Selective Bromination of Polyenes by 2,4,4,6-Tetrabromocyclohexa-2,5-dienone [1]

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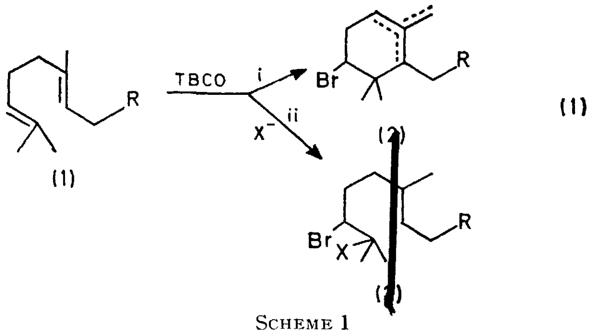
2,4,4,6-Tetrabromocyclohexa-2,5-dienone (TBCO) liberates bromonium ion when treated with polyenes to form brominated products. The results of the reaction of TBCO with simple olefins are presented. The analogous bromo-ketones, 4-bromo-2,4,6-trichloro- and 2,4,6-tribromo-4-methyl-cyclohexa-2,5-dienone, (4) *and* (5) respectively, afford the same products (3a), (6), and (7) when treated with geranyl cyanide (1; R = CN). The evidence suggests that formation of the dibromide (3a) may be due to sequential reactions. TBCO in the presence of cetyltrimethylammonium bromide serves as an excellent reagent for selective bromination of polyenes under very mild conditions.

Previous investigations from our laboratory have shown that 2,4,4,6-tetrabromocyclohexa-2,5-dienone (abbreviated as TBCO) liberates bromonium ion, when treated with various types of polyenes under mild conditions, transforming them into the brominated products. The bromination occurs at a specific position of the polyene and the product varies depending on the starting material employed. As represented in Scheme 1, the reaction consists of (i) brominative cyclization if an internal double bond can participate as a nucleophile and (ii) addition of BrX when a nucleophile (X) such as a hydroxy- or methoxy-group exists in the reaction system.

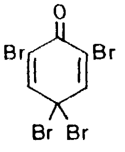


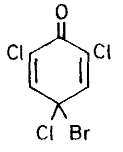
Scheme 1

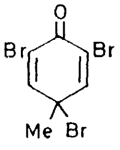
As described previously, the former reaction predominates when methyl (2*Z*)-farnesate (1; $R = CH_2CMe{=}CHCO_2Me$) is submitted to the reaction, giving the brominated cyclization product (2; $R = CH_2CMe{=}CHCO_2Me$).[1-3] On the other hand, the latter reaction predominates in the presence of ROH.[4,5]

During the course of this work, we have encountered an additional reaction of TBCO. When geranyl cyanide (1; R = CN) was stirred with an equimolar amount of TBCO at room temperature, it was converted quantitatively into the dibromide (3a).[6] In this reaction, the TBCO was converted into polymeric materials (8). This reaction can be regarded as the dibromination of a polyene by TBCO, which releases two bromine atoms per molecule. Since selective functionalization of a polyene as its dibromide is of importance in the synthetic study of terpenoids, we have further explored the reactivity of TBCO in this connection and the results are now described.

Table 1 shows the results of the reaction of simple olefins with TBCO in methylene chloride at room temperature. It is suggested that the formation of the dibromide competes with that of the allyl bromide, both of which may occur *via* a common intermediate. When the major product is the corresponding dibromide, TBCO is changed into the polymeric material (8). Considerable amounts of tribromophenol were detected when formation of the allyl bromide increased as in the cases of methyl geranate and geranyl acetate.


TBCO


(4)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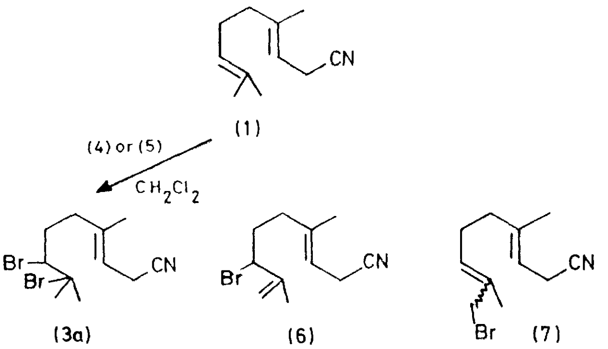
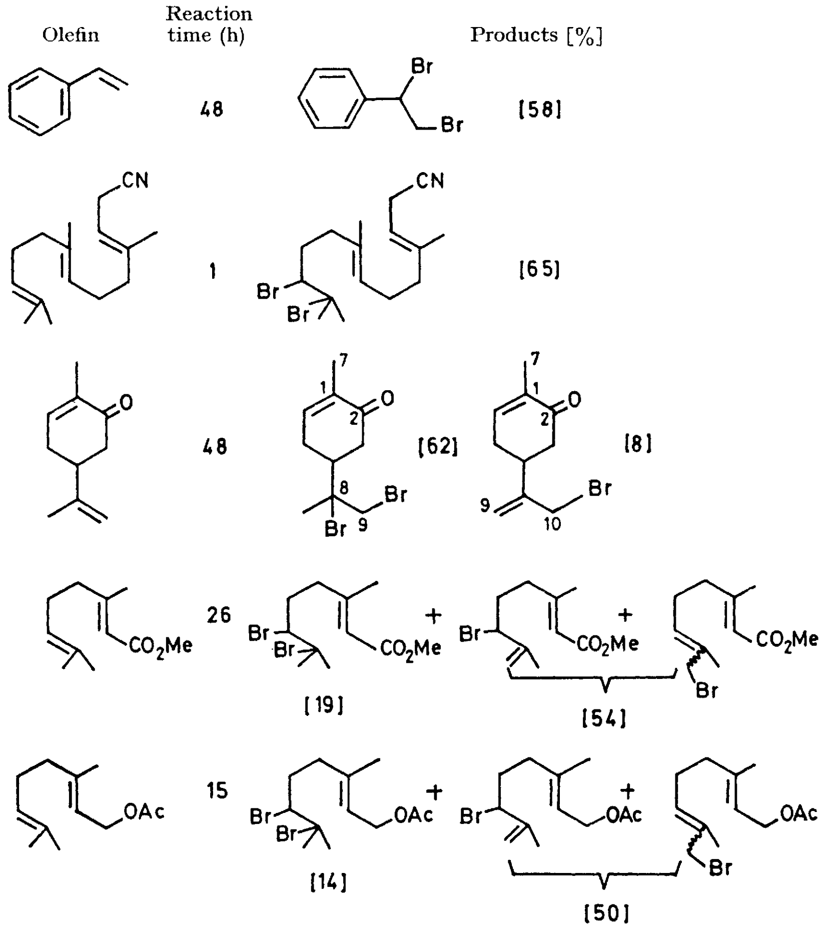


To investigate the mechanism of formation of the dibromide, we have prepared two kinds of analogous bromo-ketones (4) and (5) [7,8] and examined their reaction with geranyl cyanide. As is evident from the results in Table 2, both bromo-ketones gave the same products, a mixture of the dibromide (3a) and the allyl bromides [(6) and (7)] although their ratios were slightly different. An n.m.r. study of the crude reaction mixture indicated that only the secondary bromide was formed initially, and that it rearranged partly to the isomeric primary bromide during the separation procedure. Addition of typical

TABLE 1

Reaction of olefins with TBCO



radical traps to the reaction system did not disturb the formation of the products, indicative of an ionic rather than radical reaction. The implication from these experiments is that both the two bromine atoms of the dibromide (3a) originate in each case from the bromine at C-4 of the bromo-ketones, TBCO, (4), and (5). It is also plausible that the initial step of the reaction involves attack of Br$^+$ at the terminal double bond since formation of the dibromide is increased remarkably by the addition of Br$^-$ as shown in experiment 4 in Table 2.

The evidence described above can provide an explanation for the dibromide formation; this is shown in Scheme 2. By liberation of Br$^+$, TBCO changes into the anion$_1$ (Y = Br), which then replaces the C-4 bromine of another molecule of TBCO to give Br$^-$ and a phenoxy-ketone [equation (3)]. Since the phenoxy-ketone possesses a similar partial structure to that of TBCO, it liberates Br$^+$ and turns into anion$_2$ [equation (4)]. The sequential reactions of the resulting anion$_2$ with TBCO to release Br$^-$ followed by liberation of Br$^+$ afford anion$_n$ [the polyphenoxy-ether (8)]. The released Br$^-$ combines with the brominated carbonium ion to form the dibromide [equation (5)]. The allyl bromide (6) would be formed from the same carbonium ion as in equation (2). The reactions in Scheme 2 are corroborated by the fact that the physical data and elemental analysis of the polymeric material derived from TBCO agree with the estimated structure of the polyphenoxy-ether (8) (see Experimental section). When geranyl cyanide was treated with the analogous bromo-ketones (4) and (5), the phenoxy-ketone in equation (3) has no ability to liberate Y$^+$ (Y = Cl or Me) from its quinoid portion. Consequently, the dibromide is formed in less than 50% yield. Although the phenoxy-ketone intermediate (Y = Cl or Me) in equation (3) was not detected, presumably due to its instability,[9] the corresponding phenol derivative was isolated.

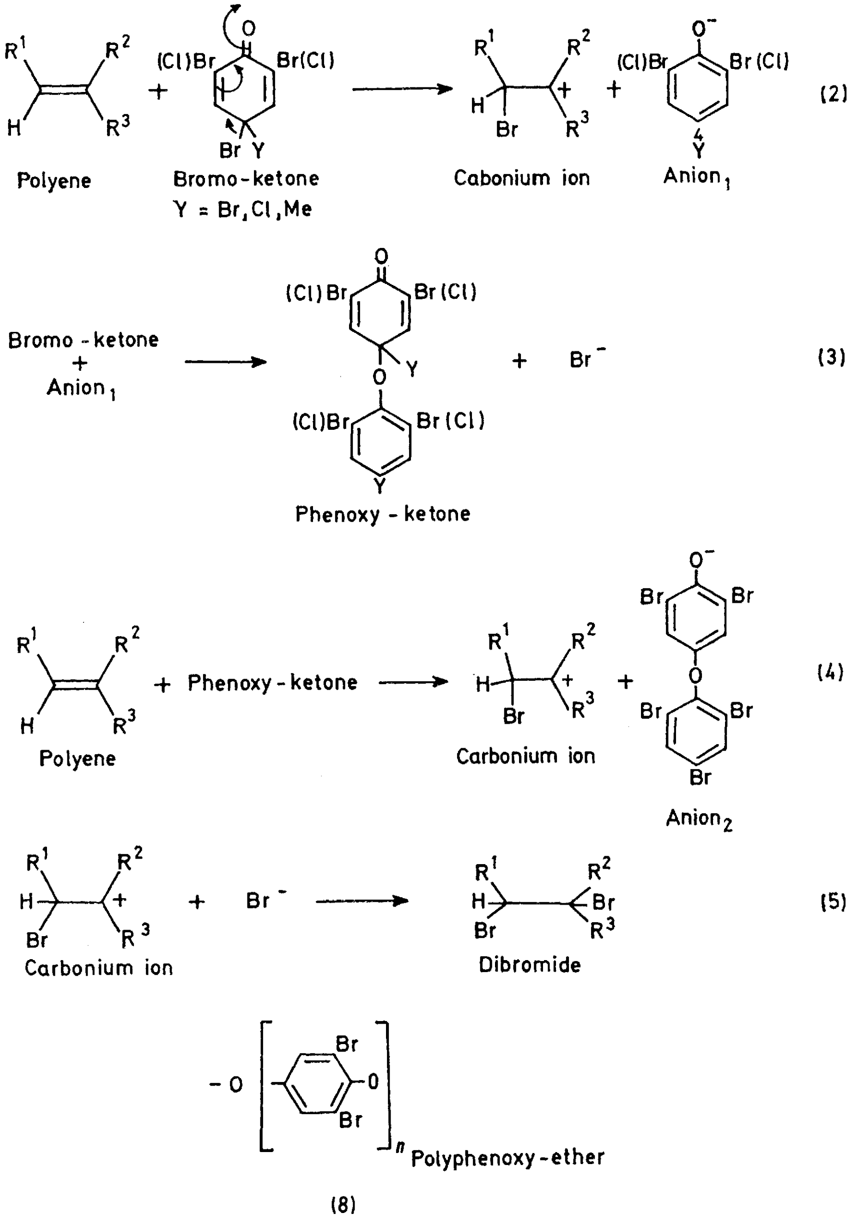
TABLE 2

Reactions of geranyl cyanide with bromo-ketones

		Products (%)			
Experiment	Bromo-ketone	(3a)	(6) + (7)	Recovered (1)	Phenol
1	TBCO	98			Polymer
2	(4)	40	10	26	46 [a]
3	(5)	45	10	36	43 [b]
4	(4) + CTAB [c]	88			

[a] Trichlorophenol. [b] 2,6-Dibromo-4-methylphenol. [c] Cetyltrimethylammonium bromide.

As indicated by experiment 4 of Table 2, the predominant formation of the dibromide was observed when the reaction was carried out in the presence of Br$^-$ as a quarternary ammonium salt. To investigate the generality of this reaction, various types of polyenes were submitted to the reaction under the same conditions and the results are summarized in Table 3. As can be seen, yields were generally high. The ring double bond in limonene was selectively brominated when 1 mol equiv. of TBCO was employed (experiment 2). By use of 2 mol equiv. of TBCO (experiment 3), the remaining double bond was brominated to form the tetrabromide as a separable mixture of diastereoisomers. As anticipated, limonene gave a complex brominated mixture under the usual bromination conditions (Br_2 in CCl_4). In the reaction of myrcene (experiment 4), the isolated double bond of the molecule reacted selectively to give the corresponding dibromide. However, decomposition during isolation of the product contributed to the lower yield.



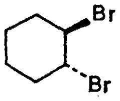
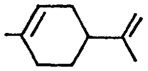
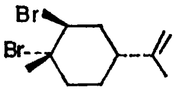
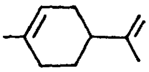
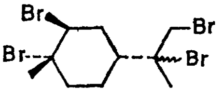
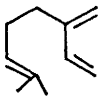
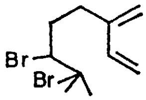
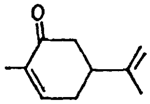
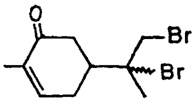
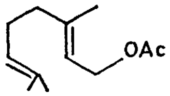
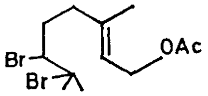
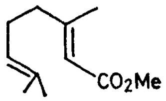
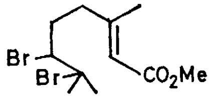
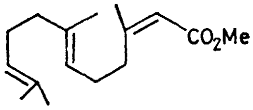
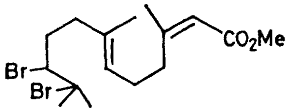
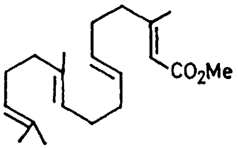
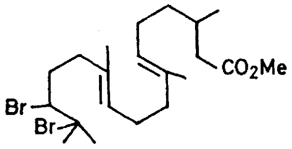
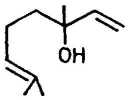
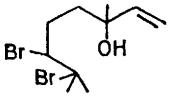
SCHEME 2

In contrast to the results shown in Table 1, polyenes such as carvone (experiment 5), geranyl acetate (experiment 6), and methyl geranate (experiment 7) were transformed into the dibromides exclusively. It should be also emphasized that the terminal bond of methyl geranylgeranate which possesses four double bonds was selective brominated in moderate yield (experiment 9).

It is seen, therefore, that TBCO serves as an excellent reagent for selective bromination of olefins under very mild conditions, permitting easy functionalization to form dibromides.

TABLE 3

Selective dibromination of polyenes

Experiment	Polyene	Molar ratio TBCO	Molar ratio CTAB[a]	Product	Yield (%)
1		1	1		91
2		1	1		77
3		2	2		87
4		1	2		36
5		1	1		97
6		1	1		95
7		1	1		82
8		1	1		73
9		1	1		62
10		1	2		22

[a] Cetyltrimethylammonium bromide.

EXPERIMENTAL

Reaction of Olefins with TBCO (*Table* 1).—*Reaction of geranyl cyanide* (1; R = CN). To a mixture of geranyl cyanide (814 mg, 5 mmol) and anhydrous dichloromethane (20 ml) was added TBCO[10] (2.05 g, 5 mmol) and the reaction mixture stirred at room temperature for 1 h. The mixture was diluted with ether and the resulting precipitates [polymeric materials (8)] were removed. The ethereal solution was washed with aqueous NaOH and aqueous NaCl, dried ($MgSO_4$), and evaporated. The residue was passed through a short SiO_2 column with n-hexane–EtOAc (10 : 1) as eluant to give (*E*)-6,7-dibromo-3,7-dimethyloct-2-ene-1-carbonitrile (3a) (1.60 g, 98%) as a colourless oil (Found: C, 40.8; H, 5.2; N, 4.3. $C_{11}H_{17}Br_2N$ requires C, 40.9; H, 5.3; N, 4.35%). In addition to its satisfactory physical data [δ ($CDCl_3$) 4.09 (dd, *J* 1.5 and 10 Hz, CHBr) and 1.82 and 1.99 (each sharp s, $CBrMe_2$)], the structure of the dibromide (3a) was confirmed by transforming it (316 mg, 1 mmol) in ether (2 ml) into geranyl cyanide (160 mg, 100%) using zinc dust (120 mg, 1.8 mmol) and AcOH at room temperature. The polymeric materials (8) showed δ ($CDCl_3$) 7.3 (m) and 7.8 (m) in the ratio 1 : 1, $\nu_{max.}$ (KBr) 3 090, 2 930, 1 590, 1 430, 1 230, and 1 180 cm^{-1} [Found: C, 28.95; H, 1.05. $(C_6H_2Br_2O)_n$ requires C, 28.85; H, 0.8%].

Reaction of styrene. Styrene (138 mg, 1.32 mmol) in dichloromethane (13 ml) was treated similarly with TBCO (544 mg, 1.33 mmol) for 48 h. Styrene dibromide (201 mg, 58%), m.p. 71—72 °C (lit.,[11] 73—74 °C), was obtained after purification through SiO_2 with n-hexane as eluant. When 3 mol. equiv. of TBCO were employed in an n.m.r. tube, quantitative formation of styrene dibromide was observed after 48 h.

Reaction of farnesyl cyanide. Farnesyl cyanide (746 mg, 3.22 mmol) in dichloromethane (13 ml) was treated with TBCO (1.32 g, 3.22 mmol) under the same conditions for 1 h. Chromatography on SiO_2 with n-hexane–EtOAc (10 : 1) as eluant afforded 10,11-dibromo-3,7,11-trimethyldodeca-2,6-diene-1-carbonitrile [(818 mg, 65%), δ 4.12 (dd, *J* 1.5 and 11 Hz, CHBr) and 1.81 and 1.97 (each sharp s, $CBrMe_2$) (Found: C, 48.95; H, 6.35; N, 3.55. $C_{16}H_{25}Br_2N$ requires C, 49.15; H, 6.45; N, 3.6%)].

Reaction of (—)-*carvone.* To a solution of (—)-carvone (1.5 g, 10 mmol) in dichloromethane (30 ml) was added TBCO (4.2 g, 10 mmol) and the mixture kept for 48 h. After addition of ether, the solution was washed with aqueous NaOH and then aqueous NaCl. From the NaOH solution was obtained tribromophenol methyl ether (1.24 g, 35%) after sequential procedures of acidification, extraction with ether, etherification with CH_2N_2, and finally separation by SiO_2 column chromatography. The neutral residues were passed through a SiO_2 column (CH_2Cl_2 as eluant) to isolate 8,9-*dibromo*-p-*menth*-6-*en*-2-*one* (1.93 g ,62%, mixture of diastereoisomers), δ 1.75 (br d, *J* 1.5 Hz, 1-Me), 1.92 (s, 8-Me), 3.78, 3.82, and 3.95 (each d, *J* 10 Hz, 9-H_2 diastereoisomeric mixture), and 6.63 (m, 6-H) (Found: C, 38.05; H, 4.4. $C_{10}H_{14}Br_2O$ requires C, 38.75; H, 4.55%); 10-*bromo*-p-*mentha*-6,8(9)-*dien*-2-*one* (260 mg, 8%), M^+ 228 and 230, δ 1.72 (br s, 1-Me), 3.99 (br s, 10-H_2), 5.04 and 5.28 (C=CH_2), and 6.66 (m, 6-H), and recovered (—)-carvone (210 mg, 14%).

Reactions of methyl geranate and geranyl acetate. A mixture of methyl geranate (225 mg, 1.24 mmol), CH_2Cl_2 (12 ml), and TBCO (510 mg, 1.24 mmol) was kept for 26 h and then separated into acidic and neutral fractions by shaking with aqueous NaOH. From the acidic portion was obtained tribromophenol (313 mg, 76%). The neutral residues were passed through a short SiO_2 column [n-hexane–EtOAc (30 : 1) as eluant] to afford methyl 6,7-dibromo-3,7-dimethyloct-2-enoate (80 mg, 19%), M^+ 340, 342, and 344 (1 : 2 : 1)], δ (CCl_4) 1.82 and 2.01 (s, $CBrMe_2$), 2.20 (d, *J* 1.5 Hz, 3-Me), 4.14 (dd, *J* 1.5 and 10 Hz, CHBr), and 5.74 (br s, 2-H), and a mixture of methyl 6-bromo-3,7-dimethylocta-2,7-dienoate and methyl 8-bromo-3,7-dimethylocta-2,6-dienoate (175 mg, 54%).

Similarly, geranyl acetate (248 mg, 1.27 mmol) was treated with TBCO (531 mg, 1.30 mmol) in CH_2Cl_2 (13 ml) for 15 h. The acidic portion afforded tribromophenol (320 mg 75%) whilst the neutral portion gave a mixture of 6-bromo-3,7-dimethylocta-2,7-dienyl acetate and 8-bromo-3,7-dimethylocta-2,6-dienyl acetate (173 mg, 50%); 6,7-*dibromo*-3,7-*dimethyloct*-2-*enyl acetate* (63 mg, 14%), M^+ 354, 356, and 358 (1 : 2 : 1), δ (CCl_4) 1.78 (br s, 3-Me), 1.82 and 1.99 (s, $CBrMe_2$), 4.14 (dd, *J* 1.5 and 10 Hz, CHBr), 4.55 (d, *J* 7 Hz, 1-H_2), and 5.45 (t, *J* 7 Hz, 2-H); and recovered acetate (35 mg, 14%).

Each mixture of the allyl bromides obtained from methyl geranate and geranyl acetate showed only one spot on t.l.c. (SiO_2 under several conditions). Detailed inspection of the n.m.r. spectra indicated, however, that the allyl bromides (M^+ 260 and 262) from geranic ester were a *ca.* 1 : 1 mixture of secondary (methyl 6-bromo-3,7-dimethylocta-2,7-dienoate) [δ (CCl_4) 1.87 and 2.17 (7- and 3-Me), 4.50 (m, CHBr), 4.92 and 5.10 (br s, C=CH_2), and 5.66 (br s, 2-H)] and primary (methyl 8-bromo-3,7-dimethylocta-2,6-dienoate) [δ (CCl_4) 1.79 and 2.17 (7- and 3-Me), 3.93 (br s, CH_2Br), and 5.66 (br s, 2-H)] bromides. The allyl bromides from geranyl acetate [*m*/*e* 214 and 216 (*M* — AcOH), 195 (*M* — Br) and 135 (*M* — Br — AcOH)] were a 7 : 1 mixture of secondary (6-bromo-3,7-dimethylocta-2,7-dienyl acetate) [δ (CCl_4) 1.87 and 1.98 (7- and 3-Me), 4.52 (d, *J* 7 Hz, 1-H_2), 4.85 and 5.06 (br s, C=CH_2), and 5.37 (t, *J* 7 Hz, 2-H)], and primary (8-bromo-3,7-dimethylocta-2,6-dienyl acetate) [δ (CCl_4) 1.73 and 1.98 (7- and 3-Me), 3.93 (br s, CH_2Br), 4.52 (d, *J* 7 Hz, 1-H_2), and 5.37 (t, *J* 7 Hz, 2-H)] bromides, respectively.

Reactions of Geranyl Cyanide with Bromo-ketones (*Table* 2). —*Preparation of the bromo-ketones* (4) *and* (5). (a) 4-*Bromo*-2,4,6-*trichlorocyclohexa*-2,5-*dienone* (4). To a stirred mixture of 2,4,6-trichlorophenol (25 g) and MeOH–AcOH (200 ml, 1 : 1) was added bromine (25 g) during 1 h at room temperature and the stirring continued for a further 1 h. Aqueous Na_2CO_3 (300 ml; 10% w/v) was added and the resultant orange precipitate was collected and washed with water and then MeOH (100 ml). Recrystallization from n-hexane–CH_2Cl_2 afforded the bromo-ketone (4) (16 g), m.p. 109—110 °C (lit.,[7] 97 °C).

(b) 2,4,6-*Tribromo*-4-*methylcyclohexa*-2,5-*dienone* (5). 2,6-Dibromo-4-methylphenol (26.6 g) in MeOH–AcOH (100 ml 1 : 1) was similarly treated with bromine (16 g) under ice-cooling and the precipitate, obtained by addition of aqueous Na_2CO_3 (10% w/v), was recrystallized from n-hexane–CH_2Cl_2 to give the bromo-ketone (5) (15.6 g), m.p. 104—105 °C (lit.,[8] 105 °C).

Reactions of geranyl cyanide. (a) *With* 4-*bromo*-2,4,6-*trichlorocyclohexa*-2,5-*dienone* (4). A mixture of geranyl cyanide (518 mg, 3.2 mmol), dichloromethane (30 ml), and the bromo-ketone (4) (876 mg, 3.2 mmol) was stirred for 65 h at room temperature when trichlorophenol (286 mg, 46%) was removed from an acidic fraction of the reaction mixture. The neutral fraction was passed through a SiO_2 column [n-hexane–AcOEt (15 : 1) as eluant] to isolate recovered geranyl cyanide (133 mg, 26%), 6,7-dibromo-3,7-dimethyloct-2-ene-1-carbonitrile, and a 7 : 2 mixture (75 mg, 10%) of 6-bromo-3,7-dimethylocta-2,7-diene-1-carbonitrile (6), *m*/*e* 162 (*M* — Br) and 121 (*M* — Br — MeCN), δ 1.70 and 1.86 (3- and 7-Me), 3.02 (d, *J* 7 Hz, 1-H_2), 4.43 (m, CHBr), 4.91 and 5.08 (br s, C=CH_2), and 5.26 (t, *J* 7 Hz, 2-H)], and 8-bromo-3,7-dimethylocta-2,6-diene-1-carbonitrile (7), δ 1.70 and 1.77 (3- and 7-Me), 3.02 (d, *J* 7 Hz, 1-H_2), 3.93 (br s, CH_2Br), 5.26 (t, *J* 7 Hz, 2-H), and 5.54 (m, 6-H). When the reaction was carried out in an n.m.r. tube without isolation, no signal due to the primary bromide (7) was observed.

(b) *With* 2,4,6-*tribromo*-4-*methylcyclohexa*-2,5-*dienone* (5). A mixture of geranyl cyanide (268 mg, 1.64 mmol), dichloromethane (16 ml), and the bromo-ketone (5) (566 mg, 1.64 mmol) was similarly stirred for 60 h and 2,6-dibromo-4-methylphenol (185 mg, 43%) was obtained from the acidic fraction. The neutral portion gave after chromatography on SiO_2 the dibromide (3a) (236 mg, 45%), recovered geranyl cyanide (97 mg, 36%), and a mixture of the secondary (6) and primary (7) bromides (41 mg, 10%).

(c) *With the bromo-ketone* (4) *in the presence of cetyltrimethylammonium bromide.* To a vigorously stirred solution of geranyl cyanide (195 mg, 1.19 mmol) and cetyltrimethylammonium bromide (437 mg, 1.2 mmol) in dichloromethane (12 ml) was gradually added the bromo-ketone (4) (333 mg, 1.2 mmol) whereupon the mass of cetyltrimethylammonium bromide disappeared to afford at the end of the reaction a clear solution. Stirring was continued for a further 1 h, the solvent was removed *in vacuo*, and ether was added to the residue. The ethereal solution was filtered, washed with aqueous NaOH and aqueous NaCl, dried ($MgSO_4$), and evaporated. The residue was passed through a SiO_2 column [n-hexane–AcOEt (10 : 1) as eluant] to give 6,7-dibromo-3,7-dimethyloct-2-ene-1-carbonitrile (3a) (338 mg, 88%) as a colourless oil.

Reactions of Olefins with TBCO in the Presence of Cetyltrimethylammonium Bromide (*Table* 3).—*General procedure.* To a 0.1M solution of each olefin in dichloromethane was added the required amount of cetyltrimethylammonium bromide and chloroform was added until the mixture became a clear solution ($CHCl_3 : CH_2Cl_2 = 1 : 4$ v/v for 1 mol. equiv. of cetyltrimethylammonium bromide but 1 : 2 for 2 mol. equiv.). To the stirred solution was gradually added TBCO. As soon as TBCO was added, the reaction mixture became green, and changed to orange after *ca.* 1 min. When the mixture became orange, more TBCO was added and the operation continued until all the required TBCO had been consumed. After removal of the solvents *in vacuo* (35 °C at 300 mmHg), n-hexane was added to the residue and insoluble materials were removed by filtration through Celite. The n-hexane solution was washed with aqueous NaOH and aqueous NaCl, dried ($MgSO_4$), and evaporated, and the residue was purified by distillation and/or chromatography on SiO_2

Experiment 1. 1,2-Dibromocyclohexane [12] was prepared from cyclohexene (214 mg) in 91% yield, b.p. 106 °C (oil bath) at 36 mmHg (Found: C, 29.65; H, 4.2. Calc. for $C_6H_{10}Br_2$: C, 29.8; H, 4.15%).

Experiment 2. (+)-Limonene dibromide (1,2-dibromo-*p*-menth-8-ene) [13] was prepared from (+)-limonene (371 mg) in 77% yield, b.p. 45 °C (oil bath) at 2.5 mmHg (Found: C, 40.8; H, 5.5 Calc. for $C_{10}H_{16}Br_2$: C, 40.55; H, 5.45%).

Experiment 3. (+)-Limonene tetrabromide (1,2,8,9-tetrabromo-*p*-methane) was prepared from (+)-limonene (182 mg) in 87% yield and was separated into oily (Found: C, 26.55; H, 3.7. Calc. for $C_{10}H_{16}Br_4$: C, 26.35; H, 3.55%) and crystalline diastereoisomers by recrystallization from MeOH. The crystalline tetrabromide had m.p. 103 °C (lit.,[14] 104—105 °C) (Found: C, 26.45; H, 3.65).

Experiment 4. Myrcene-6,7-dibromide (6,7-dibromo-7-methyl-3-methyleneoct-1-ene), prepared from myrcene (247 mg), was fairly unstable on the SiO_2 column and pure specimens were obtained in 36% yield, δ 1.80 and 1.98 (sh s, $CBrMe_2$), 4.21 (d, *J* 10 Hz, CHBr), 4.9—5.5 (m, $C=CH_2 \times 2$), and 6.37 (dd, *J* 11 and 18 Hz, 2-H) (Found: C, 40.5; H, 5.35. $C_{10}H_{16}Br_2$ requires C, 40.55; H, 5.45%).

Experiment 5. (−)-Carvone dibromide (8,9-dibromo-*p*-menth-6-en-2-one) [15] was prepared from (−)-carvone (256 mg) in 97% yield, b.p. 40 °C (oil bath) at 0.05 mmHg (Found: C, 38.95; H, 4.75. Calc. for $C_{10}H_{14}Br_2O$: C, 38.75; H, 4.55%).

Experiment 6. Geranyl acetate dibromide (6,7-dibromo-3,7-dimethyloct-2-enyl acetate) was prepared from geranyl acetate (227 mg) in 95% yield, b.p. 30 °C (oil bath) at 0.04 mmHg (Found: C, 40.45; H, 5.8. $C_{12}H_{20}Br_2O_2$ requires C, 40.45; H, 5.65%).

Experiment 7. Methyl geranate dibromide (methyl 6,7-dibromo-3,7-dimethyloct-2-enoate) was prepared from methyl geranate (178 mg) in 82% yield, b.p. 30 °C (oil bath) at 0.03 mmHg (Found: C, 38.7; H, 5.4. $C_{11}H_{18}Br_2O_2$ requires C, 38.6; H, 5.3%).

Experiment 8. Methyl (2*Z*)-farnesate dibromide [methyl (2*Z*)-10,11-dibromo-3,7,11-trimethyldodeca-2,6-dienoate] was prepared from methyl (2*Z*)-farnesate (209 mg). The brominated products were purified by chromatography on SiO_2 with n-hexane–EtOAc (30 : 1) as eluant to give the *dibromide* (250 mg, 73%), δ 1.80 and 1.98 (sh s, $CBrMe_2$), 4.12 (dd, *J* 2 and 11 Hz, CHBr), 1.89 (d, *J* 1.5 Hz, 3-Me), 5.59 (br d, *J* 1.5 Hz, 2-H), and 5.26 (t, *J* 7 Hz, 6-H) (Found: C, 47.15; H, 6.35. $C_{16}H_{26}Br_2O_2$ requires C, 46.85; H, 6.4%), and the tetrabromide [methyl (2*Z*)-6,7,10,11-tetrabromo-3,7,11-trimethyldodec-2-enoate] (41 mg, 9%).

Experiment 9. Methyl geranylgeranate dibromide [methyl (2*E*,6*E*,10*E*)-14,15-dibromo-3,7,11,15-tetramethylhexadeca-2,6,10-trienoate] was prepared from the methyl ester (749 mg) in 62% yield (694 mg) accompanied by recovered ester (109 mg, 15%) and the tetrabromide (221 mg, 15%). Chromatography on SiO_2 with n-hexane–EtOAc (40 : 1) as eluant gave the *dibromide*, M^+ 476, 478, and 480 (1 : 2 : 1), δ 1.80 and 1.97 (sh s, $CBrMe_2$), 2.13 (d, *J* 1.5 Hz, 3-Me), 4.12 (br d, *J* 10 Hz, CHBr), 5.10 (br s, 6- and 10-H), and 5.59 (br s, 2-H). The dibromide (41 mg, 0.086 mmol) was quantitatively converted into methyl geranylgeranate by zinc dust (58 mg, 0.89 mmol) in AcOH (0.2 ml).

Experiment 10. (−)-Linalol dibromide (6,7-dibromo-3,7-dimethyloct-1-en-3-ol) was prepared from (−)-limonene (270 mg) in 22% yield (Found: C, 38.15; H, 5.7. $C_{10}H_{18}Br_2O$ requires C, 38.2; H, 5.8%), δ 1.30 (COH*Me*), 1.81 and 1.98 ($CBrMe_2$), 4.17 (br d, *J* 9 Hz, CHBr), and 4.9—6.1 (3 H, m, $CH=CH_2$).

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