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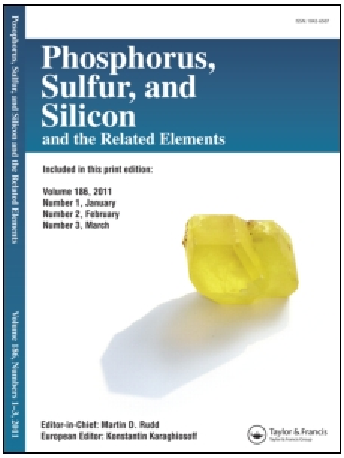

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THE SYNTHESIS OF BICYCLIC PHOSPHONIUM SALTS

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Bicyclic phosphonium salts (**1–6**), (**9**) and (**15**) have been prepared by three routes, i.e. the Diels Alder cycloaddition reactions of vinyltriphenylphosphonium bromide with cyclopentadiene and anthracene and its derivatives; the alkylation of tertiary phosphines by 2- and 7-bromotrinorbornanes; and via the free-radical addition of diphenylphosphine to trinorbornene followed by the alkylation of the resultant 2-trinornyldiphenylphosphine using iodomethane and iodoethane. Chromatographic methods were developed for the purification of the salts which were characterised by ^{1}H, ^{13}C and ^{31}P n.m.r. spectroscopy.

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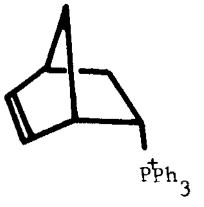
INTRODUCTION

Phosphonium salts have been prepared by many routes and most commonly by the reaction of alkyl halides with tertiary phosphines.[1] Here we describe the application of three methods to the synthesis of a series of compounds in which the phosphonium group is attached to a rigid bicyclic system. The salts were required for a study of the relationship of the dihedral PC and PH angles to the NMR vicinal coupling constants and to evaluate shielding effects of phosphonium groups in relation to adjacent nuclei.[2]

DISCUSSION

Some work has been done towards the preparation of trinorbornyl phosphonium salts, involving the cycloaddition of cyclopentadiene with vinyl phosphonium salts.[3,4] Ruden *et al.*[4] have described the reaction of cyclopentadiene with vinyltriphenylphosphonium bromide as giving 4 : 1 isomeric mixture of adducts. We have re-investigated and extended this work to include the reactions of anthracene, 9-methylanthracene, 9,10-dimethylanthracene, anthracen-9-al, hexachlorocyclopentadiene, tetraphenylcyclone and furan. The salts (**1–5**) were isolated in a wide range of yields (25–100%) from reactions carried out at 150°C under pressure in acetonitrile. Hexachlorocyclopentadiene, tetraphenylcyclone and anthracen-9-al did not react with the vinyl salt, whilst furan gave decomposition products due to the high reaction temperature.

The *endo* configuration of the trinorbornenyl salt (**1**) was confirmed by ^{13}C nmr from the characteristic PC(7) coupling constant, 12.5 Hz for 150° dihedral angle (N.B., the corresponding dihedral angle for the *exo* salt would be ca. 90° and $^3J_{PC(7)}$ ca. 0 Hz). The saturated salt (**6**) was prepared by catalytic hydrogenation of (**1**); its



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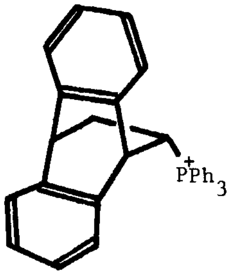

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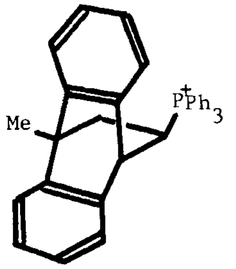

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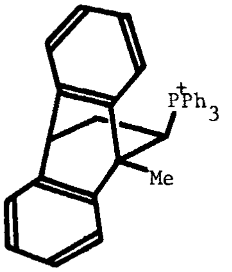

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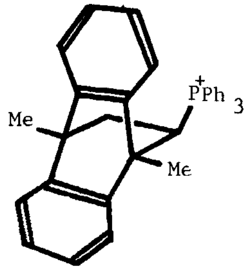

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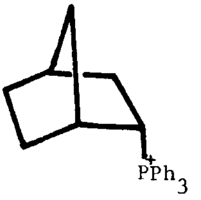

(6)

^{13}C nmr spectrum showed $^3J_{PC(7)} = 15.1$ Hz confirming the retention of the *endo* configuration. 4-Methylanthracene gave an isomeric mixture of salts, (**3**) and (**4**), in a 4 : 1 ratio. Attempts to separate the mixture by chromatography was unsuccessful.

Trinorbornyl and trinorbornenylphosphonium salts have also been prepared from halotrinorbornane derivatives,[5] either through organometallic intermediates, or through carbocations produced by the action of silver salts. Direct alkylation by phosphines has not been reported. We find that a wide range of tertiary phosphines are alkylated by *exo*-2-bromotrinorbornane (**7**, X = Br) and 7-bromotrinorbornane (**8**). (See Table.) Once again, the yields of phosphonium salts varied widely and frequently there were a number of by-products due to thermolysis and oxidation.

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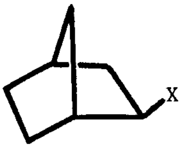

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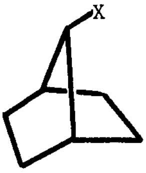

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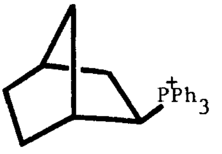
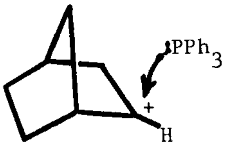


(9)

However, on a 0.1 molar scale, triphenylphosphine and *exo* bromide (**7**, X = Br) gave a quantitative yield of *exo*-2-trinorbornyltriphenylphosphonium bromide (**9**). Its configuration was established from its ^{13}C nmr spectrum which showed $^3J_{PC(7)} = 0$ Hz corresponding to a dihedral angle of 90°, whilst $^3J_{PC(6)} = 14.6$ Hz corresponding to a dihedral angle of 180°.

It is well known that alkyl halides undergo nucleophilic substitution reactions involving gradations of S_N1 and S_N2 behaviour. For *exo*-2-bromotrinorbornane (**7**, X = Br) ionisation should be much preferred[6] and the retention of configuration can be rationalised by having less hindered approach of the phosphine to the trinorbornyl cation (**10**) from the *exo* direction. This is consistent with the conversion of exo-2-chlorotrinorbornane (**7**, X = Cl) in hot aqueous silver nitrate to the corresponding alcohol (**7**, X = OH).[7] On the other hand both the *syn* and *anti* 7-bromobenzotrinorbornanes solvolyse in aqueous dioxan to their corresponding alcohols with retention of configuration.[8] Perhaps in this case hydrogen bonding assists π-participation and species such as (**11**) and (**12**) are involved.



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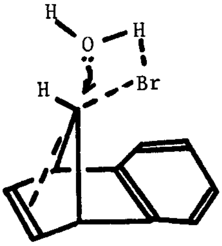

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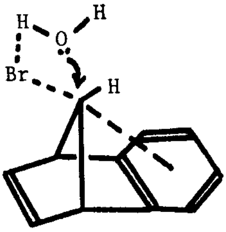

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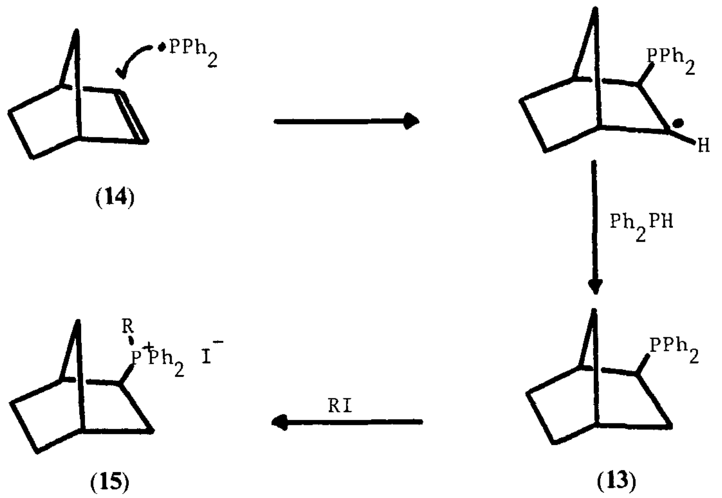
The 7-bromotrinorbornanes (**8**) did not react with triphenylphosphine. This is attributed to the small C1, C7, C4 bond angle which cannot approach the desired 120° angle for the S_N1 carbocationic intermediate and also to steric hindrance. The alkylarylphosphines with less steric demands gave low yields of the desired 7-substituted phosphonium salts.

An alternative route to 2-trinorbornyl phosphonium salts involved the initial preparation of 2-trinorbornyl diphenylphosphine (**13**) by radical catalysed addition of diphenylphosphine to trinorbornene (**14**). Reports of acid,[9] base[10] and radical [11] catalysed addition of primary and secondary phosphines[9,11] and dialkyl phosphonates to unsaturated systems are well known but these methods have not been applied to the formation of trinorbornyl phosphines. We find that *exo* (**13**) can be prepared in a 35% yield using azobisisobutyronitrile as the radical initiator. Alkylation with methyl and ethyl iodides gave quantitative yields of the corresponding *exo* salts (**15**, R = Me) and (**15**, R = Et). Again the *exo*-configurations were evident from the ^{13}C nmr spectra; i.e. for the iodide (**16**, R = Me) $^{3}J_{PC(6)} = 14.7$ Hz (dihedral angle 180°), $^{3}J_{PC(7)} = 0$ Hz (dihedral angle 90°), and for the iodide (**16**, R = Et) $^{3}J_{PC(6)} = 15.3$ Hz and $^{3}J_{PC(7)} = 0$ Hz. The preference for the *exo* configuration is in accordance with less hindered approach of the phosphino radical towards the *exo* face of the trinorbornene (**14**).



Whilst phosphonium salts are generally crystalline solids they frequently resist purification by recrystallisation. We found that thick layer (1 mm) chromatography using Kieselguhr G and a 1 : 1 mixture of diethyl ether and chloroform afforded a satisfactory method of purification. The salts were observed under u.v. light at low R_F on the plates. The required bands of Kieselguhr were extracted with chloroform using a Soxlet apparatus. Where necessary the process was repeated until ^{1}H, ^{13}C and ^{31}P nmr spectroscopy showed the salt to be pure.

EXPERIMENTAL

N.m.r. spectra were recorded using a JEOL FX100 spectrometer. The ^{1}H and ^{13}C spectra will be the subject of a separate paper.

(*Endo-2-Trinorbornenyl*)*triphenylphosphonium Bromide* (**1**). Vinyltriphenylphosphonium bromide (1 g), cyclopentadiene (0.2 g) and hydroquinone (ca. 0.05 g) in acetonitrile (5 ml) were sealed in a thick glass tube and heated at 150°C for 7 days. After cooling, the tubes were carefully opened and the contents washed out with a little dichloromethane. Diethyl ether was added to precipitate the salt in a quantitative yield, m.p. 219–221°C (220–223°C).[12]

2-[5,6,7,8-Dibenzobicyclo(2,2,2)octadienyl]triphenylphosphonium Bromide (**2**). Prepared by above procedure replacing the cyclopentadiene by anthracene (0.5 g). The bromide, δ_P 26.7 ppm, was obtained in a 25% yield* and was characterised by ^{1}H and ^{13}C nmr spectroscopy.

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*It was not possible to remove small amounts of anthracene which contaminated the salts and therefore satisfactory analyses and melting points were not obtained.

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2- and 3-[1-Methyl-5,6,7,8-dibenzobicyclo(2,2,2)octadienyl]triphenylphosphonium Bromides (**3**) *and* (**4**). Prepared as above procedure using 9-methylanthracene (0.5 g) as the diene. A mixture of isomeric bromides, δ_P 26.96 and 24.0 ppm, was obtained in 30% yield* and were characterised by ^{1}H and ^{13}C nmr spectroscopy.

2-[1,4-Dimethyl-5,6,7,8-dibenzobicyclo(2,2,2)octadienyl]triphenylphosphonium Bromide (**5**). Prepared as above procedure using 9,10-dimethylanthracene (0.5 g). The bromide was isolated in 40% yield,* δ_P 26.65, and was characterised by ^{1}H and ^{13}C nmr spectroscopy.

(Endo-2-Trinorbornyl)triphenylphosphonium Bromide (**6**). (Endo-2-Trinorbornenyl)triphenylphosphonium bromide (**1**) (5.0 g) and palladium/charcoal catalyst (0.4 g) in ethanol (100 ml) was hydrogenated at 100 p.s.i. over a period of 12 h at 20°C. After removing the catalyst and solvent the solid residue was taken up in chloroform and precipitated with diethyl ether. The colourless salt (5.0 g; 100%) had δ_P 25.2, m.p. 242–244°C and was characterised by ^{1}H, ^{13}C and ^{31}P nmr spectroscopy. Anal. found: C, 70.4; N, 5.7. $C_{25}H_{26}PBr$ requires C, 68.6; H, 5.9.

(Exo-2-Trinorbornyl)triphenylphosphonium Bromide (**9**). Exo-2-Bromotrinorbornane[13] (8.78 g) and triphenylphosphine (13.1 g) in benzonitrile (10 ml) was refluxed 4 days. After cooling, crystallisation by the addition of diethyl ether, gave the salt (21.8 g; 99.8%), δ_P 26.75, m.p. 259–261°C. (Anal. found: C, 67.25; H, 5.96. $C_{25}H_{26}PBr$ requires C, 68.6; H, 5.9). It was further characterised by ^{1}H and ^{13}C nmr spectroscopy.

Alkylation of Tertiary Phosphines by Bicyclic Bromoalkanes. The phosphines listed in the table and either 2-bromotrinorbornane or 7-bromotrinorbornane were reacted as follows. Molar equivalents of tertiary phosphine and bicyclic halide (approximately 0.5 g total material) in acetonitrile (5 ml) were sealed in a thick walled glass tube and heated at 180°C for 7 days. After cooling, the contents of the tube were removed and the solvent evaporated. The residue was taken up in a minimum of chloroform and the salt precipitated by the addition of ether. The salts were purified by thick layer chromatography using Kieselguhr G (see discussion). The ^{31}P n.m.r. chemical shifts of the salts are given in the table.

TABLE

^{31}P Chemical shifts of phosphonium salts obtained from the reaction of tertiary phosphines and bromotrinorbornanes

Halide	Phosphines								
	Ph_3P	$(p\text{-Anisyl})_3P$	Ph_2PMe	Ph_2PEt	Ph_2PBu	$PhPMe_2$	$PhPEt_2$	$PhPBu_2$	Bu_3P
(**7**, X = Br)	26.7	20.8	26.1	32.3	30.0	25.8	34.7	31.1	10.4
(**13**)	27.1	—	22.0	28.2	25.8	23.8	32.7	28.5	33.1
	20.1						31.9	28.2	31.9

(Exo-2-Trinorbornyl)diphenylphosphine (**14**). Diphenylphosphine (4.3 g), trinorbornene (4.7 g), and azo-bis-isobutyronitrile (0.2 g) in toluene (50 ml) were refluxed 72 h. The toluene was removed and the residue distilled to give the phosphine (1.5 g), b.p. 114–116°C (0.5 Torr), δ_P −6.5 ppm $\delta_{^{13}C}$ {^{1}H} (trinorbornyl C atoms) 29.1 (s) 31.4 (d, J_{PC} 7.3), 35.4 (d, J_{PC} 11.8), 36.8 (d, J_{PC} 16.9), 36.9 (d, J_{PC} 12.5), 39.3 (s) and 39.8 (d, J_{PC} 5.9 Hz) ppm.

(Exo-2-Trinorbornyl)methyldiphenylphosphonium Iodide (**16**, *R* = *Me*). (Exo-2-Trinorbornyl)diphenylphosphine was added to excess iodomethane in diethyl ether. The salt, which precipitated quantitatively over a period of 5 min, had m.p. 197–8°C, δ_P 25.8 and was characterised by ^{1}H and ^{13}C nmr spectroscopy. Anal. found: C, 56.2; H, 5.6. $C_{20}H_{24}PI$ requires C, 56.9; H, 5.7%.

(Exo-2-Trinorbornyl)ethyldiphenylphosphonium Iodide (**16**, *R* = *Et*). Prepared as above using iodoethane in place of iodomethane. The salt had m.p. 172–174°C, δ_P 32.4 and was characterised by ^{1}H and ^{13}C nmr spectroscopy. Anal. found: C, 56.2; H, 5.6. $C_{21}H_{26}PI$ requires C, 57.8; H, 6.0%.

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