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BROMINE INDUCED AUTOXIDATION AND BROMINATION STUDIES OF CHLORINATED NORBORNENES

GOPALPUR NAGENDRAPPA*

Engler-Bunte Institut, Bereich Petrochemie
Universität Karlsruhe, 7500 Karlsruhe, West Germany.

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Summary: Atmospheric oxygen easily oxidises 2,3-dichloro-2-norbornene in presence of bromine radicals. But 2,3-dichloro-2,5-norbornadiene and 2-chloro-2-norbornene fail to add oxygen. All three chloronorbornenes undergo bromination under radical and ionic conditions to yield products of rearrangement and bond migrations.

Chloroolefins, on account of their diverse application in industry, agriculture, health management etc, find their way into the environment and contribute their mite to environmental pollution. Their interaction with molecular oxygen is important in understanding their atmospheric chemistry and such studies as also those of autoxidation of various other organic compounds are receiving much attention.[1] Autoxidation of halo-olefins may also lead to useful products.[1m]

Oxygenation of some chloroolefins has been brought about by light induced, chlorine radical-catalysed molecular oxygen addition through free radical chain processes.[1i-o] In biological systems superoxide radical ion is believed to effect the chloroolefin oxidation.[1n,o]

Bromine radical is also considered to play an important role in atmospheric chemistry on account of bromine being potentially more active than chlorine, since HBr is less stable than HCl, which allows more bromine to remain in the active forms Br and BrO.[2]

We have earlier reported on the oxidation of 2,3-dichloronorbornene (1) by different oxidising agents.[3] We have now observed that oxidation of 1 can be accomplished by bromine radical induced oxygenation. In addition we have made product studies of reactions of 1 and related compounds (2 and 3) with bromine and HBr, the results of which are reported here.

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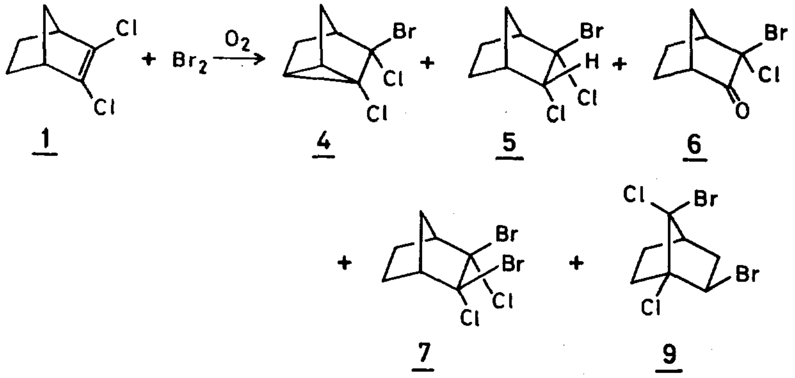
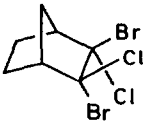
* Address for correspondence: Department of Chemistry, Bangalore University (Central College), Bangalore-560 001, India.

RESULTS AND DISCUSSION

Bromination of 2,3-dichloronorbornene (1) was carried out in methylene chloride, chloroform and carbon tetrachloride under nitrogen or oxygen or ambient atmosphere. The reaction required 8-10 h for completion when the reaction flask was covered[4] and about the same time when not covered. The products, 3-bromo-2,3-dichloronortricyclene (4), 2,3-dibromo-2,3-dichloronorbornane (7) and 2,7-dibromo-1,7-dichloronorbornane (9), were obtained as common major products in presence of oxygen or under nitrogen atmosphere in chloroform or methylene chloride. The fourth major product in experiments run in presence of oxygen or ambient atmosphere was 3-bromo-3-chloro-2-norbornanone (6), and that in experiments run under nitrogen atmosphere was approximately equivalent amount of 2-bromo-2,3-dichloronorbornane (5),(Scheme 1). Thus 5 and 6 are formed in a mutually exclusive way depending on the absence or presence of oxygen. In addition, small amounts of 3-4 products were formed, which could not be isolated in sufficient quantity and purity for identification. Table 1 summarises the results of bromination of 1. The major compounds were isolated in pure form by chromatographing on silica gel column followed by recrystallisation and/or vacuum sublimation, and their identities were established by microanalysis, IR, NMR (^{1}H and ^{13}C) and mass spectral data. The structural assignment of 5

Scheme : 1





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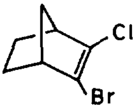

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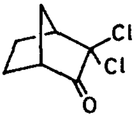

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Table-1: Bromination of 2,3-dichloro-2-norbornene (1)

Conditions		Products[a] (ratio, %)				
		4	5	6	7	8
Ambient atmosphere	CH_2Cl_2[b]	20-22	< 1	8-10	33-36	28-30
	$CHCl_3$	31-32	-	12-14	21-22	21-22
	CCl_4	16-20	< 3	9-10	10-12	33-38
Oxygen atmosphere	CH_2Cl_2/dark[c]	21-24	-	11-13	28-34	30-34
	$CH_2Cl_2/h\nu$[d]	5-6	13-16	21-23	27-30	7-8
	$CHCl_3$	30-40	< 3	7-9	7-10	32-47
	CCl_4/dark	26-28	< 2	11-13	9-12	33-36
	$CCl_4/h\nu$	< 3	14-15	22-25	25-27	< 2
Nitrogen atmosphere	CH_2Cl_2/dark	21-22	12-14	-	6-8	58-60
	$CH_2Cl_2/h\nu$	< 2	< 1	-	84-88	8-9
	$CHCl_3$	28-32	8-10	-	12-16	44-48
	CCl_4/dark	-	-	-	90-95	3-8
Nitrogen stream	$CHCl_3$/dark	20-23	-	-	56-59	20-21

[a] Minor and unidentified products are not included. [b] The reaction flask was not covered in these reactions. [c] Flask was covered with aluminium foil. [d] The flask was illuminated with 200 W tungsten lamp.

and 9 was based on the chemical shift values[5] of the protons on C-3 and C-2 respectively, and on analogy and mechanistic considerations.[5e] The configuration on C-2 and C-3 of 2,3-dibromo-2,3-dichloronorbornane could be either *cis* or *trans*. ^{13}C NMR indicates it to be a mixture of both, one being in large excess over the other. We favour the *cis* configuration (7) for the larger component, because: (i) *exo*-*cis* addition is more common,[6] and (ii) when this compound was refluxed with magnesium in ether, 1 and 20 were obtained in about 4:1 ratio. Assuming that *exo*-*cis*-elimination is the predominant mode of elimination,[7] 7 would be expected to lead essentially to 1, and 20 would be formed from the minor *trans*-isomer.

All the products of bromination seem to be kinetically controlled, since the product composition remained the same even when the reaction mixture was kept stirred for long periods (70-80 h) after the reaction completed, except for very slow formation, in runs under oxygen, of an as yet unidentified compound, but closely related to 9 as shown by its chromatographic behaviour (GC, TLC and CC) and mass spectrum.

The proportion of nortricyclene 4 is 20-22% in experiments run in CH_2Cl_2 and 30-40% in $CHCl_3$, under nitrogen or oxygen atmosphere. In CCl_4, however, 4 is formed to the extent of 25-30% only in 'dark', under oxygen. But if the reaction is run in 'dark' under nitrogen or with illumination (200 W tungsten lamp) under oxygen, only traces of 4 were observed indicating that radical conditions are not conducive to its formation. Bromination with illumination in CH_2Cl_2 also produced only traces of 4. This suggests that in CH_2Cl_2 and $CHCl_3$, the major part of bromination is going through an ionic mechanism even under nitrogen atmosphere in dark. The formation of 6, however, clearly points to the fact that the reaction is also going through radical intermediates. Such a combination of radical and ionic components is not uncommon in reactions of norbornenes,[8,9] and we presume that this situation is prevailing here.

In all the bromination reactions performed with illumination under nitrogen atmosphere, the major product (>90%) was 7, and 9 formed as a minor product. In contrast, bromination with illumination under oxygen gave ~70% of 7, ~25% of 6 and <5% of 9. Though 7 was formed in larger proportion in all the light aided reactions, it is unlikely that it is produced only through radical processes, because no consistent pattern could be discerned from the amount of 7 formed under different conditions. It seems that, in addition to the influence of oxygen, HBr also plays some role in this outcome, and it is not easy to fully rationalise these variations. Nevertheless, what emerges from these results is that 9 is a product of ionic intermediates, and radical conditions would lead to preferential formation of 7.

Light, oxygen and HBr - all the three seem to influence the ratio of 7:9. The role of light is clear, but that of oxygen and HBr is not quite so. However, from the observed results, it seems likely that oxygen and HBr[10] react more competitively than bromine with radical intermediates - thus both acting as efficient radical scavengers - leading bromination to occur mainly by ionic mechanism. This interpretation gets some support from the fact that when HBr formed in the reaction is driven out by bubbling nitrogen gas slowly,[11] 7 was obtained as the major product, and 4 and 9 formed as minor products.

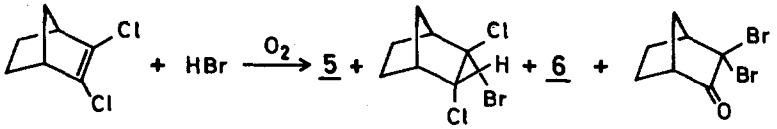
In addition, the solvents CH_2Cl_2 and $CHCl_3$ may also help ionic reaction by acting as radical scavanger, but CCl_4 remains indifferent.[5c] It may also be noted that consistently high proportions of nortricyclene 4 were formed in CH_2Cl_2 and $CHCl_3$ even under nitrogen atmosphere indicating that these solvents support ionic route.

In CCl_4, bromination of 1 with illumination under oxygen atmosphere gave ∽15% of 5, ∽24% of 6 and ∽25% of 7, along with small amounts of 4 and 9. A few more (∽5-6) minor products were also present, three of which seem to be 10, 20 and 22 from their chromatographic behaviour and mass spectral data. The compound 20 is produced initially, which then undergoes further reaction to give other products including 6.

Attempt to brominate 1 under UV irradiation produced a product mixture that contained not less than 30 components and was not analysed.

The formation of 5 in nitrogen atmosphere and of 6 in presence of oxygen to about the same extent and the near absence of 5 in the latter reaction indicated that HBr, in presence of oxygen, is mainly consumed in the autoxidation process. In a separate experiment, it was also found that passing dry HBr through chloroform solution of 1 under ambient conditions produced 5, 6 and 10 in the ratio of 15:4:1, the proportion of 6 being double that obtained in the bromination reaction,[12] (Scheme 2).

Scheme : 2



5a 10

When HCl was used instead of HBr, no reaction occurred. We also tried direct oxidation by passing oxygen into chloroform solution of 1 at 25° and 50° for upto 15 h with illumination using 200 W lamp, but the starting compound was recovered unchanged. The results point out that 1 undergoes oxygenation easily by atmospheric oxygen when induced by bromine radicals and HBr seems to have profound catalytic influence.[13]

To elicit the structural features that influence the efficacious autoxidation of the vinyl halide function under similar condition, bromination of 2-chloronorbornene (2), 2,3-dichloro-2,5-norbornadiene (3) and 1,2-dichlorocyclohexene was carried out.

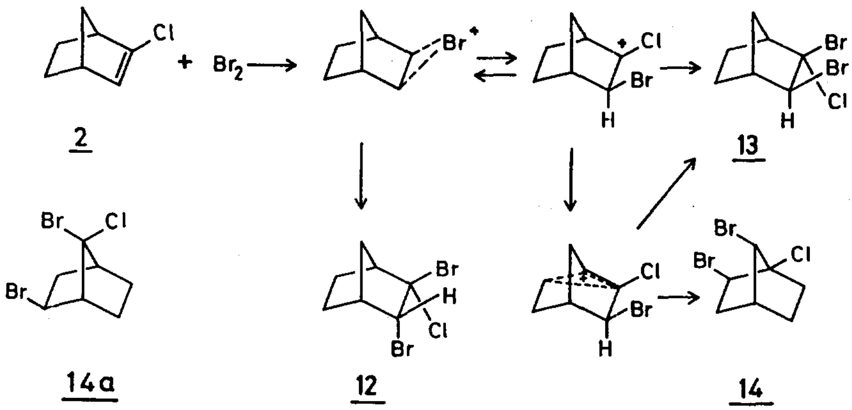
1,2-Dichlorocyclohexene (21) underwent very facile bromination under ambient conditions giving a complex mixture of products, complete identification of which has not been possible, but IR and GC-MS data do indicate some minor amounts of oxygenated products like carbonyl compounds, phenolic compounds etc. Probably, because of reactive allylic positions[14] and higher reactivity of 21, the product is not as simple a mixture as in the case of 1.

The bromine addition to 2-chloronorbornene (2) was performed under ambient conditions, and it was found that bromine was consumed instantaneously. Two major compounds were isolated, which constituted 50-55%

and 31-38% of the product mixture. The former is identified as a mixture of equal quantities[15] of 12 and 13, and the latter as 14. A minor compound, composing 7-8% of the product, is identified as nortricyclene 11.[16] No ketonic or any other oxygenated product was isolated. Thus no observable autoxidation of 2 takes place under the same conditions which bring about oxidation of 1.

The bromination of 2 in nitrogen atmosphere yielded 68-70% of 12+13 and 25-28% of 14. This suggests that 14 is a product of ionic bromination and 12 and 13 are products of ionic and/or radical bromination (Scheme 3). It is interesting to note that 14 is a single product and the other possible product of Waagner-Meerwein rearrangement with 4,5-bond migration, 14a, is not formed.[16] This suggests that the positive charge on bromine-bridged intermediate is essentially concentrated on C-2 due to its stabilization by chlorine.[17]

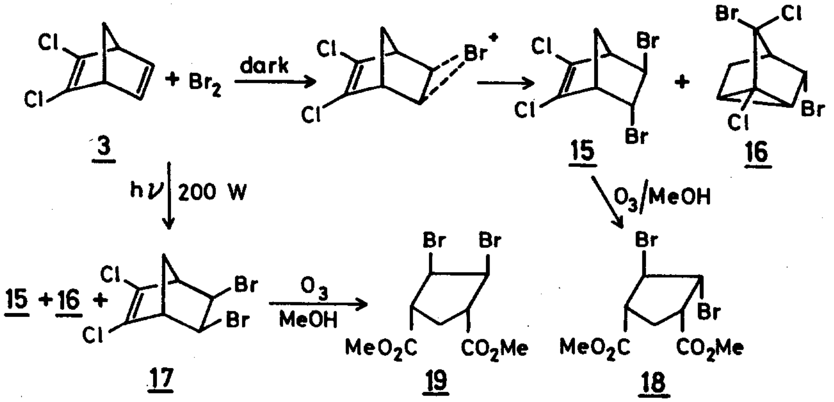
Scheme : 3



Bromination of 2,3-dichloro-2,5-norbornadiene (3) at 0° under ambient atmosphere was instantaneous and gave a mixture of 53% of 15 and 46% of 16, which were easily separated on silica gel column and identified by spectral characteristics, elemental analysis and ozonolysis, (Scheme 4). When the bromination product mixture was ozonised in methanol,[18] 15 was converted to the dimethyl ester 18, which was isolated and identified. When 3 was brominated with exposure to 200 W lamp, 45% of 15, 42% of 17 and only 13% of 16 were formed. The compound 17 was identified by its spectral data and ozonolysis. However, in both cases no oxygen containing compound was observed, although radical intermediates seem to be involved at least in the case of bromination under illumination.

The observed results are consistent with the expected initial attack of bromine on the unchlorinated double bond (Scheme 4).

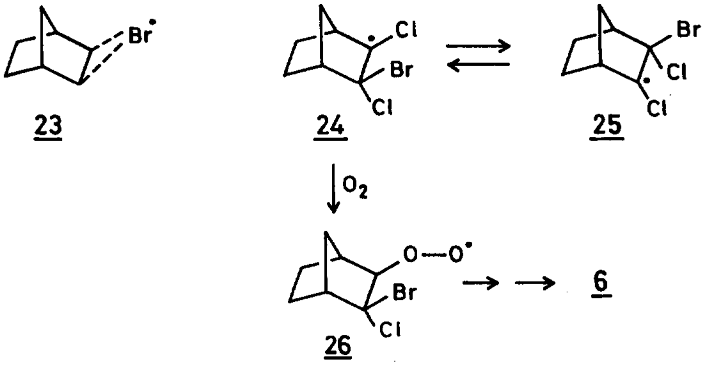
Scheme : 4



The foregoing results indicate that for the facile autoxidation of chlorinated norbornene two vinylic chlorines are necessary and a radical initiator is required to start the reaction. One can imagine similar oxidation taking place even in the atmosphere as bromine atoms are available.[2]

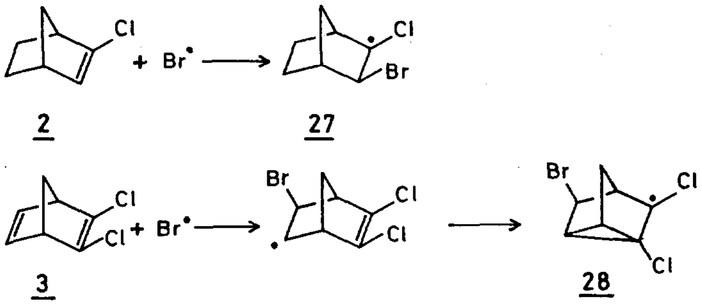
The addition of bromine atom to 1 is likely to produce a bridged radical 23 having symmetrical structure,[19] or a rapidly equilibrating system of 24 and 25, both being stabilised by α-chlorine.[20] Oxygen then adds to 24/25 producing the peroxy radical 26 which undergoes further transformation to give 6 (Scheme 5). The mechanism resembles the one proposed for autoxidation of haloethylenes.[1a]

Scheme : 5



Though similar chlorine stabilised radical intermediates 27 and 28 (Scheme 6) could be envisaged in the case of 2 and 3 respectively,[21] it is surprising that no significant amount of oxygenation product is formed in either case.

Scheme : 6



EXPERIMENTAL SECTION

The required chlorobicyclics, 2,3-dichloro-2-norbornene (1),[3a] 2-chloro-2-norbornene (2) and 2,3-dichloro-2,5-norbornadiene (3)[21] were prepared by known methods. The solvents, dichloromethane, chloroform and carbon tetrachloride were distilled from phosphorus pentoxide. Infrared (IR) spectra were recorded on Beckmann Acculab 1 spectrometer. Nuclear magnetic resonance (^{1}H and ^{13}C NMR) spectra were obtained on Bruker Data System Model MTC-20 instrument with tetramethylsilane as internal standard. Mass spectra (MS)[22] were obtained on Varian Mat 111 gas chromatograph/mass spectrometer system. The gas chromatographic (GC) analyses were performed on Varian Aerograph 1400 and Shimadzu 6A instruments using 3 m Nitrilsilicone oil column with temperature programme and nitrogen as carrier gas. Column chromatography (CC) was carried out using silica gel 60 or Kieselgel 60 (70-230 mesh size) with pentane and pentane-ether as eluents and each solid product was purified finally by vacuum sublimation. The melting points (m.p.) are uncorrected. The elemental analyses were carried out at the analytical laboratories of Prof. Dipl. Ing. Dr. H. Malissa & G. Reuter, Engelkirchen, and Dipl. Chem. R. Glier, Rothlein, West Germany.

General experimental procedure: A three necked flask fitted with a gas inlet adaptor, a dropping funnel and a reflux condenser connected to a mercury trap was used. The apparatus was flushed with dry nitrogen or oxygen if required and same atmosphere was maintained, otherwise ambient atmosphere was maintained. 'Dark' reactions were run by covering the flask with thick aluminium foil. The source of light for reactions under illumination was a 200 W tungsten lamp. The compound (300 mg to 3.25 g was used in various experiments) was added to the flask followed by 10-25 ml of the solvent. Nitrogen or oxygen was bubbled in when either atmosphere was required. Then a solution of bromine (10-20 mol % excess) in the same solvent (5-10 ml) was added dropwise over 15-30 min with stirring and the reaction was followed by GC. When the starting compound had been consumed, the excess bromine was destroyed by dropwise addition of a 10% solution of $NaHSO_3$. The organic layer was then separated, washed successively with 10% $NaHCO_3$ soln, water and satd NaCl soln. After drying over $MgSO_4$ the solvent was removed on a rotary evaporator and the residue was chromatographed. The yields were generally more than 95%.

Bromination of 2,3-dichloro-2-norbornene (1). The following compounds were isolated from the product of bromination of 1. The percentage composition of these compounds under various reaction conditions is given in Table 1.

2-Bromo-2,3-dichlorobicyclo[2.2.1]heptane (5). This was the first major component eluted with pentane, m.p. 86-87°. (Found: C, 34.30; H, 3.70; Br, 32.82; Cl, 29.00; $C_7H_9BrCl_2$. Requires: C, 34.42; H, 3.69; Br, 32.78; Cl, 29.10%). NMR ($CDCl_3$), δ 5.00 (d, with fine splitting, 1 H, $J \sim 4$ Hz), 3.15 (m, 1 H), 2.55 (m, 1 H), 2.40-1.20 (m, 6 H). MS, m/z, 248, 246, 244, 242 (M^+); 167, 165, 163 (M^+-Br); 138, 136, 134 ($C_5H_4Cl_2$); 129, 127 (C_7H_8Cl); 101, 99 (C_5H_4Cl), 91 (C_7H_7).[22]

3-Bromo-2,3-dichlorotricyclo[2.2.1.$0^{2,6}$]heptane (4). Eluted with pentane after 5. It was contaminated with 5 and one or two other minor components. Repeated chromatography gave only about 90% pure compound. NMR and MS are quite satisfactory. NMR ($CDCl_3$), δ 2.55 (narrow m, 2 H), 2.35 (broad s, 1 H), 1.90 (s, 2 H), 1.60 (s, 1 H), 1.40 (s, 1 H). MS, m/z, 246, 244, 242, 240 (M^+); 165, 163, 161 (M^+-Br); 137, 135, 134 ($C_5H_3Cl_2$).

2,3-Dibromo-2,3-dichlorobicyclo[2.2.1]heptane (7). This was eluted with pentane after 4, m.p. 178°. (Found: C, 25.89; H, 2.43; Br, 49.27; Cl, 22.07; $C_7H_8Br_2Cl_2$. Requires: C, 26.04; H, 2.49; Br, 49.50; Cl, 21.96%). ^1H NMR ($CDCl_3$), δ 3.14 (m, 2 H), 2.70-1.36 (m, 6 H). ^{13}C NMR ($CDCl_3$), ppm 90.74 (s), 59.82 (d), 35.79 (t), 24.71 (m). MS, m/z, 328, 326, 324, 322, 320 (M^+); 247, 245, 243, 241 (M^+-Br); 209, 207, 205 (C_7H_7BrCl); 183, 181, 179 (C_5H_5BrCl); 165, 163, 161 ($C_7H_7Cl_2$); 157, 155, 153 (C_3H_3BrCl); 139, 137, 135 (C_5H_5Cl); 127, 125 (C_7H_6Cl); 101, 99 (C_5H_4Cl).

2,7-Dibromo-1,7-dichlorobicyclo[2.2.1]heptane (9). This was eluted with 5:95 ether-pentane, m.p. 145°. (Found: C, 26.22; H, 2.54; Br, 49.30; Cl, 21.80; $C_7H_8Br_2Cl_2$. Requires: C, 26.04; H, 2.49; Br, 49.50; Cl, 21.96%). ^1H NMR ($CDCl_3$), δ 4.58-4.23 (m, 1 H), 3.0-1.2 (m, 7 H). ^{13}C NMR (acetone-d_6), ppm 85.45 (s), 78.02 (s), 52.34 (d), 50.39 (d), 42.36 (t), 36.88 (t), 26.72 (t). MS, m/z, 328, 326, 324, 322, 320 (M^+); 247, 245, 243, 241 (M^+-Br); 209, 207, 205 (M^+-BrCl); 183, 181, 179 (C_5H_5BrCl); 165, 163, 161 ($C_7H_7Cl_2$); 157, 155, 153 (C_3H_3BrCl); 139, 137, 135 ($C_5H_5Cl_2$); 127, 125 (C_7H_6Cl); 101, 99 (C_5H_4Cl).

3-Bromo-3-chlorobicyclo[2.2.1]heptan-2-one (6). This was eluted with 10:90 ether-pentane, m.p. 87-89°. Found: C, 37.59; H, 3.68; Br, 35.80; Cl, 16.00; C_7H_8BrClO. Requires: C, 37.58; H, 3.58; Br, 35.79; Cl, 15.88%). IR (KBr pellet), 1770, 1745 cm^{-1}. ^1H NMR ($CDCl_3$), δ 3.75 (m, 1 H), 2.85 (m, 1 H), 2.55-1.60 (m, 6 H). The IR and NMR were similar to those of 3,3-dichloro-2-norbornanone.[3b] MS, m/z, 226, 224, 222 (M^+); 198, 196, 194 (M^+-C_2H_4); 158, 156, 154 (C_2BrClO); 117, 115 (C_5H_4ClO).

Reaction of 1 with HBr. The apparatus was a glass tube with sintered glass bottom and was fitted at the top with a condenser having $CaCl_2$ guard tube. The reaction tube was well covered with aluminium foil to prevent any light, and ice-cold water was circulated in the condenser. A slow stream of HBr (dried by bubbling through conc H_2SO_4) was passed through the sintered glass into the solution of 1 (3-5 mmol) in $CHCl_3$ (10-15 ml) at room temperature. The reaction was monitored by GC. When the reaction was complete, the solution was washed successively with water, 10% $NaHSO_3$ soln, water, 10% $NaHCO_3$ soln, water, and finally satd NaCl soln. After drying over $MgSO_4$, the solvent was stripped under vacuum. The residue (yield, > 95%) showed three peaks in GC in 75:20:5 ratio, which were separated on a silica gel column. Elution with pentane gave the major component which was identified as 5. (The ^1H NMR indicated the presence of an isomeric compound likely to be 5a to the extent of 10-15% of 5 estimated from an additional doublet at δ 4.65, J ~4 Hz). Elution with 9:1 pentane-ether provided the other major component identified to be 6. The minor component was not fully characterised, but seems to be 10 by its MS and chromatographic properties.

Bromination of 2,3-dichlorobicyclo[2.2.1]hepta-2,5-diene (3). To a solution of 0.90 g (5.6 mmol) of 3 in 10 ml CH_2Cl_2 cooled in ice-water bath was added dropwise a solution of 1.04 g (6.5 mmol) of bromine, which disappeared as added, unlike in the case of 1. At the end of addition the bromine colour persisted. The mixture was stirred for another 30 min and worked up to get a solid (yield, 2.30 g, 96%) showing two peaks in GC.

The products were separated on a Kieselgel 60 column using pentane as eluent. The nortricyclene 16 eluted first followed by 15.

3,5-Dibromo-2,3-dichlorotricyclo[2.2.1.$0^{2,6}$]heptane (16). M.p. 70-71°. (Found: C, 26.26; H, 1.87; Br, 49.70; Cl, 22.00; $C_7H_6Br_2Cl_2$. Requires: C, 26.20; H, 1.87; Br, 49.81; Cl, 22.10%). ^{1}H NMR ($CDCl_3$), δ 4.82 (narrow q, 1 H), 2.79 (narrow septet, 1 H), 2.6-2.0 (four overlapping m, 4 H). ^{13}C NMR ($CDCl_3$), ppm 80.83 (s), 54.84 (d), 50.27 (d), 31.34 (s), 30.25 (t), 26.30 (d), 25.38 (d). MS, m/z, 326, 324, 322, 320, 318 (M^+); 245, 243, 241, 239 (M^+-Br); 219, 217, 215, 213 ($C_5H_4BrCl_2$); 207, 205, 203 (C_7H_5Cl); 126, 124 (C_7H_5Cl).

trans-4,5-Dibromo-2,3-dichlorobicyclo[2.2.1]hept-2-ene (15). M.p. 55-57°. (Found: C, 26.28; H, 1.84; Br, 49.70; Cl, 22.20; $C_7H_6Br_2Cl_2$. Requires: C, 26.20; H, 1.88; Br, 49.81; Cl, 22.10%). IR (KBr pellet), 1600 cm^{-1}. ^{1}H NMR ($CDCl_3$), δ 4.37 (m, 1 H, *exo*), 3.95 (ddd, 1 H, *endo*), 3.35 (m, 1 H), 3.10 (m, 1 H), 2.95-2.15 (m, 2 H). MS same as that of 16.

Ozonolysis of 15 in methanol gave the dibromodimethyl ester 18. IR (film), 1745 cm^{-1}. ^{1}H NMR ($CDCl_3$), δ 4.73-4.28 (two overlapping t, 2 H), 3.85 (s, 3 H), 3.78 (s, 3 H), 3.73-3.23 (overlapping q and dd, 2 H), 2.60 (d, 1 H), 2.45 (dd, 1 H). MS, m/z, 346, 344, 342 (M^+); 315, 313, 311 (M^+-OCH_3); 284, 282, 281 (M^+-2 OCH_3); 265, 263 (M^+-Br); 234, 232 (M^+-(CH_3O+Br)); 203, 201 (M^+-(Br+2 OCH_3)); 175, 173.

Bromination of 3 under illumination with 200 W lamp gave a mixture of three components in the ratio 14:42:44, which was ozonised in methanol directly, and the product was chromatographed on silica gel. Elution with pentane gave the unozonised minor component 16. Elution carefully with 3:1 pentane-ether gave 18 and 19. IR of 19, 1740 cm^{-1}. ^{1}H NMR ($CDCl_3$), δ 4.8 (d, with fine splitting, 2 H), 3.78 (s, 6 H), 3.9-3.2 (m, 2 H), 3.0-2.0 (m, 2 H). MS, same as that of 18.

Bromination of 2-chlorobicyclo[2.2.1]hept-2-ene (2). To a solution of 0.66 g (5.1 mmol) of 2 in 8 ml of CH_2Cl_2 stirred under ambient conditions was added dropwise a solution of 0.85 g (5.3 mmol) of bromine in 5 ml of CH_2Cl_2. Bromine disappeared instantaneously. After further stirring for 30 min, the product was isolated as usual, yield, 1.39 g (94%). GC showed four peaks in the ratio 3:7:53:31. The IR of the crude product showed only a very weak band around 1720 cm^{-1}, but GC-MS indicated no oxygenated product. The major components were isolated by chromatographing on Kieselgel 60 column.

2,3-Dibromo-2-chlorobicyclo[2.2.1]heptane (12+13). They were eluted together using pentane. (Found: C, 29.05; H, 3.09; Br, 55.25; Cl, 12.52; $C_7H_9Br_2Cl$. Requires: C, 29.12; H, 3.14; Br, 55.41; Cl, 12.29%). ^{1}H NMR ($CDCl_3$), δ 4.55 (d, $J \sim 2.5$ Hz, 0.55 H), 4.28 (d,

$J \sim 2.5$ Hz, 0.45 H), 3.19 (m, 1 H), 2.50 (m, 1 H), 2.20 (m, 1 H), 2.05-1.20 (m, 5 H). ^{13}C NMR ($CDCl_3$), ppm 87.95, 85.57; 68.41, 67.31; 58.43, 57.94; 49.91, 49.54; 36.15, 34.45; 28.42, 28.18; 27.45, 24.77. MS, m/z, 255, 253, 251 (M^+-Cl); 211, 209, 207 (M^+-Br); 183, 181, 179 (C_5H_5BrCl); 174, 172 (C_7H_9Br); 157, 155, 153 (C_3H_3BrCl); 145, 143 (C_5H_4Br); 130, 128 (C_7H_9Cl); 101, 99 (C_5H_4Cl); 93 (C_7H_9).

3-Bromo-2-chlorotricyclo[2.2.1.0^{2,6}]heptane (11). Eluted with pentane after 12 and 13. ^{1}H NMR ($CDCl_3$), δ 4.10 (m, 1 H), 2.25 (m, 2 H), 1.71-1.25 (m, 5 H). MS, m/z, 210, 208, 206 (M^+); 157, 155, 153 (C_3H_3BrCl); 129, 127 (C_7H_8Cl); 101, 99 (C_5H_4Cl).

1-Chloro-2,7-dibromobicyclo[2.2.1]heptane (14). Eluted with pentane-ether (95:5), m.p. 98-102°. (Found: C, 29.35; H, 3.16; Br, 55.47; Cl, 12.29; $C_7H_9Br_2Cl$. Requires: C, 29.15; H, 3.14; Br, 55.41; Cl, 12.29%). ^{1}H NMR ($CDCl_3$), δ 4.40-4.10 (m, 2 H), 3.20-1.45 (m, 7 H). ^{13}C NMR ($CDCl_3$), ppm 72.06 (s), 59.40 (d), 52.65 (d), 42.91 (d), 42.18 (t), 37.30 (t), 26.66 (t). MS, m/z, 292, 290, 288, 286 (M^+); 211, 209, 207 (M^+-Br); 183, 181, 179 (C_5H_5BrCl); 174, 172 (C_7H_9Br); 157, 155, 153 (C_3H_3BrCl); 145, 143 (C_5H_4Br); 130, 128 (C_7H_9Cl); 101, 99 (C_5H_4Cl); 93 (C_7H_9).

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