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NEW HIGHLY STRAINED UNSATURATED PROPELLANES, [4.2.2]PROPELLA-2,4,7-TRIENES

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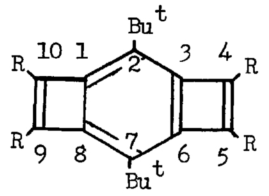
Cycloaddition of tetracyanoethylene to the benzene nucleus of 2,7-di-tert-butyl-4,5,9,10-tetra(p-halophenyl)tricyclo[6.2.0.0^{3,6}]deca-1,3(6),4,7,9-pentaene (1) afforded the title propellane, 2,7-di-tert-butyl-11,11,12,12-tetracyano-4,5,9,10-tetra(p-halophenyl)tetracyclo[6.2.2.0.0^{3,6}]dodeca-2,4,6,9-tetraene (2).

The most highly strained unsaturated propellane which has been isolated so far is [4.2.2]propella-3,7-diene.[1] We now report the isolation of two derivatives (2a and 2b) of more strained unsaturated propellane (3), and some thermal reactions of them.

Stirring of a 1:1 mixture of 4,5,9,10-tetra(p-bromophenyl)-2,7-di-tert-butyltricyclo-[6.2.0.0^{3,6}]deca-1,3(6),4,7,9-pentaene (1a)[2] and tetracyanoethylene (TCNE) in p-xylene under N_2 at room temperature for 0.5 h afforded 4,5,9,10-tetra(p-bromophenyl)-2,7-di-tert-butyl-11,11,12,12-tetracyano[6.2.2.0.0^{3,6}]dodeca-2,4,6,9-tetraene (2a)[3] in a 66% yield; λ_{max} 251 (ε 44700), 317 sh (7800), and 340 sh nm (3500); m/e (rel intensity) 986 (M^+, 100) and 858 (M^+- TCNE, 60); ^{1}H-NMR δ 1.02 (s, Bu^t, 18H) and 7.0-7.7 ppm (m, Ar, 16H); ^{13}C-NMR δ 31.6 (CH_3), 33.8 ($\overset{*}{C}(CH_3)_3$), 45.4 ($C_{1,8}$), 66.7 ($C_{11,12}$), and 111.4 and 112.1 ppm (CN). The same treatment of the Cl-analog of 1a (1b) with TCNE gave 2b in an 84% yield. By heating, 2a and 2b decomposed gradually without melting. This cycloaddition of TCNE to the 3,6-positions of 1a and 1b is in contrast to the previously reported cycloaddition of TCNE to the 4,5-positions of 1c which affords 5c.[4] This contrast would be due to an inductive effect of halogen, which would reduce electron density of the 4,5-positions of 1 and then prevent the cycloaddition to these positions.

Heating of 2a under reflux in p-xylene under N_2 for 0.5 h afforded 2,3,7,8-tetra(p-bromophenyl)-5,10-di-tert-butyl-11,11,12,12-tetracyanotetracyclo[4.4.2.0^{1,4}.0^{6,9}]dodeca-2,4,7,9-tetraene (4a) in a 44% yield; λ_{max} 244 (ε 21500) and 318 nm (39600); m/e (rel intensity) 986 (M^+, 1) and 858 (M^+-TCNE, 100); ^{1}H-NMR δ 0.92 (s, Bu^t, 18H) and 7.1-7.7 ppm (m, Ar, 16H); ^{13}C-NMR δ 31.1 (CH_3), 35.3 ($\overset{*}{C}(CH_3)_3$), 56.9 ($C_{1,6}$), 61.9 ($C_{11,12}$), and 111.6 and 114.3 ppm (CN), and 5a in a 40% yield, mp 286-288 °C. Similarly, 2b gave 4b (56%) and 5b (25%). Both 4a and 4b did not show clear melting point due



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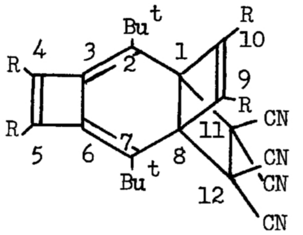

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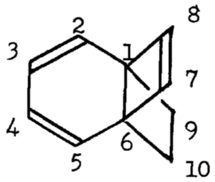

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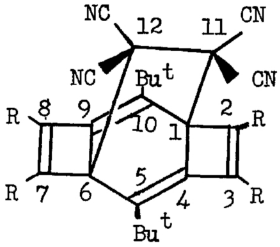

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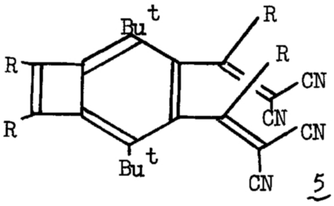

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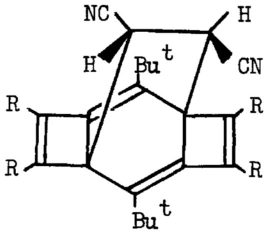

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a: R = p-Br-C_6H_4- ; b: R = p-Cl-C_6H_4- ; c: R = C_6H_5-

to their thermal isomerizations. The spectral data of 4 were comparable to those of analogous compounds.5) The thermal rearrangement of 2 to 4 and 5 would proceed successively through the cycloreversion of 2 into 1 and TCNE, and through the cycloaddition of TCNE to the 3,8- and 4,5-positions which finally affords 4 and 5, respectively. These pathways are supported by the following experiment. Heating of 2a in the presence of an equimolar amount of 1c afforded 1a in a 63% yield in addition to small amounts of 4c and 5c.

Although 4 was not converted into 5 under the above thermolysis conditions, heating of 4a and 4b under reflux in o-dichlorobenzene under N_2 for 0.5 h afforded 5a and 5b, respectively, both in 88% yields. This relative instability of 4 would be due to steric repulsion between Bu^t and CN groups, because 6a which had been prepared in a 72% yield (mp 308 °C) by the thermal cycloaddition of trans-1,2-dicyanoethylene to 1a was stable up to 180 °C.

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References and Notes

1) L. A. Paquette and R. W. Houser, J. Am. Chem. Soc., 93, 4522 (1971).

2) F. Toda and M. Ohi, J. Chem. Soc., Chem. Commun., 506 (1975); F. Toda and Y. Takahara, Bull. Chem. Soc. Jpn., 49, 2515 (1976).

3) UV and NMR spectra were measured in $CHCl_3$ and $CDCl_3$, respectively. All new compounds gave satisfactory elemental analyses.

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