Tetrahedron Letters No. 18, pp 1545 - 1548, 1978. 0040-4039/78/0429-1545. $02.00/0.

THE REACTION OF BIS(p-METHOXYPHENYL)DIAZOMETHANE WITH SULFUR DIOXIDE — SOLVENT EFFECT AND NOVEL C-C BOND FISSION —

Toyoshige Tanabe and Toshikazu Nagai*
Institute of Chemistry, College of General Education,
Osaka University, Toyonaka, Osaka 560, Japan

(Received in Japan 20 February 1978; received in UK for publication 14 March 1978)

In a series of our investigations on the reaction of diazo compounds with sulfur dioxide in the presence of the nucleophilic reagents, such as enamine or alcohol, we have clarified that this reaction proceeds via a sulfene intermediate($R^1R^2C{=}SO_2$) and that the product distribution and the stereochemistry of the product depend much on the electronic character of the substituting group (R^1 and R^2).[1]

In connection with our work, we are interested in the behavior of the sulfene bearing an electron-releasing substituent, since such sulfene may be more stabilized than that of an electron-withdrawing substituent,[2] and is expected to reveal the different reactivity. We chose bis(p-methoxyphenyl)diazomethane (1) as one of the typical examples of sulfene precursor possessing such a character, and wish to report here on the reaction of 1 with sulfur dioxide to give a novel C-C bond fission product, depending on solvents.

The reaction was generally carried out by passing gaseous sulfur dioxide through the solution consisted of 5 mmol of 1 and 100 ml of the anhydrous solvent. There observed an immediate decolorization and an evolution of N_2. After the removal of the solvent, reaction mixtures were submitted to silica gel column chromatography, and the structures of the products were established by elemental analyses, ir, nmr, mass spectra, and by the comparison with those of the authentic specimens. The results are summarized in Scheme 1 and the table.

$$\underset{\textstyle 1}{(p\text{-}CH_3OC_6H_4)_2C{=}N_2} + SO_2 \longrightarrow$$

$$\underset{\textstyle 2}{(p\text{-}CH_3OC_6H_4)_2C{=}C(C_6H_4OCH_3\text{-}p)_2} + \underset{\textstyle 3}{(p\text{-}CH_3OC_6H_4)_2C{=}O} + \underset{\textstyle 4}{(p\text{-}CH_3OC_6H_4)_2S}$$

Scheme 1

TABLE

The Reaction of Bis(p-methoxyphenyl)diazomethane(1) with Sulfur Dioxide.

Solvent	Product (mol %)[a]		
	2	3	4
C_6H_6	61	3	6
CCl_4	64	18	12
THF	69	21	ND[b]
DMF	56	35	8
CH_3CN	11	67	ND
CH_3OH	ND	59	35
C_2H_5OH	ND	35	50

[a] Yields are in mol % based on 1 used for 3 and 4, and based on a half mole of 1 used for 2.

[b] Not detected.

As may be seen in the table, tetrakis(p-methoxyphenyl)ethylene(2) or 4,4'-dimethoxybenzophenone(3) was obtained as the major product in aprotic solvents.

2: colorless prisms(from benzene-ether); mp 187-188°C(lit, 184-185°C)[3]; nmr($CDCl_3$): δ 3.73(12H, s, OCH_3), and 6.67 and 6.98(each 8H, d, J=8.5Hz, phenyl).

3: colorless needles(from ethanol); mp 143-144°C(lit, 143-144°C)[4]; ir(KBr): 1640 cm^{-1}(C=O); nmr($CDCl_3$): δ 3.87(6H, s, OCH_3), and 6.97 and 7.81(each 4H, d, J=9Hz, phenyl).

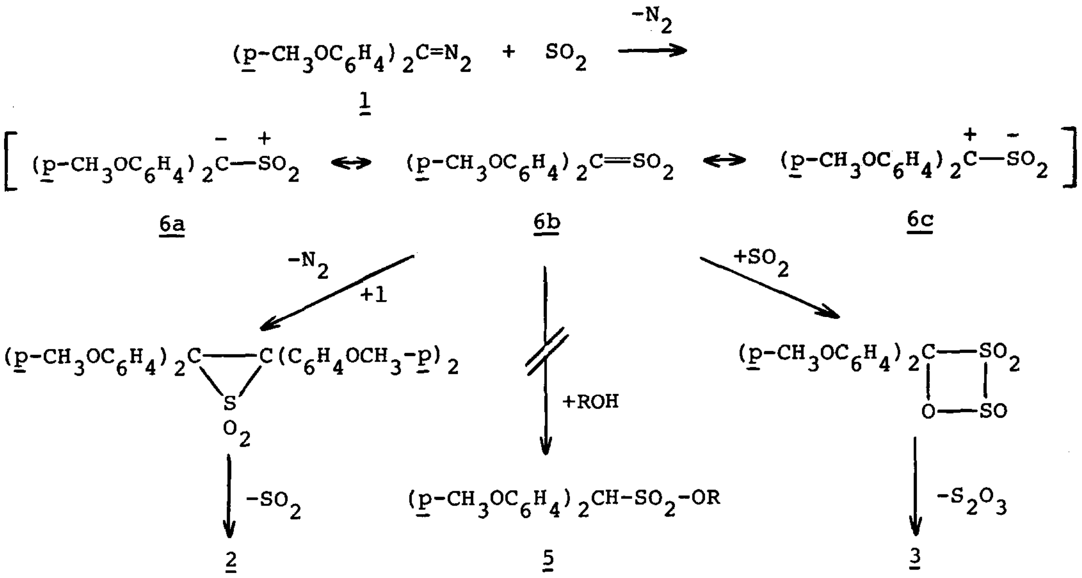
The yields of ketone increased obviously together with the increasing solvent polarity.

In contrast to these results, bis(p-methoxyphenyl)sulfide(4) was afforded in a relatively good yield in alcohol.

4: colorless needles(from methanol); mp 44-45°C(lit, 45-46°C)[5]; nmr($CDCl_3$): δ 3.74(6H, s, OCH_3), and 6.80 and 7.22(each 4H, d, J=9Hz, phenyl); mass: m/e=246(M^+).

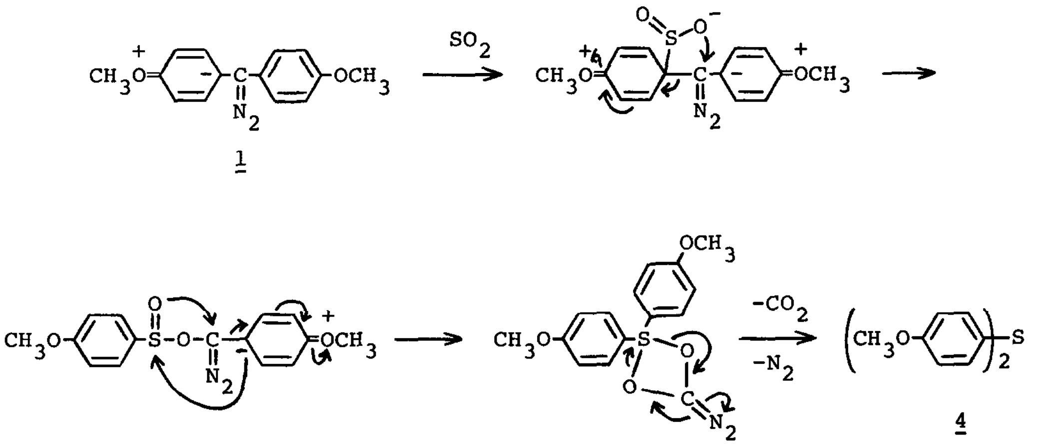
The formation of 4, the C-C bond fission product, from a diazoalkane appears to be the first observation. And it is also interesting that no corresponding sulfonate(5) was yielded at all in such nucleophilic medium.

The formation of 2 or 3 is interpreted by the reaction of sulfene(6) towards 1 or sulfur dioxide[6](Scheme 2).



Scheme 2

As for the formation of 3, the reverse ylide(6c) plays an important role, whose structure is stabilized in the polar solvents. Although a conclusive process could not be proposed here for the formation of 4, which is quite a novel reaction accompanied with the C-C bond cleavage and the loss of a carbon atom, it may be postulated that the initial stage of the reaction is the electrophilic attack of sulfur dioxide not on the α-carbon atom but on the phenyl-carbon atom in 1, as shown in Scheme 3.



Scheme 3

Further work is in progress with regard to the scope and limitation, and the details of the results will be provided in the latter papers.

REFERENCES

1. (a) T. Tanabe and T. Nagai, Bull. Chem. Soc. Jpn., **50**, 1179 (1977); (b) T. Tanabe and T. Nagai, ibid., **51**, (1978), in press.
2. (a) J. P. Snyder, J. Org. Chem., **38**, 3965 (1973); (b) K. N. Houk, R. W. Strozier, and J. A. Hall, Tetrahedron Lett., **1974**, 897.
3. H. W. Whitlock, Jr., J. Am. Chem. Soc., **84**, 2807 (1962).
4. R. Kitamura, J. Pharm. Soc. Jpn., **57**, 893 (1937).
5. H. Rheinboldt and E. Giesbrecht, J. Am. Chem. Soc., **68**, 973 (1946).
6. For a review, see (a) G. Opitz, Angew. Chem. Int. Ed. Engl., **6**, 107 (1967); (b) N. H. Fischer, Synthesis, **1970**, 393, and references cited therein.