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GENERATION AND REACTIONS OF ANTI-TRICYCLO[6.1.0.0^{2,4}]NON-5-EN-7-YLIDENE AND ANTI, ANTI-TETRACYCLO[7.1.0.0^{2,4}.0^{5,7}]-DECAN-8-YLIDENE

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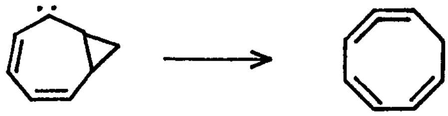
Due to high reactivity of carbene and to strain of cyclopropane ring, cyclopropyl carbenes undergo fragmentations and rearrangements rather than additions and insertions.[1] We have recently reported the facile rearrangement of bicyclo-[5.1.0]octa-2,4-diene-6-ylidene 1 to cycloocta-1,2,4,6-tetraene 2.[2] We here describe the generation of the title carbenes, 3 and 4, whose behaviors differ each other and also from those of 1.



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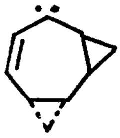

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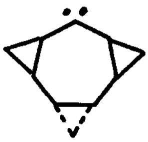
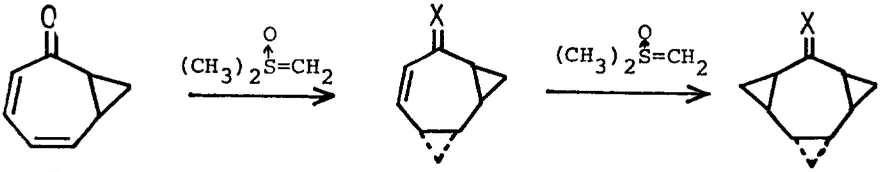


4

Preparations of the precursors:

Reaction of 2,3-σ-homotropone 5[3] with one equiv. of dimethylsulfoxonium methylide in dimethyl sulfoxide gave anti-2,3;4,5-bis-σ-homotropone 6 in 72-86% yield (b.p. 90-92°C/0.3 torr.). Further treatment of 6 with one equiv. of the reagent or treatment of 5 with two equiv. of the reagent gave anti, anti-2,3;4,5;6,7-tris-σ-homotropone 7 (m.p. 65°C) in 30-45% yield. The assigned structures were deduced from the spectral data (Table 1) and some chemical bases.[4] The homotropone 6 was then converted into the tosyl hydrazone 8 (m.p. 135°C) in 51% yield by reaction with p-toluenesulfonyl hydrazide in refluxing benzene (NH_4OAc as a catalyst). The tosyl hydrazone 9 (m.p. 179°C decomp.) was obtained from 7 in 98% yield (p-$TsNHNH_2$, pyridine, 60°C).



5

6 X=O
8 X=NNHTs

7 X=O
9 X=NNHTs

anti-Tricyclo[6.1.0.$0^{2,4}$]non-5-en-7-ylidene **3** (Scheme 1):

Irradiation of the sodium salt of **8**, obtained as solids by treatment with sodium hydride, in tetrahydrofuran (THF) in the presence of either dimethyl fumarate (DMF) or maleate (DMM) (five equiv.) yielded two *trans* adducts, **10a** (m.p. 88°C) and **10b** (m.p. 118°C) (27%:30% (DMF): 13%:15% (DMM)). The adducts were also obtained in similar yields and ratios, respectively, on a thermal condition of refluxing dioxane. The *trans* stereochemistry was suggested by the coupling constants between the vicinal cyclopropane protons (6.3 Hz in **10a** and 6.0 Hz in **10b**; see Table 1).[5] Cycloheptatrienylidene has been reported to give only *trans* adduct with both the olefins, though it adds to fumaro- and maleinitrile stereospecifically at careful conditions.[6,7] It is yet uncertain which adduct is assignable to the structure **10a** or **10b**.

On the other hand, when thermally generated in the presence of diphenylisobenzofuran (DPIBF), the carbene **3** gave two, stereoisomeric Diels-Alder adducts, **12a** (18%, m.p. 210°C) and **12b** (33%, m.p. 127°C), via transformation to highly strained dehydro-tris-σ-homobenzenes (*anti*-tetracyclo[6.1.0.$0^{2,4}$.$0^{5,7}$]non-9-enes), **11a** and **11b**. The PMR spectra indicate the absence of olefin protons. The PMR signals at δ 2.67 in **12a** and 2.47 in **12b** could be assigned to Hb in each adduct (see the Figure), whose lower field appearance relative to the other cyclopropane protons suggests its proximity to the oxygen bridge. Such a proximity effect has been observed in related systems.[8] The relatively small J_{Ha-Hb} in both the adducts (3.5 Hz in **12a** and 3.2 Hz in **12b**) indicate *trans* relationship of these protons.[5] The large difference in the J_{Hb-Hc} (8.0 Hz in **12a** and nearly zero in **12b**) leads to a conclusion that the relationships between these protons of **12a** and **12b** are *cis* and *trans*, respectively, since the cyclohexane rings can be regarded essentially planar.[9]

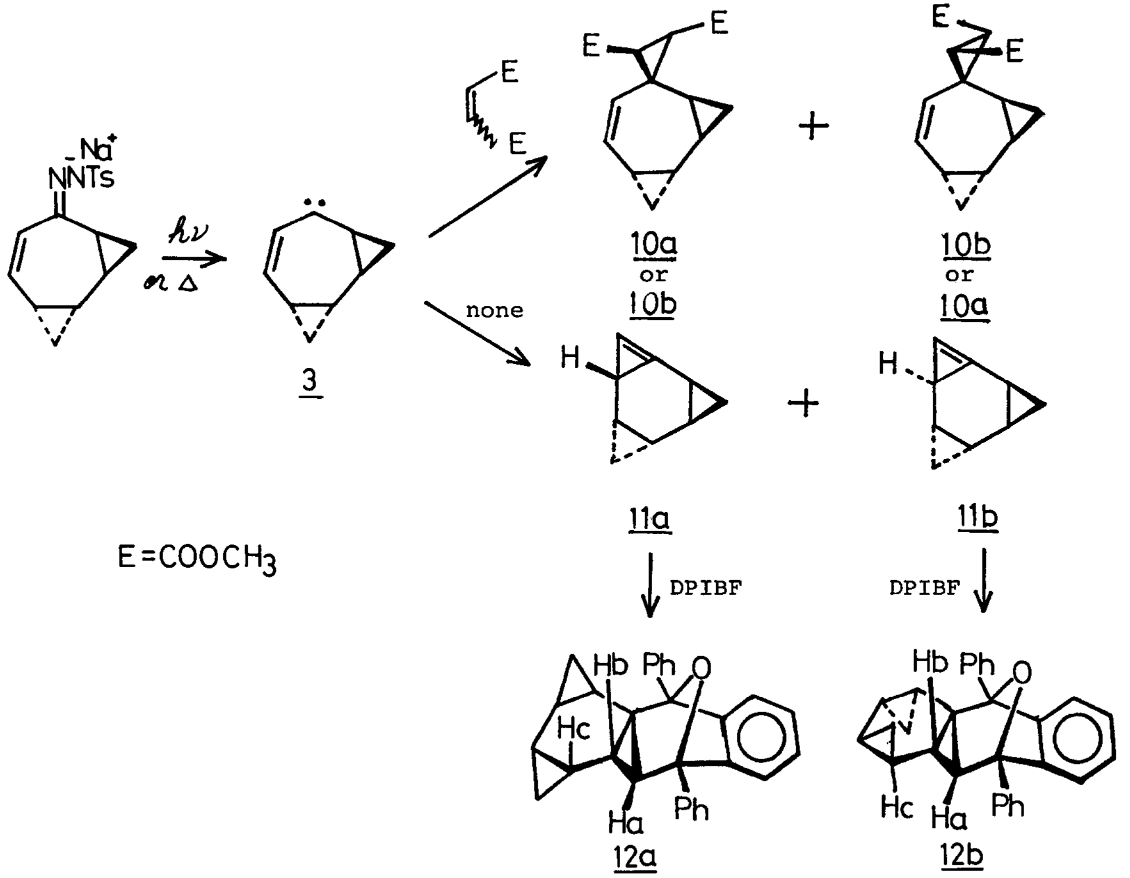
In the absence of trapping agents, the carbene **3** gave only a trace amount of volatile compounds whose structures have been yet uncertain.

Intramolecular cycloadditions of carbenes to double bonds leading to cyclopropenes are well documented.[1] As a related system, fused cycloproenes have been strongly supported as the intermediates in carbene-carbene rearrangement of cycloheptatrienylidenes and benzyl carbenes.[8, 10]

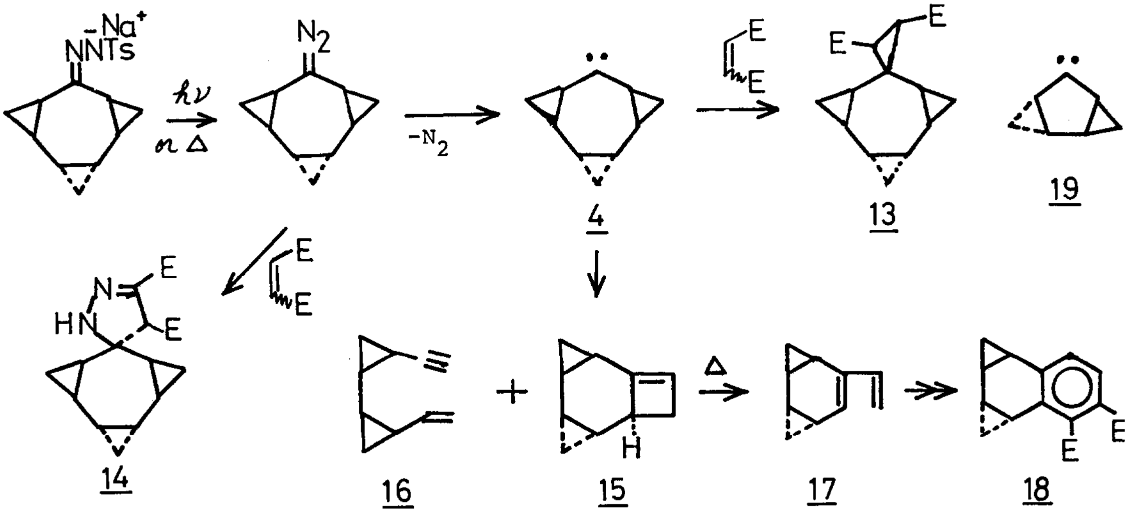
anti, *anti*-Tetracyclo[7.1.0.$0^{2,4}$.$0^{5,7}$]decan-8-ylidene **4** (Scheme 2):

Thermal decomposition of the sodium salt of **9** in refluxing dioxane in the presence of either DMF or DMM gave the adduct **13** (1.2-3.5%, m.p.74°C) and the dihydropyrazole **14** (90.8-91.4%, m.p. 156°C). The streochemistrys were tentatively assigned as shown in view of the results on **3** and steric hindrance.

However, irradiation of the salt in THF alone yielded two hydrocarbons, **15** (28%, oil) and **16** (3%, oil). The spectral data (Table 1) support their structures. Conclusive evidence on **15** was obtained by its thermal reaction. Heating of **15** in toluene (1.5 h) gave quantitatively the ring opened compound **17** which was in turn led to the bis-σ-homonaphthalene **18** (80%) by reaction with dimethyl



Scheme 1



Scheme 2

acetylenedicarboxylate followed by dehydrogenation with DDQ.

The predominant ring contraction of 4 over fragmentation contrasts with the exclusive fragmentation of anti-tricyclo[4.1.0.0^{2,4}]heptan-5-ylidene 19.[11] The latter's result may be because the similar ring contraction would produce a highly strained molecule and hence be energitically disfavored.

Table 1. Selected spectral data of the products.

6: ν (oil) 1640, 1620 cm^{-1}; λ (EtOH) 262.5 nm (log ε 3.63); δ (CCl$_4$) 0.69 (1H, m), 1.15-2.15 (7H, m), 5.28 (1H, dd, J=12.5, 1.5 Hz), 6.45 (1H, dd, 12.5, 7.3).

7: ν (KBr) 1690 cm^{-1}; λ (EtOH) 280 nm (log ε 1.83); δ (CDCl$_3$) 0.03 (1H, m), 0.5-1.2 (9H, m), 2.22 (2H, ddd, J=8.5, 8.5, 7.5 Hz).

10a: δ (CDCl$_3$, 100 MHz) 0.4-1.7 (8H, m), 2.56 (2H, narrow AB quartet, J=6.3 Hz) 3.68 (3H, s), 3.70 (3H, s), 4.80 (1H, d, J=12.0), 5.90 (1H, dd, 12.0, 6.5)

10b: δ (CDCl$_3$, 100 MHz) 0.3-1.3 (8H, m), 2.52 (2H, narrow AB quartet, J=6.0 Hz), 3.67 (3H, s), 3.73 (3H, s), 5.43 (1H, d, 10.5), 5.80 (1H, br. d, 10.5).

12a: δ (CDCl$_3$) 0-1.30 (8H, m), 1.33 (1H, d, J=3.5 Hz), 2.67 (1H, dd, 8.5, 3.5), 7.1-8.2 (14H, m).

12b: δ (CDCl$_3$) -0.42 (1H, ddd, J=4.8, 4.8, 4.5 Hz), 0-1.10 (7H, m), 1.18 (1H, d, 3.2), 2.47 (1H, d, 3.2), 7.0-7.9 (14H, m).

13: δ (CDCl$_3$) 0-0.5 (12H, m), 3.15 (2H, s), 3.67 (3H, s), 3.83 (3H, s).

14: ν (KBr) 3355, 1720, 1700 cm^{-1}; δ (CDCl$_3$) 0.2-1.5 (12H, m), 3.73 (3H, s), 3.83 (3H, s), 3.97 (1H, s), 6.25 (1H, br., NH).

15: ν (oil) 1640 cm^{-1}; δ (CCl$_4$) 0.10 (1H, m), 0.8-1.2 (5H, m), 1.41 (1H, m)m 2.1-2.3 (2H, m), 2.75 (1H, ddd, J=12.4, 3.8, 3.8 Hz), 5.83 (1H, structured s).

16: ν (oil) 3310, 2125, 1635 cm^{-1}; δ (CCl$_4$) 0.3-1.5 (8H, m), 1.63 (1H, d, J=1.8 Hz, CH), 4.7-5.6 (3H, m, vinyl).

17: ν (oil) 1635, 1600 cm^{-1}; λ (EtOH) 254 nm (log ε 4.18); δ (CCl$_4$) 0.3-1:7 8H, m), 4.82 (1H, ddd, J=10.5, 1.6, 0.8 Hz), 5.15 (1H, ddd, 17.5, 1.6, 0.5), 6.55 (1H, br. d, 4,0), 6.20 (1H, dd, 17.5, 10.5)

18: δ (CCl$_4$) 0.5-1.3 (4H, m), 1.6-1.9 (4H, m), 3.80 (6H, s), 7.12 (1H, d, J=8.0 Hz), 7.56 (1H, d, 8.0).

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