The Stereochemistry of the 2 + 2 and 2 + 4 Cycloadditions of Benzyne[1,2]

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Abstract: Orbital symmetry considerations predict that the symmetric benzyne **1** will undergo a nonconcerted 2 + 2 cycloaddition while the 2 + 4 reaction should be stereospecific. The opposite results are predicted for the antisymmetric singlet **2**. Benzyne adds to the 1,2-dichloroethylenes in a nonstereospecific fashion to give dichlorobenzocyclobutenes with moderate, but not complete loss of the original stereochemistry. *cis*-Olefin gives 35% of the *trans*-benzocyclobutene and *trans*-olefin gives 20% of the *cis*-benzocyclobutene. By contrast, the Diels–Alder reaction of benzyne with either *trans,trans*-2,4-hexadiene or the dimethyl ester of *trans,trans*-muconic acid is stereospecific. These data imply that the structure of benzyne is the symmetric singlet state **1**.

The structure of benzyne has been the subject of considerable speculation, but with few exceptions[2b,5] it is generally agreed[6] that the ground state is a singlet. It has recently been pointed out by Hoffmann that two singlets are possible and calculated[7] that the singlet lower in energy is the one symmetric with respect to a C_2 axis interconverting the two sp^2-like orbitals containing the "free" electrons. Woodward and Hoffmann's earlier formulations on the control of pericyclic reactions exercised by orbital symmetry[8] allow a prediction of the stereochemical results of cycloadditions of both the symmetric singlet (**1**) and the antisymmetric singlet (**2**). Thus an experimental determination becomes possible. It might be mentioned here that Hoffmann's calculations of the structure of 1,8-dehydronaphthalene as the antisymmetric singlet agree with the experimental determinations of Rees and Storr and Hoffmann, *et al.*[9a–c] For the calculated symmetric state of benzyne, orbital symmetry considerations lead to the prediction of a nonconcerted thermal $2_\pi S + 2_B S$ (B = benzyne) cycloaddition to give benzocyclobutenes with scrambled stereochemical label, and a concerted $4_\pi S + 2_B S$ reaction with dienes to give 1,4-dihydronaphthalenes with retained configuration. The "rules" here predict the same results as for cycloadditions of ethylene.[10] The antisymmetric state on the other hand should undergo a concerted $2_\pi S + 2_B S$ cycloaddition but a nonconcerted $4_\pi S + 2_B S$ reaction.

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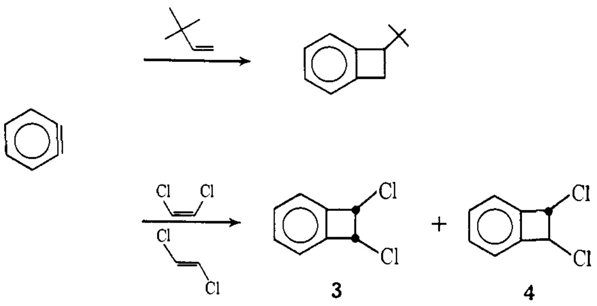
The 2 + 2 cycloaddition reaction of benzyne has been known for some time.[11] Strangely, although the related addition of carbenes to olefins has been intensely studied from a stereochemical point of view, the stereochemistry of the cycloaddition of benzyne to olefins has not been determined.[2a–d] Probably this was because most simple olefins lead to extensive "ene" reaction and do not yield benzocyclobutenes cleanly.[12] We find that olefins lacking allylic hydrogen give benzocyclobutenes without complication. Thus 3,3-dimethylbutene-1 gives moderate yields of 1-*t*-butylbenzocyclobutene and the dichloroethylenes give 1,2-dichlorobenzocyclobutenes. This latter observation allows a determination of the sterochemistry of the reaction. The products of the addition to the dichloroethylenes, *cis*-1,2-dichlorobenzocyclobutene (**3**) and *trans*-1,2-dichlorobenzocyclobutene (**4**), are known[13] and the stereochemistry of the *cis* compound has been determined by X-ray analysis. The similarity of the spectra of **3** and **4** leaves no doubt as to the structure of **4**. In particular, 1,1-dichlorobenzocyclobutene (**5**) is eliminated by virtue of the symmetry of the nmr signals of the aromatic protons and the chemical shift of the cyclobutyl protons. The aromatic hydrogens appear as a symmetrical multiplet (**3** τ 2.68; **4** τ 2.69) while the cyclobutyl hydrogens are un-



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[1] We greatly appreciate support of this work through National Science Foundation Grant GP-7819.

[2] Presented in part at the Symposium on Orbital Symmetry Correlations in Organic Chemistry, Cambridge, England, January 1969. Preliminary accounts of this work have appeared, as has related material. (a) M. Jones, Jr., and R. H. Levin, *Tetrahedron Lett.*, 5593 (1968); (b) I. Tabushi, R. Oda, and K. Okazaki, *ibid.*, 3743 (1968); (c) H. Wasserman, A. J. Solodar, and L. S. Keller, *ibid.*, 5597 (1968); (d) L. Friedman, R. J. Osiewicz, and P. W. Rabideau, *ibid.*, 5735 (1968); (e) R. W. Atkin and C. W. Rees, *Chem. Commun.*, 152 (1969).

[3] Alfred P. Sloan Research Fellow, 1967–1969.

[4] N. D. E. A. Fellow, 1967–1970.

[5] C. D. Campbell and C. W. Rees, *Chem. Commun.*, 192 (1965).

[6] H. E. Simmons and R. W. Hoffmann in "Dehydrobenzene and Cycloalkynes," R. W. Hoffmann, Ed., Academic Press, New York, N. Y., 1967.

[7] R. Hoffmann, A. Imamura, and W. J. Hehre, *J. Amer. Chem. Soc.*, **90**, 1499 (1968).

[8] For reviews see R. B. Woodward and R. Hoffmann, *Accounts*, **1**, 17 (1968), J. J. Vollmer and K. L. Servis, *J. Chem. Educ.*, **45**, 214 (1968), and G. B. Gill, *Quart. Rev.* (London), **22**, 338 (1968).

[9] (a) C. W. Rees and R. C. Storr, *Chem. Commun.*, 193 (1965); (b) C. W. Rees and R. C. Storr, *J. Chem. Soc.*, 765 (1969); (c) R. W. Hoffmann, G. Guhn, M. Preiss, and B. Dittrich, *ibid.*, 769 (1969).

[10] For investigations of such reactions see P. D. Bartlett and G. E. H. Wallbillich, *J. Amer. Chem. Soc.*, **91**, 409 (1969), and P. D. Bartlett and K. E. Schueller, *ibid.*, **90**, 6071 (1968), and references therein.

[11] Reference 6, p 200 ff.

[12] Reference 6, p 197 ff.

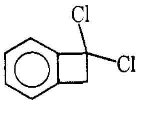
[13] G. L. Hardgrove, L. K. Templeton, and D. H. Templeton, *J. Phys. Chem.*, **72**, 668 (1968).

Table I

Olefin	% **3**	% **4**	% yield	Solvent	~Temp, °C	Hr	Source
trans (15 equiv)[a]	19	81	40	150 ml of DCE[b]	65	2	HCl[c]
trans (15 equiv)	17	83		150 ml of DCE	40	35	HCl
trans (5 equiv)	20	80		600 ml of DCE	80	2	HCl
trans (15 equiv)	20	80	32	600 ml of DCE	80	2	HCl
trans (15 equiv)	16	84		75 ml of CH_2Cl_2	40	24	Carboxylate[d]
trans (15 equiv)	20	80		75 ml of DCE	55	2	Carboxylate
trans (15 equiv)	19	81		300 ml of EtI	55	2	HCl
cis (15 equiv)[a]	68	32	5	150 ml of DCE	65	2	HCl
cis (15 equiv)	60	40		300 ml of DCE	80	2	HCl
cis (15 equiv)	70	30		300 ml of EtI	65	3	HCl

[a] Average of several runs. [b] 1,2-Dichloroethane. [c] Benzenediazonium-2-carboxylate hydrochloride. [d] Benzenediazonium-2-carboxylate.

split (**3** τ 4.34; **4** τ 4.74). By contrast, compound **6**, a model for **5**, shows its cyclobutyl hydrogens at τ 6.2.[14]



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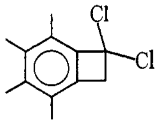

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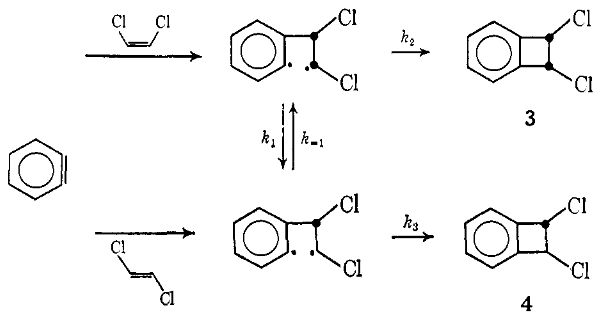
The nmr spectra of the corresponding 1,2-dibromo and 1,2-diiodo compounds have been described by Fraenkel and coworkers.[15] In these compounds as well as in **3** and **4** the *trans* isomers have their cyclobutyl hydrogens at 0.4 ppm higher field than the *cis* isomers. Compounds **3** and **4** were easily separable on a variety of gas-chromatography columns.

The results of the addition of benzyne to *cis*- and *trans*-1,2-dichloroethylene under a variety of conditions are shown in Table I. The course of the addition of benzyne to *trans*-1,2-dichloroethylene is independent of modest temperature and duration changes as well as a twelvefold dilution and use of ethyl iodide as solvent. The larger yields in the additions to this olefin reflect the approximately thirtyfold greater rate of addition to the *trans*-olefin over the *cis*. Two related precursors were used and no change in the ratio of **3**:**4** noted. The 2 + 2 addition is nonstereospecific and therefore bears out the notion that **1** is the structure of benzyne. We feel that the lack of stereospecificity is the result of a two-step cycloaddition proceeding through an intermediate diradical[16] (although the argument is not altered if polar species are involved) which lives long enough to permit some rotation about the critical carbon–carbon bond. Similar results have been obtained by others[2a,c,d] and with one exception[2b] interpreted in the same way. It is possible, using expressions similar to those developed by Bartlett, *et al.*,[17] to calculate the relative rates of cyclization and rotation in the proposed intermediate singlet diradical.



Here, in Bartlett's terminology

$$(3/4)_{cis} = p = k_2(k_{-1} + k_3)/k_1k_3 \tag{1}$$

$$(4/3)_{trans} = q = \frac{k_3(k_1 + k_2)}{k_{-1}k_2} \tag{2}$$

These equations become, where $a = k_{-1}/k_1$, $b = k_2/k_1$, $c = k_3/k_2$, $d = k_3/k_{-1}$

$$p = (a/c) + b \tag{3}$$

$$q = (c/a)(1 + b) \tag{4}$$

and thus

$$a/c = (p + 1)/(q + 1) \tag{5}$$

$$b = (pq - 1)/(q + 1) \tag{6}$$

$$d = (bc/a) = k_3/k_{-1} = (pq - 1)/(p + 1) \tag{7}$$

Equations 5–7 allow us to calculate b, the ratio of the rates of closure to rotation starting from the *cis*-olefin; d, the ratio of the rates of closure to rotation starting from the *trans*-olefin; and $^a/_c$, the *cis*/*trans* product ratio expected under conditions of complete rotational equilibrium: $b = 1.3$; $d = 2.3$; $^a/_c = 0.6$.

One group of workers[2b] has attributed the nonstereospecificity to the intervention of triplet benzyne. It was claimed that addition of methyl iodide induced intersystem crossing and thereby increased the population of triplet benzyne. We (Table I) and others[2d] find no effect of added iodide. Nonetheless, analogy can be claimed to the reactions of triplet carbenes which are indeed nonstereospecific. It is important to recognize, however, that the ratio of *cis* and *trans* adducts found in the benzyne reactions is not that typical of triplet carbene additions. The best studied of such reactions involve methylene,[18] bis(carbomethoxy)carbene,[19] a related[20] cyclic carbene derived from Meldrum's acid,[21] and the carbene derived from diazocyclohexanone.[22] In each of these cases it is the *trans* product which is

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[14] H. Hart and R. W. Fish, *J. Amer. Chem. Soc.*, **82**, 749 (1960).

[15] G. Fraenkel, Y. Asahi, M. J. Mitchell, and M. P. Cava, *Tetrahedron*, **20**, 1179 (1964).

[16] P. G. Gassman and H. P. Benecke, *Tetrahedron Lett.*, 1089 (1969).

[17] L. K. Montgomery, K. Schueller, and P. D. Bartlett, *J. Amer. Chem. Soc.*, **86**, 622 (1964).

[18] C. McKnight, P. S. T. Lee, and F. S. Rowland, *ibid.*, **89**, 6802 (1967), and references therein.

[19] M. Jones, Jr., W. Ando, and A. Kulczycki, Jr., *Tetrahedron Lett.*, 1391 (1967).

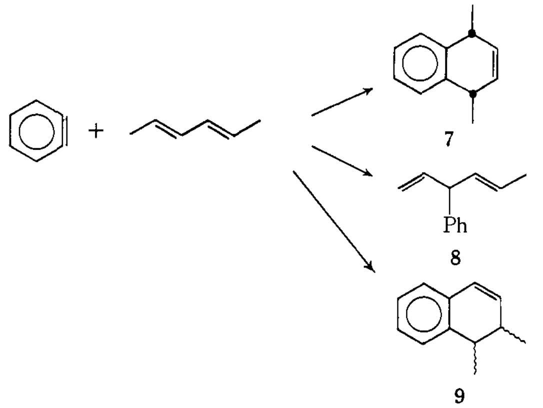
[20] P. M. Howley, unpublished work.

[21] B. Eistert and F. Geiss, *Chem. Ber.*, **94**, 929 (1961).

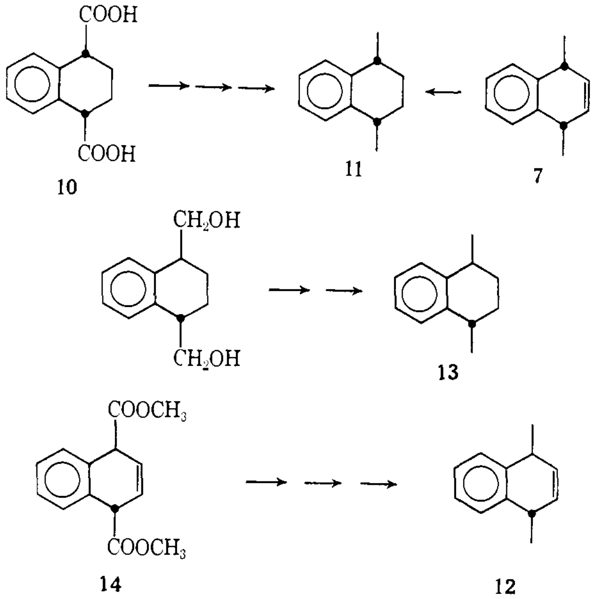
[22] M. Jones, Jr., and W. Ando, *J. Amer. Chem. Soc.*, **90**, 2200 (1968).

formed in the greater amount (between 75 and 85%) and the *trans/cis* ratio is independent of the starting olefin. The results from benzyne bear little similarity to these and it is not clear to us why, if triplets are involved, they should not. It seems if anything that a tetramethylene diradical should be more reluctant to close than trimethylene and should therefore allow more, not less, rotation.[23]

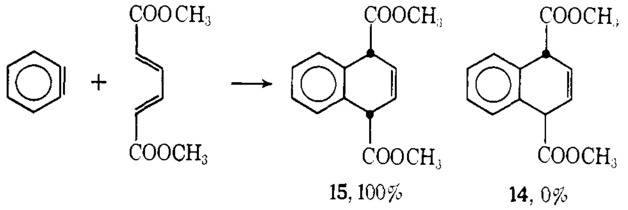
Further evidence for the absence of triplets, as well as the structure of benzyne, comes from an examination of the 2 + 4 cycloaddition. The Diels–Alder reaction of benzyne is extremely well known[24] but as with the 2 + 2 reaction, the stereochemistry received no early attention.[2e] Addition of benzyne to *trans,trans*-2,4-hexadiene leads to three products, **7, 8** and **9**.



The 2 + 4 cycloaddition product, **7**, was formed in 74% yield and constituted at least 85% of the product mixture. While we were able to find only one dihydronaphthalene it remained with prove the stereochemistry and the absence of the other isomer. Our dihydronaphthalene is identical to the compound formed by Hückel[25] by the reductive dimethylation of naphthalene but no stereochemical conclusions could be drawn. The stereochemistry was established as *cis* by conversion of the diacid **10** of known stereochemistry[26] to **11** by a route analogous to that used by Walborsky[27] followed by hydrogenation of **7** to the identical *cis*-tetrahydronaphthalene **11**. The corresponding *trans*-dihydronaphthalene **12** and tetrahydronaphthalene **13** were also synthesized.



While we were unable to separate **11** and **13** under any gas-chromatographic conditions, **7** and **12** were separable and under conditions where 1% of **12** could have been detected, none appeared.[28] An even more striking example of the specificity of this reaction involves the cycloaddition to the dimethyl ester of *trans,trans*-muconic acid.



Here, while the *cis* and *trans* isomers **15** and **14** are easily separable, they are so prone to isomerization that we have been unable to find chromatographic conditions sufficient for elution but insufficient for isomerization. However, the nmr spectra of **15** and **14** permit an analysis using the methoxy signals (**15** τ 6.32; **14** τ 6.24) to be performed on the crude product. Under conditions where an added 0.7% of **14** is easily detectible no **14** appears. The 4 + 2 cycloaddition is stereospecific within these limits of detection. Not only is this consistent with the structural calculations of Hoffmann[7] and our experiments on the 2 + 2 reactions, but it argues strongly against the intermediacy of triplet benzyne. Should triplet benzyne be involved there seems no reason to expect a stereospecific reaction. Surprisingly, the most nearly analogous reaction, the addition of carbenes to dienes has not been studied from a stereochemical point of view. The remote possibility therefore exists that there is something about the diene system which directs the addition of even triplets stereospecifically *cis*. Were this to be the case, our finding of a stereospecific *cis* addition of benzyne would not constitute evidence against the presence of triplets. Unpublished work in this laboratory shows that this is not the case. Triplet bis(carbomethoxy)carbene undergoes considerably more *trans* addition than does the singlet, which gives only the usual traces of the product of *trans* addition.

Compounds other than the Diels–Alder addition product **7** are formed in the reaction of benzyne with *trans,trans*-2,4-hexadiene. Compound **8** is the product of an "ene" reaction and was formed in 6% yield. Compound **9**, formed in only 4% yield, is assigned its structure on consideration of its spectra and will be dealt with in a separate work. Suffice it to say here that it probably finds its origin in a 2 + 2 addition to the diene followed by rearrangement.

Two final possible interpretations of our results must be mentioned. Both require the presence of two benzynes. First, while the Woodward–Hoffmann rules do not permit a concerted 2S + 2S thermal cycloaddi-

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[23] A species related to triplet tetramethylene has been generated. This species closes to *cis* and *trans* products in the ratio 1.1:1. N. J. Turro and P. A. Wriede, *J. Amer. Chem. Soc.*, **90**, 6863 (1968).

[24] Reference 6, p 208 ff.

[25] W. Hückel and J. Wolfering, *Ann.*, **686**, 34 (1965).

[26] T. M. Lyssy, *J. Org. Chem.*, **27**, 5 (1962).

[27] Y. Inouye, T. Sugita, and H. M. Walborsky, *Tetrahedron*, **20**, 1695 (1964).

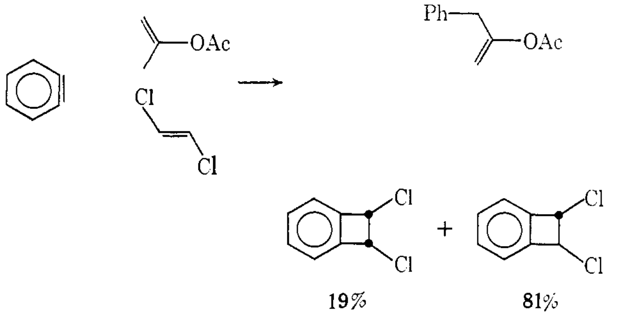
[28] We thank John Riddle and Professor J. A. Berson of the University of Wisconsin for assistance in the separation of **7** and **12** by capillary gas chromatography. Separation was finally achieved on a 250 ft Carbowax column operated at 110° with 50 psi gas pressure.

tion, they do allow a process in which one of the partners undergoes an antarafacial attack; in this case a $2_BS + 2_\pi A$ reaction. This would produce *trans*-1,2-dichlorobenzocyclobutene from *cis*-olefin and *vice versa*. Were such a process occurring, a new stereospecific source of the *cis* product must also be postulated. Two benzynes are required.

Second, even if one accepts the arguments against the existence of pure triplet benzyne, why not posit a mixture of a singlet and a triplet? The triplet might give nonstereospecific attack, the singlet stereospecific; the combination giving the observed ratios. Again, two benzynes are needed.

We have already given one argument against two benzynes. If two benzynes exist in the reaction with the dichloroethylenes, they should also be present in the Diels–Alder reaction. It is difficult to see why two products should be obtained in the 2 + 2 reaction, but only one in the 2 + 4. In either of the above two cases we would expect some component of nonstereospecific 2 + 4 addition.

Further evidence against the presence of two benzynes comes from a competition experiment. We have generated benzyne in a mixture of isopropenyl acetate and *trans*-dichloroethylene. We find the ratio of *cis*-/*trans*-benzocyclobutenes formed to be exactly that found in the absence of isopropenyl acetate. Large amounts of "ene" product are formed from the acetate. This result requires that any two benzynes have the same relative reactivities with isopropenyl acetate ("ene" reaction) and dichloroethylene (2 + 2 cycloaddition). We regard this as most unlikely and combined with the results of the 2 + 4 cycloaddition mentioned above, to argue strongly for the presence of only one benzyne, the symmetric singlet **1**.



Experimental Section

General. Nmr spectra were measured on a Varian Associates A-60-A or HA-100[29] instrument. Mass spectra were measured on an AEI MS-9 mass spectrometer.[30] Gas chromatography was performed on a Varian Aerograph A-90-P instrument: column A, 2-m 10% Dow-Corning DC-710 silicone oil on 70–80 mesh Anakrom; column B, 1-m 15% Carbowax 20M on 60–80 mesh Chromosorb P; column C, 2-m 15% Carbowax 20M on 60–80 mesh Chromosorb W; column D, 2-m 15% Carbowax 20M on 60–80 mesh Chromosorb P.

Reaction of Benzyne with 3,3-Dimethylbutene-1. Benzenediazonium-2-carboxylate hydrochloride[31] (BDC-HCl) (13.3 g, 0.072 mol)[32] was added to a mixture of 150 ml of 1,2-dichloroethane, 10 ml (0.14 mol) of propylene oxide, and 90 g (1.08 mol, 15 equiv) of 3,3-dimethylbutene-1. The resultant slurry was stirred and heated to reflux. After approximately 18 hr gas evolution had ceased and the reaction mixture was a homogeneous pale red solution. The solution was concentrated at the water pump and chromatographed directly on gas-chromatography column A at 130°. The major peak was identified as 1-*t*-butylbenzocyclobutene: nmr: τ 2.99 (4 H, m), 6.59–7.2 (3 H, m), and 9.05 (9 H, s); precise mass measurements, calcd for $C_{12}H_{16}$: 160.125194; found: 160.125309.

Reaction of Benzyne with *cis*-1,2-Dichloroethylene.[33] In a typical procedure, 6.1 g (0.033 mol) of BDC-HCl was added to 75 ml of 1,2-dichloroethane, 5 ml (0.07 mol) of propylene oxide and 39 ml (0.52 mol, 15 equiv) of *cis*-1,2-dichloroethylene. The resultant slurry was stirred and heated to reflux. After 1.25 hr gas evolution had ceased and the reaction mixture was a homogeneous pale red solution. The crude reaction mixture was analyzed by nmr spectroscopy. Addition of an internal standard was used to fix the absolute yield at 5%.

Reaction of Benzyne with *trans*-1,2-Dichloroethylene.[33] This reaction was run in a manner similar to that of the *cis* reaction. The yield of 40% was measured by the internal standard technique.

Reaction of Benzyne with *cis*- and *trans*-1,2-Dichloroethylene with Added Ethyl Iodide. These reactions were run in an identical fashion with those above with the exception that 150 ml of ethyl iodide replaced 75 ml of 1,2-dichloroethane as solvent. The initial slurry was stirred and heated to reflux. The reaction mixture turned pale yellow-grey and by the time gas evolution had ceased, a homogeneous pale red. The crude reaction mixture was concentrated and analyzed by nmr.

Reaction of Benzyne with *trans*-1,2-Dichloroethylene in the Presence of Isopropenyl Acetate. BDC-HCl (3.05 g, 0.0165 mol) was added to 75 ml of 1,2-dichloroethane, 2.5 ml (0.035 mol) of propylene oxide, 20 ml (0.52 mol, 15 equiv) of *trans*-1,2-dichloroethylene and 1.78 ml (0.0165 mol, 1 equiv) of isopropenyl acetate. The resultant slurry was stirred and heated to reflux. After 3 hr gas evolution had ceased and the reaction mixture was a homogeneous red solution. The crude reaction mixture was concentrated and analyzed by nmr which revealed *cis*- and *trans*-1,2-dichlorobenzocyclobutene in the ratio 19:81. The nmr also showed the presence of 2-acetoxy-3-phenylpropene.[34] The ratio of **3** + **4**/2-acetoxy-3-phenylpropene was *ca.* 0.15.

Reaction of Benzenediazonium-2-carboxylate with *trans*-1,2-Dichloroethylene. Anthranilic acid (3.42 g, 0.025 mol) was diazotized according to the method of Friedman.[35] The resulting benzenediazonium-2-carboxylate was added to 50 ml of dichloromethane and 26.7 ml (0.345 mol, 15 equiv) of *trans*-1,2-dichloroethylene. The slurry was stirred and heated to reflux. After 24 hr gas evolution had ceased and the solution was black and homogeneous. This was concentrated and analyzed by nmr.

Stability of *cis*-1,2-Dichlorobenzocyclobutene. Pure **3** isolated by preparative gas chromatography on column A at 150° was dissolved in 1,2-dichloroethane and refluxed for 6 hr. Gas-chromatographic analysis showed that no new compounds were formed. BDC-HCl and propylene oxide were then added and the slurry thermally decomposed under reflux. Analysis by gas chromatography showed that none of the starting *cis*-dichlorobenzocyclobutene had been destroyed.

Synthesis of *trans,trans*-Dimethylmuconate. *trans,trans*-Muconic acid (15.0 g, 0.106 mol) was placed in 600 ml of absolute methyl alcohol and 3 ml of concentrated sulfuric acid added. The slurry was heated to reflux and stirred. The reaction mixture became homogeneous and developed a black color. After 24 hr reflux it was again inhomogeneous. Refluxing was continued for an additional 6 hr and the reaction mixture allowed to stand overnight. A brown solid (mp 156–160°, lit. 163.5°,[36] 152°[37]) was isolated by filtration. The nmr spectrum of this compound was identical with that reported for *trans,trans*-dimethylmuconate.[38] The crude yield was 14 g (67%). This material was not further purified.

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[29] We thank the National Science Foundation for providing funds for the purchase of this instrument through Grant GP-5200. The Instrument Laboratory at Princeton is supported in part by Biomedical Sciences Support Grant FR-07057.

[30] We thank the National Science Foundation and the National Aeronautics and Space Administration for providing the funds for the purchase of this instrument.

[31] We thank Professor Lester Friedman and F. M. Logullo for the details of this preparation.

[32] Assuming no water of hydration.

[33] This procedure was varied in minor fashion to generate the data summarized in the table.

[34] A. J. Solodar, Ph.D. Thesis, Yale University, 1967; *Dissertation Abstr.*, **28**, 4511-B (1968).

[35] L. Friedman, *J. Amer. Chem. Soc.*, **89**, 3071 (1967).

[36] J. A. Elvidge and P. D. Ralph, *J. Chem. Soc., C*, 387 (1966).

[37] J. Tsuji, M. Morikawa, and N. Iwamoto, *J. Amer. Chem. Soc.*, **86**, 2095 (1964).

[38] L. M. Jackman, "Applications of Nuclear Magnetic Resonance

Reaction of Benzyne with *trans,trans*-Dimethylmuconate. BDC-HCl (6.5 g, 0.035 mol), 5.0 ml (0.07 mol) of propylene oxide, 200 ml of 1,2-dichloroethane and 7.0 g (0.035 mol, 1 equiv) of *trans,trans*-dimethylmuconate was stirred and heated to reflux. After 45 min gas evolution had stopped and the reaction mixture was a deep red color. Nmr analysis of the crude concentrated solution showed the presence of *cis*-1,4-dicarbomethoxy-Δ^2-dihydronaphthalene.[26] This compound is readily isomerized to the *trans* isomer[26,39] on gas chromatography on Column B (column temperature, 200°; injector, 270°; detector, 260°). The *trans* isomer could not be detected in the crude reaction mixture, however. Preparative gas chromatography afforded analytical material.

Anal. Calcd for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 67.98; H, 5.77.

Reaction of Benzyne with *trans,trans*-2,4-Hexadiene. BDC-HCL (5.0 g, 0.027 m), 5 ml (0.07 mol) of propylene oxide, 250 ml of 1,2-dichloroethane and 25 g (0.304 mol, 11.4 equiv) of *trans,trans*-2,4-hexadiene was stirred and heated to reflux. Gas evolution ceased after 1.1 hr and the reaction mixture was a homogeneous deep red color. The crude reaction mixture was concentrated, and analyzed by gas chromatography on column D at 110°. Collection gave *cis*-1,4-dimethyl-Δ^2-dihydronaphthalene in 74% yield as determined by addition of an internal standard.

Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 91.09; H, 9.05.

***trans*-1,4-Dimethyl-Δ^2-dihydronaphthalene (12).** *trans*-1,4-Dicarbomethoxy-Δ^2-dihydronaphthalene (30 g, 0.122 mol) was added to 125 ml of anhydrous ether. This slurry was then added to a slurry of 12.5 g (0.33 mol) of $LiAlH_4$ in 300 ml of anhydrous ether under nitrogen. The rate of addition was controlled so as to keep the reaction under gentle reflux. After addition was complete the slurry was allowed to stir under nitrogen over night at room temperature. Water was then added to decompose the salts and the organic layer separated and dried over sodium sulfate. The aqueous layer was continuously extracted with ether for 2 days, and the combined organic layers concentrated to give 16.5 g of a crude gummy yellow oil.

This crude diol was dissolved in 65 ml of pyridine and 17.5 ml of mesyl chloride added dropwise over 0.5 hr. The reaction was stirred for an additional 2 hr after which time the pink slurry was poured into a precooled solution of 108 ml of concentrated HCl and 216 ml of water. A viscous yellow gel settled out but was brought back into solution by addition of tetrahydrofuran. This homogeneous solution was then extracted with 600 ml of ether and the organic extract dried over sodium sulfate. The resulting milky white solution was dripped into a slurry of 25 g (0.66 mol) of $LiAlH_4$ in 500 ml of ether over 1.3 hr at such a rate as to maintain a gentle reflux. The slurry was allowed to stand overnight at room temperature and then decomposed by slow addition of water. The aqueous fraction was extracted with 400 ml of ether and the combined organic layers dried over sodium sulfate. These were then concentrated at the water pump to give a pale pink liquid. Gas chromatographic analysis on column C at 110° revealed only one peak which on collection proved to be **12**.

Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 91.25; H, 8.82.

***trans*-1,4-Dimethyltetralin (13).** Mesyl chloride (3.1 ml, 0.04 mol) was added dropwise to a solution of *trans*-1,4-bis(hydroxymethyl)tetralin[26] (3.0 g, 0.015 mol) in 12.1 ml of pyridine. After addition the solution was stirred and cooled for another 2 hr and then added to a cold solution of 20 ml of concentrated HCl and 40 ml of water. A yellow gel settled out but was brought back into solution by addition of tetrahydrofuran. The organic layer was then extracted with 500 ml of ether and the ether extract dried over sodium sulfate and concentrated to a white solid. To this was added 125 ml of anhydrous ether and the resultant slurry added to 16.0 g (0.16 mol) of $LiAlH_4$ in 60 ml of ether. The addition was controlled so as to maintain a gentle reflux. After addition the reaction mixture was stirred under nitrogen for an additional 16 hr, then decomposed by addition of water. The aqueous layer was extracted with ether, the organic layers were combined, dried over sodium sulfate and concentrated. The crude reaction product was analyzed by glpc on column D at 120°. The major peak was collected and identified as *trans*-1,4-dimethyltetralin (**13**): nmr τ 2.98 (4 H, s), 6.96–7.35 (2 H, m), 7.91–7.05 (10 H, m with superimposed doublet); precise mass measurement: Calcd for $C_{12}H_{16}$: 160.125194.Found: 160.123762.

***cis*-1,4-Dimethyltetralin (11). Procedure A.** *cis*-1,4-Tetralindicarboxylic acid[26] (51 g, 0.23 mol) was refluxed with 900 ml of methanol and 19.5 ml of concentrated H_2SO_4. After 18 hr the solution was concentrated so as to remove half the methanol. The clear liquid was extracted with two 300-ml portions of cold ether. The combined ether washings were washed with 100 ml of 1.0 *N* sodium bicarbonate, neutralized by addition of H_2SO_4 and concentrated. This liquid was then distilled (Kugelrohr) to yield 42 g (*ca.* 80%) of crude *cis*-diester. This was dissolved in 100 ml of anhydrous ether and dropped into a slurry of 12.5 g of $LiAlH_4$ in 300 ml of ether under nitrogen. The addition was controlled so as to maintain a gentle reflux and allowed to stand overnight. The salts were decomposed by addition of water, with cooling. The aqueous layer was extracted with 250 ml of ether, the organic fractions were combined, dried over sodium sulfate and concentrated. The crude *cis*-diol was converted to the dimethyl compound by a procedure exactly analogous to the one used in the *trans* series. The major peak was collected by preparative glpc on column D at 110°. The nmr spectrum was identical with that previously published.[40] Precise mass measurement: Calcd for $C_{12}H_{16}$: 160.125194, Found: 160. 12481.

Procedure B. Hydrogenation of 7. Compound **7** (0.25 ml) was hydrogenated over a catalytic amount of PtO_2 in methanol. The compound absorbed *ca.* 100% of the theoretical amount of hydrogen to give, after concentration and preparative glpc on column D at 110°, *cis*-1,4-dimethyltetralin identical with that produced by procedure A.

Spectroscopy in Organic Chemistry," Pergamon Press, Inc., New York, N. Y., 1959, p 95.

(39) G. W. Brown and F. Sondheimer, *J. Amer. Chem. Soc.*, **89**, 7116 (1967).

(40) American Petroleum Institute Research Project No. 44, spectrum No. 581 (60MHz) and 2c (100MHz).