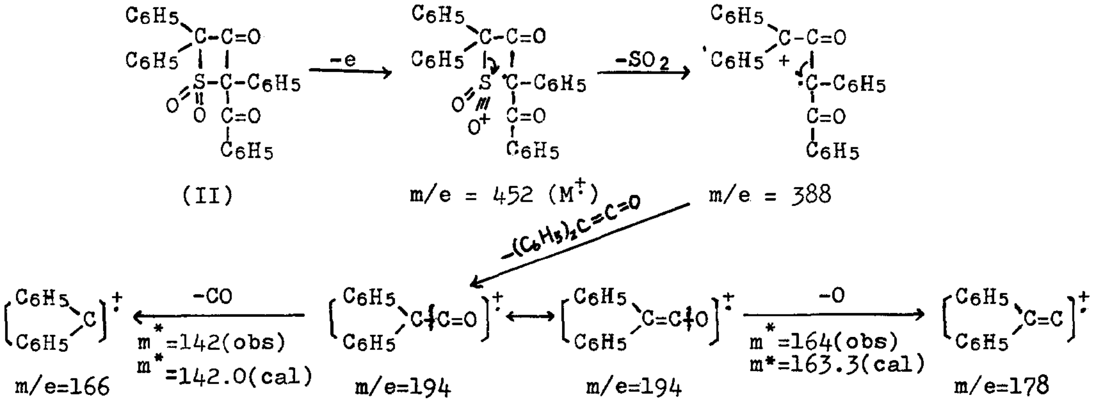
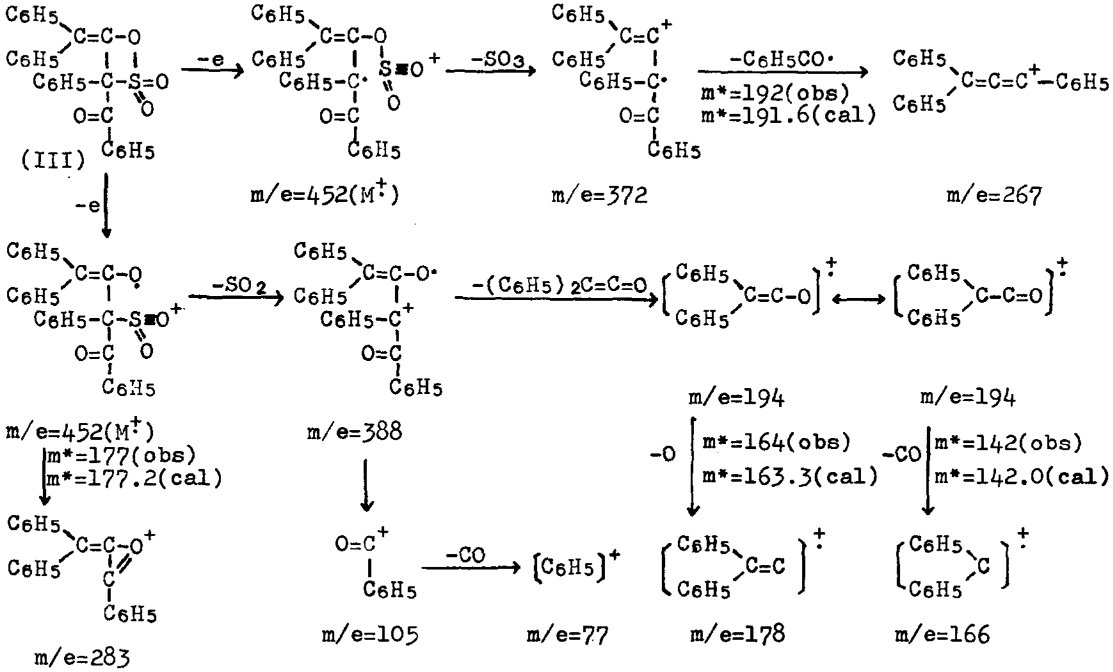
* The yields are in mole % based on I used for IV and V, and based on a half mole of I used for II and III.

The reaction of I with SO_2 did not take place below room temperature, and the reaction was carried out in refluxing benzene. To a solution of azibenzil (8.5 g) in benzene (85 ml) was introduced SO_2 gas (200 g) during 4.5 hr under reflux. The products were separated by chromatography using silica gel as the adsorbent, II, m.p. 232-233° (dec), being identified on the basis of IR, NMR and Mass spectra and elemental analysis. Two types of C=O stretching bands at 1785 ($\nu_{C=O}$ of four membered ring) and 1605 cm^{-1} ($\nu_{C=O}$ of benzoyl group) appeared in the IR spectrum of II, with bands at 1350 (ν_{as} SO_2) and 1140 cm^{-1} ($\nu_{s}SO_2$). The NMR spectrum displayed only a multiplet at τ 2.5~3.0 due to phenyl protons. (Found: C, 74.92; H. 4.41; S, 7.20. $C_{28}H_{20}O_4S$ req. C, 74.33; H, 4.46; S, 7.07 %.) The mass spectrum of II was in good agreement with the structure: a molecular ion peak of m/e = 425 appeared in the spectrum, with peaks which corresponded to the fragments as is shown below. The structure of II was further confirmed from



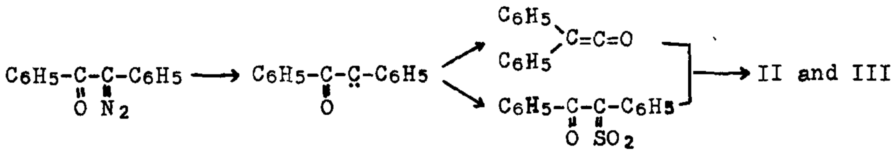
the results of the thermal decomposition and base hydrolysis: the neat decomposition of II at 280° afforded tetraphenylethylene with evolving of SO_2, the hydrolysis of II with sodium hydroxide in 1 : 1 water-dioxane yielded quantitatively diphenylmethyl phenylmethyl sulfone (VIII), m.p. 157~158° (dec). The identification of VIII was made by IR, NMR, Mass and elemental analyses. IR: 1310 (ν_{as} SO_2) and 1130 cm^{-1} (ν_s SO_2). NMR: τ 2.4~2.9 (15H, multiplet, phenyl), 4.85 (1H, singlet, methine) and 5.85 (2H, doublet, methylene). Mass spectrum of VIII was also in good agreement with the structure: m/e = 258 (M^+- SO_2) appeared in the spectrum, with major peaks at m/e = 167 ($(C_6H_5)_2CH^+$) and 91 ($C_6H_5CH_2^+$). (Found: C, 74.52; H, 5.56; S, 10.28. $C_{20}H_{18}O_2S$ req. C, 74.53; H, 5.59; S, 9.95 %.)

Confirmation of III was achieved in a manner paralleling that employed above for II. M.p. 173~174° (dec). IR: 1605 ($\nu_{c=o}$), 1585 ($\nu_{c=c}$), 1350 (ν_{as} SO_2) and 1130 cm^{-1} (ν_s SO_2). (Found: C, 74.11; H, 4.78. $C_{28}H_{20}O_4S$ req. C, 74.33; H, 4.46 %.) Mass spectrum of III was in good agreement with the structure as is shown in the chart.



Compounds IV and V were readily identified by mixed m.p. methods.

It has been well known that diazoketones decompose thermally to undergo the Wolff rearrangement to give ketenes. Accordingly, under the present conditions, the interaction of phenyl benzoyl carbene with SO_2 will be considered in competition with the Wolff rearrangement to the ketene. Compounds II and III most probably arises by cycloaddition of the ketosulfene to the ketene.



The formation of II and III should be noted, because, to date, attemps to isolate cycloadducts from sulfenes and ketenes have not yet been successful[2] as far as we know.

A photochemical reaction of I with SO_2 in benzene was also carried out under irradiation by a high-pressure mercury lamp for 28 hr at -5~-20°, giving III in a higher yield (35 %) than that obtained under the thermal decomposition, in addition to IV (44 %) and V(13 %). The preferential formation of III might be interpreted in terms of a porlarization of the type $=\overset{+}{C}-\overset{-}{O}$ of the ketene by photo-activation.

Further work is in progress with regard to scope and limitation of this reaction.

References

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2. W. E. Truce, J. J. Breiter, D. J. Abraham and J. R. Norell, J. Am. Chem. Soc., 84, 3030 (1962).