# Remarkably Stereoselective Formation of *cis*-Stilbenes from the Lithium Bromide-catalysed Decomposition of Aryldiazomethanes

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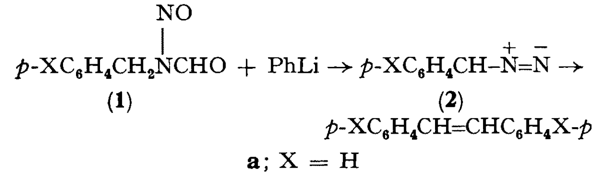
*Summary* Lithium bromide catalyses the decomposition of aryldiazomethanes (**2**) in ether at room temperature to *cis*-stilbenes as the major products, possibly *via* 'sandwich'-type compounds.

DURING our investigation of the reaction of *N*-nitrosamides with organometallic reagents, we observed the formation of *cis*- and *trans*-stilbenes from the action of phenyl-lithium on *N*-benzyl-*N*-nitrosoformamide (**1a**).[1] The structure of these olefins clearly suggested the benzyl group of (**1a**) as the source of these products. In related studies, we had demonstrated the formation of phenyldiazomethane (**2a**)[2] in the reaction of (**1a**) with hydrides, and had also observed the characteristic red colour of (**2a**) during the reaction of (**1a**) with phenyl-lithium. In view of the recent interest in the dimerization of aryldiazomethanes to the corresponding olefins,[3,4] our observations were notable because the olefins were formed in relatively large amounts and *cis*-stilbene was the predominant isomer.

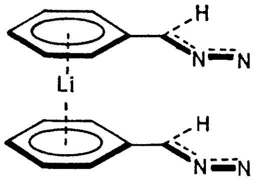


$$\underset{(\mathbf{1})}{p\text{-}XC_6H_4CH_2\overset{NO}{\overset{|}{N}}CHO} + PhLi \rightarrow \underset{(\mathbf{2})}{p\text{-}XC_6H_4CH\text{-}\overset{+}{N}{=}\overset{-}{N}} \rightarrow p\text{-}XC_6H_4CH{=}CHC_6H_4X\text{-}p$$

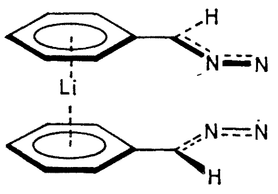
**a**; X = H
**b**; X = OMe
**c**; X = Cl

It seemed to us that neither the carbene nor a corresponding carbenoid could possibly account for the stereochemistry.[5] Thus, the only other possibility was that the lithium bromide generated from the preparation of phenyl-lithium was in some way acting as a remarkably efficient catalyst for the decomposition of phenyldiazomethane to the olefins. Surprisingly, not only did the reaction of phenyldiazomethane (**2a**)[6] with 1 equiv. of lithium bromide in ether at room temperature (4 days) proceed in high yields, but the product also consisted essentially of pure *cis*-stilbene.† Such remarkable stereoselectivity is unprecedented as far as we know.[4]

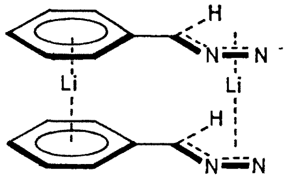
The formation of *cis*-stilbene as the major product suggested that the intermediate leading to *cis*-stilbene has to be highly ordered, probably through complexation with the lithium ion. While one can envisage ordering by



(A)



(B)



(C)

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† Only trace amounts of *trans*-stilbene and benzylideneazine could be detected by n.m.r. spectroscopy.

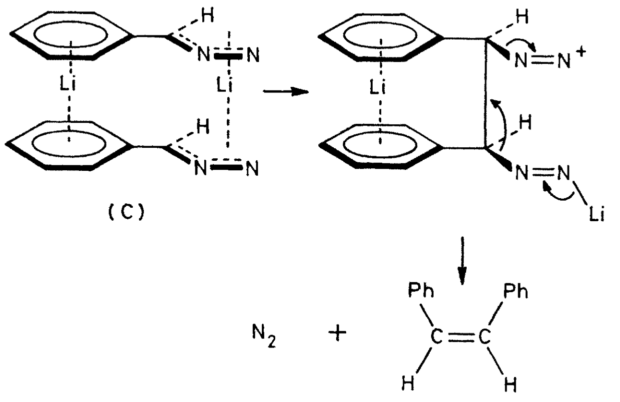
TABLE. Reaction of aryldiazomethanes with salts.[a]

| Run | $ArCHN_2$ | Salt | Ratio (to salt **2**) | Time/ days | Product yield/% $ArCH=CHAr$[b] *cis* | *trans* | PhCHO | ArCH=NN=CHAr | $ArCHN_2$ (recovered) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | (**2a**) | LiBr | 1·0 | 6 | 68(90) | + | — | — | 24 |
| 2 | (**2a**) | LiBr | 0·5 | 7 | 37(76) | + | — | — | 52 |
| 3 | (**2a**) | LiBr[d] | 1·0 | 4 | 72[e] | 36[e] | — | 7[e] | — |
| 4 | (**2a**) | LiBr[f] | 1·0 | 6 | 27(58) | + | 6[e] | 17[e] | 53[e] |
| 5 | (**2a**) | NaBr | 1·0 | 6 | — | — | 41[e] | — | 51[e] |
| 6 | (**2a**) | KBr | 1·0 | 6 | — | — | 45[e] | — | 50[e] |
| 7 | (**2b**) | LiBr | 4·0[g] | 4 | 64 | 4 | — | — | — |
| 8 | (**2c**) | LiBr | 1·0 | 11 | 61 | 15 | — | 20 | — |

[a] Unless otherwise noted, all the reactions were performed at room temperature in flasks protected with a drying tube and covered with aluminium foil A plus sign signifies that the compound was detected by t.l.c. while a minus sign means that it could not be detected by t.l c. The times given are approximate (±2—3 h). [b] Unless otherwise noted, the yields of stilbenes are those of isolated products and those in parentheses are corrected for recovered starting materials. [c] Recovered and determined as the acetates. [d] At ether reflux. [e] By n.m.r. integration. [f] Carried out in the presence of 1 equiv. of 18-crown-6 ether. [g] *p*-Methoxyphenyldiazomethane is quite unstable and a reaction run with a slight excess (1·3) of lithium bromide resulted in nearly quantitative formation of the azine, the stilbenes being detected only by t.l.c.

'sandwiching' of the lithium ion between the $\pi$-system of the aryl groups of (**2a**) (A), there is no obvious reason why the arrangement depicted in (A), necessary to lead to the *cis*-isomer, should be preferred over the alignment shown in (B). Therefore, one must postulate a second complexation at the other end of the sandwich, namely between the $\pi$-electron system of the diazoalkane unit (C),‡ in order to account for the formation of the less stable *cis*-stilbene. Thus, substituents on the phenyl rings would be expected to influence the reaction, with electron-donating groups favouring and electron-withdrawing substituents hindering the putative complexation process.

The results shown in the Table suggest that the effect of the concentration of lithium bromide does not contradict the proposed complexation at *two* sites. Similarly, the expected effect of substituents was substantiated by the fact that the reaction of *p*-methoxyphenyldiazomethane (**2b**) proceeded more readily,[7] while the decomposition of *p*-chlorophenyldiazomethane (**2c**) was slower. The specificity of the effect of a lithium ion was demonstrated by the failure of sodium and potassium bromide to induce formation of olefins. A reaction carried out in the presence of 18-crown-6 ether confirmed the critical role played by the lithium ion (Table, run 4). As might be expected, an increase in temperature should not favour a delicate and highly ordered complex such as (C). Indeed the ratio of *cis*-to *trans*-stilbene decreased in a reaction carried out at reflux in ether (Table, run 3). The apparent necessity for *double* complexation was emphasized by the failure of t-butyldiazomethane[8] to give any olefin when similarly treated with lithium bromide in ether.§



SCHEME

Thus, on the basis of the present data, we suggest the mechanism shown in the Scheme as a rationalization for the formation of *cis*-stilbenes.

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‡ Although not depicted it is probable that ether molecules assist in the stabilization of the complex.

§ A complex mixture of products, none of which was the expected *dimeric* olefin 2,2,5,5-tetramethylhex-3-ene, b.p. 125—150 °C (*cis*- and *trans*-isomers), was formed.

[1] M. Nakajima and J.-P. Anselme, unpublished results.

[2] M. Nakajima and J.-P. Anselme, *J. Org. Chem.*, 1980, **45**, in the press.

[3] D. S. Wulfman, G. Linstrumelle, and C. F. Cooper 'The Chemistry of Diazonium and Diazo Groups,' in 'The Chemistry of Functional Groups,' ed. S. Patai, Wiley Interscience, New York, 1978, p. 912.

[4] T. Shirafugi, Y. Yamamoto, and H. Nozaki, *Tetrahedron*, 1971, **27**, 5353; H. Nozaki, R. Nogori, and K. Sisida, *ibid.*, 1964, **20**, 1125; W. S. Trahanovsky, M. D. Robbins, and D. Smick, *J. Am. Chem. Soc.*, 1971, **93**, 2086; T. Oshima and T. Nagai, *Tetrahedron Lett.*, 1979, 2789; C. D. Gutsche, G. L. Bachman, and R. S. Coffey, *Tetrahedron*, 1962, **18**, 617.

[5] We considered carbenoid mechanisms similar to that suggested very recently (T. Oshima and T. Nagai, *Tetrahedron Lett.*, 1980, 1251) and found them unconvincing as a possible rationalization of our results.

[6] J.-P. Anselme, *Org. Prep. Proc.*, 1969, **1**, 73.

[7] Closs *et al.* (S. H. Goh, L. E. Closs, and G. L. Closs, *J. Org. Chem.*, 1969, **34**, 25) had already noted that *p*-tolyldiazomethane reacted more readily (with lithium bromide and zinc halides) than phenyldiazomethane; however neither the yield nor the ratio of isomers of the stilbenes were reported.

[8] G. M. Kaufman, J. A. Smith, G. G. Vander Stouw, and H. Shechter, *J. Am. Chem. Soc.*, 1965, **87**, 935.