

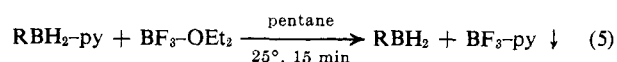
Table I. Preparation of Representative Monoalkylboranes from 2-Alkyl-1,3,2-benzodioxaboroles *via* Reaction with Lithium Aluminum Hydride or Aluminum Hydride and Their Conversion into Amine-Monoalkylboranes and Mixed Trialkylboranes^a

Monoalkylborane, RBH ₂ , R substituent	Amine-monoalkylborane			Mixed trialkylborane, RBH ₂ + olefin	RBR' ₂ yield, ^d %	RR' ₂ CB- (OCH ₂) ₂ (2) yield, %
	Yield, ^c %	Bp, °C (mm)	n _D ²⁰			
1-Butyl	85	48 (0.5)	1.4320 ^e	Isobutylene	90	88
1-Butyl	83	48 (0.5)	1.4320 ^{b,e}	2-Butene ^b	85	80 ^g
1-Butyl	90		1.5155 ^f	11-Chloro-1-hendecene	75	70
1-Butyl				4-Penten-1-ol acetate	85	70
Isobutyl	87	40 (0.5)	1.4305 ^e	Isobutylene	99	
Isobutyl	93		1.5100 ^f	2-Butene	90	86
Isobutyl				2-Butene ^b	90	78 ^g
Isobutyl				11-Chloro-1-hendecene	75	
2-Butyl	81	36 (0.3)	1.4342 ^e	Isobutylene	92	88
2-Butyl				Isobutylene ^b	86	75 ^g
2-Butyl				4-Penten-1-ol acetate	80	70
Cyclopentyl	90	67 (0.5)	1.4640 ^e	Isobutylene	88	
Cyclopentyl				2-Butene	85	
Cyclohexyl	90	84 (0.5) ^{e,h}				
<i>exo</i> -Norboryl	85		1.5440 ^f	Allyl ethyl ether	85	
<i>exo</i> -Norboryl	95	93 (0.2) ^{b,e}				

^a Unless otherwise mentioned, aluminum hydride was used as the reducing agent. ^b Lithium aluminum hydride was used as the reducing agent. ^c By isolation. ^d By glpc analysis. ^e Trimethylamine-monoalkylborane derivative. ^f Pyridine-monoalkylborane derivative. ^g The corresponding trialkylcarbinol product. ^h Mp 42°; lit.⁵ mp 42°.

benzodioxaborole (1.76 g, 10 mmol) in pentane (10 ml) was treated with a clear solution of AlH₃ in THF¹⁶ (7.3 ml of 1 M, 10% excess) at 0° under nitrogen for 30 min. After dilution with pentane (10 ml), the mixture was filtered through Celite under nitrogen. Evaporation of the solvent at 0° gave 0.68 g (97%) of a clear liquid, *n*-butylborane: ν (CCl₄) 2550 (B-H, terminal), 1590 (B-H-B, bridge) cm⁻¹. Upon reaction with methanol, 19.0 mmol of hydrogen gas was evolved. Glpc analysis of the reaction mixture then indicated the presence of dimethyl 1-butylboronate in 90% yield. No other organoboron compounds were discernible in the glpc chromatogram. The addition of an olefin instead of methanol to the monoalkylborane product completes the formation of the corresponding mixed trialkylborane in nearly quantitative yield. For example, *sec*-butylborane (25 mmol) prepared as described above was treated with 4-penten-1-ol acetate (6.4 g, 50 mmol). The usual carbonylation in the presence of ethylene glycol then produced the corresponding 2-trialkylcarbinyl-1,3,2-dioxaborolane in 70% yield: bp 146° (0.1 mm); n_D²⁰ 1.4685.

The monoalkylboranes should be utilized soon after preparation. They can be transformed into relatively stable amine derivatives by treatment either with trimethylamine or pyridine. The pyridine-monoalkylboranes permit a ready regeneration of the parent monoalkylborane upon treatment with boron trifluoride etherate¹³ (eq 5).



The preparation of several representative monoalkylborane transformation products is given in Table I.¹⁷

(16) N. M. Yoon and H. C. Brown, *J. Amer. Chem. Soc.*, **90**, 2927 (1968).

(17) All the compounds were analyzed by ir and nmr spectroscopy. All the new compounds, in addition, gave satisfactory elemental analyses.

The present development provides, for the first time, a general and highly straightforward synthesis of monoalkylboranes, and some of their transformation products of considerable synthetic importance.

(18) Postdoctorate research associate on Grant No. GM-10937 provided by the National Institutes of Health.

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Received May 29, 1971

Geometry of the *anti*-Tricyclo[3.1.0.0^{2,4}]hexane and Cyclohexa-1,4-diene Systems

Sir:

Several examples of photoinduced dimerization of cyclopropenes are known.^{1a} In particular, photolysis of 3-monosubstituted 1,2-diphenylcyclopropenes with or without sensitizer proceeds readily to afford one or two dimeric products, to which the tricyclo[3.1.0.0^{2,4}]hexane skeleton was assigned.^{1b-e} The stereochemistry of the photoproducts, however, was either undetermined or assigned only on the basis of mechanistic considerations, and, further, in some cases even proposed structures appeared to be insecure.^{1c} Because of (i) the absence of unambiguous evidence to establish the stereochemistry of these compounds and (ii) our interest in the exact geometry of this intriguing tricyclo system, we have undertaken X-ray analysis of photodimers obtained from 3-carbomethoxy-1,2-diphenylcyclopropene (**1**).

The direct irradiation of **1** (Pyrex filter, THF solvent, 6 hr, room temperature) provided dimers A and B in 56 and 25% yields, respectively.² Both A and B were

(1) (a) H. H. Stechl, *Chem. Ber.*, **97**, 2681 (1964); (b) N. Obata and I. Moritani, *Bull. Chem. Soc. Jap.*, **39**, 2250 (1966); (c) J. Trotter, C. S. Gibbons, N. Nakatsuka, and S. Masamune, *J. Amer. Chem. Soc.*, **89**, 2792 (1967); (d) C. Deboer and R. Breslow, *Tetrahedron Lett.*, 1033 (1967); photolysis of triphenylcyclopropene with a sensitizer provided a cyclopropylcyclopropene derivative in addition to a normal dimer (tricyclohexane); (e) H. Dürr, *ibid.*, 1649 (1967).

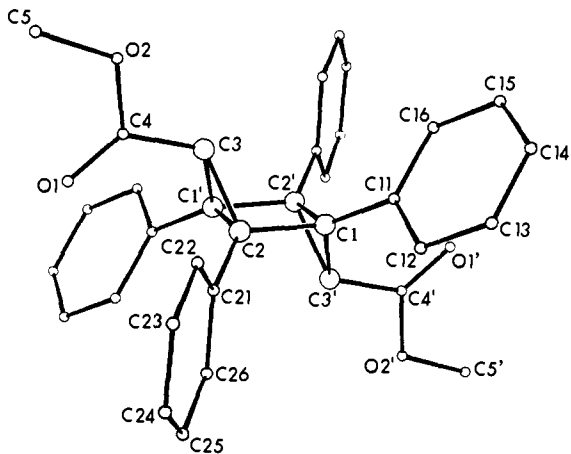


Figure 1. A perspective view of dimer A. Selected distances (ångströms) and angles (degrees) with standard deviations in parentheses are: distances, C(1)–C(2), 1.536 (4); C(1')–C(2), 1.532 (4); C(1')–C(3), 1.532 (5); C(2)–C(3), 1.525 (4); C(3)–C(4), 1.483 (5); C(1)–C(11), 1.478 (4); C(2)–C(21), 1.492 (4); angles, C(1)–C(2)–C(1'), 90.0 (3); C(2)–C(1)–C(2'), 90.0 (3); C(2)–C(3)–C(1'), 60.2 (2); C(3)–C(1')–C(2), 59.7 (2); C(1')–C(2)–C(3), 60.1 (2).

aromatized to give the same compound above 300° and were inert thermally and photochemically under the conditions used to prepare these compounds.³ Because of symmetry indicated by their nmr spectra and the similarity of the uv spectra,² four tricyclo[3.1.0.0^{2,4}]hexane and two cyclohexa-1,4-diene structures are equally possible for A and B. Raman spectra in the region 1600–1700 cm⁻¹ provided useful information. Isomer A had only one strong absorption at 1600 cm⁻¹ which could be attributed to the carbonyl group, while B showed an additional strong absorption at 1680 cm⁻¹, a value consistent with the cyclohexa-1,4-diene structure.⁴ Therefore, these results indicate that A is very likely to be a tricyclohexane derivative, while B possesses the cyclohexadiene skeleton. The crystal-structure determinations of both A and B were undertaken to provide (1) a precise geometry of the novel tricyclo system, and (2) additional evidence concerning the planarity of the cyclohexa-1,4-diene ring.^{5–7}

Dimer A crystallizes in space group $P2_1/n$ with unit cell dimensions $a = 10.044$ (4), $b = 9.500$ (2), $c = 14.172$ (4) Å, $\beta = 104.38$ (2)°, and two molecules per unit cell. The structure was solved by application of direct methods⁸ to 1022 significant reflections which were measured on a Picker manual diffractometer (Cu K α radiation, $0 < 2\theta \leq 120^\circ$). The structure was found to be *anti*-1,2,4,5-tetraphenyl-3,6-dicarbomethoxytricyclo[3.1.0.0^{2,4}]hexane, as shown in Figure 1, and has refined to a conventional R factor of 0.040.

(2) Preliminary experiments were performed by S. M. at Mellon Institute, Pittsburgh, Pa. (1963–1964). Physical properties of these products were: dimer A, mp 257–258°; $\lambda_{\text{max}}^{\text{THF}}$ 236.5 nm (log ϵ 4.69); nmr (CDCl₃, 100 MHz) τ 2.78 (20 H), 6.30 (s, 2 H), 6.71 (s, 6 H); dimer B, mp 256–257°; $\lambda_{\text{max}}^{\text{THF}}$ 242.7 nm (log ϵ 4.68); nmr τ 2.92 (20 H), 5.00 (s, 2 H), 6.93 (s, 6 H).

(3) This control experiment does not necessarily eliminate the possibility that excited 1* converts A into B or *vice versa*. Several attempts to isomerize A to B thermally failed and resulted invariably in the formation of the aromatic compounds.

(4) H. D. Stidham, *Spectrochim. Acta*, **21**, 23 (1965).

(5) G. Dallinga and L. H. Toneman, *J. Mol. Struct.*, **1**, 117 (1967).

(6) R. J. Jandacek and S. H. Simonsen, *J. Amer. Chem. Soc.*, **91**, 6663 (1969).

(7) H. Oberhammer and S. H. Bauer, *ibid.*, **91**, 10 (1969).

(8) J. Karle and I. L. Karle, *Acta Crystallogr.*, **21**, 849 (1966).

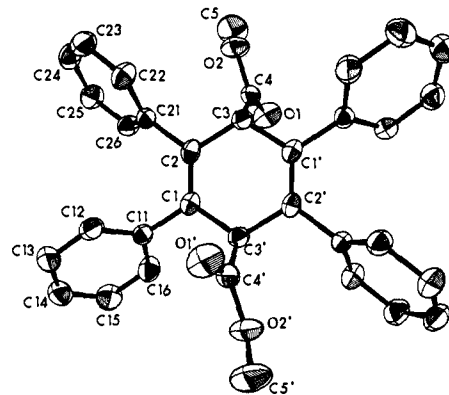


Figure 2. Perspective view of dimer B. Selected bond distances (ångströms) and angles (degrees) together with their standard deviations in parentheses are: distances, C(1)–C(2), 1.326 (5); C(2)–C(3), 1.521 (5); C(1)–C(3'), 1.513 (4); C(1)–C(11), 1.500 (5); C(2)–C(21), 1.502 (4); C(3)–C(4), 1.539 (6); angles, C(3')–C(1)–C(2), 122.3 (3); C(1)–C(2)–C(3), 122.2 (3); C(2)–C(3)–C(1'), 115.4 (3).

The molecules occupy inversion centers in the crystal which require the central four-membered ring to be rigorously planar. The dihedral angle between the three- and four-membered rings is 117°. The bond lengths within the three- and four-membered rings are definitely different from those found in unfused rings. More specifically the average distance of 1.530 Å observed in the three-membered ring is longer than typical values of ~ 1.51 Å^{9,10} and the distances in the four-membered ring (1.534 Å average) are generally shorter than the normal values of ~ 1.55 Å.^{11–15}

All distances within the tricyclohexane framework are equal within experimental error. It seems probable that this feature would be better investigated by a molecular orbital treatment of the tricyclo system as a whole rather than of its component ring fragments. The tricyclo system certainly shows the common characteristic of formally strained systems in that the bond distances to the substituent groups are approximately 0.02 Å shorter than values calculated from conventional covalent radii.^{16,17}

Dimer B crystallizes in the monoclinic space group $I2/a$ with unit cell dimensions $a = 20.052$ (1), $b = 5.756$ (1), $c = 22.782$ (2) Å, $\beta = 95.74$ (7)°, and four molecules per unit cell. Experimental procedures as used for the determination of dimer A produced 1065 significant reflections.

The structure was solved by direct methods⁸ and dimer B was identified as *anti*-1,2,4,5-tetraphenyl-3,6-dicarbomethoxycyclohexa-1,4-diene. The structure which has been refined to a value for $R = 0.043$ is shown in Figure 2. All bond distances are essentially in agreement with accepted values.

(9) R. E. Long, H. Maddox, and K. N. Trueblood, *ibid.*, *Sect. B*, **25**, 2083 (1969).

(10) A. Hartman and F. L. Hirschfeld, *ibid.*, **20**, 80 (1966).

(11) A. A. Almenningen, O. Bastiansen, and P. N. Scanche, *Acta Chem. Scand.*, **15**, 711 (1961).

(12) E. Benedetti, P. Corradini, and C. Pedone, *Acta Crystallogr.*, *Sect. B*, **26**, 493 (1970).

(13) E. Adman and T. N. Margulis, *J. Phys. Chem.*, **73**, 1480 (1969).

(14) B. Greenberg and B. Post, *Acta Crystallogr.*, *Sect. B*, **24**, 918 (1968).

(15) E. Adman and T. N. Margulis, *J. Amer. Chem. Soc.*, **90**, 4517 (1968).

(16) C. J. Fritchie, Jr., *Acta Crystallogr.*, **20**, 27 (1966).

(17) M. J. S. Dewar, *Tetrahedron*, 1817 (1965).

The molecules are situated at crystallographic inversion centers, hence any deviations from planarity for the cyclohexa-1,4-diene ring lead to a chair structure. The deviations from planarity are small (each atom lies approximately 0.01 Å from the least-squares plane), but significant in a statistical sense. These results are in good agreement with those of the X-ray study of a glycine derivative of cyclohexa-1,4-diene.⁶ It is convenient to redefine the reference plane by the four olefinic (sp^2) carbon atoms and to discuss deviations of the methylenic (sp^3) carbon atoms from this plane since this allows immediate comparison of the boat and chair forms. This structure shows a deviation of 0.03 Å for C-3 for this reference plane. Dallinga and Toneman⁵ considered chair, boat, planar, and skew conformations in the preliminary stages of their electron diffraction study but pursued only the planar form to completion. However the suggested deviations from the plane were ≤ 0.05 Å. On the other hand Oberhammer and Bauer⁷ favored the boat conformation with a dihedral angle of 160° giving a deviation of 0.23 Å from the diene plane for the methylenic (sp^3) carbon atoms. While the cyclohexa-1,4-diene ring in this structure is not severely constrained as it would be in a fused ring system it remains a legitimate question as to whether the observed geometry reflects the inherently preferred structure for the cyclohexa-1,4-diene ring or whether it results from either intermolecular forces in the condensed phase or intramolecular forces due to the bulky substituents (particularly the phenyl-phenyl repulsions).

Having established the face-to-face geometry of two phenyl substituents of A, one can readily understand the 236-nm uv maximum of this compound. In a manner analogous to the case of the bicyclobutane system,¹⁸ the two groups in this geometry couple rather strongly through the p-rich σ bond common to the three- and four-membered rings of the system. The carbomethoxy group appears not to exert any significant steric repulsion to distort this unique alignment.^{18d,e} The hypsochromic shift of the stilbene chromophore of B is obvious in the geometry shown and requires no further comment.

Acknowledgment. We thank the Research Council of Canada and the Defense Research Board for financial support.

(18) (a) S. Masamune, *J. Amer. Chem. Soc.*, **86**, 735 (1964); (b) for the X-ray analysis of 1,5-diphenyltricyclo[2.1.0.0^{2,5}]pent-3-yl *p*-bromobenzoate, see ref 1c; (c) S. Masamune, *Tetrahedron Lett.*, 945 (1965); (d) R. B. Woodward and D. L. Dalrymple, *J. Amer. Chem. Soc.*, **91**, 4613 (1969); (e) J. M. Schulman and G. J. Fisanick, *ibid.*, **92**, 6654 (1970). In the cases of esters of *exo*-1,3-diphenylbicyclobutanecarboxylic acid, uv maxima are shifted to shorter wavelengths (*ca.* 220 nm) from the normal position (*ca.* 270 nm) apparently due to the steric hindrance between the carbomethoxy and phenyl groups.

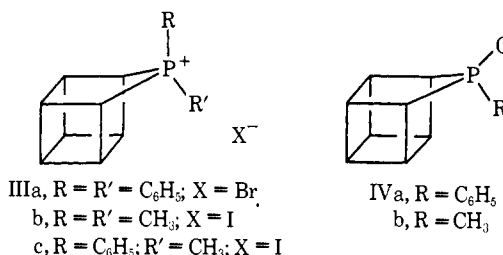
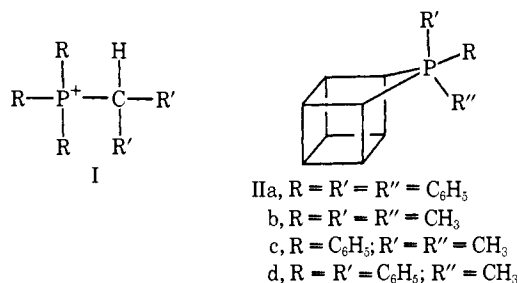
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A Stable Pentaalkylphosphorane

Sir:

Although pentaarylphosphoranes can be prepared by treating tetraarylphosphonium salts with aryllithium reagents,¹ no pentaalkylphosphorane has yet been pre-

pared in this or any other way. Thus, tetramethylphosphonium iodide reacts with methylolithium or phenyllithium in ether to give not the phosphorane, but the ylide,² and there are numerous analogous reactions,³ many of which are the basis of the Wittig reaction.⁴ Consider the general phosphonium salt, I, the precursor of anylide, and suppose that two of the substituents, say R and R', are joined in a ring so small that it strains the carbon-phosphorus-carbon angle. When base approaches this molecule it can relieve the strain if, instead of removing the hydrogen atom from the carbon adjacent to phosphorus, it bonds to the phosphorus instead.⁵ This would account, for example, for the stability of the phosphorane IIa⁶ and would explain why the phosphonium salt IIIa,⁶ unlike tetraphenylphosphonium salts,⁷ can be prepared from the phosphine oxide IVa⁸ and phenyllithium.⁹



It would also mean that if one of the substituents in the phosphonium salt had a potentially reactive hydrogen atom and two *other* substituents on the phosphorus atom, say the groups labeled R in structure I, were joined in a small ring, base would react not with the hydrogen atom, but would add to the phosphorus instead. We have verified this hypothesis by showing that the phosphoranes IIb, IIc, and IIId are easily synthesized and stable at room temperature, and we

(1) (a) G. Wittig and M. Rieber, *Justus Liebig's Ann. Chem.*, **562**, 187 (1949); (b) G. Wittig, *Bull. Soc. Chim. Fr.*, 1162 (1966).

(2) G. Wittig and M. Rieber, *Justus Liebig's Ann. Chem.*, **562**, 177 (1949).

(3) (a) G. Wittig and G. Geissler, *ibid.*, **580**, 44 (1953); (b) D. Seyferth, W. B. Hughes, and J. K. Heeren, *J. Amer. Chem. Soc.*, **87**, 2847 (1965); (c) A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966.

(4) A. Maercker, *Org. React.*, **14**, 270 (1965).

(5) This hypothesis is derived from Westheimer's account for the rate of hydrolysis of small-ring phosphorus esters: F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968); R. Kluger and F. H. Westheimer, *J. Amer. Chem. Soc.*, **91**, 4143 (1969).

(6) T. J. Katz and E. W. Turnblom, *ibid.*, **92**, 6701 (1970).

(7) (a) G. Wittig and H.-J. Cristau, *Bull. Soc. Chim. Fr.*, 1293 (1969); (b) H. Gilman and G. E. Brown, *J. Amer. Chem. Soc.*, **67**, 824 (1945).

(8) T. J. Katz, J. C. Carnahan, Jr., G. M. Clarke, and N. Acton, *ibid.*, **92**, 734 (1970).

(9) It also accounts for the ease with which bisbiphenylphosphonium salts can be prepared¹⁰ and for the stability of the alkylbisbiphenylphosphoranes.^{10,11} See also ref 6, footnote 22.

(10) D. Hellwinkel, *Chem. Ber.*, **102**, 548 (1969); **98**, 576 (1965).

(11) M. Schlosser, T. Kadibelban, and G. Steinhoff, *Justus Liebig's Ann. Chem.*, **743**, 25 (1971).