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SYNTHESIS AND REACTIONS OF NEW HIGHLY STRAINED UNSATURATED PROPELLANES, [4.2.1]PROPELLA-2,4,7-TRIENES

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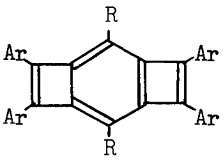
The title propellane, 2,7-di-tert-butyl-11,11-dichloro-4,5,9,10-tetraaryltetracyclo[6.2.1.0.0^{3,6}]undeca-2,4,6,9-tetraene (3), was prepared by cycloaddition of dichlorocarbene to the benzene nucleus of 2,7-di-tert-butyl-4,5,9,10-tetraaryltricyclo[6.2.0.0^{3,6}]deca-1,3(6),4,7,9-pentaene (1). On Ag$^+$-induced methanolysis and acetolysis of 3a, its endo-Cl reacted easily and endo-methoxy (6) and endo-acetoxy derivative (9) were obtained, respectively, probably via bishomoallyl cation of pyramidal structure (5). Hydrolysis of 3a and 9 afforded 1a.

The most highly strained unsaturated propellane which has been isolated so far is derivative of [4.2.2]propella-2,4,7-triene (2c, 2d)1) prepared by cycloaddition of tetracyanoethylene to 2,7-di-tert-butyl-4,5,9,10-tetra(p-halophenyl)tricyclo[6.2.0.0^{3,6}]deca-1,3(6),4,7,9-pentaene (1c, 1d). We now report the isolation and some novel reactions of derivative (3) of more strained unsaturated propellane, [4.2.1]propella-2,4,7-triene (4). We also report Ag$^+$-induced methanolysis and acetolysis of 3a which afford the endo-11-methoxy (6) and endo-11-acetoxy derivative (9), respectively, probably via bishomoallyl cation of pyramidal structure (5), and hydrolysis of 3a and 9 which affords 1a.



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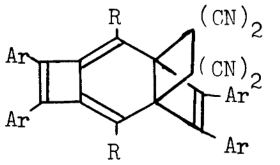

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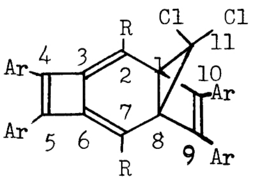

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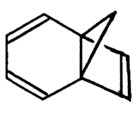

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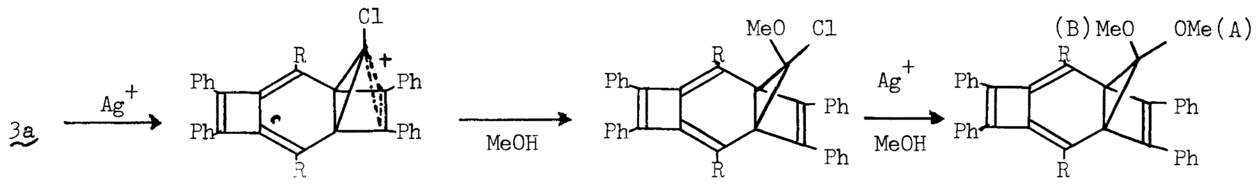
a: Ar = Ph ; b: Ar = p-Me-C$_6$H$_4$- ; c: Ar = p-Cl-C$_6$H$_4$- ; d: Ar = p-Br-C$_6$H$_4$- ; R = $\overset{12}{\mathrm{C}}(\overset{13}{\mathrm{C}}\mathrm{H}_3)_3$

Stirring of a mixture of **1a** (1 g), 50% aqueous KOH (30 ml), $CHCl_3$ (30 ml), and a catalytic amount of benzyltriethylammonium chloride under N_2 at room temperature for 2 h afforded **3a** (0.23 g; 20%) as colorless needles, after purification by column chromatography on Al_2O_3 (CCl_4); mp 218-219 °C; λ_{max}[2] 254 (ε 33800) and 320 sh nm (7300); ^1H-NMR δ 0.92 (s, tBu, 18H) and 7.08-7.80 (m, Ph, 20H); ^{13}C-NMR (for ^{13}C-isotope enriched sample, 20% each carbon of C_1, C_3, C_6, and C_8) δ 30.4 (C_{13}), 34.0 (C_{12}), 47.3 ($C_{1,8}$), and 140.7 ppm ($C_{3,6}$). Similar treatments of **1b**, **1c**, and **1d** afforded **3b** (29%, mp 217-218 °C), **3c** (24%, mp 236-237 °C), and **3d** (18%, mp 205-206 °C), respectively.

Treatment of **3a** with excess $AgClO_4$ in MeOH at room temperature for 10 min afforded the 11-methoxy derivative (**6**) as colorless needles in 70% yield; mp 189-191 °C; λ_{max} 260 (ε 31700) and 319 sh nm (10600); ^1H-NMR δ 0.96 (s, tBu, 18H), 3.73 (s, OMe, 3H), and 7.22 (bs, Ph, 20H). Further treatment of **6** under the same conditions for 12h afforded the 11,11-dimethoxy derivative (**7**) as colorless prisms in 70% yield; mp 188-189 °C; λ_{max} 248 (ε 33600) and 321 sh nm (9200); ^1H-NMR δ 0.96 (s, tBu, 18H), 3.51 and 3.70 (each s, OMe, 3H), and 7.0-7.7 (m, Ph, 20H). On the same treatment of **6** for 1 h, however, **6** was recovered unchanged in 85% yield. Of the two MeO signals of **7**, the one at relatively higher magnetic field (δ 3.51) can be ascribed to exo-methoxy group (A) which is shielded by Ph groups on the C_9- and C_{10}-positions. The MeO groups of **6** should be at the endo-position, because its chemical shift (δ 3.73) is comparable to that of the endo-MeO (B) of **7** (δ 3.70). Similar treatments of **3a** with $AgClO_4$ in EtOH for 10 min and 12 h afforded ethoxy-analog of **6** (67%, mp 188-190 °C) and diethoxy-analog of **7** (43%, mp 169-170 °C), respectively.

Extremely faster conversion of **3a** into **6** than that of **6** into **7**, can well be interpreted by assuming bishomoallyl cation of pyramidal structure (**5**) as an intermediate, which is formed by Ag^+-induced elimination of the endo-Cl accompanied by participation of p-orbitals of cyclobutene ring. In the case of **6**, with syn-relationship of Cl and p-orbitals, however, such the neighboring group participation would not occur efficiently. Intermediacy of bishomoallyl cation in the solvolysis of various substituted carbocycles, but not of propellane, has well been documented.[3] Treatments of **3a** with MeMgI in ether at room temperature for 2 h and with AgOAc in AcOH under reflux for 1 h afforded its methyl-derivative (**8**) in 42% yield; mp 199-200 °C; λ_{max} 251 (ε 24200) and 323 sh nm (6500); ^1H-NMR δ 0.92 (s, tBu, 18HO, 2.44 (s, Me, 3H), and 7.45 (bs, Ph, 20H) and acetoxy-derivative (**9**) in 51% yield; mp 202 °C; λ_{max} 252 (ε 34400) and 325 sh nm (9200); ^1H-NMR δ 0.96 (s, tBu, 18H), 2.29 (s, OAc, 3H), and 7.41 (s, Ph, 20H), respectively. Neither **8** nor **9** was caused further substitution reaction by prolonged reaction. Both **8** and **9** would also be produced by the reaction pathway which proceeds via the bishomoallyl cation (**5**), and their Me and AcO groups would also be at endo-positions.



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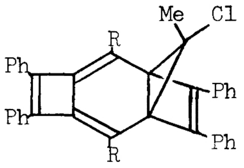

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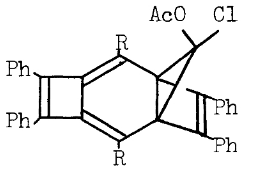

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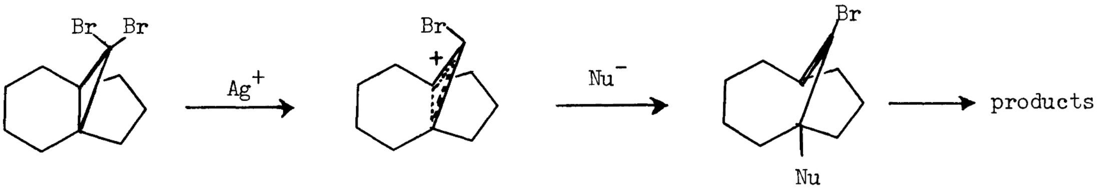
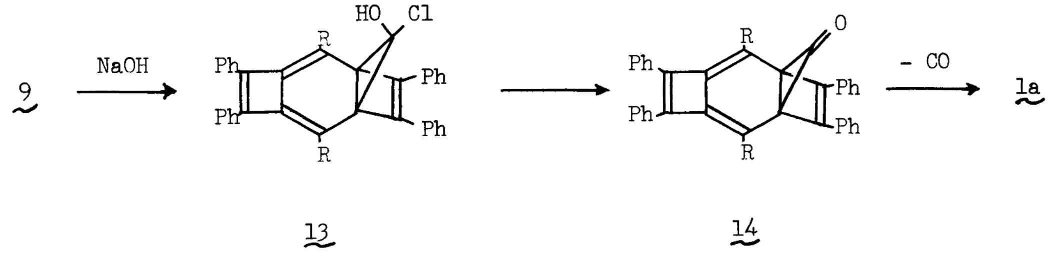
R = C(CH$_3$)$_3$

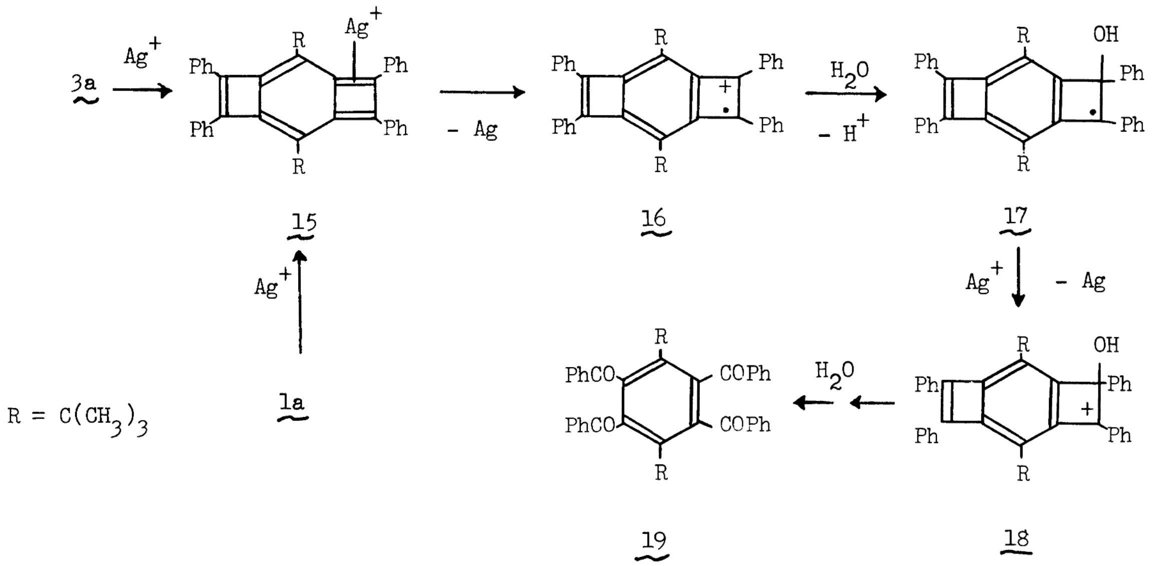


10 11 12

All the above mentioned Ag$^+$-induced substitution reactions of 3a and 6 are in contrast to those of Ag$^+$-induced solvolysis of saturated propellane. For example, it has been reported that Ag$^+$-induced reaction of 10 with nucleophile (Nu$^-$) affords various products successively via homoallyl cation (11) and bridge-head olefin intermediate (12).4)

The most interesting reaction of the propellanes is hydrolysis of 3a and 9 to 1a. Heating of 9 in acetone containing a small amount of aqueous NaOH under reflux for 2.5 h afforded 1a in 72% yield. This reaction probably proceeds by decarbonylation of propellanone (14) which was initially produced by hydrolysis of 9 into 13 followed by elimination of HCl. Reaction type of the decarbonylation of 14 is similar to that of the previously reported thermal cycloreversion of 2 into 1 and tetracyanoethylene.1) Treatment of 3a with excess AgClO$_4$ in wet tetrahydrofuran (THF) resulted in a greenish blue solution, and this color disappeared gradually and finally afforded AgCl, Ag-metal, and 2,3,5,6-tetrabenzoyl-1,4-di-tert-butylbenzene (19)5) in 27% yield. This color is probably attributed to a 1:1 complex of Ag$^+$ and 1a which was derived from 3a successively via 13 and 14, because a solution of 1a and an equimolar amount of AgClO$_4$ in dry benzene showed the same color (λ_{max} 592 nm; ^{1}H-NMR δ 1.09 and 1.24 (each s, tBu, 9H)), and because decomposition of a solution of 1a and excess AgClO$_4$ in dry benzene with water gave Ag-metal and 19 in 66% yield. Magnetic nonequivalence of the two tBu groups suggests that this complex is unsymmetrical as depicted (15). Although mechanism of the conversion of 15 into 19 is not clear, a plausible pathway is that proceeds via cations such as 16 and 18, because the formation of Ag metal supports production of cation by one-electron oxidation process, and because THF easily polymerized when a solution of 15 in THF was kept at room temperature. It has been reported that Lewis acid-catalyzed polymerization of THF is accerelated by cyclic compound which easily undergoes cationic ring-opening reaction.[6]





References and Notes

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