Tetrahedron Vol. 42, No. 9, pp. 2519 to 2522, 1986
Printed in Great Britain.

0040-4020/86 $3.00+.00
Pergamon Journals Ltd.

BROMINATION OF OCTAMETHYLCYCLOPENTENE - THE IRREGULAR REACTIVITY OF A STERICALLY HINDERED CYCLOALKENE

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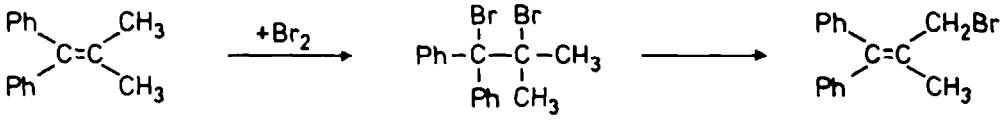
(*Received in Germany 28 December* 1985)

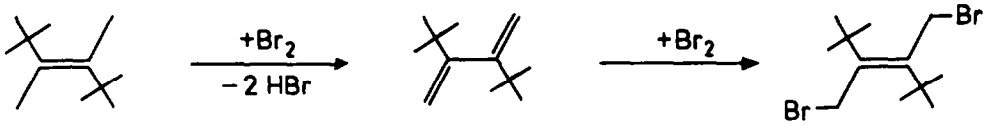
Abstract: The title compound **7** reacts with bromine under mild conditions (CCl_4, 20°C) to give the substitution products **9** and/or **10** via an electrophilic process. The tetrabromo compound **11** is formed from **7** and bromine in refluxing CCl_4 via a radical mechanism.

The addition of bromine is one of the best known reactions of unsaturated nonaromatic hydrocarbons. While most alkenes react smoothly with formation of addition products, a different behaviour is encountered with sterically hindered double bonds. Adamantylidene adamantane, for example, was reported to yield a crystalline bromonium tribromide when treated with Br_2.[2] The bromination of di- and polyarylethylenes gave charge transfer complexes or bromonium ions, sometimes in equilibrium with the reactants and regular addition products.[3] Meisenheimer reported that an allylic substitution product **3** was formed from **1** and bromine.[4] This reaction was later demonstrated by Ziegler and Bähr to proceed via bromine addition (→ **2**), HBr elimination and allylic rearrangement.[5]



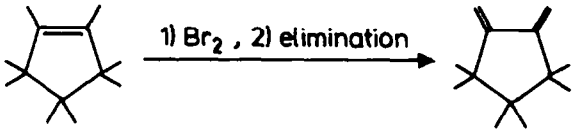
1 **2** **3**

Lenoir reported the formation of 2,3-di-tert.butyl-1,3-butadiene (**5**) by treatment of **4** with one equivalent of bromine and the formation of **6** from **4** and two equivalents of bromine.[6]



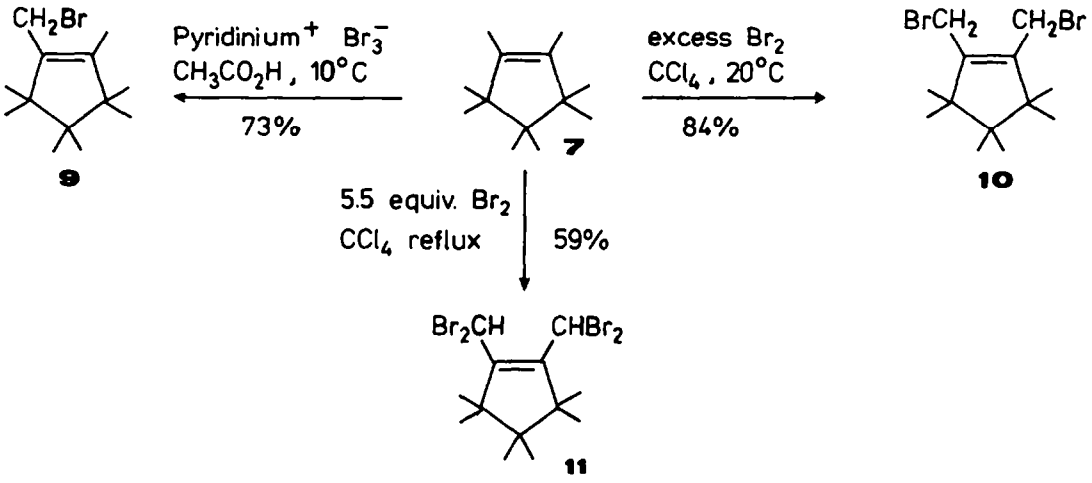
4 **5** **6**

In this paper we report the course of the bromination of **7**, which we observed during an attempt to convert the readily available octamethylcyclopentene **7** [7] into **8** by a bromination elimination sequence. The latter compound was required for the mechanistic study of cycloaddition reactions of 2,3-shielded cisoid 1,3-dienes.[8]



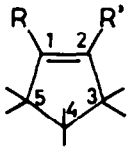
7 **8**

Products. When **7** was treated with 1 equivalent of Br_2 in CCl_4 at room temperature, bromine was consumed instantaneously, and a mixture of **7**, **9** and **10** (1 : 2.4 : 1) was observed in the ^1H NMR spectrum. An addition product could not be detected. The selective monobromination was achieved by treating **7** with 1 equivalent of pyridinium tribromide in acetic acid.



The crude material, obtained from **7** and 5 equivalents of Br_2 in CCl_4 at room temperature showed a ^1H-NMR spectrum with only 3 signals (6 : 12 : 4), indicating the presence of **10**. When a 5 : 1 mixture of **7** and Br_2 was heated in CCl_4 at reflux, preferably in the presence of a radical starter like azoisobutyronitrile, **11** was formed in fair yield. The temperature dependent ^1H and ^{13}C NMR spectra of **11** indicate hindered rotation of the $-CHBr_2$ groups. At low temperature C-1, C-2 as well as C-3, C-5 and the attached groups are nonequivalent. The rotational barrier ($\Delta G^{\neq}$) of the dibromomethyl groups was calculated [9] to be 57 kJ/mol from the coalescence of the methine protons in the 60 MHz NMR spectrum at 12°C. The conformational equilibria of **11** are presently under investigation.

Table: ^{13}C **NMR Spectra of Some Octamethylcyclopentene Derivatives** ($CDCl_3$)



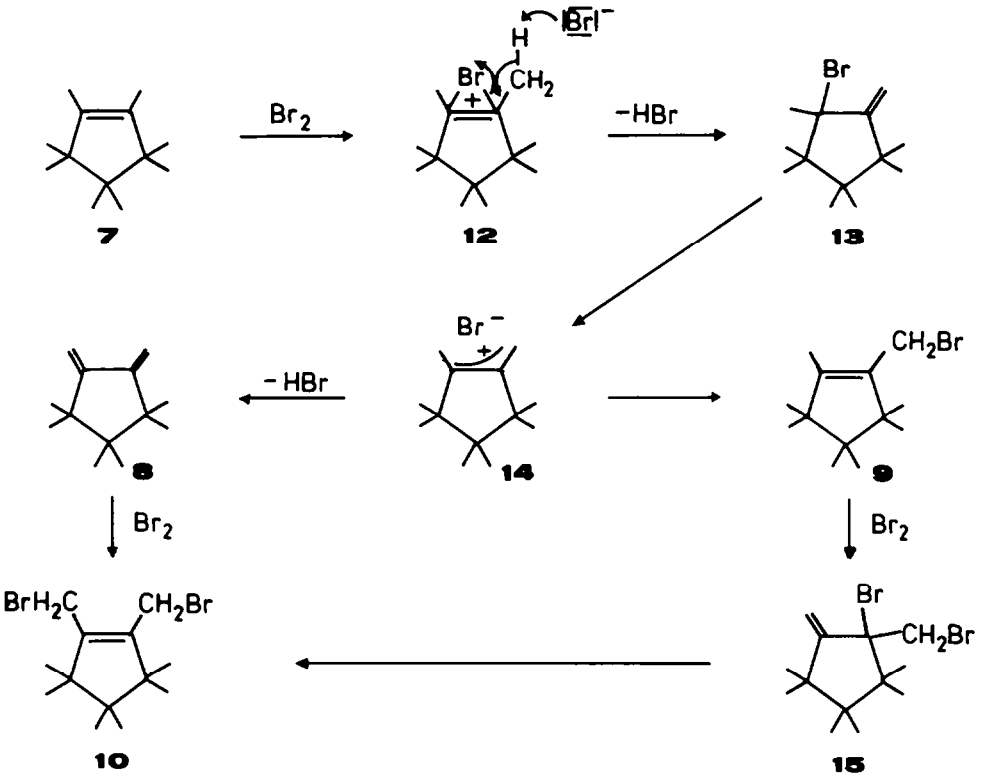
	R	R'	C-1	1-R	C-2	2-R'	C-3	3-CH_3	C-4	4-CH_3	C-5	5-CH_3
7	CH_3	CH_3	135.0	10.0	135.0	10.0	49.8	24.2	45.7	21.7	49.8	24.2
9	CH_2Br	CH_3	146.7	26.7	135.7	10.6	49.7	23.9	46.3	21.3	50.1	24.8
10	CH_2Br	CH_2Br	144.7	23.4	144.7	23.4	50.1	24.5	46.9	21.0	50.1	24.5
11 [a]	$CHBr_2$	$CHBr_2$	143.8	29.7	146.7	34.7	50.2	23.5	47.9	20.3	52.8	25.0

a) -20°C; the relative assignments of C-1,2, C-3,5 and the attached groups are uncertain.

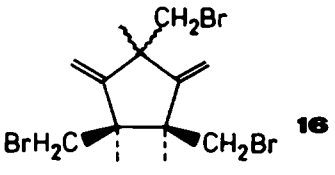
Reaction Mechanism. The formation of **9** and **10** is best explained by an ionic pathway, comparable to the mechanism suggested by Wynberg for the halogenation of tetraalkylethylenes with N-halosuccinimides.[10] The alternative radical mechanism is excluded since the reaction proceeds fast at low temperature and was not inhibited by 2,4,6-tri-tert.butyl phenol.

The initial formation of the bromonium ion **12**, which is suggested in the Scheme is in accord with the behaviour of other sterically hindered alkenes.[8] Successive deprotonation yields the tertiary allylic bromide **13**, which rearranges to the allylic isomer **9**. An analogous mechanism

9 → 15 → 10 may explain the production of 10 from 9 and bromine in CCl_4 at 20°C. In accord with the relative electron releasing effects of CH_3 and CH_2Br, 9 was observed to consume Br_2 less rapidly than 7.



However, there must be an additional route from 7 to 10, as the dibromo compound 10 was also formed during the treatment of 7 with 0.2 equivalents of Br_2 in CCl_4 at 20°C (10 : 9 = 1 : 3). Since 9 is less reactive than 7, a pathway is required, which avoids the intermediacy of 9. As suggested in the Scheme, deprotonation of 14 may yield 8, which was found to add bromine instantaneously with formation of 10. This route is analogous to that observed by Lenoir.[6] When the HBr elimination from 14 was suppressed by saturating the CCl_4 solution of 7 with HBr, prior to adding 0.5 equivalents of bromine at 0°C, the exclusive formation of 9 was found.



16

Bromination of 7 in more polar solvents (CH_2Cl_2, $CHCl_3$, CH_3CO_2H) gave several side products, probably because of rearrangements of intermediate carbenium ions. When 7 was allowed to stand with 5 equivalents of bromine in $CHCl_3$ at 20°C for 1 hour, a complex mixture containing 9, 10 and 4% of the tribromo compound 16 was isolated.

Carbenium ion rearrangements are unfavourable in CCl_4. Even under reflux conditions the tetrabromo compound 11 was the only product isolated from 7 and excess bromine. Since this reaction was accelerated by azobisisobutyronitrile, the formation of 11 is explained by a radical mechanism.

The conversion of 9 - 11 into 2,3 shielded 1,3-dienes will be reported in a subsequent paper.

We thank Dr. H. Klein for exploratory experiments and the Fonds der Chemischen Industrie for financial support.

EXPERIMENTAL

^{1}H NMR spectra: JNM-C-60-HL (JEOL). ^{13}C NMR spectra: JNM-PS-100 (JEOL). TMS as internal standard. Mass spectra: CH 4 B MAT (Varian) and 311 A MAT (Varian); only the most intensive mass peaks are listed.

Octamethylcyclopentene (7) was prepared via [3+2] cycloaddition of the 1,1,2,3-tetramethylallyl cation to 2,3-dimethyl-2-butene.[7] The published procedure [7] was modified by reducing the alkene/alkyl chloride ratio from 3.2 to 1.3 (yield: 74%).

1-Bromomethyl-2,3,3,4,4,5,5-heptamethyl-1-cyclopentene (9). Pyridinium tribromide (11.6 g, 36 mmol) was added in small portions to a stirred solution of **7** (5.0 g, 28 mmol) in 50 ml glacial acetic acid while the temperature was kept below 15°C. After 30 min, the solution was poured onto 300 mL of water. The product was extracted with ether, and the ethereal layer was washed with dilute aqueous HCl, water, and aqueous $NaHCO_3$ solution. After drying with $MgSO_4$, the solvent was evaporated and the residue was distilled to give **9** (5.3 g, 73%) as a colourless liquid with b.p. 55 - 65°C (bath) / 0.1 mmHg. - ^{1}H NMR (CCl_4): δ 0.79 (s, 6 H), 0.92 (s, 6 H), 1.03 (s, 6 H), 1.63 (s, 3 H), 3.92 (s, 2 H). - Mass spectrum (96 eV): m/e = 260, 258 (13%, 13%, M^+), 245, 243 (41, 43, $C_{12}H_{20}Br$), 179 (100, $C_{13}H_{23}$), 163 (94, $C_{12}H_{19}$), 135 ($C_{10}H_{15}$), 123 (44), 121 (53), 99 (21), 97 (40). **Anal.** Calcd. for $C_{13}H_{23}Br$: C, 60.23; H, 8.94. Found: C, 60.57; H, 9.15.

1,2-Di(bromomethyl)-3,3,4,4,5,5-hexamethyl-1-cyclopentene (10). A solution of bromine (17.6 g, 110 mmol) in 30 mL of CCl_4 was added dropwise to a solution of **7** (9.00 g, 50.0 mmol) in 50 mL of CCl_4 at 20°C. After 15 h, a nitrogen stream was passed through the solution to remove HBr and the solvent was evaporated. Distillation gave **10** (14.3 g, 84%), a colourless liquid with bp. 95 - 100°C (bath) / 0.05 mmHg. - ^{1}H NMR (CCl_4): δ 0.83 (s, 6 H), 1.09 (s, 12 H), 4.05 (s, 4 H). - Mass spectrum (70 eV): m/e = 340, 338, 336 (3%, 7%, 3%, M^+), 325, 323, 321 (19, 41, 20, $C_{12}H_{19}Br_2$), 259, 257 (21, 21, $C_{13}H_{22}Br$), 245, 243 (10, 13, $C_{12}H_{20}Br$), 178 (24, $C_{13}H_{22}$), 177 (37, $C_{13}H_{21}$), 163 (100, $C_{12}H_{19}$). - **Anal.** Calcd. for $C_{13}H_{22}Br_2$: C, 46.18; H, 6.56. Found: C, 46.17; H, 6.33.

1,2-Bis(dibromomethyl)-3,3,4,4,5,5-hexamethyl-1-cyclopentene (11). A solution of **7** (5.0 g, 28 mmol) and bromine (24 g, 0.15 mol) in 600 mL CCl_4 was heated at reflux for 6 h. During this period small amounts (~ 50 mg) of azoisobutyronitrile were added every hour. When the solvent was evaporated, **11** instantaneously crystallized to yield colourless prisms (8.2 g, 59%) which were recrystallized from hexane. mp. 150 - 152°C. - ^{1}H NMR ($CDCl_3$, +60°C): 0.83 (s, 6 H), 1.23 (s, 12 H), 6.83 (br. s, 2 H); (-60°C): 0.87 (s, 6 H), 1.07 (s, 3 H), 1.40 (s, 3 H), 6.06 (s, 1 H), 7.56 (s, 1 H). - Mass spectrum (70 eV): m/e = 500, 498, 496, 494, 492 (3%, 11%, 17%, 13%, 3%, M^+), 485, 483, 481, 479, 477 (4, 18, 27, 19, 5, $C_{12}H_{19}Br_4$), 419, 417, 415, 413 (12, 35, 36, 12, $C_{13}H_{20}Br_3$), 338, 337, 336, 335, 334, 333 (34, 44, 68, 54, 34, 21, $C_{13}H_{20}Br_2$ und $C_{13}H_{19}Br_2$), 297, 295, 293, 291 (20, 54, 47, 17, $C_{10}H_{15}Br_2$, $C_{10}H_{13}Br_2$), 281, 279, 277 (20, 43, 23, $C_9H_{11}Br_2$), 257, 255 ($C_{13}H_{19}Br$), 215, 213 (79, 85, $C_{10}H_{14}Br$), 176 (85, $C_{13}H_{20}$), 161 (85, $C_{12}H_{17}$), 57 (100, C_4H_9). - **Anal.** Calcd. for $C_{13}H_{20}Br_4$: C, 31.49; H, 4.06. Found: C, 31.38; H, 3.84.

Bromination of 7 in $CHCl_3$. A 2M solution of bromine in $CHCl_3$ (12.5 mL, 25 mmol) was added dropwise to a solution of **7** (1.00 g, 5.5 mmol) in 12.5 mL $CHCl_3$ at 20°C. The mixture was washed with aqueous $NaHSO_3$ solution, dried, and the solvent evaporated. Chromatographic separation (Silica 60, petroleum ether/40 - 60°C) yielded **16** (80 mg, 4%) besides **9**, **10** and nonidentified products.

r-1,c-2,c or t-4-tri(bromomethyl)-1,2,4-trimethyl-3,5-dimethylene-cyclopentane (16). Colourless viscous oil. - ^{1}H NMR ($CDCl_3$): δ 1.28 (s, 6 H), 1.41 (s, 3 H), 3.40 (s, 2 H), 3.43 and 3.62 (AB system of 1,2-CH_2Br with J = 10.5 Hz), 5.16 (d, J = 0.8 Hz, 2 H), 5.30 (d, J = 0.8 Hz, 2 H). - ^{13}C NMR ($CDCl_3$): δ 22.6 (q, 1,2-CH_3), 30.0 (q, 4-CH_3), 39.6 (t, 1,2-CH_2Br), 44.2 (t, 4-CH_2Br), 47.0 (s, C-4), 51.9 (s, C-1,2), 111.7 (t, =CH_2), 158.4 (s, C-3,5). - Mass sprectrum (70 eV): m/e = 337, 335, 333 (13%, 24%, 11%, M^+-Br), 323, 321, 319 (50, 100, 56, $C_{12}H_{17}Br_2$), 133 (85, $C_{10}H_{13}$). - No UV-absorption for λ > 200 nm. - **Anal.** Calcd. for $C_{13}H_{18}Br_2$: C, 37.62; H, 4.61. Found: C, 36.96; H, 4.55.

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