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FORMATION OF STILBENES AND SPIRO-OXETANES IN THE REACTIONS OF PHENYLDIAZOMETHANES WITH CHLORANIL

Takumi Oshima and Toshikazu Nagai*

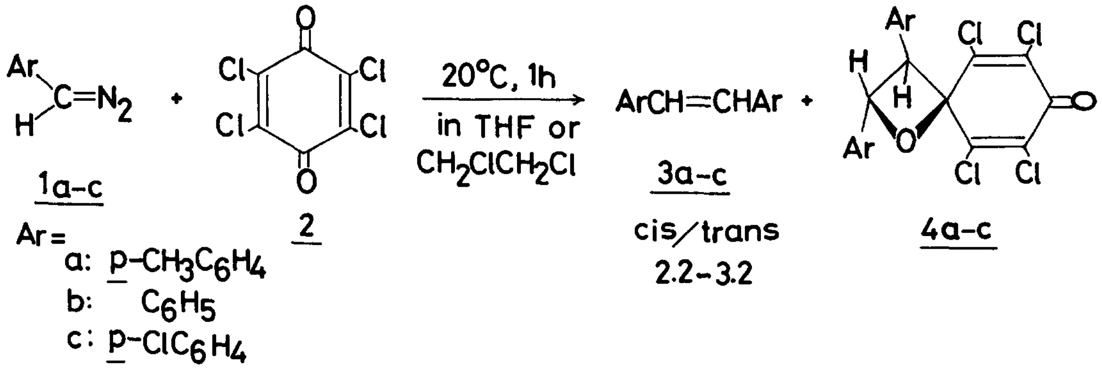
Institute of Chemistry, College of General Education,
Osaka University, Toyonaka, Osaka 560, Japan

Summary: The reactions of several phenyldiazomethanes with chloranil gave stilbenes and spiro-oxetanes at 20°C. Stilbenes were major products and the thermodynamically less stable cis-isomers prevailed about 2 to 3 times more than trans-ones depending on the solvents and the substituents of phenyldiazomethanes. On the other hand, stable trans-isomers were obtained exclusively in the case of the oxetanes. The stereochemistry and the mechanism of these reactions will be discussed.

B. Eistert and G. Bock[1] have obtained the 1:1 addition product, epoxide, in the reaction of diazomethane with chloranil.

We wish to report here that the reactions of several phenyldiazomethanes(1) with chloranil(2) give cis- and trans-stilbenes(3) and 2,3,5,6-tetrachlorospiro-[2,5-cyclohexadiene-trans-3',4'-diaryl-2'-oxacyclobutane]-4-one(4) as seen in Scheme 1.

Scheme 1



The substituent and solvent effects on these product distributions are summarized in Table 1.

Table 1. The substituent and solvent effects on the formations of stilbenes(3) and oxetanes(4).

$ArCH=N_2$ (1)	Solv.	Stilbenes(%) (*cis*/*trans*)* (3)	Oxetanes(%) (4)
1a	THF	69.0 (2.4)	15.6
1b	"	75.5 (2.8)	8.1
1c	"	72.3 (3.2)	6.2
1a	CH_2ClCH_2Cl	60.0 (2.2)	31.7
1b	"	59.7 (2.5)	26.4
1c	"	59.5 (2.9)	20.6

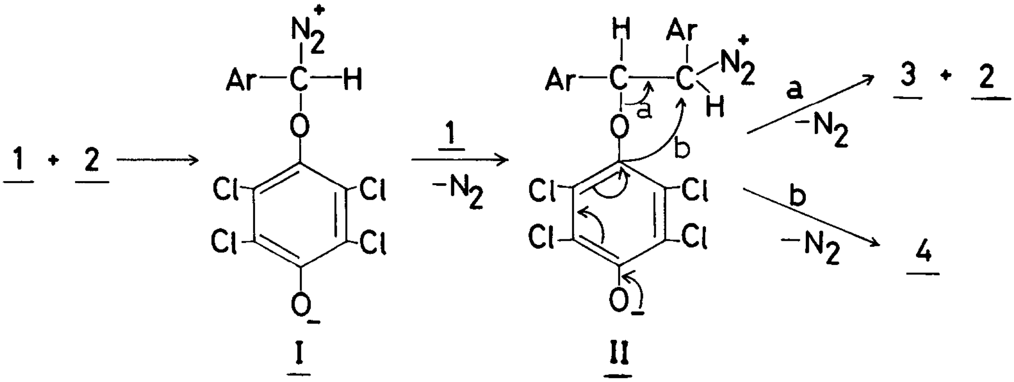
*) *Cis*- and *trans*-3 were separated by column chromatographic treatment on silica gel.

In both THF and dichloroethane, 3 were major products. The yield of spiro-oxetanes(4) considerably increased in dichloroethane than in THF. Here, particular attention should be paid for the fact that the thermodynamically less stable *cis*-3 prevailed about 2 to 3 times more than *trans*-3 depending on the solvents and the substituents.[2] On the contrary, in the case of 4 more stable *trans*-isomers were obtained exclusively. The structure of 4 was confirmed by the comparison with authentic sample given in the photoaddition of *trans*-3 and 2 and by the thermal decomposition of 4 giving *trans*-3 and 2.[3]

The formations of 3 and 4 can be formulated in Scheme 2. The diazonium betains(I) are first given in the reactions of 1 with 2 and the resulting I undergoes nucleophilic attack by another 1 to turn out to the next betains(II). If the type (a) electron migration occurs, II gives 3 and the regenerated 2. On the other hand, the type (b) electron migration leads to the formation of 4.

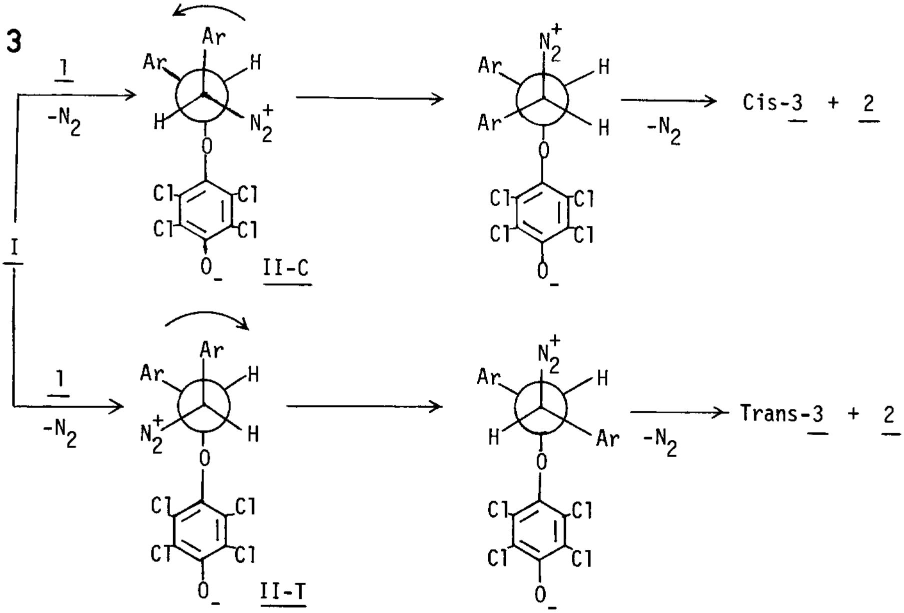
Why does the major type (a) process preferentially yield *cis*-isomers than *trans*-ones? This is well interpreted by considering the transition state

Scheme 2



leading to II. Nucleophilic attack of 1 to I should occur favorably in the manner where the steric repulsion is as small as possible and the resulting opposite charges stabilize mutually. According to these restrictions, the upper configuration(II-C) is more produced than the lower one(II-T) as shown in Newman projections(Scheme 3). If trans elimination of nitrogen and 2 is favored, II-C gives cis-3 and II-T gives trans-3.

Scheme 3



Though type (b) process is minor one in the both solvents, significant increase of 4 in dichloroethane may be attributable to the less-solvating ability of this medium where the opposite charges of II should come closely to promote the type (b) process. The problem of selective formation of *trans*-4 can be resolved by the assumption that the nitrogen elimination is prior to the bond making process in contrast to the stilbene formation. In this intramolecular S_N1 type reaction, the resulting carbonium betains are stable enough to allow the rotation along C-C bond before the ring closure, so that the two aryl rings locate in the stable *trans* position.

As to the mechanism giving I, formation of radical ion pair was supported by the detection of anion radical of 2.[4] However, the participation of 1,3,4-oxadiazoline intermediate or direct combination between the diazo-carbon and the oxygen atom of 2 can not be ruled out completely. These problems are now under investigation.

REFERENCES AND NOTE

1. B. Eistert and G. Bock, Chem. Ber., 92, 1247(1959).
2. W. S. Trahanovsky *et al*. have reported the high *cis* to *trans* ratio of stilbenes in the decomposition of phenyldiazomethanes with catalytic amounts of ceric ammonium nitrate. But unequivocal explanation for the formation of high yield of *cis*-isomer is lacking, W. S. Trahanovsky, M. D. Robbins, and D. Smick, J. Amer. Chem. Soc., 93, 2086 (1971).
3. The irradiation of a nitrogen saturated solution of *trans*-stilbene(1.0 g) and chloranil(1.0 g) in benzene(100 ml) in a Pyrex tube at 15°C for 3 hr (high pressure mercury lamp) gave only *trans*-4b in 77.8% yield, and the respective thermal decompositions of 4a(160°C), 4b(160), and 4c(180) for 1 min gave only *trans*-3 and the regenerated 2.
4. T. Oshima, A. Yoshioka, and T. Nagai, Tetrahedron Letters, 1789(1977).

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