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ISOLATION OF 5-OXA-, 5-THIA-, AND 5-TOSYLAZA-2,8-DI-t-BUTYL-4,6,10,11-TETRAPHENYLTRICYCLO[7.2.0.0^{3,7}]UNDECA-1,3,6,8,10-PENTAENES, THEIR $HClO_4$ SALTS, AND 4-SELENA-2,8-DI-t-BUTYL-5,6,10,11-TETRAPHENYLTRICYCLO[7.2.0.0^{3,7}]UNDECA-1,3(7),5,8,10-PENTAENE: NEW ANTIAROMATIC SYSTEMS[1)]

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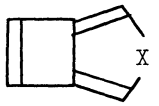
The title new antiaromatic compounds were prepared by unusual insertion reactions of O, S, N, and Se to 2,7-di-t-butyl-4,5,9,10-tetraphenyltricyclo-[6.2.0.0^{3,6}]deca-1,3(6),4,7,9-pentaene.

Of two 8π-electron cyclobutadienoheterocycles (1, 2), two unstable derivatives of 1, 3-oxa-bicyclo[3.2.0]hepta-1,4,6-triene (1a)[2)] and 6,7-diphenyl-3-thiabicyclo[3.2.0]hepta-1,4,6-triene[3)] have been isolated. Benzologs of 1 and 2 are also interesting hitherto unknown antiaromatic systems.[4)] We report isolation of stable benzologs of 1 (3a-c and 4a-b) and of 2 (5). The onium ion salts derived from 3 and 4 are expected to be stable, because 3 and 4 are released from their antiaromaticities by the formation of the onium ions. We also report isolation of $HClO_4$ salt of 4 (6).

Heating of 2,7-di-t-butyl-4,5,9,10-tetraphenyltricyclo[6.2.0.0^{3,6}]deca-1,3(6),4,7,9-pentaene (7)[5)] under reflux in dimethyl sulfoxide under N_2 for 3 h afforded 5-oxa-2,8-di-t-butyl-4,6,10,11-tetraphenyltricyclo[7.2.0.0^{3,7}]undeca-1,3,6,8,10-pentaene (3a) as yellow needles in 54% yield: mp 284 °C; λ_{max}^{ϵ} 260 nm (ε 25,200), 296 (30,700), and 370 (8600); ^{1}H NMR δ 0.95 (s, Bu^t). A plausible reaction pathway is that proceeds successively via 8 and 9 (Scheme 1). Similar S-insertion occurs when 7 is heated with elemental sulfur. Heating of 7 and S-powder under reflux in p-xylene under N_2 for 2 h afforded 5-thia-analog of 3a (3b) as yellow prisms in 43% yield: mp 266 °C; λ_{max} 257 nm (ε 23,100), 318 (28,900), and 390 (4200); ^{1}H NMR δ 0.89 (s, Bu^t).



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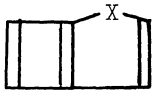

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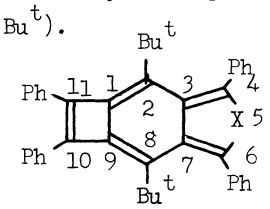

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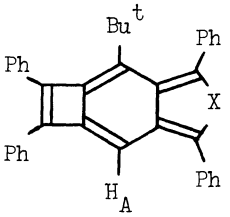

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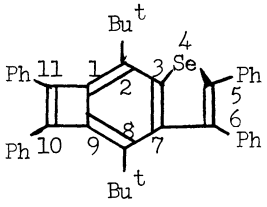

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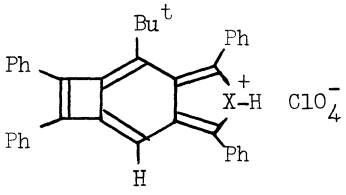

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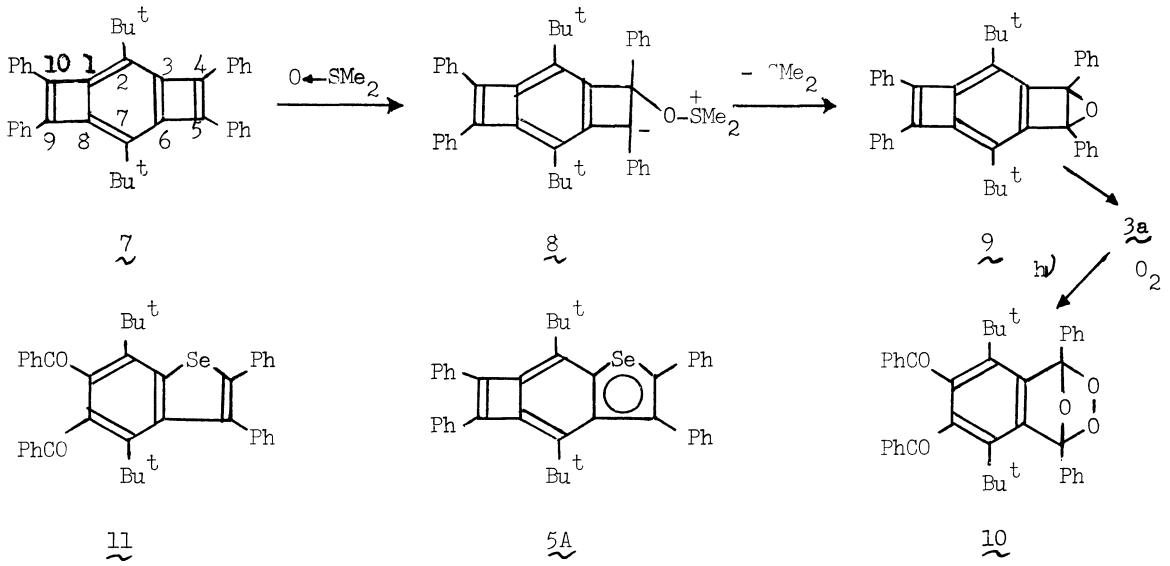
a : X = O; b : X = S; c : X = NTs; d : X = Se

Scheme 1

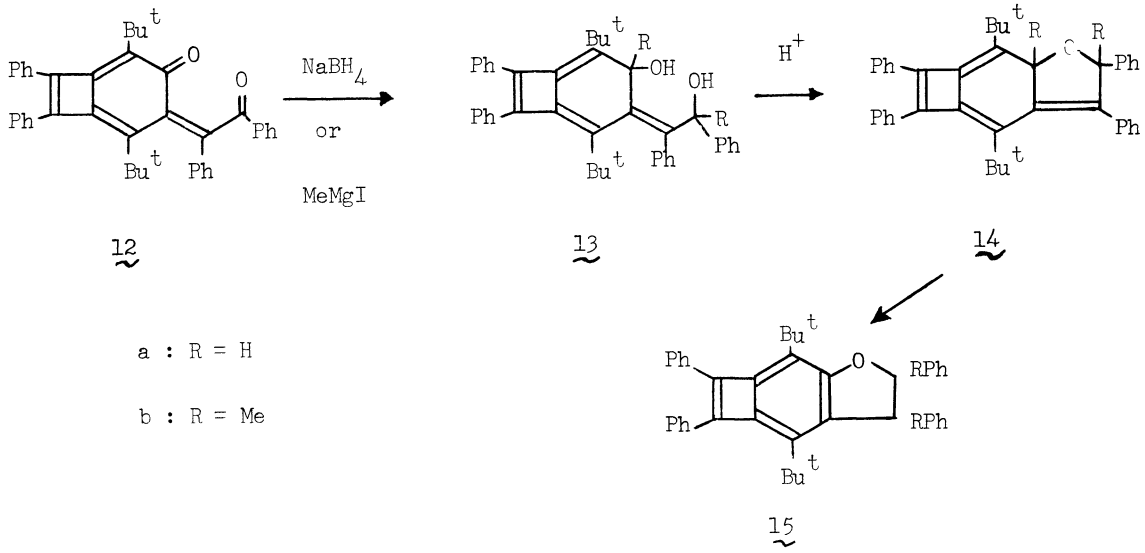


When 7 and TsN_3 were heated at 80 °C in p-xylene for 1 h, 5-tosylaza-analog of 3a (3c) was obtained as yellow prisms in 56% yield: mp 195 °C; λ_{max} 243 nm (ε 26,700), 260 (26,300), 309 (35,400), and 377 (7200); ^{1}H NMR δ 0.72 (s, Bu^t) and 2.32 (s, Me). This reaction is contrasted with the addition of dichlorocarbene to the 3,6-positions of 7 to afford a highly strained unsaturated propellane.[7] Tosylnitrene might not be the main reactive species in this reaction, because it has been reported that tosylazide is not effectively decomposed into tosylnitrene even at 155 °C.[8]

Compounds 3a-c are stable. Photooxidation of 3a in benzene afforded dibenzoylisobenzofuran peroxide (10)[9] in 47% yield. This photooxidation is analogous to that of 1,3-diphenylisobenzofuran to its peroxide.[10] However, 3b and 3c were inert to the photooxidation.

In contrast with the above insertions, Se is inserted into the 3,4-positions of 7. Heating of 7 and Se-powder under reflux in p-xylene under N_2 for 0.5 h afforded 4-selena-2,8-di-t-butyl-5,6,10,11-tetraphenyltricyclo[7.2.0.0^{3,7}]undeca-1,3(7),5,8,10-pentaene (5) in 89% yield as orange prisms: mp 276-277 °C; λ_{max} 265 nm (ε 19,200), 323 (2800), and 415 (430); ^{1}H NMR δ 0.55 and 0.99 (s, Bu^t). This contrast may be due to larger atomic radius of Se. Te did not react with 7. The hypothetical 4,5-positions Se-inserted compound (3d) may have serious steric crowding between Bu^t and Ph on the selenophene ring. High reactivity of 7 for such the insertion reaction can also be seen in the reaction of 7 with SeO_2. Heating of 7 and a half molar amount of SeO_2 under reflux in p-xylene under N_2 for 0.5 h afforded 3a, 5, and quinomethide derivative (12)[9] in 14, 32, and 22% yields, respectively. Compound 5 is sensitive to oxygen even in the crystalline state. When crystals of 5 were exposed to air for 2 days, dibenzoylbenzoselenophene (11) (mp 251-253 °C) was obtained in quantitative yield. In order to compare the oxygen sensitivity of 5 with that of benzocyclobutadiene which is fused to saturated five-membered heterocycle, 15a was prepared. Treatment of the diol (13a) (mp 134 °C), which was initially prepared by $NaBH_4$ reduction of 12, with catalytic amount of HCl afforded 15a as orange prisms in quantitative yield: mp 240-242 °C; λ_{max} 265 nm (ε 23,600), 304 (26,900), 355 (sh) (11,100), and 425 (sh) (1500); ^{1}H NMR δ 0.76 and 1.16 (s, Bu^t), and 2.65 and 3.70 (d, J=11 Hz, CH). Formation of 15a from 13a can be interpreted by prototropic rearrangement of 14a which was initially produced by dehydration of 13a. It is surprising that benzocyclobutadiene derivative can easily be formed by allylic rearrangement. Intermediacy of 14a was

Scheme 2

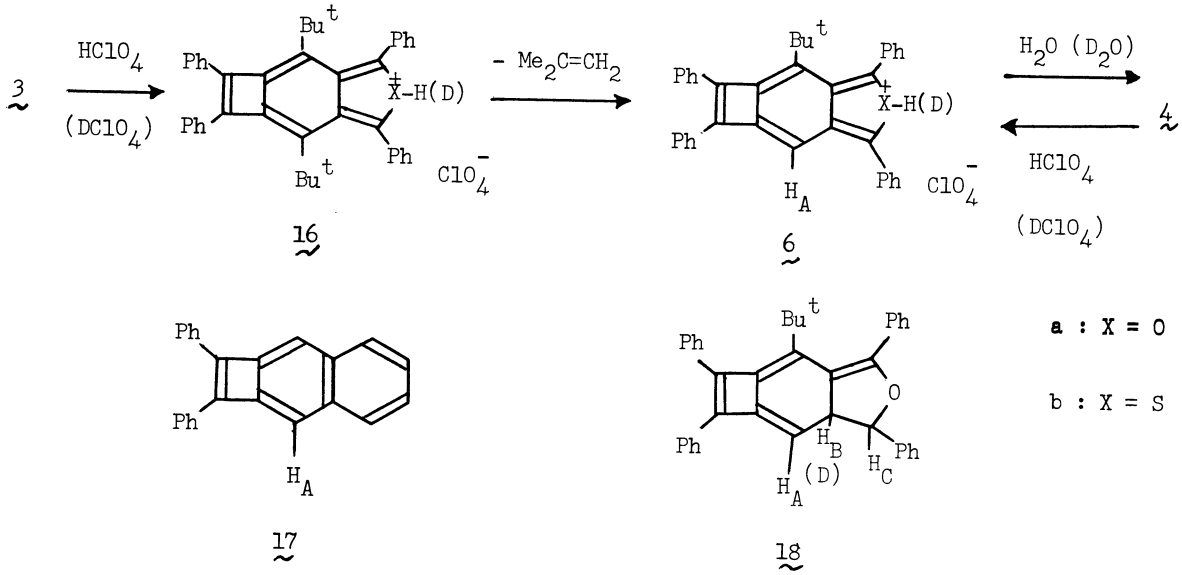


indirectly proven by isolating 14b (62% yield; mp 235-237 °C; λ_{max} 256 nm (ε 22,600), 275 (21,100), and 320 (sh) (11,500); ^{1}H NMR δ 0.88 and 1.22 (s, Bu^t), and 1.86 and 3.60 (s, Me)) upon HCl-catalyzed dehydration of 12b (not isolated) prepared by the reaction of 12 with MeMgI. Compound 15a is stable enough to be purified by recrystallization in air. Therefore, sensitivity of 5 to oxygen suggests that contribution of the canonical structure (5A) is not important.

In order to estimate antiaromaticity of 3 by ^{1}H NMR spectrum, H-substituted derivative (4) was prepared. Treatment of 3a with 70% $HClO_4$ in benzene afforded $HClO_4$ salt of 4a (6a) as golden yellow plates in quantitative yield: mp 220-221 °C; λ_{max} (CH_2Cl_2) 298 nm (ε 26,000), 331 (21,000), 400 (12,000), 632 (21,000), and 700 (sh) (13,000); ^{1}H NMR (CD_2Cl_2) δ 1.05 (s, Bu^t) and 5.85 (s, =O$^+$-H, disappeared for $DClO_4$ salt). Salt 6a was decomposed with water to afford free base 4a in 73% yield; mp 186-187 °C; ^{1}H NMR δ 0.85 (s, Bu^t) and 6.50 (s, H_A). Treatment of 4a with 70% $HClO_4$ in benzene afforded 6a again. Upon treatment of 3b with 70% $HClO_4$ in $CDCl_3$, deep blue color solution of 6b was obtained: λ_{max} 426 nm (ε 69,000), 560 (86,500), 650 (sh) (12,400), and 694 (sh) (7200); ^{1}H NMR δ 0.93 (s, Bu^t) and 6.13 (s, =S$^+$-H, disappeared for $DClO_4$ salt), though 6b could not be isolated in pure state. Treatment of the solution with water afforded 4b in quantitative yield: mp 223-224 °C; ^{1}H NMR δ 0.79 (s, Bu^t) and 6.39 (s, H_A). The same blue color solution of 6b was obtained by dissolving 4b in $CDCl_3$ containing 70% $HClO_4$. In both cases of 6a and 6b, ^{1}H NMR signal of H_A was not detected, probably because of overlapping to signals of aromatic hydrogens. UV absorption bands of 4a (292 nm (ε 28,400), 330 (22,300), and 436 (8500)) and 4b (294 nm (ε 22,100), 337 (23,200), and 432 (5000)) appeared at longer wave-length region than those of 3a and 3b, respectively. This is probably due to a serious steric crowding in 3. The δ-values of H_A of 4a and 4b are comparable to that of H_A of naphthocyclobutadiene (17) (δ 6.50).[11] These data suggest that 3 and 4 have paramagnetic ring current and then show antiaromaticity. Nevertheless, 3c, 5, and 15a did not form any $HClO_4$ salt.

It was proven that H_A of 4 comes from methyl of the Bu^t group of 3 but not from $HClO_4$. Treatment of 3 with $DClO_4$ and then with D_2O afforded 4 but not its deuterated one (Scheme 3). When the reaction of 3 with $HClO_4$ in CD_2Cl_2 was followed by ^{1}H NMR spectrum, signals of isobutylene (δ 1.68 (s, Me) and 4.60 (s, $=CH_2$)) appeared initially and turned gradually to the signal of Bu^{t}OH$_2$ (δ 1.32 (s, Bu^t)). This substitution reaction of the Bu^t group with the hydrogen might be accelerated by partly delocarized positive charge on the six-membered ring and by steric crowding in the onium

Scheme 3



salt (16). Delocarization of positive charge seems likely, because 6a was easily reduced with $NaBH_4$ to afford 18 in 40% yield: mp 225-226 °C; λ_{max} 298 nm (ε 18,900), 311 (19,600), and 375 (sh) (8800); ^1H NMR δ 0.98 (s, Bu^t), 4.81 (d, J=9 Hz, H_C), 5.16 (dd, J=3 and 9 Hz, H_B), and 6.60 (d, J=3 Hz, H_A). In this reaction, H^- attacks on the β-carbon of the oxonium ion, and 18-d (^1H NMR δ 0.99 (s, Bu^t), 4.70 (s, H_C), and 6.55 (s, H_A)) was obtained when 6a was reduced with $NaBD_4$. However, neither 3 nor 4 was reduced with $NaBH_4$.

To our best knowledge, no $HClO_4$ salts of heterocyclic compounds have yet been isolated.[12] Stability of 6 might be due to releasing from antiaromaticity of 4 by protonation.

REFERENCES AND NOTES

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