Tetrahedron Letters No.34, pp. 3743-3747, 1968. Pergamon Press. Printed in Great Britain.

NONSTEREOSPECIFIC CYCLOADDITION OF BENZYNE WITH CIS- AND TRANS- PROPENYL METHYL ETHER

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(Received in Japan 1 April 1968; received in UK for publication 27 May 1968)

We wish to report hitherto unknown nonstereospecific 1,2-1,2-cycloaddition of "benzyne" with cis- and trans-propenyl methyl ether.

"Benzyne" has been investigated by many organic chemists since it was recognized as a likely unstable intermediate (1) and the investigations have mostly been concentrated to preparative purposes. Thus Diels-Alder reactions with appropriate dienes (2), addition to ammonia (3) or other amines (4), addition to alcohols (5) and thiols (6) were often reported and symmetricity of the intermediate was sometimes proved (7).

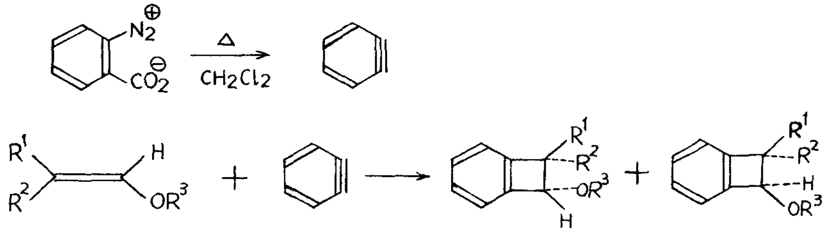
However, much fewer works have been done on "benzyne" from the physical-organic aspects (8) and though benzyne is formally an eight electron system, there was not obtained any experimental evidence to elucidate its electronic structure.

In contrast, carbenes or carbenoids have attracted much attention from theoretical as well as from experimental viewpoints (9) where stereospecificity of the addition took a very important role especially in the beginning of the theoretical approach (10).

We are much interested in the reported 1,2-1,2-cycloaddition of "benzyne" to vinyl ether or vinyl acetate (11) because the reaction should afford stereochemical information if 1,2-disubstituted ethylene is employed, which may allow to elucidate its electronic structure.

Thus a solution of 6.0 g (0.083 mole) of propenyl methyl ether (isomer composition is shown in the Table) and ca. 3.0 g (12) (ca. 0.02 mole) of benzenediazonium-2-carboxylate (according to Stiles' procedure (5)) in 100ml of methylene

Scheme I



I	II	III
a. $R^1=R^3=CH_3$, $R^2=H$	a.	a. (=IIb)
b. $R^2=R^3=CH_3$, $R^1=H$	b.	b. (=IIa)

chloride were kept at 40° with stirring under nitrogen for 3 hours. During the period, ca. 750 ml (0.031 mole) of gas was evolved. Usual work up gave a distillate (48-50° at 5-6 mmHg, (27% based on the starting diazoniumcarboxylate and 35% based on the gas evolution.)) which was a sharp single peak in VPC by using common columns. But it consisted of two isomers A and B, (both are novel compounds) the presence of which was evident by investigating its nmr spectrum : A; 1.27δ doublet (6.5 cps), CH_3 proton on cyclobutane ring (H_A); 3.43δ singlet, proton on OCH_3 (H_B); 4.78δ doublet (5.4 cps) with structure, cyclobutane proton α- to OCH_3 (H_C); multiplet ranging from 3.2-3.9δ, cyclobutane proton α- to CH_3; multiplet ranging from 6.9δ to 7.3δ, phenyl protons. B; 1.37δ doublet (6.9 cps) (H_A), 3.38δ singlet (H_B), 4.35δ doublet (1.2 cps) with structure (H_C) (13), multiplet at 3.2-3.9δ and multiplet at 6.9-7.3δ. All of the peaks were in expected intensities. Elemental analysis and mass-spectroscopy (148, parent; 133, parent minus CH_3; 117, parent minus CH_3O) of these were also satisfactory.

Isomer composition (A, cis-3-methoxy-4-methyl-1,2-benzocyclobutane and B, the corresponding trans isomer) determined by three pairs of nmr characteristic absorption intensities are selfconsistent as shown in the Table. From the results, nonstereospecificity to a considerable extent of the addition is evident (14).

The product composition was consistent with the expected value, which was calculated on the basis that a complete nonstereospecific addition would give 78.4% cis- and 21.6% trans-adducts (16) and that nonstereospecificity of the reaction in our condition was 65% from the experimental isomer composition on the pure cis starting olefin (see Table II) by assuming that reactivities of cis and trans olefins are approximately equal. (65%=14.0/21.6 × 100)

Therefore, our results affords the first experimental evidence for the prediction that benzyne should involve aromatic diradical species (8c). Relatively poor inversion to the trans adduct from the cis olefin may be interpreted from the assumption of higher stability of the cis-adduct (or a cis-conformed biradical) than the trans (18). Our results of ready insertion of

Table I

Set No	Starting propenyl methyl ether (15)		Product composition		Estimation basen on:
	cis	trans	cis(IIb)	trans(IIa)	
1	100%	0%	86	14	H_B
2	91%	9%	78.4	21.6	H_B
			76.2	23.8	H_C
			79.5	20.5	H_A
3	68%	32%	72.3	27.7	H_B
			70.8	29.2	H_C
			71.6	28.4	H_A
4	27.2%	72.8%	60.5	39.5	H_B

Table II

starting olefin		expected isomer composition			obs. (average)	
cis	trans	cis	trans	(17)	cis	trans
100	0	86.0	14.0		86.0	14.0
91	9	83.0	17.0		78.0	22.0
68	32	74.8	25.2		71.6	28.4
27	73	60.6	39.4		60.5	39.5
57.5	42.5	—	—	(in CH_3I)	78.4	21.6

benzyne (generated from benzenediazoniumcarboxylate) into various N-H bonds (19) (ca. 15%) were also in accordance with the assumption of some singlet contribution from the analogy to carbene chemistry. Remarkable heavy atom solvent effect observed by the authors also serves another evidence for some singlet contribution in a light solvent and it excludes the alternative that nonstereospecificity might arise from dipolar intermediate.

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8b. Similar conclusion from massspectroscopy; I.P.Fisher and F. P. Lossing, ibid., 85, 1018 (1963). Consideration of energetics suggests that benzyne has an aromatic diradical character rather than dipolar character.

8c. H.E.Simmons, J. Am. Chem. Soc., 83, 1657 (1961).

9. See "Carbene chemistry" by W.Kirmse, and H.M.Frey, Academic Press, 1964.

10. Usually, stereospecific and nonstereospecific addition are considered to correspond to singlet and triplet carbene, respectively. But there is criticism to too simple understanding of the multiplicity of carbene species; See e.g., S.Murahashi, I.Moritani and M.Nishino, *J. Am. Chem. Soc.*, **89**, 1257 (1967).
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12. The dry diazonium carboxylate was very dangerous (explosive) so that the amount was not weighed accurately.
13. Vicinal coupling constant of cyclobutane protons are in expected order of magnitude, i.e., 5.4 cps for cis and 1.2 cps for trans. E.g., M.Karplus, *J. Chem. Phys.*, **30**, 11 (1959) showed the angle dependency of coupling constant of vicinal protons.
14. In the reaction condition, the product composition was observed practically unchanged. Starting olefin was isomerized in the condition but only to minor extent. E.g., recovered olefin from experiment no. 1 (from pure cis-olefin) contained only negligible amount of trans olefin.
15. The isomer composition was determined by vpc (PEG column) and nmr (cis; 8.50τ doublet of doublets (J=6.6 and 2.1 cps), 3 protons; 6.48τ singlet, 3 protons; multiplet centered at 5.76τ, one proton; and 4.25τ doublet with fine structures (J=6.0 cps), one proton; trans; 8.48τ, doublet of doublets (J=6.6 and 1.5 cps), 3 protons; 6.58τ, singlet, 3 protons; multiplet centered at 5.40τ, one proton; doublet with fine structure (J=13.8 cps), one proton), both of which were quite consistent.
16. The composition was what was observed by the authors in a solvent of heavy atom such as methyl iodide. Triplet content would not be 100% but very high in the condition.
17. Small deviations may arise from the assumption that cis and trans olefins have equal reactivities.
18. Dimerization of 1,2-dichloro-1,2-difluoroethylene gave the corresponding cis-adduct predominantly although a biradical intermediate was involved; See J.D.Roberts et al., *J. Am. Chem. Soc.*, **72**, 3300 (1950).
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