matographed on silica gel (chloroform–acetone, 20:1). A broad, yellowish brown zone was collected and evaporated. The residue was crystallized from acetone–ether as described above; yield 180 mg, total yield of **22b** 349 mg, (7.5%), mp 247–252° dec with a change at about 220° from fine yellow needles to long thick yellow needles.

Anal. Calcd for $C_{23}H_{22}ClNO_8$: C, 58.05; H, 4.66; N, 2.94; Cl, 7.45; mol wt, 475.9. Found: C, 58.18; H, 4.73; N, 2.89; Cl, 7.53.

The ultraviolet spectrum showed $\lambda\lambda_{\max}^{\text{MeOH}-0.1M\,\text{Na}_2\text{B}_4\text{O}_7}$ after 1 hr equilibration 453 (33,800), 345 (5400), 310 (6500), and 261 mμ (ε 9000);[19] $\lambda\lambda_{\max}^{0.01N\ \text{methanol}-\text{HCl}}$ after 1 hr equilibration 427 (31,300), 327 (6600), and 215 mμ (ε 22,200).

Michael Adduct i. Triethylamine (2.8 ml) was added to a solution of **1** (5 g) and dimethyl 3-oxoglutarate (**2**) (4.0 ml) in dry benzene (75 ml), and the mixture was kept at room temperature for 24 hr. The reaction mixture was then washed with water and very dilute HCl until the water layer had a pH of 4. The benzene layer was dried over sodium sulfate and evaporated *in vacuo*. The yellowish, oily residue was triturated with ether and the crystalline i was collected (1.61 g, 19%), mp 135–137°; after one crystallization from ether, 137°.

Anal. Calcd for $C_{23}H_{21}NO_7$: C, 65.24; H, 5.00; N, 3.31; mol wt, 423.4. Found: C, 65.44; H, 4.91; N, 3.11.

Spectral results were as follows: ultraviolet $\lambda_{\max}^{\text{ethanol}}$ 230 mμ (ε 18,800); infrared $\lambda_{\max}^{\text{CHCl}_3}$ 2.8 (broad), 3.28 (broad), 5.56, 5.75, 5.83, 6.02, 6.26, 6.32, 6.62, 6.73, and 6.93 μ; nmr, two methyl singlets at τ 6.34 and 6.21.

Transformation of i into 3. Potassium *t*-butoxide was added to a solution of i (300 mg) in tetrahydrofuran (5 ml). The mixture was stirred at room temperature for 25 hr and then worked up as described in the preparation of **3**, yield 134 mg (45% of **3**), identical in every respect with compound **3** described earlier.

Improved Method for the Preparation of Thiobenzoylglycine. Ethylthiobenzoylglycine (30 g), pyridine (60 ml) and phosphorus pentasulfide (15 g) were refluxed for 2 hr. After further addition of phosphorus pentasulfide (5 g), the mixture was refluxed for another hour. After addition of benzene (500 ml) the mixture was filtered and the filtrate washed twice with 10% aqueous NaOH (150 ml) and several times with dilute HCl. The benzene was removed *in vacuo*, and the oily residue was dissolved in ethanol (100 ml). Aqueous KOH (15%, 50 ml) was added to this solution, and the mixture was kept at room temperature for 4 days. Most of the ethanol was then removed *in vacuo* and the residue was diluted with water (100 ml), washed thrice with ether–benzene (1:1), and acidified slowly in an ice bath with 2 *N* HCl. The crystalline solid was collected and recrystallized once from hot water, mp 150–154°; $\lambda\lambda_{\max}^{\text{methanol}}$ 240 mμ (ε 10,900) and 286 mμ (ε 7300).

Acknowledgment. Financial support given by the National Institutes of Health, Grant No. A1-07626-01, the National Science Foundation, Grant No. GP-6626, and Charles Pfizer and Company, an unrestricted research grant, is gratefully acknowledged.

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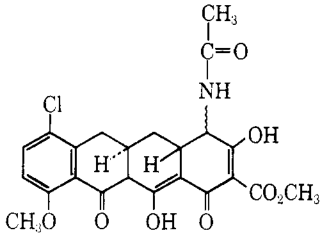
[19] Recent findings in our laboratory by Mr. J. Philip Bays suggest that the maximum at 345 mμ may be attributable to a small amount of an isomer of structure ii.



ii

The Preparation and Properties of 1,2-Bis(triphenylphosphoranyl)benzocyclobutene[1,2]

Alfred T. Blomquist and Victor J. Hruby[3]

Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14850. *Received April 11, 1967*

Abstract: The preparation of *trans*-1,2-bis(triphenylphosphonio)benzocyclobutene dibromide and its conversion to 1,2-bis(triphenylphosphoranyl)benzocyclobutene are described. Treatment of the dibromide salt with base followed by reaction with a benzaldehyde affords different results that depend upon the nature of the solvent. In ethanol as the major solvent, the principal products are the *cis*- and *trans*-1-benzylidenebenzocyclobutenes corresponding to the particular benzaldehyde used, together with triphenylphosphine oxide; in DMF or DMSO, the major products are the *cis,cis*- and/or *cis,trans*- and/or *trans,trans*-1,2-bisbenzylidenebenzocyclobutenes corresponding to the benzaldehydes used, as well as triphenylphosphine oxide. In both instances a number of minor products are obtained. The structure and stereochemistry of the major products are in accord with the chemical and physical data reported herein.

It has been predicted that benzocyclobutadiene (I; Y and Z = H), an 8π-electron system, should possess some cyclobutadiene character, exhibit considerable resonance energy, and have a singlet ground state.[4,5] Other considerations[6,7] suggest that the hydrocarbon will have little resonance stabilization and thus might simply act as a highly reactive olefin. Indeed, several derivatives of benzocyclobutadiene have been prepared

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[1] Taken from the Ph.D. Thesis of V. J. Hruby, Cornell University, 1965. The partial support of the National Science Foundation Grant G-18902 is gratefully acknowledged.

[2] For a preliminary report of some of this work, see A. T. Blomquist and V. J. Hruby, *J. Am. Chem. Soc.*, **86**, 5041 (1964).

[3] American Viscose Fellow, summer 1963; National Science Foundation Predoctoral Research Fellow, 1963–1964; National Science Foundation Predoctoral Cooperative Fellow, 1964–1965; Mobil Company Fellow, summer 1965.

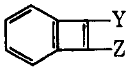
[4] J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, *J. Am. Chem. Soc.*, **74**, 4579 (1952).

[5] H. S. Lee, *Chemistry* (Taipei), 22 (1963), and subsequent papers; *Chem. Abstr.*, **59**, 14719*g* (1963).

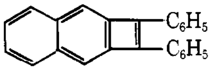
[6] M. E. Vol'pin, *Russ. Chem. Rev.*, **29**, 129 (1960); *Chem. Abstr.*, **54**, 17234*i* (1960).

[7] D. Ginsburg, Ed., "Non-benzenoid Aromatic Compounds," Interscience Publishers, Inc., New York, N. Y., 1959, pp 65–101.

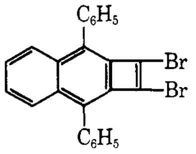
in situ (I: Y and Z = H;[8-10] Y and Z = Br;[8a,11] Y = H, Z = Br;[12] Y = H, Z = I;[13] Y = CH_3 Z = C_6H_5[14]), but efforts to isolate a *bona fide* benzocyclobutadiene have failed. On the other hand, recently two naphthocyclobutadiene derivatives, compounds II[15] and III,[16] have been synthesized and isolated.



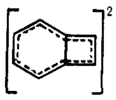
I



II



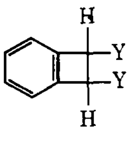
III



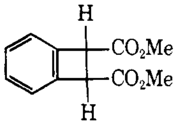
IV

The benzocyclobutadiene dianion (IV), a 10π-electron bicyclic system, might be predicted to be aromatic although electron compressional energies would probably far exceed any aromatic stabilization. Whatever the case, the recent isolation of a metal complex of the hydrocarbon I[17] (Y and Z = H) and isolation of the compounds II and III encourages efforts to prepare an isolable benzocyclobutadiene and substances containing the benzocyclobutadiene dianion for a general study of their properties.

For this purpose the preparation of 1,2-disubstituted benzocyclobutenes (V) that possess strong electron-withdrawing groups was undertaken. Particularly appealing substituents for the compounds of type V were the nitro, phosphonium, and sulfonyl groups; preparation of the diester VI was not considered in view of an earlier failure.[18] The present article describes the preparation and properties of the bisphosphonium salt VIIIa.



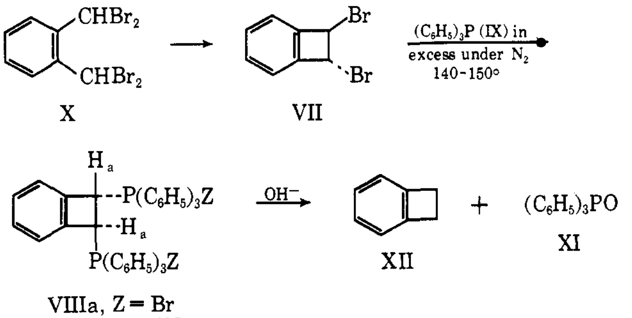
Va, Y = $P^+(C_6H_5)_3Br^-$
b, Y = NO_2
c, Y = SO_2R



VI

Results and Discussion

For this study $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*o*-xylene is converted to pure *trans*-1,2-dibromobenzocyclobutene (VII) *via* a modification of the procedure of Cava, *et al.*;[19] reaction of the dibromide VII with excess triphenylphosphine (IX) at 150°, under nitrogen, gives the desired 1,2-bis(triphenylphosphonio)benzocyclobutene dibromide (VIIIa) in nearly quantitative yield. Under the usual conditions for the preparation of phosphonium salts, *i.e.*, nonexclusion of air, there is obtained a mixture of salts and triphenylphosphine oxide (XI) or gummy oils.

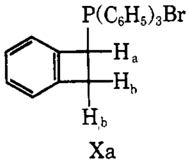


X VII

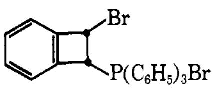
VIIIa, Z = Br
b, Z = ClO_4

XII XI

The nmr spectrum[20] of the bisphosphonium salt VIIIa exhibits absorption at 6.65 ppm (bm, possible quartet) indicative of the aliphatic hydrogens H_a and at 7.7 ppm (bm) characteristic of the aromatic hydrogen atoms; the integrated ratio of these absorptions is 1:17. The spectrum of the compound VIIIa, which contains some of the monophosphonium salt Xa, shows an additional peak at 2.55 ppm due to the H_b absorptions. The salt VIIIa probably has a *trans* configuration on the basis of its observed stability and its synthesis from *trans*-VII. It is pertinent to note that the nmr spectra of all samples of the bis salt VIIIa indicate the complete absence of *cis*-1-bromo-2-(triphenylphosphonio)benzocyclobutene bromide (XIII), regardless of the preparative method used to obtain VIIIa. The infrared and ultraviolet absorption spectra of VIIIa (see Experimental Section) support the structural assignment. Finally, hydrolysis of the bis salt VIIIa with aqueous alkali affords benzocyclobutene (XII) together with the oxide XI, and metathesis with cold 50% perchloric acid gives 1,2-bis(triphenylphosphonio)benzocyclobutene diperchlorate (VIIIb).



Xa



XIII

Solutions of the salt VIIIa in the solvents N,N-dimethylformamide (DMF) or dimethyl sulfoxide (DMSO), when treated with bases such as lithium ethoxide, potassium *t*-butoxide, *n*-butyllithium, and sodium amide, afford deep carmine-colored solutions of 1,2-bis(triphenylphosphoranyl)benzocyclobutene

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[8] (a) M. P. Cava and K. Muth, *Tetrahedron Letters*, 140 (1961); (b) M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **79**, 1701 (1957); (c) M. P. Cava and D. R. Napier, *ibid.*, **78**, 500 (1956).

[9] (a) C. D. Nenitzescu, M. Avram, and D. Dinu, *Ber.*, **90**, 2541 (1957); (b) C. D. Nenitzescu, M. Avram, and D. Dinu, *Chem. Ind.* (London), 257 (1959); (c) M. Avram, D. Dinu, C. D. Nenitzescu, and F. Mateescu, *Ber.*, **93**, 1789 (1960); (d) M. Avram, I. G. Dinulescu, D. Dinu, and C. D. Nenitzescu, *Chem. Ind.* (London), 555 (1962).

[10] G. W. Griffin and D. F. Veber, *ibid.*, 1162 (1961).

[11] F. R. Jensen and W. E. Coleman, *Tetrahedron Letters*, No. 2, 7 (1959).

[12] M. P. Cava and J. F. Stucker, *J. Am. Chem. Soc.*, **79**, 1706 (1957).

[13] M. P. Cava, K. W. Ratts, and J. F. Stucker, *J. Org. Chem.*, **25**, 1101 (1960).

[14] A. T. Blomquist and C. G. Bottomley, *J. Am. Chem. Soc.*, **87**, 86 (1965).

[15] M. P. Cava, B. Hwang, and J. P. Van Meter, *ibid.*, **85**, 4032 1963).

[16] M. P. Cava and B. Hwang, *Tetrahedron Letters*, 2297 (1965).

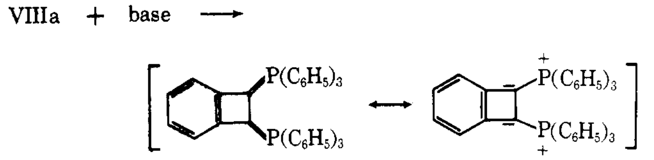
[17] G. F. Emerson, L. Watts, and R. Pettit, *J. Am. Chem. Soc.*, **87**, 131 (1965).

[18] A. T. Blomquist, Y. C. Meinwald, C. G. Bottomley, and P. W. Martin, *Tetrahedron Letters*, No. 24, 13 (1960).

[19] M. P. Cava, A. A. Deana, and K. Muth, *J. Am. Chem. Soc.*, **81**, 6458 (1959).

[20] All nmr spectra are determined by a Varian A-60 spectrometer and the absorption peaks are given in ppm downfield from tetramethylsilane (TMS). Coupling constants are given in cps. Abbreviations used here include: s = singlet; d = doublet; t = triplet; q = quadruplet; m = multiplet; b = broad; c = complex; u = unsymmetrical.-

(XIV) which are unstable when exposed to air or moisture but which appear to be stable indefinitely at low temperatures (< −30°) in an inert atmosphere.[21] It has not been possible to isolate the bis ylid XIV. The nmr spectrum of the bis ylid XIV is best determined

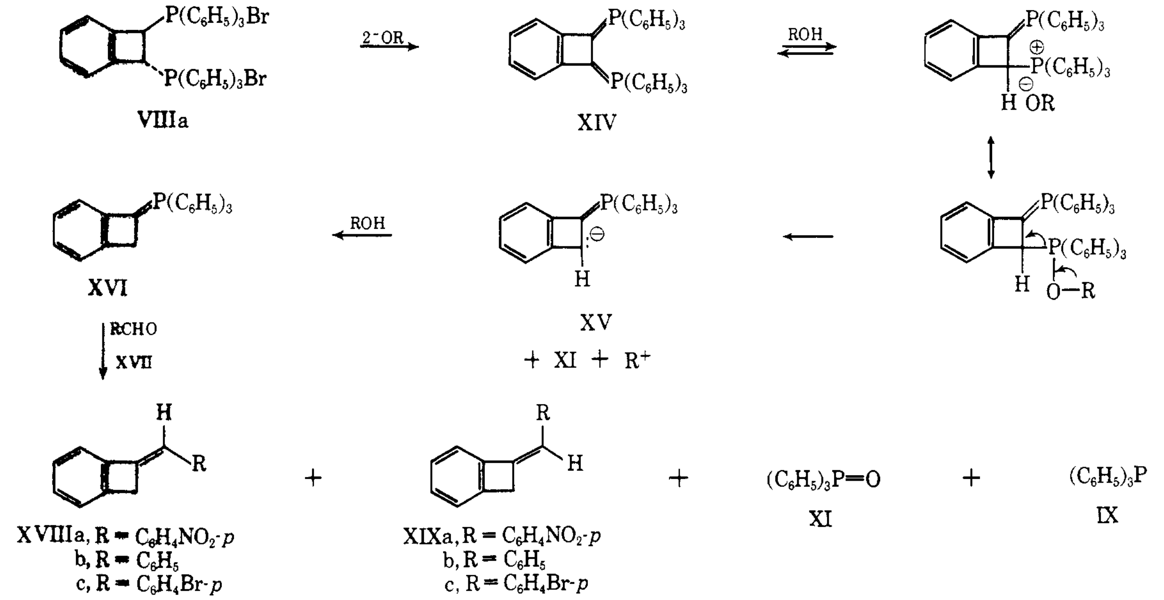


XIV

by treating the salt VIIIa with excess potassium *t*-butoxide in DMSO. A broad multiplet centered at 7.47 ppm containing two distinct maxima at 7.38 and 7.57 ppm is observed, but no absorption is seen below about 7.0 ppm.[22] The ultraviolet spectrum of a DMF solution of XIV shows absorptions at 435 (sh, log ε 3.64), 315 (sh, 4.18), and 308 mμ (sh, 4.21). A DMSO solution of XIV shows no electron spin resonance absorptions. Furthermore, treatment of the salt VIIIa with sodium methoxide in tetrahydrofuran at 0° provides sodium bromide in 90% yield, and addition of deuterium chloride to a solution of the bis ylid XIV leads to deuterium incorporation.

However, when a solution of the salt VIIIa in a solvent such as methanol is treated with nonaqueous base (sodium methoxide), a time-variable nmr spectrum is observed. This solution initially exhibits considerable aliphatic hydrogen absorption, and its light orange color suggests a low bis ylid concentration. Furthermore, the phosphine oxide XI is gradually formed. These results suggest that the bis ylid XIV is similar in basicity to the methoxide ion and can thus react with methanol affording the mono ylid XVI which can undergo further reaction (Chart I).

Chart I. Reactions of Salt VIIIa with Base and Benzaldehydes in Solvent Ethanol



The different behavior of the salt VIIIa and the ylid XIV in various solvents is further investigated in the following reactions.

Reactions in Solvent Ethanol. An ethanol solution of the salt VIIIa is treated with an alkoxide such as lithium ethoxide, potassium *t*-butoxide, or sodium ethoxide, and a short time later with a benzaldehyde (XVII). Reaction proceeds slowly; in two cases (addition of *p*-nitro- and *p*-bromobenzaldehyde) the *trans* products, *trans*-1-*p*-nitrobenzylidenebenzocyclobutene (XVIIIa) and *trans*-1-*p*-bromobenzylidenebenzocyclobutene (XVIIIc), respectively, slowly precipitate. When the remaining reaction mixture is worked up (see Experimental Section), both the *trans* and the *cis* monobenzylidene isomers, XVIII and XIX, respectively, the oxide XI, and, *usually*, a small amount of the phosphine IX, together with a polymeric salt, are obtained. None of the bisbenzylidene compounds are detected (*vide infra*). In all cases studied, the major isomer isolated from the above reactions is the *trans* isomer of the compounds XVIII; the relative amounts of each isomer vary with the aldehyde used.[24] Thus when *p*-nitrobenzaldehyde is used, the yield of *trans* isomer XVIIIa is 55%, and that of *cis* isomer XIXa is 34%; with benzaldehyde, the yield of *trans* isomer XVIIIb is 56% and that of the *cis* isomer XIXb is only 14%; when *p*-bromobenzaldehyde is used, the yields of *trans* isomer XVIIIc and *cis* isomer XIXc are 54 and 32%, respectively.

The structure and stereochemistry of the products XVIIIa, b, and c and XIXa, b, and c rest on their analyses, molecular weights, and the following spectral and chemical evidence. The nmr spectra (Table I) agree with the assigned structures. Of particular interest are the allylic hydrogens (H_a's) and the vinylic hydrogens (H_b's). The proximity of H_a and H_b to aromatic nuclei in the *trans* compounds XVIIIa, b, and c as compared with that of the *cis* compounds XIXa, b, and c results, because of steric and/or ring current effects,[25,26] in a deshielding of 0.20–0.39 ppm for the

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(21) To the best of our knowledge this constitutes the first example of the preparation of a 1,2-bisphosphoranyl compound. Furthermore XIV might be considered to be a pseudo derivative of the 10π-electron benzocyclobutadiene dianion system.

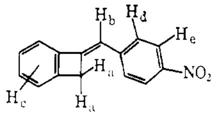
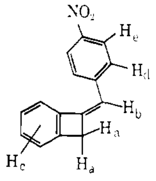
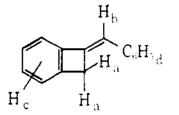
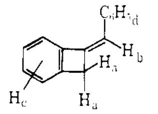
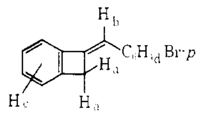
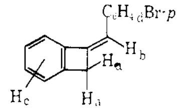
(22) For comparison, the aromatic H's of triphenylphosphine absorb at 7.22 ppm and those of triphenylphosphine oxide at 7.5 ppm. See also ref 23.

(23) A. W. Johnson, *J. Org. Chem.*, **24**, 282 (1959).

(24) S. Trippett, *Quart. Rev.* (London), **17**, 406 (1963).

(25) Examples of proximity effects in deshielding are reported by W. Magata, T. Terasawa, and K. Tori, *J. Am. Chem. Soc.*, **86**, 3746 (1964).

Table I. Nmr of Monobenzylidene Compounds

Compound	Solvt	H_a	H_b	H_c	H_d	H_e
 XVIII a (*trans*)	$(CH_3)_2CO$	4.01(d)	6.67(t)	7.10(bs)	7.50(ud)	8.03(ud)
		J_{ab} = 0.8 cps			J_{de} = 8.2 cps	
 XIXa (*cis*)	CCl_4	3.62(s)	6.12(s)	7.08(cm)	7.41(ud)	8.02(ud)
					J_{de} = 8.2 cps	
 XVIIIb (*trans*)	CCl_4	3.83(d)	6.50(s)	7.09(s)	7.22(m)	
 XIXb (*cis*)	CCl_4	3.59(s)	6.14(s)	7.10(m)	7.31(m)	
 XVIIIc (*trans*)	$CDCl_3$	3.88(d)	6.55(t)	7.18(bm)	7.33(d)	
		J_{ab} = 1.6 cps				
 XIXc (*cis*)	$CDCl_3$	3.68(d)	6.18(t)	7.23(m)	7.45(m)	
		J_{ab} = 0.9 cps				

vinylic hydrogens and of 0.36–0.55 ppm for the allylic hydrogens of the *trans* isomers relative to the *cis* isomers, exactly as expected.

The ultraviolet spectra (see Experimental Section) also strongly support the structural assignments. In all cases studied, the *trans* isomers exhibit absorption maxima which are slightly bathochromic when compared with the corresponding *cis* isomers, and also show larger extinction coefficients at the long wavelength absorptions. A similar effect is observed for various *trans*- and *cis*-α-alkylstilbenes which closely resemble the products obtained here.[27–29]

The infrared spectra are also compatible with the structural assignments. DeTar and Carpino[30] have pointed out that *trans*-stilbenes generally exhibit greater absorption than the *cis* isomers in the 7–9-μ region, whereas the situation is reversed in the 10.3–13.6-μ region; Luttke[31] has suggested that *cis*-stilbene-like compounds show more fine structure in the 12–15-μ region of the infrared. The *cis* and *trans* isomers obtained here usually exhibit these same general characteristics (see Experimental Section).

It is of interest to note that the *cis* compounds XIXa, b, and c are converted in varying degree to the *trans* isomers XVIIIa, b, and c in DMF that contains triphenylphosphine oxide. A less facile isomerization of the *cis* compound XIXa is obtained in pure DMF.

N-Bromosuccinimide (NBS) treatment of *trans*-1-*p*-nitrobenzylidenebenzocyclobutene (XVIIIa) affords 1-bromo-2-*p*-nitrobenzylidenebenzocyclobutene (XX) in low yield. The stereochemistry of this product is unknown. When the *trans* isomer XVIIIa is treated with bromine, the addition product XXI is obtained. On the other hand, the addition of bromine to *cis*-1-*p*-bromobenzylidenebenzocyclobutene (XIXa) proceeds slowly, and after a 36-hr reflux in carbon tetrachloride a mixture is obtained that shows olefinic absorption in its infrared spectrum. Chromatography on alumina provides only one isolable product, *trans*-1-(α-bromo-*p*-nitrobenzylidene)benzocyclobutene (XXII). The structural assignment of the latter product is in accord with all data. Of particular interest is its nmr spectrum which shows no vinylic hydrogen absorption, but instead shows two allylic hydrogens which absorb as a singlet at 3.9 ppm. The stereochemistry is uncertain, but mechanistic considerations predict the formation of the *trans* isomer.

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(26) J. E. Mulvaney, Z. G. Gardlund, and S. L. Gardlund, *J. Am. Chem. Soc.*, **85**, 3897 (1963); D. Y. Curtin, H. Gruen, and B. A. Shoulders, *Chem. Ind.* (London), 205 (1958), for similar effects.

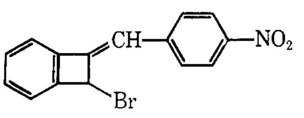
(27) H. Suzuki, *Bull. Chem. Soc. Japan*, **33**, 396 (1960).

(28) A. V. Dombrovskii, Y. G. Bal'on, and K. G. Tashchuk, *Zh. Obshch. Khim.*, **32**, 603 (1962); *Chem. Abstr.*, **58**, 1383*e* (1963).

(29) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, pp 276, 424–434.

(30) D. F. DeTar and L. A. Carpino, *J. Am. Chem. Soc.*, **78**, 475 (1956).

(31) W. Luttke, *Ann. Chem.*, 184 (1963).



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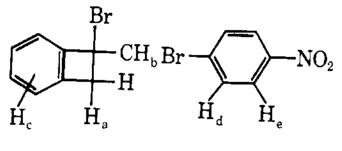
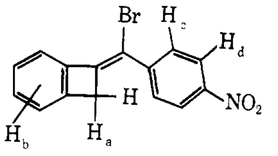
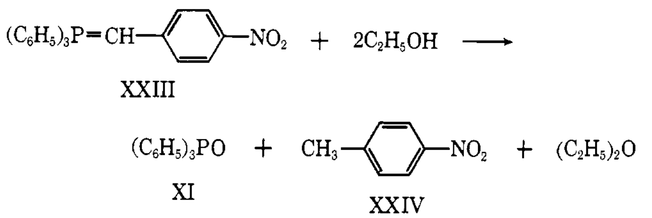


XXI



XXII

A possible mechanism by which the monobenzylidene products XVIII and XIX form is given in Chart I. The previous work of Grayson and Keough[32] provides a simple example of the kind of reaction suggested. They report that when the phosphorane XXIII is treated with alcohol a facile hydrolysis results, and triphenylphosphine oxide (XI), *p*-nitrotoluene (XXIV), and diethyl ether are formed. Furthermore, they observe that $Ph_3P{=}CHPh$ is hydrolyzed much more slowly than the phosphorane XXIII, whereas alkylphosphoranes such as $Ph_3P{=}CH{-}$alkyl do not hydrolyze in alcohols. This suggests that considerable stability must attend formation of the anionic intermediate XV in our scheme. Although predominance of the *trans* isomer XVIII suggests that the phosphorane XVI should be quite stable, it could not be isolated.

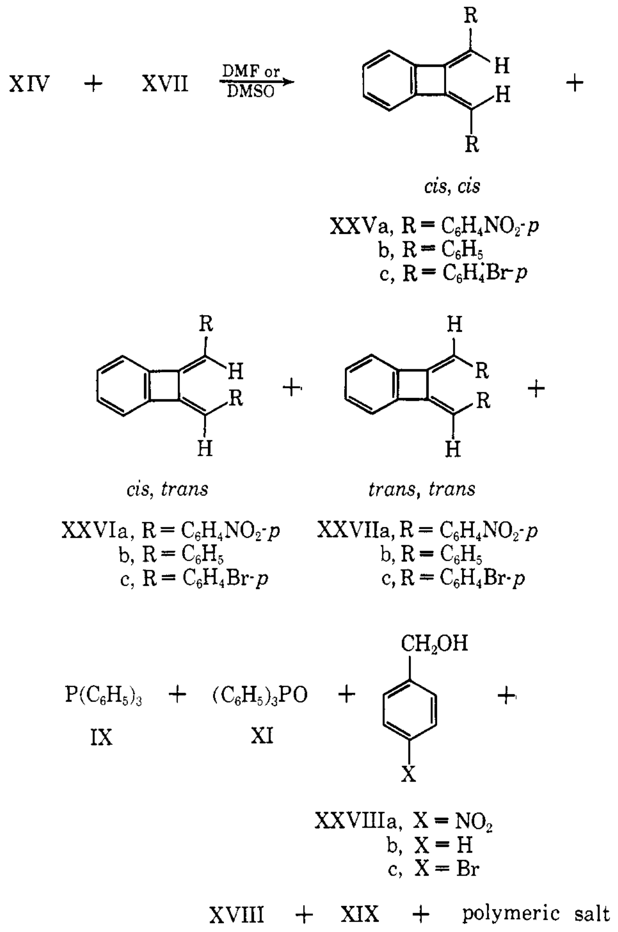


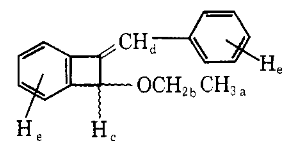
Reactions in DMF or DMSO. Treatment of DMF or DMSO solutions of 1,2-bis(triphenylphosphoranyl)-benzocyclobutene (XIV) with the same aldehydes used above leads to quite different results from those obtained in alcohol (compare Charts I and II). The major products isolated in this case are the bisbenzylidene compounds XXV and/or XXVI and/or XXVII, as well as triphenylphosphine oxide. Under various conditions minor amounts of triphenylphosphine,[2] the monobenzylidene products XVIII and XIX, the benzyl alcohol XXVI, and polymer salt are obtained.

Treatment of the phosphorane XIV with *p*-nitrobenzaldehyde (XVIIa) provides one of the monobenzylidene isomers, the *trans* product XVIIIa, small amounts of triphenylphosphine, *p*-nitrobenzyl alcohol (XXVIIIa), and polymer salt. The major products are triphenylphosphine oxide, and the three bisbenzylidene isomers *cis,cis*-1,2-bis(*p*-nitrobenzylidene)benzocyclobutene (XXVa), *cis,trans*-1,2-bis(*p*-nitrobenzylidene)-benzocyclobutene (XXVIa), and *trans,trans*-1,2-bis-(*p*-nitrobenzylidene)benzocyclobutene (XXVIIa). Only minor quantities of the *trans,trans* isomer XXVIIa are obtained. The relative amounts of the *cis,cis* isomer XXVa and of the *cis,trans* isomer XXVIa vary somewhat from run to run owing to the ready isomerization (see Experimental Section) of the latter isomer.[33]

On the other hand when the ylid XIV is treated with benzaldehyde (XVIIb), 17% of *trans*-1-benzylidenebenzocyclobutene (XVIIIb), 1% of *cis*-1-benzylidenebenzocyclobutene (XIXb), some triphenylphosphine, and polymer salt are obtained. The only bisbenzylidene compound isolated is *cis,cis*-1,2-dibenzylidenebenzocyclobutene (XXVb). (Another isomer is indicated in the initial chromatographic fraction as admixture with XXVb since an nmr spectrum exhibits a small auxiliary vinyl hydrogen peak and a few aromatic peaks in addition to those found for pure XXVb; on recrystallization of this product only the pure isomer XXVb is obtained.) Triphenylphosphine oxide (XI)[2] and what appears to be impure 1-benzylidene-2-ethoxybenzocyclobutene (XXIX, see Experimental Section) are also obtained. The latter product cannot be purified.

Chart II. Reactions of the Phosphorane XIV with Aldehydes in DMF or DMSO





XXIX

When the bis ylid XIV and *p*-bromobenzaldehyde (XVIIc) react, only small amounts of the monobenzyl-

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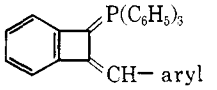
(32) M. Grayson and P. T. Keough, *J. Am. Chem. Soc.*, **82**, 3919 (1960).

(33) This ready isomerization also prevents a complete purification of XXVIa, though infrared and nmr spectral data suggest that about 95% purity is obtained. Likewise, *cis,trans*-1,2-bis(*p*-bromobenzylidene)benzocyclobutene (XXVIc) can be isomerized, though with considerable difficulty, to the *cis,cis* isomer XXVc.

idene compounds XVIIIc (0–5.8%) and XIXc (0–3.7%) are obtained. No triphenylphosphine results, and only trace amounts of *p*-bromobenzyl alcohol (XXVIc) and the polymer salt are obtained.[34] The major products isolated are *cis,cis*-1,2-bis(*p*-bromobenzylidene)benzocyclobutene (XXVc), *cis,trans*-1,2-bis(*p*-bromobenzylidene)benzocyclobutene (XXVIc), and triphenylphosphine oxide (XI).

p-Nitrobenzyl alcohol (XXVIIIa) and *p*-bromobenzyl alcohol (XXVIIIc) are formed by reduction of the corresponding benzaldehydes on an alumina column. This reduction occurs when solvents such as chloroform or alcohol are used as eluent for alumina columns containing absorbed benzaldehydes.[35] Triphenylphosphine (IX) and the polymer salt can form in a number of ways, but we have no evidence to indicate the particular path followed.[2]

The formation of the monobenzylidene products XVIII and XIX undoubtedly occurs in much the same way as it does when the bis salt VIIIa is treated with alkoxide in alcohols, because in most of the cases cited alkoxide is used in the production of bis ylid XIV, and thus small amounts of alcohol are present in the reaction mixture. Alternatively they might arise from hydrolysis of intermediates such as XXX during the reaction or during work-up.



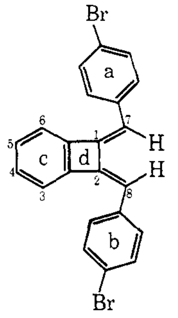
XXX

The isolation of only *trans*-1-*p*-nitrobenzylidenebenzocyclobutene (XVIIIa) is fortuitous since we find that the *cis* isomer XIXa is readily isomerized to XVIIIa under the experimental conditions.[36]

The structure and stereochemistry of the bisbenzylidene products XXVa, b, and c, XXVIa and c, and XXVIIa rest on their analyses, molecular weights, and the following chemical and physical data.

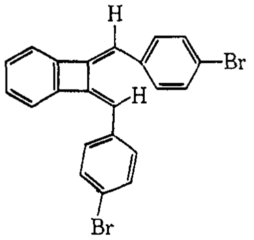
The somewhat unexpected nmr and ultraviolet spectra which are observed for the bisbenzylidene products make unequivocal assignment of their stereochemistry difficult (*vide infra*).[2] However, the solubility of the two stable isomers of 1,2-bis(*p*-bromobenzylidene)benzocyclobutene (XXVc and XXVIc) in carbon tetrachloride makes it possible to determine the stereochemistry by dipole moment measurements. These results can then be used in conjunction with other evidence to deduce the stereochemistry of all the bisbenzylidene isomers isolated.

In calculating the theoretical dipole moments, the following assumptions are made: (1) all phenyl rings are considered "normal;" (2) the benzocyclobutadiene component of the molecule, that is, rings c and d together with the C–C bonds 1–7 and 2–8, closely resembles dimethylenebenzocyclobutene, and thus the bond lengths can be estimated from the bond orders determined for this system;[5] (3) the major contribution to the dipole moment will be the *p*-bromostyrene portion of the molecule (*p*-bromostyrene has a dipole moment of 1.52 D.[37]). The calculated dipole moments for XXVc, XXVIc, and XXVIIc are given below.[38]



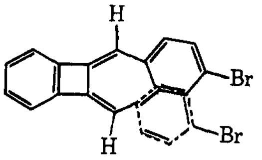
XXVc

0.79 D.



XXVIc

2.15 D.



XXVIIc

2.94 D.

The dipole moment of the high-melting isomer (191–192°) is found to be 0.69 ± 0.18 D. (0.70 ± 0.30 D. by an independent method, see Experimental Section) in good agreement with that calculated for the *cis,cis* isomer XXVc, while the observed dipole moment of the low-melting isomer (150–151°) is 2.30 ± 0.02 D. (2.21 ± 0.12 D. by independent method), in good agreement with that calculated for the *cis,trans* isomer XXVIc.

Further structural assignments can be made by comparison of the ultraviolet spectra. The absorption maxima of the *cis,cis* isomer XXVc are slightly bathochromic compared with those of the *cis,trans* structure XXVIc; also the long and short wavelength absorptions of the former are more intense, and the midrange maxima show slightly smaller extinction coefficients (see Experimental Section). A similar result is obtained for the two major isomers of 1,2-bis(*p*-nitrobenzylidene)benzocyclobutene, with the stable isomer (*vide supra*) exhibiting more intense and slightly bathochromic long and short wavelength maxima compared with the easily isomerized isomer. Though no midrange maxima are observed in this case, the *cis,cis* structure XXVa is assigned to the former isomer and the *cis,trans* stereochemistry to the easily isomerized product XXVIa. The low-yield orange isomer (*vide supra*) which exhibits its most intense maximum in the visible region (432.5 mμ), and a good deal of fine structure throughout the spectrum is assigned *trans,trans* stereochemistry (*i.e.*, XXVIIa). The ultraviolet spectrum of 1,2-dibenzylidenebenzocyclobutene has characteristics of both *p*-bromobisbenzylidene isomers, but

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(34) Small amounts of a phosphorus compound, mp 162.5–163.5°, which analyzed for $C_{18}H_{15}PO_2$ and had no aliphatic hydrogens (nmr analysis) are obtained, but its structure is not known.

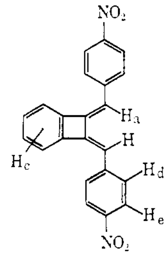
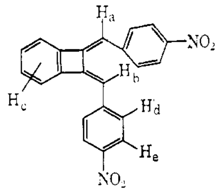
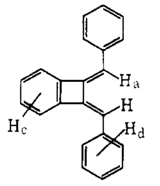
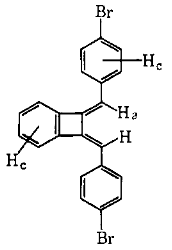
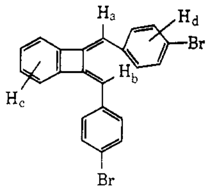
(35) V. J. Hruby, *N. Dakota. Acad. Sci.*, 28 (1962).

(36) The more facile isomerization of the *cis* isomers XIX to the *trans* isomers XVIII in the presence of triphenylphosphine oxide than in its absence suggests that betaine decomposition in the Wittig reaction may be reversible in certain cases. Though other explanations may be evoked, the matter deserves added investigation.

(37) K. B. Everard, L. Kumar, and L. E. Sutton, *J. Chem. Soc.*, 2807 (1951).

(38) The assistance of Professor C. F. Wilcox, Jr., is gratefully acknowledged.

Table II. Nmr Spectra of Dibenzylidenebenzocyclobutene Isomers

Compound	Solvt	H_a	H_b	H_c	H_d	H_e
	DMSO	6.82(s)		7.37(m)	7.53(ud)	8.11(ud)
					J_{de} = 8.5 cps	
	CDCl$_3$	6.72(s)	6.84(s)	7.42(m)	7.77(ud)	8.33(ud)
					J_{dc} = 8.5 cps	
	CCl$_4$	6.72(s)		7.41(cm)	7.65(bm)	
	DMSO	6.92(s)		7.53(cm)	7.73(bm)	
	CDCl$_3$	6.65(s)		7.58(bs)		
	DMSO	6.95(s)		7.79(s)		
	CDCl$_3$	6.57(s)		7.22(cm)	7.36(bm)	
	DMSO	6.87(s)	6.97(s)	7.56(bd)	7.73(bs)	

since it is stable and the only isomer isolated, it is undoubtedly the *cis,cis* product XXVb.

The nmr spectra of these compounds (the spectrum of *trans,trans*-1,2-bis(*p*-nitrobenzylidene)benzocyclobutene (XXVIIa) could not be determined due to its low solubility) support the structural sssignments made (see Table II). Of particular interest are the vinyl hydrogen absorptions. The *cis,cis* isomers XXVa, b, and c all exhibit singlets, while the *cis,trans* products XXVIa and XXVIc exhibit doublets; that is, the two vinyl hydrogens are chemically not equivalent. (Note, however, that the latter compound gives a singlet in chloroform-*d*.) The assignments for the vinyl hydrogens in the *cis,trans* isomers are made on the assumption that the H_b's are more susceptible to steric and/or ring current deshielding effects. The reason for the large downfield shift (*ca.* 0.6 ppm) of the H_a's in the bisbenzylidene compounds XXVa, b, and c as compared with the similar hydrogens (H_b's) in the monobenzylidene compounds XVIIIa, b, and c (compare Charts I and II) is not easily explained, but is possibly due to ring current effects and/or increased aromatic-like character in the former compounds.

Oxidative degradation of the 1,2-bisbenzylidene products under mild conditions does not afford any of the desired 1,2-benzocyclobutenedione (XXXI), but only starting material. Under more vigorous conditions, however, the principal products obtained are *o*-phthalic acid (XXXII) and the corresponding benzoic acid derivative XXXIII.

Work by Blomquist and Meinwald[39] on dimethylenecyclobutanes and dimethylenecyclobutenes suggested the possibility of obtaining a Diels–Alder adduct from one of the *cis,cis* isomers XXV; that is, the diene XXV might react with the activated dienophile affording a benzocyclobutadiene which would be sufficiently sterically hindered to prevent dimerization. However, treatment of *cis,cis*-1,2-dibenzylidenebenzocyclobutene (XXVb) with N-phenylmaleimide or tetracyanoethylene gives only starting materials, though in the latter case highly colored complexes are formed.

Although the initial step of an oxidative Diels–Alder reaction[40] of the diene XXV with 1,4-naphthoquinone

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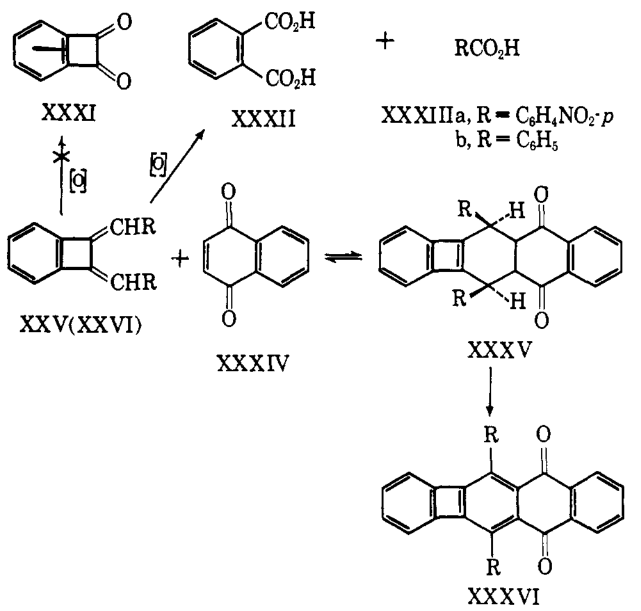
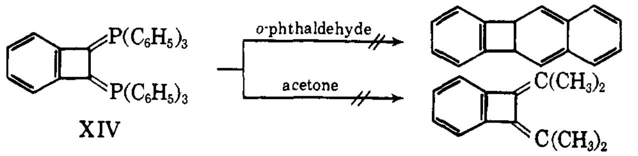
[39] A. T. Blomquist and Y. C. Meinwald, *J. Am. Chem. Soc.*, **82**, 3619 (1960), and preceding papers.

[40] E. Bergmann, L. Haskelberg, and F. Bergmann, *J. Org. Chem.*, **7**, 303 (1942).



is not expected to occur easily, the possibility exists that the intermediate, the substituted benzocyclobutadiene XXXV, will be sufficiently long-lived for the oxidation to the biphenylene derivative XXXVI to occur. However, when the reaction is attempted in boiling nitrobenzene, only starting materials are obtained. Furthermore, an attempt to react the *cis,cis* isomer XXVc with N-phenylmaleimide using aluminum chloride as catalyst does not result in formation of the desired product.

Attempts to prepare benzo[*b*]biphenylene (XXXVII) and 1,2-bis(isopropylidene)benzocyclobutene (XXXVIII) by reaction of the bisphosphorane XIV with *o*-phthalaldehyde and acetone, respectively, are unsuccessful.



Experimental Section

Melting points and boiling points are uncorrected. Analyses were done by Scandinavian Microanalytical Laboratory, Herlev, Denmark, or by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. The analyses of phosphorus compounds were done by Alfred Bernhardt Microanalytical Laboratories, Max Planck Institute, Mulheim (Ruhr), Germany. Infrared spectra were recorded by a Perkin-Elmer Infracord or by a Perkin-Elmer Model 337 grating infrared spectrophotometer. Ultraviolet and visible spectra were recorded by a Cary Model 14 recording spectrophotometer. The nmr spectra were determined using a Varian A-60 spectrometer. Chloroform-*d* was prepared by standard literature methods.[41,42] Solvents were purified by standard methods.

***trans*-1,2-Dibromobenzocyclobutene (VII).** A stirred, warm (60°) solution of 84.4 g (0.5 mole) of $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*o*-xylene in 550 ml of N,N-dimethylformamide (DMF) was treated with 200 g (1.3 moles) of sodium iodide according to the method of Cava, *et al.*[19] The crude dibromide VII obtained was treated with 35 g of bromine in 200 ml of carbon tetrachloride for 2 days. The bromine was destroyed with aqueous sodium thiosulfate; the organic layer was dried over magnesium sulfate and the solvent removed *in vacuo*. The oil obtained was distilled *in vacuo*, bp 95° (1.8 mm) or 70° (0.3 mm), and the entire bromine treatment was repeated. Finally the light yellow oil obtained was fractionally crystallized from petroleum ether (bp 30–60°) to afford 32.31 g (60%) of the pure dibromo compound VII, mp 50.5–52° (lit.[19] mp 52°). In succeeding fractions, 14.2 g (26%) of mixtures of *trans*- and *cis*-1,2-dibromobenzocyclobutene were obtained.

1,2-Bis(triphenylphosphonio)benzocyclobutene Dibromide (VIIIa). To a fire-dried flask, purged with nitrogen, were added 10.48 g (40 mmoles) of VII and 62.88 g (240 mmoles) of IX; the flask was then plunged into an oil bath at 100°. The stirred solution was warmed to 145° over a 1-hr period and then stirred for 24 hr at 145–155°. Care was taken to exclude all air and moisture. The slurry was cooled to *ca.* 40°; ether was added and the light tan powder obtained recrystallized from methylene chloride–ether to afford 30.80 g (98%) of the dibromide VIIIa as colorless plates, mp 228–230° slight dec. A further recrystallization gave an analytical sample (the salt must be dried at 100° to remove methylene chloride), mp 230.5–232° slight dec.

The infrared spectrum (KBr pellet) showed $\lambda_{\max}$ 3.22, 3.33, 3.41, 3.53, 6.16, 6.28, 6.75, 6.98, 7.62, 8.43, 8.63, 9.02, 10.03, 13.31, 13.78, and 14.57 μ. The ultraviolet spectrum (log ϵ in parentheses) had $\lambda_{\max}^{95\%\,\mathrm{EtOH}}$ 278 (3.86), 271.5 (3.92), 266 (3.81), 232 (sh, 4.06), and 230 mμ (sh, 4.07).

Anal. Calcd for $C_{44}H_{32}P_2Br_2$: C, 67.19; H, 4.61; P, 7.88; Br, 20.32. Found: C, 67.04; H, 4.73; P, 8.00; Br, 20.50.

Preparations similar to the one described above but carried out in the presence of air gave a mixture of salts and triphenylphosphine oxide (XI).

Upon admixture of a solution of the salt VIIIa in water–ethanol to 70% perchloric acid, the *diperchlorate salt* VIIIb precipitated as fine colorless needles, mp 278–280° dec. The nmr spectrum of VIIIb (in methylene chloride) showed absorption at 6.69 ppm (bm, H_a) and 7.63 ppm (bm, aromatic H) in relative ratio 1:17. The ultraviolet spectrum of VIIIb (log ϵ in parentheses) had $\lambda_{\max}^{95\%\,\mathrm{EtOH}}$ 277 (3.76), 269.5 (3.82), 264 (sh, 3.71), and 220 mμ (4.65).

Hydrolysis of the Salt VIIIa. A solution of 2.36 g (3 mmoles) of the salt VIIIa in 50 ml of distilled water mixed with a solution of 0.28 g (7 mmoles) of sodium hydroxide in 50 ml of water was refluxed for 9 hr, cooled to room temperature, and extracted with petroleum ether. The petroleum ether extracts were dried over magnesium sulfate, the solvent was removed, and the oil which remained was extracted with cyclohexane. The latter extract contained 0.04 g (13%) of benzocyclobutene (XII) which had $\lambda_{\max}^{C_6H_{12}}$ 271.5, 265.5, 260, and 255 mμ (sh) identical with that of authentic XII.[43] The remaining material was crystallized from benzene–petroleum ether to afford 1.50 g (91%) of colorless microneedles of XI, mp 155–156° (lit.[44] mp 156°), identical with an authentic sample of XI as shown by infrared comparison and mixture melting point determination.

1,2-Bis(triphenylphosphoranyl)benzocyclobutene (XIV). Preparations from the Salt VIIIa by Reaction with Nonaqueous Bases. A. *n*-Butyllithium in DMSO. To a solution of 0.086 g (0.11 mmole) of the salt VIIIa in 1 ml of anhydrous DMSO (this solution showed two peaks in the nmr: one at 6.7 ppm (m) and another at 7.8 ppm (m) in a relative ratio of 1:17) was added 0.15 ml of 1.46 *N* *n*-butyllithium (0.22 mmole). A deep red solution of the phosphorane XIV was obtained. This solution had an nmr spectrum that comprised a broad multiplet at 7.55 ppm, but no absorption between 7.0 and 4.7 ppm.

B. Potassium *t*-Butoxide in DMSO. A DMSO solution of the salt VIIIa showed nmr absorptions centered at 6.68 ppm (poorly resolved quartet, H_a's) and at 7.76 ppm (multiplet centered at 7.43 ppm with distinct maxima at 7.68 and 7.83 ppm, aromatic H's). Addition of 2 equiv of potassium *t*-butoxide to the foregoing gave a red solution of XIV whose nmr spectrum had a multiplet centered at 7.43 ppm with distinct maxima at 7.29, 7.47, and 7.55 ppm. A similar result was obtained with DMF as solvent. Other bases such as lithium ethoxide, sodium amide, and lithium N-methylpiperazide also reacted with VIIIa to form solutions of the phosphorane XIV.

C. Sodium Methoxide in Tetrahydrofuran (THF). A stirred slurry of 0.940 g (1.2 mmoles) of VIIIa in 30 ml of anhydrous THF was cooled to 0° under nitrogen and 0.110 g (2.4 mmoles) of sodium methoxide in 20 ml of anhydrous THF was added. After this solution slurry had been stirred for 2 hr at 0° and for 2 hr at room temperature, the colorless precipitate was filtered and thoroughly washed with ethanol–ether. This gave 0.226 g (90%) of sodium bromide.

Nmr Study of Reaction of the Salt VIIIa with Sodium Methoxide in Methanol. A methanol solution of the salt VIIIa showed absorp-

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(41) R. C. Lord, B. Nolin, and H. D. Stidham, *J. Am. Chem. Soc.*, **77**, 1365 (1955).

(42) M. H. Earing and J. G. Cloke, *ibid.*, **73**, 769 (1951).

(43) M. P. Cava and D. R. Napier, *ibid.*, **80**, 2255 (1958).

(44) R. Sauvage, *Compt. Rend.*, **139**, 674 (1904).

tions at 6.70 ppm (poorly resolved quartet, H_a's) and 7.62 ppm (bm, aromatic H's). The nmr tube was filled with nitrogen and 2 equiv of sodium methoxide was added. The following spectra were observed at the time intervals indicated. (a) After 5 min, aliphatic H's centered at 6.70 ppm were still present in about 50% of the original concentration. The aromatic absorptions were somewhat displaced with increased absorptions at high fields (around 7.3 ppm) and decreased absorption at low fields (around 7.9 ppm). A new peak appeared at 7.5 ppm due to the formation of triphenylphosphine oxide and the possible presence of a small amount of the bisphosphorane XIV. (b) After 15 min, less than 10% of the original peak centered at 6.7 ppm remained. The peak centered at 7.5 ppm, essentially the only one present (not including solvent), was quite broad and skewed to the right. (c) After 1 hr, the spectrum was essentially equivalent to the previous one except that the major peak had somewhat narrowed. Similar spectra were obtained after 2 hr and 1 day. An infrared spectrum confirmed the presence of triphenylphosphine oxide (XI).

Electron Spin Resonance of the Phosphorane XIV. A solution of 0.12 g (0.15 mmole) of the salt VIIIa in 1.5 ml of anhydrous DMSO was thoroughly purged with nitrogen, 0.2 ml of 1.46 *N* *n*-butyllithium (0.30 mmole) was added, and the red solution was transferred to a 2-mm optical density tube filled with nitrogen. The tube was evacuated and the esr spectrum determined.[45] It showed that no free radicals were present in any significant concentration.

Reactions of the Phosphorane XIV with Certain Benzaldehydes in Ethanol. A. With Benzaldehyde (XVIIb). A solution of lithium ethoxide prepared from 9.4 ml of 1.44 *N* *n*-butyllithium (13.5 mmoles) and 15 ml of anhydrous ethanol was added to a cooled solution (0°) of 4.72 g (6 mmoles) of the salt VIIIa in 80 ml of anhydrous ethanol. The mixture was stirred for 1 hr; a solution of 1.46 g (14 mmoles) of XVIIb in 20 ml of absolute ethanol was added. The reaction mixture was then stirred for 1 hr at 0°, 1.5 hr at room temperature, and 3 hr at 50–60°. After the solvent had been removed *in vacuo*, the semisolid residue was taken up in 150 ml of methylene chloride–ether, the organic solution was washed with water (two 50-ml portions), and finally dried over sodium sulfate. Removal of solvents on a steam bath left a semisolid that was chromatographed on a 1.5 × 75 cm column containing 100 g of Alcoa No. 71707 alumina packed in petroleum ether. The products obtained, eluent solvents in parentheses, were: (1) 0.16 g (13.9%) of *cis*-1-benzylidenebenzocyclobutene (XIXb) (petroleum ether) as a colorless oil, whose infrared spectrum showed λ_{max} 3.27, 3.41, 6.02, 6.25, 6.70, 6.92, 7.06, 7.36, 8.55, 9.25, 9.70, 10.00, 10.27, 10.93, 11.52, 11.75, 11.99, 13.36, 13.51, 14.20, and 14.41 μ; its ultraviolet spectrum (log ε in parentheses): $\lambda_{max}^{95\%\,EtOH}$ 321 (4.05), 307 (4.15), 293 (4.03), 279 (4.02), 241 (sh, 3.52), 232.5 (sh, 3.96), 225.5 (4.10), and 222 mμ (sh, 4.09); (2) 0.64 g (55.6%) of *trans*-1-benzylidenebenzocyclobutene (XVIIIb) (petroleum ether) as colorless microneedles, mp 124.5–126°, whose infrared spectrum (Nujol) showed λ_{max} 6.04, 6.30, 6.91, 8.50, 10.91, 11.40, 11.46, 13.16, 14.13, and 14.45 μ; the ultraviolet spectrum (log ε in parentheses): $\lambda_{max}^{95\%\,EtOH}$ 322.5 (4.33), 308.5 (4.45), 291 (4.28), 280.5 (4.25), 241.5 (3.57), 233.5 (4.02), 226.5 (4.12), and 220.5 mμ (4.09) (*Anal.* Calcd for $C_{15}H_{12}$: C, 93.71; H, 6.29; mol wt, 192. Found: C, 93.69; H, 6.33; mol wt (Rast), 182); (3) 0.05 g (3.2%) of triphenylphosphine (IX) (0–10% benzene–petroleum ether) as microneedles, mp 77–79° (lit.[46] mp 80°), which was identical with an authentic sample of IX, by infrared comparison and did not depress the melting point on admixture with an authentic specimen; (4) 2.98 g (89.1%) of triphenylphosphine oxide (XI) (ether) as colorless needles when crystallized from benzene–hexane, mp 154–156°, identical in all respects with an authentic sample; and (5) 0.32 g of a light tan polymer-like phosphonium salt (methanol).

B. With *p*-Nitrobenzaldehyde (XVIIa). To a solution of 2.36 g (3 mmoles) of the salt VIIIa in 40 ml of anhydrous ethanol, cooled to 0° and blanketed with nitrogen, was added a solution of lithium ethoxide (prepared by adding 3.8 ml (5.54 mmoles) of 1.46 *N* *n*-butyllithium to 12 ml of absolute ethanol) over a 15-min period. After stirring for 1 hr, a solution of 0.68 g (4.5 mmoles) of XVIIa in 20 ml of absolute ethanol was added dropwise. This mixture was stirred for 1 hr at 0° and for 4 hr at room temperature. The 0.25 g of *trans*-1-*p*-nitrobenzylidenebenzocyclobutene (XVIIIa) which precipitated during this time was isolated by filtration. The solvent from the reaction mixture was removed *in vacuo;* the residual oil was taken up in ether (300 ml) and the ether solution was washed with water (two 50-ml portions) and finally dried over sodium sulfate. After the solvents were removed, the semisolid was dissolved in a few milliliters of benzene and chromatographed on a 1.5 × 75 cm column containing 60 g of Fisher alumina packed in petroleum ether. The following products were obtained (eluent solvents in parentheses): (1) 0.08 g (10%) of IX (petroleum ether) as colorless needles from benzene–petroleum ether, mp 78–80°; (2) 0.24 g (34%) of *cis*-1-*p*-nitrobenzylidenebenzocyclobutene (XIXa) (20–30% benzene–petroleum ether) as a light yellow powder, mp 82–86°, after crystallization from hexane. (The melting point range could not be narrowed on multiple recrystallizations since the product existed in two clearly visible crystalline forms which always coprecipitated in varying amounts.)

The infrared spectrum (Nujol) had λ_{max} 6.02, 6.27, 6.64, 7.50, 9.01, 11.39, 11.55, 13.05, 13.25, 13.45, 13.82, 14.10, and 14.45 μ; the ultraviolet spectrum (log ε in parentheses): $\lambda_{max}^{95\%\,EtOH}$ 357 (4.02), 352.5 (4.03), 281 (sh, 3.54), 265.5 (sh, 3.74), 263.5 (3.75), 252 (3.76), 248 (sh, 3.78), and 242 mμ (3.80) (*Anal.* Calcd for $C_{15}H_{11}NO_2$: C, 75.94; H, 4.67; mol wt, 237. Found: C, 75.73; H, 4.81; mol wt (Rast), 234); (3) 0.14 g (55%) of XVIIIa (50% benzene–petroleum ether) as fluffy yellow needles when crystallized from benzene–hexane, mp 150.5–151.5°.

The infrared spectrum (Nujol) had λ_{max} 6.03, 6.26, 6.32, 6.62, 7.52, 9.01, 11.22, 11.53, 11.80, 12.03, 12.98, 14.02, and 14.52 μ; the ultraviolet spectrum (log ε in parentheses): $\lambda_{max}^{95\%\,EtOH}$ 359.5 (sh, 4.34), 355 (4.35), 353 (sh, 4.34), 348 (4.31), 270 (sh, 3.88), 264 (3.91), 262 (sh, 3.90), and 238.5 mμ (3.95) (*Anal.* Calcd for $C_{15}H_{11}NO_2$: C, 75.94; H, 4.67; mol wt, 237. Found: C, 76.04; H, 4.78; mol wt (Rast), 222); (4) trace amounts of other olefinic nitro-containing product(s) which could not be purified; (5) 1.67 g (82%) of XI (ether) as colorless needles from benzene–hexane, mp 153–154°; (6) 0.06 g (8.8%) of *p*-nitrobenzyl alcohol (ether–methanol) as pale yellow needles from chloroform–hexane, mp 89–90.5° (lit.[47] mp 93°), identical in all respects with an authentic specimen; and (7) 0.065 g of the brown glassy polymer salt (methanol).

C. With *p*-Bromobenzaldehyde (XVIIc). A mixture of 2.46 g (22 mmoles) of potassium *t*-butoxide in 50 ml of absolute ethanol was added to a solution of 7.08 g (9 mmoles) of the salt VIIIa in 75 ml of absolute ethanol cooled to 0° under an atmosphere of nitrogen. This solution was stirred for 1 hr at 0° and during this time potassium bromide precipitated. A solution of 3.70 g (20 mmoles) of XVIIc in 50 ml of absolute ethanol was then added dropwise and the mixture stirred for 2 hr at 0° and for 3 hr at 35–45°. The mixture that precipitated is filtered and digested with 25 ml of boiling benzene to dissolve the organic material. Subsequent filtration gave 1.62 g (76%) of potassium bromide. The benzene solution was concentrated to a few milliliters, and addition of hexane afforded 0.87 g of *trans*-1-*p*-bromobenzylidenebenzocyclobutene (XVIIIc), identical with the product later obtained (*vide infra*). The original mother liquors were concentrated *in vacuo*, and the residual oil was dissolved in 500 ml of methylene chloride–ether; the solution was washed with water (three 50-ml portions) and dried over sodium sulfate. The solvent was removed and the semisolid was taken up in carbon tetrachloride and chromatographed on a 2 × 100 cm column containing 120 g of Alcoa No. 71707 alumina packed in petroleum ether. The following products were obtained (eluent solvents in parentheses): (1) 0.80 g (32%) of *cis*-1-*p*-bromobenzylidenebenzocyclobutene (XIXc) (0–5% benzene–petroleum ether) as colorless microcrystals from 80% ethanol, mp 66–67°.

The infrared spectrum (KBr) had λ_{max} 3.26, 3.43, 6.00, 6.30, 6.71, 6.88, 6.94, 7.08, 7.16, 8,51, 9.08, 9.29, 9.90, 11.52, 11.62, 11.82, 12.18, 13.28, 13.98, and 14.34 μ; the ultraviolet spectrum (log ε in parentheses): $\lambda_{max}^{95\%\,EtOH}$ 326.3 (4.37), 311.5 (4.49), 300 (sh, 4.34), 294.5 (4.32), 285 (4.29), 231.5 (sh, 4.30), and 227.5 mμ (4.33) (*Anal.* Calcd for $C_{15}H_{11}Br$: C, 66.44; H, 4.09; Br, 29.47; mol wt, 271. Found: C, 66.15; H, 4.10; Br, 29.43; mol wt (Rast), 251); (2) 1.32 g (54.1%) of *trans*-1-*p*-bromobenzylidenebenzocyclobutene (XVIIIc) (5–10% benzene–petroleum ether) as a microcrystalline powder on recrystallization from 95% ethanol, mp 153–153.5°.

The infrared spectrum (KBr) had λ_{max} 3.29, 3.48, 3.52, 6.03, 6.30, 6.75, 6.90, 6.94, 7.05, 7.16, 7.48, 7.60, 8.48, 8.53, 8.75, 8.80, 9.00, 9.13, 9.36, 9.98, 10.04, 10.44, 10.72, 11.36, 11.91, 12.23, 13.22, 13.35, 13.94, and 14.82 μ; the ultraviolet spectrum (log ε in paren-

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(45) We sincerely thank Professor David Geske for performing this experiment.

(46) I. M. Heilbron, Ed., "Dictionary of Organic Compounds," Vol. III, Oxford Press, New York, N. Y., 1938, p 887.

(47) Reference 46, p 104.

theses): $\lambda_{max}^{95\%EtOH}$ 328 (4.59), 313 (4.62), 299.5 (4.40), 292.5 (4.41), 284 (4.37), 242 (3.67), 234.5 (4.07), 227.5 (4.14), and 222.5 mμ (sh, 4.09) (*Anal.* Calcd for $C_{15}H_{11}Br$: C, 66.44; H, 4.09; Br, 29.47; mol wt, 271. Found: C, 66.40; H, 4.17; Br, 29.36; mol wt (Rast), 261); (3) 4.66 g (91%) of XI (ether) as colorless needles from benzene–petroleum ether, mp 154–155°; (4) 0.22 g (6%) of *p*-bromobenzyl alcohol (XXVIIIc) (chloroform) as a somewhat impure colorless solid, identical with an authentic sample by infrared comparison; and (5) 0.25 g of the impure polymer salt as a light brown semisolid glass (methanol).

1-Bromo-2-*p*-nitrobenzylidenebenzocyclobutene (XX). A mixture of 0.24 g (1 mmole) of the *trans*-olefin XVIIIa, 0.16 g (1 mmole) of N-bromosuccinimide, and catalytic amounts of benzoyl peroxide in 12 ml of carbon tetrachloride was refluxed for 5 hr. After filtration, the solution was concentrated to 5 ml and chromatographed on a 1 × 50 cm column containing 13 g of Alcoa No. 71707 alumina packed in petroleum ether. The third 40-ml fraction of petroleum ether eluent contained 0.02 g (6.3%) of the product XX, 178–180.5°. A few recrystallizations from carbon tetrachloride–petroleum ether gave light yellow microcrystals, mp 182.5–183°.

The infrared spectrum (Nujol) had λ_{max} 6.00, 6.26, 6.62, 7.45, 7.49, 9.00, 11.17, 11.31, 11.47, 11.77, 11.90, 12.65, 13.08, 13.27, 13.42, and 14.35 mμ; the ultraviolet spectrum (log ε in parentheses): $\lambda_{max}^{95\%EtOH}$ 358 (sh, 4.21), 356.5 (4.22), 351.5 (sh, 4.22), 265 (sh, 3.77), 262 (sh, 3.79), and 257 mμ (sh, 3.81) with strong end absorption.

Anal. Calcd for $C_{15}H_{10}NO_2Br$: C, 56.98; H, 3.19. Found: C, 56.56; H, 3.47.

1-Bromo-1-(α-bromo-*p*-nitrobenzyl)benzocyclobutene (XXI). A solution of 0.24 g (1 mmole) of XVIIIa and 0.16 g (1 mmole) of bromine in 15 ml of carbon tetrachloride was refluxed until most of the bromine color had disappeared (14 hr). The mixture was concentrated to *ca.* 5 ml, and 15 ml of petroleum ether was added. Cream-colored plates of XXI (0.35 g, 85%) precipitated, mp 125–129°. A further crystallization from carbon tetrachloride–petroleum ether afforded an analytical sample of XXI in the form of colorless plates, mp 132–133°.

The infrared spectrum (Nujol) showed λ_{max} 6.22, 6.58, 7.43, 7.64, 8.55, 8.65, 9.01, 10.28, 11.50, 11.59, 12.07, 12.72, 13.18, 14.05, and 14.31 μ; the ultraviolet spectrum (log ε in parentheses): $\lambda_{max}^{95\%EtOH}$ 279 (3.98), 276.5 (4.00), 275 (4.00), and 273 mμ (3.99) with strong end absorptions; the nmr spectrum had absorptions at 3.80 (s, H_a's), 5.50 (s, H_b), 7.2 (cm, H_c's), 7.63 (ud, H_d's), and 8.22 ppm (ud, H_e's) in relative ratios of 2.1:1:4.3:2.3:2.1 with J_{de} = 8.2 cps.

Anal. Calcd for $C_{15}H_{11}NO_2Br_2$: C, 45.37; H, 2.79; N, 3.53; Br, 40.25; mol wt, 397. Found: C, 45.16; H, 2.86; N, 3.63; Br, 40.45; mol wt (Rast), 404.

***trans*-1-(α-Bromo-*p*-nitrobenzylidene)benzocyclobutene (XXII).** Bromine (0.16 g, 1 mmole) was added to 0.24 g (1 mmole) of the olefin XIXa in 15 ml of carbon tetrachloride, and the mixture refluxed for 36 hr. The solution was concentrated to 3 ml and treated with petroleum ether. A light tan semisolid precipitated which melts over a wide range even after repeated recrystallizations. Since an infrared spectrum showed no olefinic absorption, the material was chromatographed on a 1 × 50 cm column containing 12 g of Alcoa No. 71707 alumina. Using 60% benzene–petroleum ether as eluent, 0.22 g (60.6%) of XXII was obtained as light yellow needles, mp 148.5–150°. A recrystallization from carbon tetrachloride–petroleum ether afforded the analytical sample, mp 149.5–150.5°.

The infrared spectrum (Nujol) showed λ_{max} 6.09, 6.28, 6.64, 7.09, 7.14, 7.47, 8.05, 8.70, 9.02, 11.35, 11.62, 11.80, 13.03, 13.28, 14.09, and 14.48 μ; the ultraviolet spectrum (log ε in parentheses): $\lambda_{max}^{95\%\ EtOH}$ 352.5 (4.25), 348 (4.25), 344.5 (4.26), 342 (4.26), 336 (4.27), 262.5 (sh, 4.37), 258.5 (4.39), 255 (sh, 4.38), and 234.5 mμ (4.48). The nmr spectrum (chloroform-*d*) had absorptions at 3.90 (s, H_a's), 7.35 (m, H_b's), 7.78 (ud, H_c's), and 8.25 ppm (ud, H_d's) with J_{de} = 8.2 cps. The relative ratios were 1:1.94:1.15:1.01.

Anal. Calcd for $C_{15}H_{10}NO_2Br$: C, 56.98; H, 3.19; N, 4.43; Br, 25.28; mol wt, 316. Found: C, 56.93; H, 3.30; N, 4.43; Br, 25.34; mol wt (Rast), 320.

Isomerization of *cis*-1-*p*-Nitrobenzylidenebenzocyclobutene (XIXa). A. In DMF with Added Triphenylphosphine Oxide (XI). A solution of 0.12 g (0.5 mmole) of XIXa and 0.28 g (1 mmole) of XI in 60 ml of anhydrous DMF was stirred under nitrogen for 11 hr. The solution was poured into 500 ml of ice–water and the slurry was extracted with ether (three 150-ml portions). The combined organic layers were dried over sodium sulfate and the solvents were removed. The resulting solid mixture was chromatographed on 30 g of silica gel to give 0.08 g (67%) of the *trans* compound XVIIIa, mp 150–151.5°, identical with an authentic sample in all respects, and 0.04 g (33%) of unisomerized starting material XIXa.

B. In DMF Only. A mixture of 0.10 g of the isomer XIXa in 40 ml of anhydrous DMF was stirred for 12 hr at room temperature under an atmosphere of nitrogen, poured into 250 ml of ice–water, and worked up as in A above. The products obtained were 0.085 g (85%) of the unisomerized *cis* isomer XIXa and 0.015 g (15%) of the *trans* isomer XVIIIa.

Isomerization of *cis*-1-Benzylidenebenzocyclobutene (XIXb). A solution of 0.09 g (0.4 mmole) of the isomer XIXb and 0.22 g (0.8 mmole) of XI in 20 ml of anhydrous DMF was stirred under nitrogen for 12 hr at 25–30°. The mixture was worked up as in the previous cases except that 20 g of Fisher alumina was used. The products obtained were 0.063 g (70%) of the unisomerized starting material XIXb, 0.014 g (17%) of the *trans* isomer XVIIIb, and 0.22 g of XI.

Isomerization of *cis*-1-*p*-Bromobenzylidenebenzocyclobutene (XIXc). A solution of 0.190 g (0.7 mmole) of the olefin XIXc and 0.388 g (1.4 mmoles) of XI in 60 ml of anhydrous DMF was stirred for 12 hr at room temperature under a nitrogen atmosphere, poured into 400 ml of ice–water, and worked up as above except that Alcoa No. 71707 alumina was used. The products obtained were 0.130 g (68%) of the unisomerized starting material XIXc, 0.046 g (24%) of the *trans* isomer XVIIIc, and 0.370 g of XI.

1,2-Bis(benzylidene)benzocyclobutenes by Reaction of the Phosphorane XIV with Various Benzaldehydes. A. From *p*-Nitrobenzaldehyde (XVIIa). A stirred solution of 4.72 g (6 mmoles) of the dibromide VIIIa in 75 ml of freshly distilled DMF was cooled to −50° under an atmosphere of nitrogen, and a solution of lithium ethoxide was prepared from 8.2 ml of 1.46 *N* *n*-butyllithium (12.4 mmoles) and 8 ml of absolute ethanol was added. After stirring the deep red solution for 20 min, a solution of 2.12 g (14 mmoles) of XVIIa in 25 ml of dry DMF was added rapidly. The mixture was maintained at −50 to −30° for 2 hr, at 0° for 3 hr, and then poured into 1 l. of ice–water. The slurry was extracted with methylene chloride (two 300-ml portions) and ether (two 300-ml portions); the combined organic layers were washed with water (four 150-ml portions) and dried over sodium sulfate. After removal of the solvents the semisolid residue obtained was taken up in 75 ml of benzene. The insoluble material was filtered to give 0.39 g of slightyl impure *cis,cis*-1,2-bis(*p*-nitrobenzylidene)benzocyclobutene (XXVa), identical with the material obtained by chromatography (*vide infra*). The benzene solution was concentrated to 40 ml and chromatographed on a 2 × 100 cm column containing 140 g of Alcoa No. 71707 alumina. Elution afforded the following products (eluent solvents in parentheses): (1) 0.06 g (4%) of IX (petroleum ether) which crystallized from 95% ethanol as colorless needles, mp 77°, identical with an authentic sample of IX by infrared comparison and mixture melting point determination; (2) 0.14 g of XVIIa (20–30% benzene–petroleum ether) as a light yellow solid; (3) 0.19 g (12%) of XVIIIa (60–70% benzene–petroleum ether) as yellow needles from 95% ethanol, mp 150–151°, identical with an authentic sample (*vide supra*); (4) 0.62 g (27.9%)[48] of *cis,trans*-1,2-bis(*p*-nitrobenzylidene)benzocyclobutene (XXVIa) (50% benzene–petroleum ether) as a light yellow powder, mp 190–210°. The wide melting point range indicated the presence of small amounts of the *cis,cis* isomer XXVa. All attempts at purification either by recrystallization or by chromatography afforded a mixture of the two isomers. However, the product was at least 90% pure as shown by its distinct nmr (see Table II) and infrared spectra. The ultraviolet spectrum (log ε in parentheses) showed $\lambda_{max}^{CHCl_3}$ 381 (sh, 4.36), 371.5 (4.38), and 247.5 mμ (4.33); the infrared spectrum (Nujol) had λ_{max} 5.98, 6.08, 6.26, 6.66, 7.41, 9.00, 11.40, 11.59, 11.69, 12.01, 13.33, 13.55, 14.38, and 14.55 μ; (5) 0.56 g (0.95 g total, 42.8%) of *cis,cis*-1,2-bis(*p*-nitrobenzylidene)benzocyclobutene (XXVa) (90% benzene–petroleum ether) as light yellow needles from chloroform–benzene, mp 282–284°.

The infrared spectrum (Nujol) had λ_{max} 6.09, 6.27, 6.34, 6.62, 7.47, 9.00, 11.32, 11.44, 11.51, 11.72, 13.41, 14.35, and 14.56 μ; the ultraviolet spectrum (log ε in parentheses): $\lambda_{max}^{CHCl_3}$ 381 (sh, 4.58), 378 (4.59), 374 (4.59), 368 (4.58), 278 (sh, 4.09) and 246 mμ (4.46) (*Anal.* Calcd for $C_{22}H_{14}N_2O_4$: C, 71.35; H, 3.81; N, 7.56. Found: C, 71.06; H, 4.06; N, 7.44); (6) 0.06 g (2.5%) of *trans,trans*-1,2-bis(*p*-nitrobenzylidene)benzocyclobutene (XXVIIa)

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(48) Difficulty in separating these three isomers probably results in considerable manipulation losses.

as red-orange needles on crystallization from acetone, mp 263–264.5° dec.

No nmr could be taken because of its low solubility in all organic solvents. The infrared spectrum (Nujol) showed λ_{max} 6.02, 6.10, 6.28, 6.63, 7.46, 7.65, 8.11, 9.01, 9.85, 11.63, 11.75, 13.27, 13.51, and 14.54 μ; the ultraviolet spectrum (log ϵ in parentheses): $\lambda_{max}^{CHCl_3}$ 436 (sh, 4.35), 432.5 (4.36), 415 (sh, 4.30), 358.5 (sh, 4.21), 351 (4.27), 330 (4.18), 311.5 (4.17), 302 (4.16), 284 (sh, 4.07), and 265 mμ (4.09) (*Anal.* Calcd for $C_{22}H_{14}N_2O_4$: C, 71.35; H, 3.81; N, 7.56. Found: C, 69.94; H, 3.78; N, 7.31); (7) 3.13 g (93.7%) of XI (ether) as colorless microneedles on recrystallization from benzene–petroleum ether, mp 154.4–155.5°, identical with an authentic sample in all respects. A methanol solution of the product showed an nmr peak at 7.50 ppm; (8) 0.06 g (2.8%) of XXVIIIa (chloroform), as pale yellow needles, identical with an authentic sample by infrared comparison; and (9) 0.40 g of a light brown semisolid glass (methanol). The infrared spectrum indicated the presence of phosphonium and nitro groups.

Similar though less easily purified mixtures were obtained when the reaction was carried out in DMSO using *n*-butyllithium as base or in DMF using lithium N-methylpiperazide as base.

B. From Benzaldehyde (XVIIb). A solution of the bisphosphorane XIV was prepared in the usual manner from 4.72 g (6 mmoles) of the salt VIIIa in DMF. To this cold (−50°) solution was added 1.48 g (14 mmoles) of XVIIb in 25 ml of freshly distilled DMF. The resulting solution was maintained at −50° for 3.5 hr, at 0° for 2.5 hr, and finally at 40° for 2 hr. The mixture was worked up as before except that chromatographic separation was accomplished on a 2 × 100 cm column packed with 110 g of Fisher alumina.[49] The following products were obtained, eluent solvents in parentheses: (1) 0.10 g (1%) of XIXb (petroleum ether) as a colorless oil, identical with the product obtained from the reaction in ethanol (*vide supra*); (2) 0.15 g (9%) of IX (petroleum ether); (3) 0.20 g (17.4%) of XVIIIb (petroleum ether) as colorless microcrystals from 95% ethanol, mp 124–125°, identical with the product obtained when ethanol was used as solvent (*vide supra*); (4) 0.84 g (50%) of *cis,cis*-1,2-dibenzylidenebenzocyclobutene (XXVb) as colorless needles when crystallized from 95% ethanol. (Nmr analysis of the product obtained directly from the chromatographic column suggested the presence of a small amount of another isomer since a minor absorption in the methylene hydrogen region at 6.25 ppm and general smearing of the other peaks were seen before crystallization.) The melting point was 113–114°.

The infrared spectrum (Nujol) showed λ_{max} 6.07, 6.25, 6.71, 6.90, 7.00, 8.60, 9.23, 9.75, 9.92, 10.82, 11.52, 11.62, 11.80, 12.92, 13.10, 13.64, and 14.32 μ; the ultraviolet spectrum (log ϵ in parentheses): $\lambda_{max}^{95\%\,EtOH}$ 335 (4.21), 332.5 (4.22), 307 (4.13), 282 (4.26), 238.5 (4.35), and 232.5 mμ (4.39) (*Anal.* Calcd for $C_{22}H_{16}$: C, 94.25; H, 5.75; mol wt, 280. Found: C, 94.25; H, 5.72; mol wt, 270 (Rast), 280 (mass spectrum));[50] (5) 0.22 g of a light yellow oil (20–30% benzene–petroleum ether) which appeared to be a mixture of the olefin XXVb and, according to the nmr in CCl_4, a good deal of 1-ethoxy-2-benzylidenebenzocyclobutene (XXIX) since it showed peaks at 1.31 (t, H_a), 3.63 (q, H_b), 5.95 (s, H_c), 6.80 (s, H_d), and 7.50 ppm (cm, H_e) in relative ratios of 3.8:2.2:1:1:17. All attempts to purify this oil failed; (6) 0.10 g of the nearly colorless starting aldehyde XVIIIb (40–100% benzene–petroleum ether) as an oil; (7) 3.02 g (90.4%) of XI (ether) as colorless microneedles from benzene–petroleum ether, mp 155–156°; and (8) 0.42 g of a light brown polymer salt (methanol).

C. From *p*-Bromobenzaldehyde (XVIIc). A cold solution of the bisphosphorane XIV was prepared as above from 7.87 g (10 mmoles) of the salt VIIIa in 60 ml of DMF except that 2.68 g (24 mmoles) of potassium *t*-butoxide in 80 ml of dry DMF was used as base. After adding 4.44 g (24 mmoles) of XVIIc, the mixture was stirred for 1 hr at −50 to −30°, for 1.5 hr at ice-bath temperature, and for 4 hr at 30–40°. The mixture was worked up as in A except that, when the solvent extracts were evaporated to about 100 ml, a crystalline precipitate of the olefin XXVc was formed which could be filtered off and recrystallized from benzene–hexane to afford 1.10 g of colorless needles, mp 191–192°, identical with the product obtained later (*vide infra*). Chromatographic separation was accomplished on a 2.5 × 100 cm column containing 140 g of Alcoa No. 71707 alumina. The following products were obtained, eluent solvents in parentheses: (1) 0.10 g (3.7%) of XIXc (3–5% benzene–petroleum ether) as colorless microneedles from 95% ethanol, mp 65–66°, identical with an authentic sample (*vide supra*); (2) 0.16 g (5.8%) of XVIIIc (5–10% benzene–petroleum ether) as a colorless powder from absolute ethanol, mp 152–153°, identical with the product obtained from reaction in ethanol (*vide supra*); (3) 1.74 g (40%) of *cis,trans*-1,2-bis(*p*-bromobenzylidene)benzocyclobutene (XXVIc) (12–15% benzene–petroleum ether) as colorless needles when crystallized from benzene–hexane, mp 150–151°.

The infrared spectrum (KBr) showed λ_{max} 3.28, 3.39, 5.25, 6.06, 6.28, 6.70, 6.84, 7.14, 7.35, 7.67, 7.86, 8.62, 8.94, 9.10, 9.32, 9.89, 10.32, 11.05, 11.41, 11.50, 11.72, 12.06, 12.24, 12.35, 12.80, 13.26, 13.45, 14.06, and 14.65 μ; the ultraviolet spectrum (log ϵ in parentheses): $\lambda_{max}^{95\%\,EtOH}$ 335.5 (4.31), 280 (sh, 4.52), 240.5 (sh, 4.34), 233 (4.38), 224.5 (4.37), and 219 mμ (4.38) (*Anal.* Calcd for $C_{22}H_{14}Br_2$: C, 60.30; H, 3.22; Br, 36.48; mol wt, 438. Found: C, 60.43; H, 3.38; Br, 36.63; mol wt (Rast), 421); (4) 1.09 g (2.19 g total, 50%) of *cis,cis*-1,2-bis-(*p*-bromobenzylidene)benzocyclobutene (XXVc) (15–25% benzene–petroleum ether) as light cream needles which were recrystallized from carbon tetrachloride–hexane to afford colorless needles, mp 191–192°.

The infrared spectrum (KBr) showed λ_{max} 3.27, 3.32, 5.28, 6.04, 6.29, 6.35, 6.87, 7.00, 7.12, 7.69, 7.84, 8.80, 8.96, 9.34, 9.92, 10.72, 11.24, 11.68, 11.93, 12.21, 12.32, 13.19, 13.41, and 14.17 μ; the ultraviolet spectrum (log ϵ in parentheses): $\lambda_{max}^{95\%\,EtOH}$ 340.5 (4.55), 317.5 (sh, 4.43), 303 (sh, 4.42), 286 (4.49), 241.5 (4.52), 235.5 (4.51), and 218 mμ (4.54) (*Anal.* Calcd for $C_{22}H_{14}Br_2$: C, 60.30; H, 3.22; Br, 36.48; mol wt, 438. Found: C, 60.21; H, 3.32; Br, 36.56; mol wt (Rast), 405); (5) a colorless crystalline phosphorus-containing product (30% benzene–petroleum ether) which was recrystallized from carbon tetrachloride–petroleum ether to afford 0.15 g of colorless needles, mp 162.5–163.5°. An nmr spectrum (chloroform-*d*) exhibited a 22-line multiplet centered at 7.55 ppm.

Anal. Found: C, 73.55, 73.69; H, 5.04, 4.95; P, 10.46; mol wt (Rast), 292.

An empirical formula of $C_{18}H_{15}PO_2$ was calculated, but the structure is unknown; (6) 0.65 g of XVIIc (benzene–ether), recovered as colorless microneedles; (7) 5.15 g (98%) of XI (ether) as colorless microneedles from benzene–hexane, mp 155°; (8) trace amounts of *p*-bromobenzyl alcohol (XXVIIIc) (chloroform), identical with an authentic sample by infrared comparison; and (9) 0.20 g of the light brown polymeric phosphonium salt (methanol).

D. Reaction with Other Aldehydes and Ketones. Treatment of the bisphosphorane XIV with acetone or *o*-phthalaldehyde afforded olefinic products, but none of these could be separated and identified. That some of the desired benzo[*b*]biphenylene (XXXVII) was obtained in the latter case was indicated by the formation of a red complex when the small amounts of hydrocarbon oil were treated with 2,4,7-trinitrofluorenone.[51] In this case larger size hydrocarbon products were also indicated.

Oxidation of the Bisbenzylidene Compound XXVb with Periodate–Permanganate under Neutral Conditions.[52] To a rapidly stirred solution–slurry of 0.09 g (0.56 mmole) of potassium permanganate, 3.22 g (14 mmoles) of potassium metaperiodate, and 1.0 g (8.3 moles) of magnesium sulfate in 80 ml of water, was added a solution of 0.22 g (0.8 mmole) of the olefin XXVb in 60 ml of purified *p*-dioxane and 40 ml of benzene. The solution was stirred for 1 day and the organic layer was separated and continuously extracted with ether. The ether layer was dried over sodium sulfate, and the solvents were removed to afford a gummy product which was chromatographed on a 1.5 × 60 cm column containing 35 g of silica gel packed in petroleum ether. Elution afforded 0.12 g (60% chloroform–benzene as eluent) of benzoic acid which was crystallized from water to give colorless needles, mp 120–121°, mmp 120–122°, identical in all respects with an authentic specimen. When acetone–chloroform was used as eluent, 0.06 g (46%) of phthalic acid was obtained, mp 189–191° dec (lit.[53] mp 191° dec).

A similar oxidation of the olefin XXVa afforded only starting materials.

Chromic Oxide Oxidation of Bisbenzylidene Products. A. Compound XXVa. A slurry of 0.30 g (0.8 mmole) of the olefin XXVa in 15 ml of glacial acetic acid was added to a solution of

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[49] To obtain the separation reported here, a second chromatography of the early fractions is generally necessary.

[50] We sincerely thank Mr. L. R. Jimenez, B. F. Goodrich Co., Brecksville, Ohio, for this determination.

[51] W. Baker, J. W. Barton, J. F. W. McOmie, and R. J. G. Searle, *J. Chem. Soc.*, 2633 (1962).

[52] According to the procedure of R. U. Lemieux and E. von Rudloff, *Can. J. Chem.*, 33, 1701, 1704, 1714 (1955).

[53] Reference 46, 1938, p 475.

0.40 g (4 mmoles) of chromium(VI) oxide in 30 ml of glacial acetic acid and 1 ml of water. The mixture was heated at 90–100° for 3 hr and then poured into 200 ml of ice–water. This mixture was continuously extracted with ether for 5 days and the resulting organic layer dried over sodium sulfate. Removal of the solvents and chromatography of the residue on 35 g of silica gel afforded 0.23 g (85%) of *p*-nitrobenzoic acid (80–100% chloroform–benzene as eluent) which was crystallized from water to give yellow leaflets, mp 240–240.5° (lit.[54] mp 238°), and 0.10 g (77%) of phthalic acid (acetone–chloroform as eluent), mp 191° dec, which was identical with the material previously obtained (*vide supra*). Also obtained were 0.03 g of unreacted starting material and *ca.* 0.02 g of a ketone-containing product (infrared) which could not be purified.

B. Compound XXVIa. An oxidation similar to that in A resulted in the formation of 0.14 g (52%) of *p*-nitrobenzoic acid and 0.06 g (46%) of phthalic acid as well as some of the starting material XXVIa.

Isomerization of the *cis,trans*-Bisbenzylidene Compounds. A. The Olefin XXVIa. A solution of 0.11 g (0.3 mmole) of the olefin XXVIa and 0.17 g (0.6 mmole) of XI in 40 ml of anhydrous DMF was stirred under nitrogen for 48 hr at room temperature. When the solution was poured into 150 ml of ice–water, a yellow precipitate formed, which, when filtered and crystallized from benzene–carbon tetrachloride, gave 0.075 g (68%) of the *cis,cis* isomer XXVa, mp 282–284°, identical with an authentic sample by infrared comparison. The benzene–carbon tetrachloride solution was evaporated to dryness and *ca.* 0.03 g of the slightly impure starting material XXVIa was obtained. By extracting the water solution with ether, 0.14 g (82.4%) of the oxide XI was obtained.

A similar, though less facile, isomerization could be accomplished in boiling solvents such as acetone, benzene, and chloroform.

B. The Olefin XXVIc. A solution of 0.11 g (0.25 mmole) of the *cis,trans* isomer XXVIc and 0.14 g (0.5 mmole) of the compound XI in 15 ml of anhydrous DMF was treated as in A. The ice–water slurry was extracted with ether (three 100-ml portions), and the combined ether solutions were dried over sodium sulfate. The ether was evaporated, and the semisolid mixture obtained was chromatographed on a 1 × 50 cm column containing 20 g of Alcoa No. 71707 alumina to afford 0.066 g (60%) of the unisomerized *cis,trans* isomer XXVIc, 0.015 g (13.6%) of the isomerized *cis,cis* isomer XXVc, and 0.13 g of the oxide XI.

Dipole Moments of *cis,cis*- and *cis,trans*-Bisbenzylidene Compounds XXVc and XXVIc.[55] Dielectric constant measurements of the compounds XXVc and XXVIc in solvent carbon tetrachloride at 25 ± 0.01° provide the data necessary to obtain dipole moments calculated by the method of Halverstadt and Kumler.[56] The terms P_{E_2} and P_{A_1} are calculated by the methods reported in the literature (ref 57 and 58, respectively). According to the above, for XXVc and XXVIc, $\mu = 0.69 \pm 0.18$ and 2.301 ± 0.017 D., respectively. The less precise index of refraction method[59,60] gives, correspondingly, $\mu = 0.70 \pm 0.30$ and 2.21 ± 0.12 D.

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(54) Reference 46, p 100.

(55) We sincerely thank Professor C. F. Wilcox, Jr. for his help in obtaining the dipole moments.

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The Isomerization of Perfluoro-α,ω-bisazomethines

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Abstract: Perfluoro-α,ω-bisazomethines isomerize readily in the presence of fluoride ions to produce the corresponding terminal trifluoromethylbisazomethines. In general, an SN2′ mechanism is thought to be operative in these isomerizations; however, the results indicate that, in some cases, this may not be true. The geometrical isomerization of some of the materials is discussed in terms of the F^{19} nuclear magnetic resonance spectral data. The spectral properties of several novel perfluorobisazomethines are reported.

We[1] have recently reported the preparation of several perfluoro-α,ω-bisazomethines from the photolysis of tetrafluoro-2,3-diazabuta-1,3-diene in the presence of fluoroolefin or fluorocarbene coreactants.

Fluoroolefins containing terminal double bonds have been shown to isomerize in the presence of fluoride ion.[2] No such isomerization has yet been reported for perfluoroazomethines, although the terminal $CF_2{=}N$ group is susceptible to attack by fluoride ion as indicated by the dimerization of perfluoro-2-azapropene, $CF_3N{=}CF_2$.[3]

Results and Discussion

Perfluoro-2,4-diazapenta-1,4-diene (I) and perfluoro-2,5-diazahexa-1,5-dienes[1] have been found to isomerize readily in the presence of fluoride ions to the corresponding bis(trifluoromethyl)carbodiimide (II) and 2,5-diazahexa-2,4-dienes, respectively. In general, treatment of a perfluoro-α,ω-bisazomethine with cesium

$$\underset{\text{I}}{CF_2{=}NCF_2N{=}CF_2} \xrightarrow{F^-} \underset{\text{II}}{CF_3N{=}C{=}NCF_3}$$

$$CF_2{=}NCFXCFXN{=}CF_2 \xrightarrow{F^-} CF_3N{=}CXCX{=}NCF_3$$

$$X = F, CF_3$$

fluoride causes complete isomerization; however, partially isomerized material or starting material was obtained in some cases. The boiling points of the isomerized bisazomethines were generally observed (see Table I) to be lower than those of the α,ω-bisazomethine starting materials. This observation is consistent with the boiling point differences noted by Miller[2] for terminal and internal perfluorodienes.

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