Tetrahedron Letters Vol. 21, pp 1251 - 1254
0040-4039/80/0322-1251$02.00/0
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STEREOCHEMISTRY OF THE COPPER PERCHLORATE OR COPPER BROMIDE-CATALYZED DECOMPOSITION OF ARYLDIAZOMETHANES TO STILBENES

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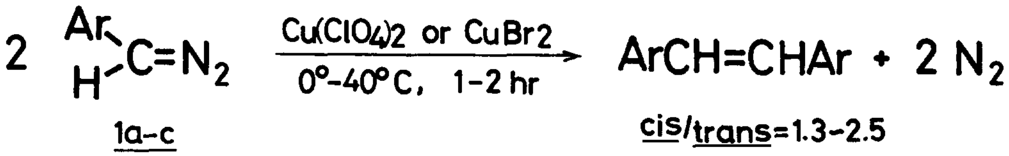
Summary: Several phenyldiazomethanes easily decompose to cis- and trans-stilbenes when treated with catalytic amounts of copper perchlorate or copper bromide at 20°C. The preferential formation of cis isomer is particularly noteworthy. The stereochemistry and the mechanism of these reactions will be discussed.

There is continuing interest in the decomposition of diazoalkanes induced by copper-containing catalysts, particularly with regard to the formation of copper carbenoids and the oxidation state of copper in such species.[1]

We wish to report that the thermodynamically less stable cis-stilbenes are produced in yields that are about 1.3 to 2.5 times greater than the yields of trans isomers in the copper perchlorate or copper bromide-catalyzed decomposition of some phenyldiazomethanes(1a-c) as formulated in Scheme 1.

Scheme 1



$$2\ \underset{\mathbf{1a\text{-}c}}{\mathrm{Ar(H)C{=}N_2}} \xrightarrow[0^\circ\text{-}40^\circ\mathrm{C},\ 1\text{-}2\ \mathrm{hr}]{\mathrm{Cu(ClO_4)_2\ or\ CuBr_2}} \underset{\textit{cis}/\textit{trans}=1.3\text{-}2.5}{\mathrm{ArCH{=}CHAr}} + 2\ N_2$$

Ar=p-$CH_3C_6H_4$(1a), C_6H_5(1b), p-ClC_6H_4(1c)

It was found that the cis to trans ratio of stilbenes was somewhat greater in the decomposition by copper perchlorate than in that by copper bromide. Moreover, this ratio increased with the electron withdrawing ability of the substituents on 1a-c and also increased as the reaction temperature was lowered (Table 1).

Table 1. Yields of Stilbenes from the Reactions of Phenyldiazomethanes(1a-c) with Copper Perchlorate or Copper Bromide in Acetonitrile[a)]

Ar	$ArCH=N_2$ (mmol)	Catalyst[b)] (mmol)	Temp. (°C)	Reaction time (hr)	ArCH=CHAr Yield(%)(cis/trans)[c)]
		$Cu(ClO_4)_2$			
p-$CH_3C_6H_4$(1a)	2.10	0.01	20	1	80.2±2.5(1.59±0.03)
C_6H_5(1b)	2.00	0.01	40	1	73.5±1.0(1.74±0.01)
C_6H_5(1b)	2.00	0.01	20	1	86.2±2.5(1.81±0.01)
C_6H_5(1b)	2.00	0.01	0	2	81.9±0.9(1.93±0.02)
p-ClC_6H_4(1c)	2.60	0.01	20	1	92.5±3.5(2.47±0.02)
		$CuBr_2$			
p-$CH_3C_6H_4$(1a)	2.10	0.01	20	1	79.5±1.3(1.36±0.02)
C_6H_5(1b)	2.00	0.01	20	1	77.2±0.2(1.52±0.02)
p-ClC_6H_4(1c)	2.60	0.01	20	1	85.5±1.6(2.23±0.06)

a: In 10 ml of solvent. b: Acetonitrile solution(0.2-0.3 ml) was added.

c: Determined by high pressure liquid chromatography using naphthalene as an internal standard.

The high yield of the cis isomer has already reported by W. S. Trahanovsky and his colleagues in the cerium(IV)-catalyzed decomposition of phenyldiazomethanes to stilbenes.[2] They proposed an oxidative chain reaction for this decomposition in analogy with an electrochemical oxidation of diphenyldiazomethane[3] but an unequivocal explanation for the formation of high yield of the cis isomer is still lacking. The oxidative chain mechanism was also introduced by D. Bethell and his co-workers for the copper perchlorate-catalyzed decomposition of diphenyldiazomethane to tetraphenylethylene.[4] In these chain reactions, the corresponding dimeric alkenes are thought to arise from the reaction of the diazoalkane radical cation with further diazoalkane as outlined in Scheme 2. In view of the thermodynamic stability, however, this process seems to predominantly lead to the stable trans isomer because of the free rotation of the intermediate(I) around the central C-C bond.

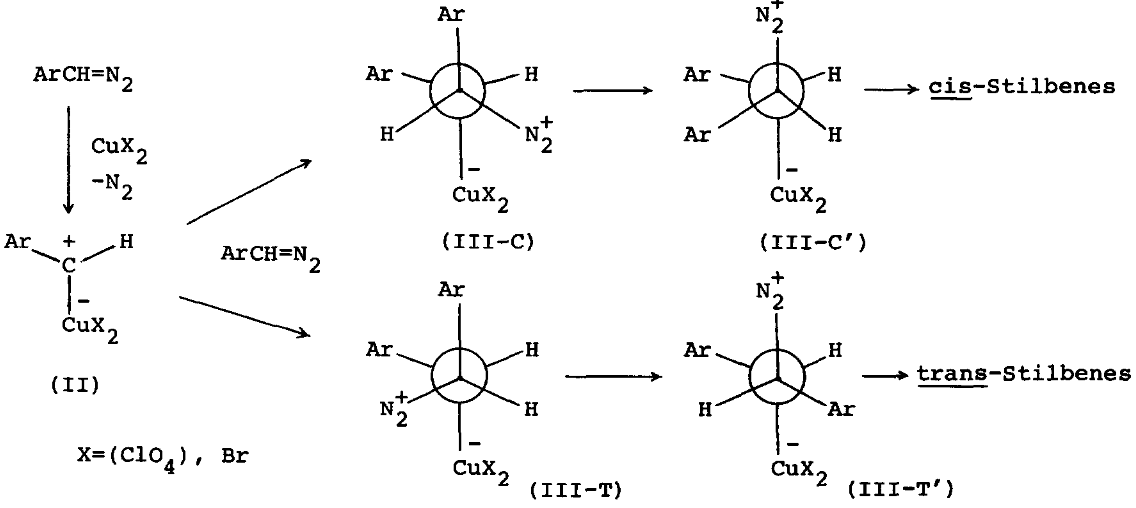
Scheme 2

$$R_1R_2\dot{C}{-}N_2^+ \quad + \quad R_1R_2C{=}N_2 \longrightarrow \underset{\text{(I)}}{R_1R_2\overset{\cdot\,+}{C}{-}CR_1R_2} \quad + \quad 2\ N_2$$

$$\text{I} \quad + \quad R_1R_2C{=}N_2 \longrightarrow R_1R_2\dot{C}{-}N_2^+ \quad + \quad R_1R_2C{=}CR_1R_2$$

Mechanistically, copper carbenoid intermediate can be put forward for the present decomposition in contrast to the above radical ion formation. Therefore, the intriguing stereochemical results can be reasonably explained by considering the subsequent reaction of phenyldiazomethanes with the resulting carbenoid on the basis of the steric and the electronic effects. A similar explanation was successfully made to describe the preferential formation of cis stilbenes from the reaction of 1a-c with chloranil.[5]

Scheme 3



Namely, the nucleophilic attack of 1a-c to the carbenoid(II) should occur favorably through the transition state where the steric repulsion is as small as possible and the resulting opposite charges stabilize mutually, giving such stable conformers as III-C and III-T(Scheme 3). It should be noted here that the III-C is more stable than III-T because the former can release some of the steric repulsion by placing the small H atom on the most crowded position between the aryl group and the copper catalyst moiety. If the trans elimination of N_2 and $Cu(ClO_4)_2$ or $CuBr_2$ is more favored than the cis elimimation, major conformer III-C is transformed into the conformational isomer III-C′ which will give cis stilbenes. On the other hand, minor III-T will lead to trans stilbenes.

The phenomena that the cis to trans ratio increased in the order 1a < 1b < 1c and also increased at a lower temperature seem to be the result of the increasing selectivity in the process giving III-C or III-T due to the decreasing reactivity of phenyldiazomethanes.

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(Received in Japan 14 December 1979)