

mass spectrum, infrared (Nujol and in carbon tetrachloride), and mixture melting point comparison with a sample prepared independently by oxidation with 30% hydrogen peroxide of the reaction mixture obtained from *t*-butylmagnesium chloride (2 moles) and phosphorus trichloride (1 mole).<sup>2</sup>

*Anal.* Calcd. for  $C_8H_{18}ClOP$ : C, 48.86; H, 9.23; Cl, 18.03; P, 15.75. Found: C, 48.84; H, 9.23; Cl, 18.02; P, 15.57.

The mass spectrum of compound I, determined at approximately 10 e.v. with an ionizing current of 20  $\mu$ a., showed significant peaks at  $m/e = 198$  and 196 (molecular weight ions) in the correct relative intensities for the chlorine isotopic distribution, and two large fragmentation peaks at 139 and 141 which arise from the loss of one *t*-butyl group from the parent compound.

The proton magnetic resonance spectrum of I, obtained on a Varian A-60 instrument in carbon tetrachloride solution, showed only a doublet at 1.25 and 1.52 p.p.m. downfield from tetramethylsilane. The observed  $J_{P-H}$  of 17 c.p.s. is in excellent agreement with assigned values obtained<sup>3a,b</sup> from more complex spectra.

A second product isolated from the alkylation of white phosphorus with *t*-butyl chloride was identified as di-*t*-butylphosphine oxide<sup>4</sup> by its infrared spectrum ( $P-H$ , 2300  $cm^{-1}$ , s;  $P=O$ , 1150  $cm^{-1}$ , vs; in Nujol), its mass spectrum ( $m/e = 162$  and 105), and by oxidation with air or bromine to di-*t*-butylphosphinic acid, m.p. 208–209.5° (lit.<sup>2</sup> 208–210°),  $m/e = 178$ . The factors determining the relative amounts of these two alkylation products have not yet been completely established.

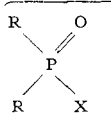
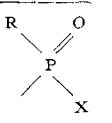
Other alkyl halides and Lewis acids also alkylate elemental phosphorus. With *t*-butyl bromide and aluminum tribromide, di-*t*-butylphosphinic bromide (II), m.p. 98–99°, was obtained. The structure of II was established by its mass spectrum, which had significant peaks at  $m/e = 240$  and 242 (molecular weight ions), 183 and 185 (molecular weight ions minus one *t*-butyl group), with both sets of relative intensities having the correct bromine isotopic ratio, by identical infrared spectra in Nujol and an undepressed mixture melting point with a sample prepared unambiguously from phosphorus tribromide and *t*-butylmagnesium bromide by a procedure similar to that utilized for compound I. The n.m.r. spectrum of II was identical with that of I. Ferric chloride and titanium tetrachloride also effected alkylation of white phosphorus with *t*-butyl chloride although much lower yields of I (about 3%) were obtained. Zinc chloride, zirconium tetrachloride, and mercuric chloride gave no alkylation under these conditions.

The alkylation of white phosphorus with *t*-amyl chloride gave di-*t*-amylphosphinic chloride ( $m/e = 224, 226; 153, 155$ ), di-*t*-butylphosphinic chloride ( $m/e = 196, 198; 139, 141$ ), and *t*-amyl-*t*-butylphosphinic chloride ( $m/e = 210, 212; 153, 155; 139, 141; 71$ ) as well as the corresponding secondary phosphine

oxides. Several recent papers<sup>5–7</sup> and older literature<sup>3</sup> report similar disproportionations with *t*-amyl chloride and other tertiary chlorides under the influence of aluminum trichloride.

White phosphorus may be alkylated with other alkyl chlorides. For example, in the presence of aluminum chloride the elemental phosphorus was entirely consumed upon the addition of 1.5 moles of either isopropyl, *n*-butyl, cyclohexyl, or *n*-octyl chlorides. The mass spectra of the crude acid hydrolysis products showed significant peaks at the  $m/e$  of the corresponding phosphinic acids since these phosphinic halides, if formed, would be destroyed by the acid hydrolytic work-up procedure employed. The major  $m/e$  values obtained from the crude organic product in each of these instances are shown in Table I. In all cases,

TABLE I

R	X	$m/e$	
			
<i>t</i> -C <sub>4</sub> H <sub>9</sub>	Cl	196, 198	139, 141
<i>t</i> -C <sub>4</sub> H <sub>9</sub>	Br	240, 242	180, 185
<i>t</i> -C <sub>4</sub> H <sub>9</sub>	OH	178	121
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	Cl	196, 198	139, 141
<i>i</i> -C <sub>3</sub> H <sub>7</sub>	OH	150	107
C <sub>6</sub> H <sub>11</sub>	OH	230	147
<i>n</i> -C <sub>8</sub> H <sub>17</sub>	OH	290	177
<i>t</i> -C <sub>6</sub> H <sub>11</sub>	Cl	224, 226	153, 155

the principal fragmentation observed during the mass spectrographic analysis was the loss of one alkyl group from the parent molecule.

Control experiments run without alkyl halide failed to produce any evidence of the presence of phosphorus chlorides. White phosphorus appears to be unchanged by the action of aluminum chloride under the reaction conditions.

**Acknowledgment.**—The author is sincerely grateful to Dr. Edward J. McNelis for stimulating discussion and encouragement, Dr. A. P. Stuart for suggesting the problem, and Mr. David Baugher for the excellent mass spectrographic analyses.

(5) T. H. Siddall and C. A. Prohaska, *J. Org. Chem.*, **28**, 2908 (1963).

(6) S. H. Metzger, O. H. Basedow, and A. F. Isbell, *ibid.*, **29**, 627 (1964).

(7) G. J. Karabatsos, F. L. Vane, and S. Meyerson, *J. Am. Chem. Soc.*, **85**, 733 (1963).

RESEARCH AND DEVELOPMENT DIVISION HOWARD P. ANGSTADT  
SUN OIL COMPANY  
MARCUS HOOK, PENNSYLVANIA

RECEIVED SEPTEMBER 19, 1964

## 1,2-Bis(triphenylphosphoranyl)benzocyclobutene

Sir:

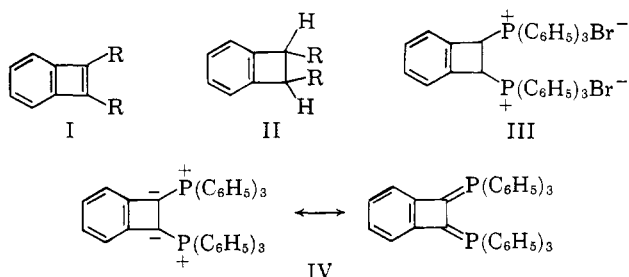
Efforts to obtain isolable derivatives of benzocyclobutadiene (I) as well as dianions of benzocyclobutadienes encouraged an investigation of the preparation and properties of a number of benzocyclobutenes of the type II ( $R = -NO_2$ ,  $-P^+(C_6H_5)_3Br^-$ ,  $-SO_2Ar$ ). This communication reports the synthesis of *trans*-1,2-bis(triphenylphosphonium)benzocyclobutene dibromide

(2) P. C. Crofts and G. M. Kosolapoff, *J. Am. Chem. Soc.*, **75**, 3381 (1953).

(3) (a) J. B. Hendrickson, M. L. Maddox, J. J. Sims and H. D. Kaesz, *Tetrahedron*, **20**, 449, (1964); (b) S. L. Manatt, G. L. Juvinall, and D. D. Elleman, *J. Am. Chem. Soc.*, **85**, 2664 (1963).

(4) The yield of this product is not known exactly, but it is estimated from an uncalibrated v.p.c. tracing to be of the same magnitude as the phosphinic chloride.

(III) and its successful transformation to the title compound IV.



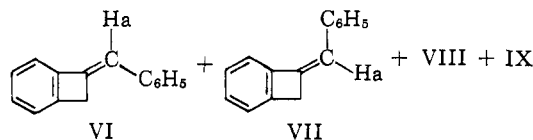
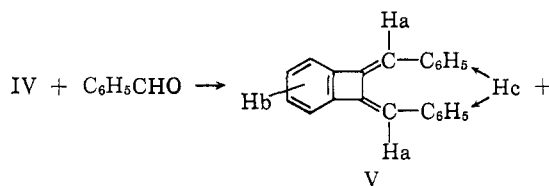
When *trans*-1,2-dibromobenzocyclobutene<sup>1</sup> is stirred under nitrogen with a 3-fold excess of triphenylphosphine at 150–160° for 24 hr., a nearly quantitative yield of a colorless powder (from methylene chloride-ether) of the salt III is obtained; m.p. 230.5–232°;  $\lambda_{\text{max}}^{\text{EtOH}}$  278.5  $\mu$  (log  $\epsilon$  3.86), 271.5 (3.92), 266 (3.81), 232 (sh, 4.06), and 230 (sh, 4.07). *Anal.* Calcd. for  $\text{C}_{44}\text{H}_{36}\text{Br}_2\text{P}_2$ : C, 67.19; H, 4.61; Br, 20.32; P, 7.88. Found: C, 67.07; H, 4.73; Br, 20.50; P, 8.00.

The n.m.r. spectrum<sup>2</sup> of compound III in dimethyl sulfoxide (DMSO) shows absorption at 6.80 (broad unresolvable quartet assigned to aliphatic H) and 7.80 p.p.m. (broad multiplet assigned to aromatic H) in the ratio 1:17.

Treatment of the salt III (1 equiv.) with either *n*-butyllithium (DMSO as solvent) or freshly prepared lithium ethoxide (dimethylformamide, DMF, as solvent) (2 equiv.) affords immediately a deep red solution of the bis-ylide IV which decomposes to a dark brown tar quite rapidly at room temperature, but appears to be quite stable at –40° for at least several hours. The n.m.r. spectrum (DMSO as solvent) of the solution of IV shows *only* a broad multiplet whose center is shifted upfield (relative to III) to 7.55 p.p.m. *No absorption is visible between 7.2 and 5.3 p.p.m.* Since triphenylphosphine absorbs at 7.22 p.p.m. in the n.m.r. (solvent, DMSO), it appears that considerable stability is afforded IV *via* electron “delocalization” within the pseudo 10 $\pi$ -electron benzocyclobutadiene dianion system.<sup>3</sup> The bis-ylide IV shows no absorption in its e.s.r. spectrum.<sup>4</sup>

A DMF solution of IV, under an atmosphere of nitrogen, when treated with excess benzaldehyde for 3.5 hr. at –50°, 2.5 hr. at 0°, and finally 2 hr. at 25–30°, affords several products. A conventional work-up of the reaction mixture gives a light yellow semisolid which was chromatographed on alumina. The following products were those obtained (elutents in parentheses) and characterized: (a) *cis*-1-benzylidenebenzocyclobutene (VII) (*ca.* 1%) (30–60° petroleum ether) as a colorless oil; (b) *trans*-1-benzylidenebenzocyclobutene (VI) (11%) (petroleum ether) as colorless plates from petroleum ether, m.p. 124.5–125.5° (*Anal.* Calcd. for  $\text{C}_{15}\text{H}_{12}$ : C, 93.71; H, 6.29; mol.

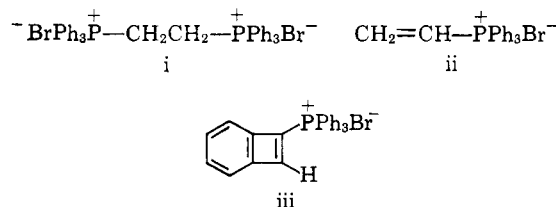
wt., 192. Found: C, 93.69; H, 6.29; mol. wt. (Rast), 182); (c) triphenylphosphine (VIII) (petroleum ether) in 17% yield (based on the assumption of a  $\beta$ -elimination of VIII from the possible monoanion derivable from the salt III, a reaction possible for 1,2-diphosphonium salts<sup>5</sup>); (d) *trans,trans*-1,2-dibenzylidenebenzocyclobutene (V) (50%) (10% benzene-petroleum



ether) as colorless needles from 95% ethanol, m.p. 114–115° (*Anal.* Calcd. for  $\text{C}_{22}\text{H}_{16}$ : C, 94.27; H, 5.76; mol. wt., 280. Found: C, 94.01; H, 5.72; mol. wt. (Rast), 270); (e) triphenylphosphine oxide (IX) (ether) in 90% yield; (f) a flaky polymeric salt (methanol) containing the phosphonium group (infrared) which melts over a wide range.

The stereochemistry of VI and VII is based on the n.m.r.<sup>6</sup> and infrared<sup>7</sup> spectra of these compounds, and agrees well with the usual predominance of the *trans* isomer in Wittig reactions.<sup>8</sup> These two products

(5) G. Wittig, H. Eggers, and P. Duffner, *Ann.*, **619**, 10 (1958). They found that 1,2-bis(triphenylphosphonium)ethylene dibromide (i) was transformed into the  $\beta$ -elimination product ii and triphenylphosphine when treated with phenyllithium. A similar reaction of salt III would produce the

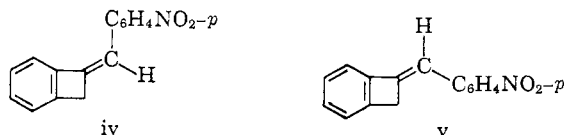


benzocyclobutadiene iii and triphenylphosphine. Attempts are being made to trap iii.

(6) See (a) J. E. Mulvaney, Z. G. Gardlund, and S. L. Gardlund, *J. Am. Chem. Soc.*, **85**, 3897 (1963); (b) D. Y. Curtin, H. Gruen, and B. A. Shoulders, *Chem. Ind. (London)*, 1205 (1958). They have shown that in compounds of this general type, the most sterically hindered olefinic hydrogens, *i.e.*, the *cis*, absorb at higher fields. In agreement with this observation, the *cis* compound's vinylic hydrogen ( $\text{H}_a$ ) absorbs at 6.14 p.p.m., while the *trans* compound's vinylic hydrogen absorbs at 6.50 p.p.m. in  $\text{CCl}_4$ .

(7) W. Luttke, *Ann.*, **668**, 184 (1963), has shown that *cis*-stilbenes show more fine structure in the 12–15  $\mu$  region than the *trans* stilbenes do. In agreement with this the *cis* compound shows five absorptions in this region, while the *trans* compound shows but three absorptions.

(8) S. Trippett, *Quart. Rev. (London)*, **17**, 406 (1963). The predominance of the *trans* isomer may be a result of energy factors in the intermediates of the Wittig reaction and/or may be due to subsequent isomerization of the *cis* to the *trans* isomer. Under our experimental conditions the latter cause appears to be of considerable importance. For example, we have found that a mixture of triphenylphosphine oxide and *cis*-*p*-nitrobenzylidenebenzocyclobutene (iv) in DMF is isomerized with 67% conversion to the *trans* isomer v after stirring for 11 hr. at 25–30°.



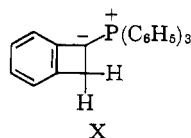
(1) M. P. Cava, A. A. Deana, and K. Muth, *J. Am. Chem. Soc.*, **81**, 6458 (1959).

(2) All n.m.r. spectra were determined on a Varian A-60 spectrometer. The chemical shifts are given in p.p.m. downfield from tetramethylsilane.

(3) To the best of our knowledge this is the first example of the preparation of a 1,2-bis-ylide, and its formation is probably aided by this added stabilization. If such stabilization did not obtain,  $\beta$ -elimination would probably be the prevailing reaction.

(4) We wish to thank Dr. David Geske for performing this experiment.

probably arise from ethanolysis of the bis-ylide IV to mono-ylide X by small amounts of ethanol present in the reaction mixture,<sup>9</sup> followed by reaction of the mono-ylide X with benzaldehyde. Studies are now underway to evaluate this hypothesis.



Aside from the analysis and expected *trans* product from the Wittig reaction, the structure of V rests on the following spectral and degradative evidence. The ultraviolet spectrum shows  $\lambda_{\text{max}}^{\text{EtOH}}$  335 m $\mu$  (log  $\epsilon$  4.21), 332.5 (4.22), 307 (4.01), 282 (4.26), 238.5 (4.35), and 232.5 (4.39). The n.m.r. spectrum in CCl<sub>4</sub> has an absorption singlet at 6.72 (H<sub>a</sub>), 7.41 (close multiplet, H<sub>b</sub>), and 7.65 p.p.m. (broad multiplet, H<sub>c</sub>) in integrated ratio of 1:2:5, respectively. The infrared spectrum shows  $\lambda_{\text{max}}^{\text{Nujol}}$  6.07 (double bond), 12.92 and 13.10 (*ortho*-disubstituted benzene ring), and 13.64 and 14.32  $\mu$  (monosubstituted benzene rings).<sup>10</sup> Prolonged periodate-permanganate oxidation of compound V in dioxane-benzene-water<sup>11</sup> produced benzoic acid (60%) and phthalic acid (50%), both identical with authentic samples, as well as a small amount of phthalic anhydride (infrared).

Work continues on the reactions and properties of the compounds III and IV and the synthesis of other benzocyclobutenes containing electron-withdrawing substituents and will be reported in due course.

**Acknowledgments.**—The support of the National Science Foundation, Grant No. G18902, is gratefully acknowledged. We sincerely appreciate helpful discussions with Dr. D. G. Farnum, Dr. A. William Johnson, and Dr. Jerrold Meinwald.

(9) See M. Grayson and P. T. Keough, *J. Am. Chem. Soc.*, **82**, 3919 (1960), for examples of similar reactions.

(10) A referee has suggested the alternate *cis,trans* structure for V, since, on steric grounds, such a structure should be more stable. We feel, however, that the *trans,trans* stereochemistry is correct for the following reasons: (i) the *cis,trans* isomer should exhibit a doublet in the n.m.r. since the two vinylic hydrogens would have different chemical environments, but we obtain only a low-field singlet, and (ii) in a case where all three isomers were obtained (when IV is treated with *p*-nitrobenzaldehyde) the *trans,trans* isomer is obtained in greatest yield and has a singlet in the n.m.r., while the *cis,trans* product exhibits a doublet in the vinylic region of the n.m.r. However, *cis,cis* stereochemistry cannot be ruled out.

(11) R. U. Lemieux and E. von Rudloff, *Can. J. Chem.*, **33**, 1701, 1710, (1955); E. von Rudloff, *ibid.*, **33**, 1714 (1955).

(12) N.S.F. Predoctoral Research Fellow, 1963–1964; N.S.F. Predoctoral Cooperative Fellow, 1964–1965.

DEPARTMENT OF CHEMISTRY  
CORNELL UNIVERSITY  
ITHACA, NEW YORK

A. T. BLOMQUIST  
VICTOR J. HRUBY<sup>12</sup>

RECEIVED AUGUST 17, 1964

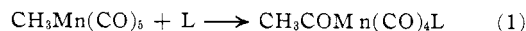
### Methyl Migration in the Reaction of Alkyl- and Acylmanganese Carbonyls

Sir:

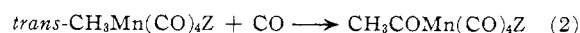
One aspect of the so-called insertion reaction<sup>1</sup> of CH<sub>3</sub>Mn(CO)<sub>5</sub> which has not received much attention is

(1) References to previous work in this field are given in R. J. Mawby, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **86**, 3994 (1964).

the mechanism by which the acetyl group is formed in reaction 1, where L is a nucleophile.

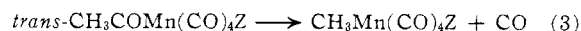


The two likely mechanisms are (a) insertion of a molecule of CO, previously bonded to the manganese, between the methyl group and the manganese, and (b) migration of the methyl group onto one of the terminal CO molecules. Although in the case of CH<sub>3</sub>Mn(CO)<sub>5</sub> it is difficult to distinguish between the two mechanisms, in the case of a complex of the type *trans*-CH<sub>3</sub>Mn(CO)<sub>4</sub>Z, where Z is some ligand other than CO, reaction 2 can be used for this purpose. If this reaction proceeds



by carbonyl insertion, the product will be *trans*-CH<sub>3</sub>COMn(CO)<sub>4</sub>Z, whereas if it proceeds by methyl migration the *cis* isomer will be formed.

Since by the law of microscopic reversibility, the reverse of this process must proceed by the same mechanism as the forward reaction, one can equally well study reaction 3. A *trans* product would in-



indicate the reverse of carbonyl insertion, a *cis* product methyl migration (see Fig. 1).

We have studied the reactions of *trans*-CH<sub>3</sub>COMn(CO)<sub>4</sub>P(Ph)<sub>3</sub> (where Ph = C<sub>6</sub>H<sub>5</sub>), which we have found to be the initial product of the reaction of CH<sub>3</sub>Mn(CO)<sub>5</sub> and P(Ph)<sub>3</sub> in either diethyl ether or tetrahydrofuran. The method of isolating this complex and the assignment of the *trans* structure were very kindly given to us prior to publication.<sup>2</sup>

The compound was prepared by treating equimolar amounts of CH<sub>3</sub>Mn(CO)<sub>5</sub> and P(Ph)<sub>3</sub> in ether at 10° for 24 hr. under nitrogen and then evaporating to near dryness under a stream of nitrogen. The yellow crystals isolated had a melting point (98°) and an infrared spectrum in hexane solution (terminal C–O stretching frequencies 2066, 1995, and 1959 cm.<sup>-1</sup>; acetyl C–O stretching frequency 1631 cm.<sup>-1</sup>) identical with those reported by Kraihanzel and Cotton.<sup>2</sup>

We found that, at 25° in hexane or tetrahydrofuran solution, *trans*-CH<sub>3</sub>COMn(CO)<sub>4</sub>P(Ph)<sub>3</sub> was converted to a new compound, which was isolated by removing the solvent and recrystallizing from chloroform-ethanol. Yellow crystals (m.p. 110°) were obtained. The infrared spectrum in hexane solution (terminal C–O stretching frequencies 2055, 1983, 1968, and 1939 cm.<sup>-1</sup>; no acetyl C–O stretching frequency) and analysis of this compound (*Anal.* Calcd. for CH<sub>3</sub>Mn(CO)<sub>4</sub>P(Ph)<sub>3</sub>: C, 62.16; H, 4.08. Found: C, 62.07; H, 4.07) showed it to be CH<sub>3</sub>Mn(CO)<sub>4</sub>P(Ph)<sub>3</sub>, previously prepared by a different method by Hieber, *et al.*,<sup>3</sup> who report an infrared spectrum for their sample which is virtually identical with that given above. We consider, in agreement with Kraihanzel and Cotton,<sup>2</sup> that the infrared spectrum (which is very similar to that reported<sup>3</sup> for the compounds *cis*-Mn(CO)<sub>4</sub>XP(Ph)<sub>3</sub>, where X = Cl, Br, or I) shows that this compound is *cis*-CH<sub>3</sub>Mn(CO)<sub>4</sub>P(Ph)<sub>3</sub>.

The simplest mechanism for the formation of *cis*-CH<sub>3</sub>Mn(CO)<sub>4</sub>P(Ph)<sub>3</sub> from *trans*-CH<sub>3</sub>COMn(CO)<sub>4</sub>P(Ph)<sub>3</sub>

(2) C. S. Kraihanzel and F. A. Cotton, private communication.

(3) W. Hieber, G. Faulhaber and F. Theubert, *Z. anorg. allgem. Chem.*, **314**, 125 (1962).