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Reactivity of *exo*- and *endo*-Tricyclo[3.2.1.0^{2,4}]octan-8-ylidenes and 7-Norbornenylidene

Shun-Ichi Murahashi,* Kazuo Okumura, Yusuke Maeda, Akio Sonoda, and Ichiro Moritani

Department of Chemistry, Faculty of Engineering Science, Osaka University, Machikaneyama, Toyonaka, Osaka, 560

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endo-Tricyclo[3.2.1.0^{2,4}]octan-8-ylidene (**2**) generated by the thermolysis of sodium salt of *endo*-tricyclo[3.2.1.0^{2,4}]octan-8-one tosylhydrazone (**5**) gave toluene (3.9%), cyclohepta-1,4-diene(**6**, 14%), cyclohepta-1,3-diene(**7**, 3.5%), bicyclo[3.3.0]octa-1,6-diene(**8**, 4.8%), bicyclo[3.3.0]octa-1,7-diene(**9**, 9.0%), and *endo*-tricyclo[3.2.1.0^{2,4}]-octane (**10**, 21%). In sharp contrast, *exo*-tricyclo[3.2.1.0^{2,4}]oct-8-ylidene (**1**) gave toluene (1.5%) and tricyclo-[5.1.0^{2,3}.0^{1,7}]oct-5-ene (**14**, 57%). The results indicate significant homoconjugative interaction between the p-orbital of the divalent carbon and the symmetric Walsh orbital of the cyclopropane. This is in line with the results of 7-norbornenylidene (**3**) in which the interaction between the divalent carbon and the carbon-carbon double bond stabilizes the nonclassical methylene. Thermolysis of sodium salt of 7-norbornenone tosylhydrazone (**18**) gave rise to cyclohexa-1,3-diene (3%), norbornene (6%), toluene (5%), spiro[2.4]hepta-4,6-diene (**19**, 10%), and bicyclo[3.2.0]hepta-1,6-diene (**21**, 56%).

Moss and Whittle reported the intramolecular reaction of 7-norbornanylidene to give norbornane (11 %), tricyclo[3.2.0.0^{2,7}]heptane (9.5%) and bicyclo[3.2.0]hept-1-ene (52%), and suggested the carbene to have normal geometry and a triplet ground state.[1] In constrast, Fisch and Pierce[2] reported bicyclo[3.3.1]-non-2-en-9-ylidene to be a singlet stabilized nonclassical methylene[3] with interaction between the carbenic bridge and the p-orbital of the double bond. In connection with this, the reactions of *exo*- and *endo*-tricyclo[3.2.1.0^{2,4}]octan-8-ylidene (**1** and **2**, respectively) and 7-norbornenylidene (**3**) are of interest, since significant homoconjugative interaction between the p-orbital of the divalent carbon and the symmetric Walsh orbital of the cyclopropane ring or the carbon-carbon double bond can be expected. Related cyclopropyl or olefinic homoconjugative participation at the developing carbonium ion center has been demonstrated,[4] kinetic results as well as extended Hückel calculations[5] on 8-tricyclo[3.2.1.0^{2,4}]octenyl cation indicating primary stabilization of the bridge cation from interaction with the cyclopropane ring rather than the double bond.[4]

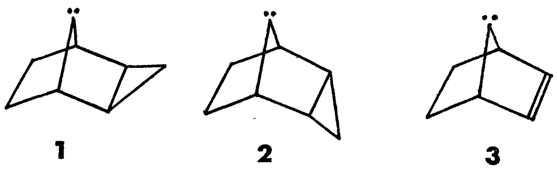
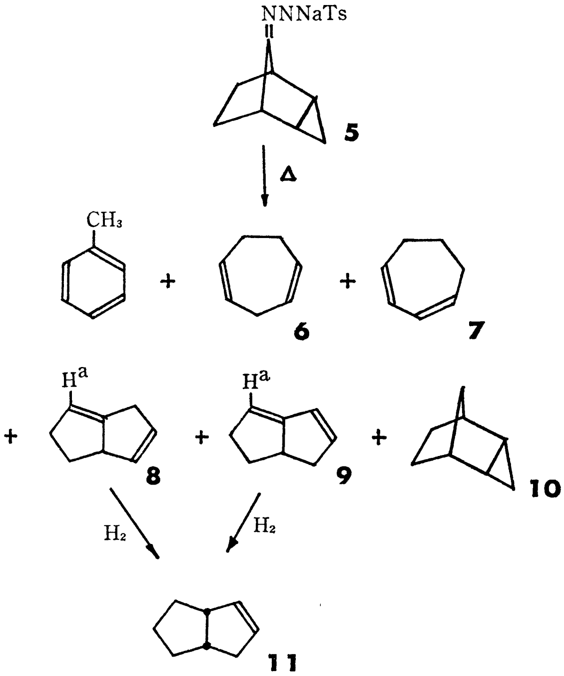


Fig. 1.

Results on the chemistry of **1** and **2** were reported by Freeman *et al.*[6] A report was made on results differing to some extent but clearly demonstrating the presence of tris-homocyclopropenyl interaction in *endo*-carbene **2**.[7] We also report results on carbene **3**, prepared from sodium salt. Moss *et al.* initially prepared it by thermolysis of lithium salt.[8] The overlapping of the vacant p-orbital of the divalent carbon with the p-orbital of the carbon-carbon double bond could be expected to stabilize sp^2 hybrid of the singlet state as in norbornenyl cation.[9]

Results and Discussion

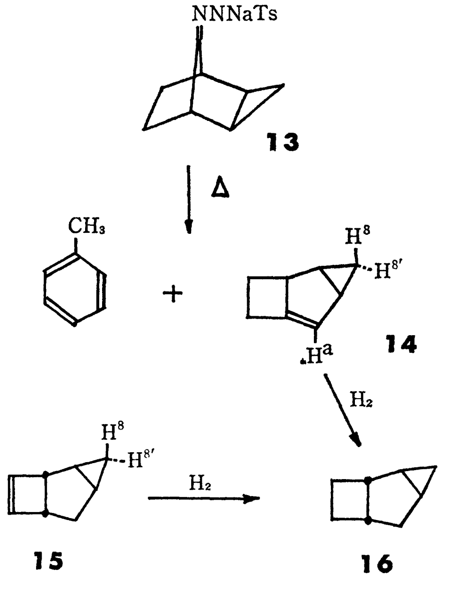
endo-Tricyclo[3.2.1.0^{2,4}]octan-8-one tosylhydrazone (**4**) was converted into sodium salt **5** by treatment with sodium hydride in THF. Salt **5**, dried at 130° *in vacuo*, was placed in a flask connected with a trap cooled at 77 °K. The flask was promptly immersed into an oil-bath which had been preheated at 180°. The volatile products (65% yield) were collected in the receiver, and subjected to careful vpc analyses. The pyrolysate was revealed to consist of six hydrocarbons as shown in Scheme 1. The first, second, third, and fifth components were readily assigned to toluene (6.9%), cyclohepta-1,4-diene (**6**, 25%),[10] cyclohepta-1,3-diene(**7**, 6.3%),[10] and *endo*-tricyclo[3.2.1.0^{2,4}]octane (**10**, 38%),[11] respectively, by comparison of their IR NMR and mass spectra, and the retention times with those of an authentic sample. Both fourth and fifth components are highly unstable olefins, and their mass spectra show the molecular peak at *m*/*e* 106. The NMR spectrum of the former component (8.6%) shows the vinyl proton resonances at δ 5.42 (multiplet, H^a)[12] and 5.75 (broad singlet, 2H) as well as signals due to



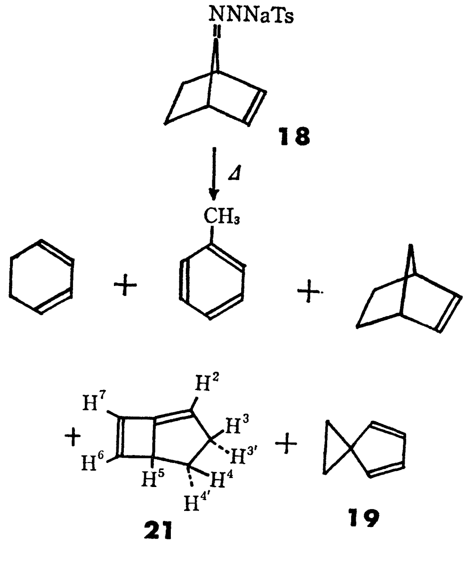
Scheme 1.

the methine proton at 3.45 (multiplet, H), double allylic protons at 2.77 (multiplet, 2H), the allylic protons at 2.34 (multiplet, 2H), and the methylene protons at 1.46 (triplet-doublet, 2H). The UV spectrum shows $\lambda_{max}^{n\text{-hexane}}$ 218 nm, indicating its non-conjugated olefin structure. Careful hydrogenation over palladium in carbon tetrachloride gave *cis*-bicyclo[3.3.0]oct-2-ene (**11**).[13] Thus, the structure was assigned to bicyclo[3.3.0]octa-1,6-diene(**8**). On the other hand, the NMR spectrum of the fifth component (16% yield) shows signals arising from the vinyl protons at δ 5.27 (multiplet, H^a) and 6.23 (singlet, 2H), the methine proton at 3.0 (multiplet, H), the allylic protons at 2.83—1.89 (multiplet, 4H), and the methylene protons at 1.49 (triplet-doublet, 2H). The UV spectrum shows $\lambda_{max}^{n\text{-hexane}}$ 246 nm, indicating the existence of a conjugated diene moiety. Its hydrogenation gave **11** again. Thus, the structure was assigned to bicyclo[3.3.0]oct-1,7-diene (**9**).[14]

A similar vacuum pyrolysis of sodium salt **13** derived from *exo*-tricyclo[3.2.1.$0^{2,4}$]octan-8-one tosylhydrazone (**12**) gave hydrocarbons (60% yield), consisting of extremely unstable tricyclo[5.1.$0^{2,5}$.$0^{1,7}$]oct-5-ene (**14**, 95.5%) and toluene (2.5%). The NMR spectrum of **14** displays multiplets at δ 5.13 (vinyl proton, H^a), 3.0—2.4 (allylic and methine, 3H), 2.3—1.5 (cyclopropyl and methylene, 4H), 1.15—0.92 and 0.55—0.35 (cyclopropyl, 1H each). Careful hydrogenation of **14** at −30—−20 °C over palladium black in carbon tetrachloride caused absorption of one equivalent of hydrogen to yield *trans*-tricyclo[5.1.$0^{2,5}$.$0^{1,7}$]octane (**15**), which was identical with a sample independently prepared by hydrogenation of *trans*-tricyclo[5.1.$0^{2,5}$,$0^{1,7}$]-oct-3-ene (**16**)[15] over palladium black in methanol. The molecular ion in the mass spectrum was found at *m/e* 108. The NMR spectrum consisted of three multiplets at δ 2.93—1.14 (10H), 0.64—0.24 (1H), and −0.22—−0.46 (1H).



Scheme 2.



Scheme 3.

Pyrolysis of sodium salt **18** derived from 7-norbornenone tosylhydrazone (**17**) at 180° gave hydrocarbons (80% yield),[16] which by careful vpc analyses was found to consist of five components in the ratio 3.7 : 8.0 : 70 : 5.7 : 12. The first, second, and fourth components were assigned to 1,3-cyclohexadiene, norbornene, and toluene, respectively, by comparison of their spectral data and the vpc retention times with those of the corresponding authentic sample. The structure of the fifth component was assigned to spiro[2.4]hepta-4,6-diene (**19**) by spectral comparison with an authentic sample.[17] For the sake of confirmation, **19** was converted into the TCNE adduct **20**. The NMR spectrum (acetone-d_6) includes signals due to the vinyl protons at δ 6.85 (triplet, 2H), the bridge protons at 3.88 (triplet, 2H), and the cyclopropyl protons at 1.05 (A_2X_2, 4H). The structure of the third, very unstable component was confirmed as follows. Hydrogenation over Pd-sponge gave bicyclo[3.2.0]pentane, which was identical with a sample prepared by hydrogenation of bicyclo[3.2.0]-hepta-2,6-diene.[18] The mass spectrum showed a molecular peak at *m/e* 92. The presence of three vinyl protons was indicated by the NMR spectrum (δ 6.67 doublet, 6.36 triplet, and 4.92 quartet). Thus, structure **21** or **22** can be considered. Double irradiation experiments showed that H_2 (δ 4.92) is not coupled to the vinyl protons, either H^6 (6.36) or H^7 (6.67), and coupled to methylene protons (H^3 and $H^{3'}$). This confirms the structure of bicyclo[3.2.0]hepta-1,6-diene (**21**) as the third component of the volatile products. Treatment of **21** with tetracyanoethylene at −78° gave rise to the TCNE-adduct, 8,8,9,9-tetracyanotricyclo[5.2.$0^{1,4}$.$0^{1,7}$]oct-2-ene (**23**). The structure of the adduct was firmly established by analysis of the IR (2260 cm^{-1}, C≡N), mass (*m/e* 220), and NMR spectra. The 100 MHz NMR spectrum ($CDCl_3$) showed absorption at δ 6.47 (H^3, doublet-doublet), 6.21 (H^2, doublet), 3.87 (H^7, multiplet), 3.63 (H^4, multiplet), 2.55 (H^5, $H^{5'}$, multiplet 2.30, and 1.80 (H^6, $H^{6'}$, multiplet). Double irradiation experiments showed that H^7 was coupled to H^6 and $H^{6'}$. Control experiments showed that norbornene, **19** and **21** are stable under the pyrolysis conditions in the presence of so-

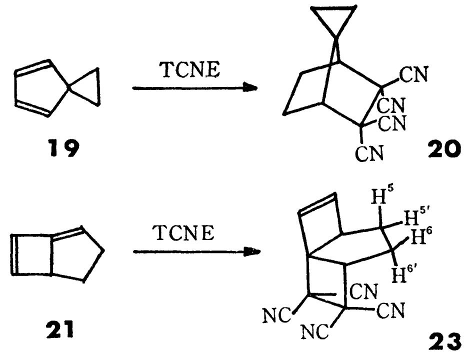
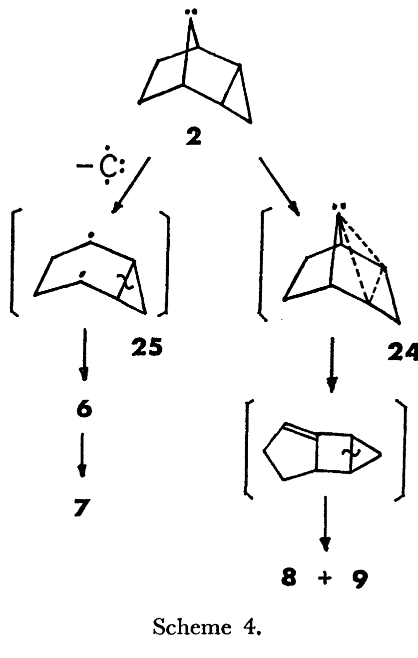


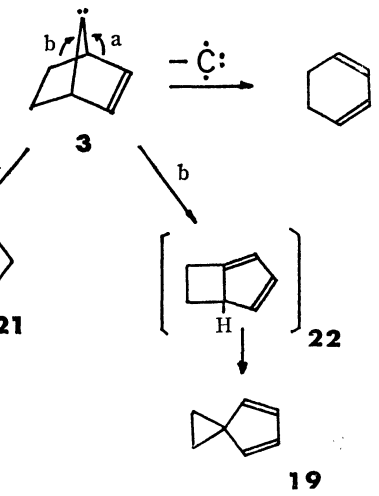
Fig. 2.

dium p-toluenesulfinate. When the pyrolysate left to stand at −20 °C, the diene **19** polymerized gradually, but other products remained unchanged.

The products of vacuum pyrolyses of **5**, **13**, and **18** are explained reasonably by assuming the intermediacy of free carbene.[1,2] However, the pyrolysis products of either **5** or **13** are different from those derived from decomposition of **5** and **13** prepared with sodium methoxide in diglyme.[6] Thus, tetracyclo[3.3.0^{2,8}.0^{4,6}]-octane, which is the main product of decomposition of **5** in diglyme, could not be detected among the products of the vacuum pyrolysis of **5**. Under the conditions of thermolysis in diglyme, two major reaction routes, a carbonium ion pathway as well as a carbene pathway, can be involved. Carbon-hydrogen and carbon-skelton rearrangements can be derived from a highly energetic cation.[19] Thus, no real chemical discrepancy between **1** and **2** can be pointed out. A favorable pathway of the reaction of **2** affording **6**—**10** can be envisioned as shown in Scheme 4. Dienes **8** and **9** can be formed by bond cleavage between C-1 and C-7 of a highly strained intermediate **24** derived from symmetrical interaction of the olefin-like cyclopropyl ring orbitals with the p-orbital of the divalent carbon. This resembles the behavior of bicyclo[3.3.1]nonen-9-ylidene[2] and indicates the nonclassical stabilization[3] of carbene **2**. It is noteworthy that tricyclo[5.1.0^{2,5}.0^{1,7}]oct-5-ene and its derivatives which can be formed *via* the 1,2-alkyl shift could not be detected among the products. Cycloheptadiene **6** can stem from cycloreversion[10] of **2** *via* the biradical intermediate **25**, accompanied by the release of a singlet carbon atom C_1. Analogous fragmentation and release of carbon atom were observed in quadricyclanylidene[20] and **3** forming cyclohexa-1,3-diene as a product. Diene **7** is an isomerization product of diene **6**.[10] Compound **10** is a hydrogen-abstraction product of carbene **2**, as norbornene arises from carbene **3**. The products from carbene **3** can be rationalized by Scheme 5. Diene **21** would arise *via* the 1,2-rearrangement (a) and diene **19** *via* the 1,2-rearrangement (b) followed by 1,5-sigmatropic rearrangement.[21] Preference of the formation of **21** to that of **19** indicates that **21** would arise fulfillment of the carbene π-bond interaction. The 1,2-rearrangement (a) of **3** finds analogies in carbonium ion chemistry.[9] It is noteworthy that the 1,3-insertion product, tricyclo[4.1.0.0^{3,7}]hept-4-ene[22] could not be detected among the reaction products; considerable 1,3-insertion products were obtained in the reaction of norbornanylidene.[1] This also suggests the presence of the carbene-π bond interaction in carbene **3**.



Scheme 4.



Scheme 5.

In sharp contrast, in the *exo*-carbene **1**, no participation of the cyclopropane ring can be observed to stabilize the carbenic center. The result was analogous to that of norbornanylidene which is suggested to have normal geometry and a triplet ground state.[1] Migration of C-7 (**26**) affording **14** is an exclusive pathway, which is presumably ascribed to steric reason.

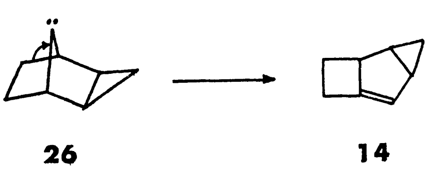


Fig. 3.

In brief, the presence of significant homoconjugative interaction between the p-orbital of the divalent carbon and either the symmetric Walsh orbital of the cyclopropane ring or the p-orbital of the carbon-carbon double bond can be demonstrated by comparative studies of the chemical reactivities of the carbenes **1**—**3** and norbornanylidene.

Experimental

All melting points are uncorrected. Infrared spectra were determined with a Hitachi 215 spectrometer, and NMR spectra with JNM-4H-100 with the use of internal tetramethylsilane. Mass spectra were taken on a Hitachi RSM-4 mass spectrometer. Vpc analyses were carried out on YANACO-550T and JEOL-20K.

endo-*Tricyclo[3.2.1.$0^{2,4}$]octan-8-one.*[11] Hydrolysis of 8,8-dimethoxy-*endo*-tricyclo[3.2.1.$0^{2,4}$]octane [bp 84°/9 mm Hg; NMR (CCl_4) δ 3.25 (s, 3H), 3.15 (s, 3H), 2.03 (m, 2H), and 1.72—0.56 (m, 8H)], with 3 M $HClO_4$ solution gave the ketone in 67% yield. IR (liquid film) 1760 cm^{-1} (C=O).

endo-*Tricyclo[3.2.1.$0^{2,4}$]octan-8-one* p-*Toluenesulfonylhydrazone (**4**).* A mixture of *p*-toluenesulfonylhydrazine (2.1 g, 11 mmol) and the ketone (1.1 g, 8.6 mmole) in ethanol (55 ml) was stirred for 40 min at 65°C. Evaporation of ethanol, followed by washing with ether and methanol gave pure tosylhydrazone (2.4 g, 94%): mp 171.5—172 °C (decomp); IR (Nujol mull) 3210 (N–H), 1685 (s), 1600(s), 1350(s), 1314(s), 1180(s), 1095(m), 980(s), and 925(s) cm^{-1}; NMR ($CDCl_3$) δ 7.77 (AX, J=8 Hz, 2H), 7.24 (AX, J=8 Hz, 2H), 2.42 (broad s, 3H), and 1.8—0.6 (m, 10H).

*Pyrolysis of the Sodium Salt (**5**) of* endo-*Tricyclo[3.2.1.$0^{2,4}$]octan-8-one* p-*Toluenesulfonylhydrazone (**4**).* To a suspension of sodium hydride (1 g, 21 mmol) prewashed with dry THF (10 ml) in a 200 ml-round flask was added a solution of tosylhydrazone **4** (5 g, 17 mmol) in THF (105 ml). The mixture was stirred under nitrogen until the evolution of hydrogen ceased. Evaporation of THF gave white powder. Further removal of THF under reduced pressure at 130 °C gave sodium salt **5**. The flask was bridged with glass tubing to a trap cooled at 77 K under reduced pressure (2 mmHg), when the salt was immersed into an oil bath preheated at 180 °C, spontaneous decomposition occurred to give the pyrolysate (1 g, 56%) in the trap. The pyrolysate was subjected to the vpc analysis (KF-96, injection temp 105 °C, detector temp 130 °C, colomun temp 60 °C). The vpc showed that six components were existent in the reaction mixture in the ratio 7 : 25 : 6 : 9 : 16 : 38, which was uncorrected for vpc detector response. The retention times of these products are 6, 11, 12, 16, 19, and 21 min, respectively. The first component was assigned to toluene, the second to cyclohepta-1,4-diene (**6**) [Mass m/e 94; NMR (CCl_4) δ 5.95—5.12 (m, 4H), 3.00—2.70 (m, 2H), and 2.35—2.14 (m, 4H); IR (liquid film) 1660 cm^{-1} (C=C)], the third to cyclohepta-1,3-diene (**7**) [Mass m/e 94; NMR (CCl_4) 5.84—6.65 (broad s, 4H) 2.55—2.16 (m, 4H), and 2.10—1.61 (m, 2H)], the sixth to *endo*-tricyclo[3.2.1.$0^{2,4}$]octane (**10**) [Mass m/e 108; IR (liquid film) 3080(m), 3030(s), 3015(s), 2960(s), 2880(s), 1480(m), 1455(m), 1440(m), 1315(s) 1250(w), 1175(w), 1150(w), 1120(m), 1075(w), 1040(m), 1015(w), 1000(m), 920(w), 900(w), 860(w), and 720(s) cm^{-1}]. Each product was collected by preparative vpc (KF-96, 20%, 6m). The extremely unstable fourth component collected in a receiver at —78° was assigned to bicyclo[3.3.0]oct-1,6-diene (**8**) according to the following data. Mass m/e 106; NMR (CCl_4) δ 5.54—5.32 (m, H), 5.81—5.70 (broad s, 2H), 3.75—3.27 (broad m, H), 2.87—2.71 (m, 2H), 2.62—2.12 (m, 2H), and 1.46 (d-t, $J_{H^4H^5}$=8 Hz, $J_{H^3H^4}$=10 Hz, 2H). Hydrogenation of the sample collected by vpc over palladium in carbon tetrachloride afforded a sample containing two products. Preative vpc (Ucon oil 20%, 2m, colomun temp 75 °C) of the main component gave *cis*-bicyclo[3.3.0]-oct-2-ene in a 65% yield. Mass m/e 108; NMR (CCl_4) δ 5.44 (m, 2H), 3.37—2.88 (m, H), 2.88—2.60 (m, H), 2.60—2.28 (m, H), 2.28—1.97 (m, H), and 1.97—0.71 (m, 6H). The minor product, mass m/e 106, was tentatively assigned to *cis*-bicyclo[3.3.0]oct-2,6-diene, which was probably derived from **8** *via* palladium induced 1,3-hydride site.[23] The fifth extremely unstable component was assigned to bicyclo-[3.3.0]oct-1,7-diene (**9**), [Mass m/e 106; NMR (CCl_4) δ 5.40—5.20 (m, H), 6.23 (broad s, 2H), 3.38—2.62 (broad m, H), 2.83—1.89 (m, 4H), and 1.49 (t-d, $J_{H^3H^4}$=11 Hz, $J_{H^4H^5}$=8 Hz, 2H)]. Hydrogenation over palladium-charcoal (5%) in carbon tetrachloride followed by preparative vpc gave *cis*-bicyclo[3.3.0]oct-2-ene in 69% yield along with *cis*-bicyclo[3.3.0]oct-2,7-diene, since hydrogenation of **8** gave the same product.

exo-*Tricyclo[3.2.1.$0^{2,4}$]octan-8-one.* To a suspension of Zn(Cu) (36 g) in dry ether (200 ml) was added freshly distilled methylene iodide (2 g) with stirring. To the mixture was added a solution of 7,7-dimethoxynorbornene(20 g) and and methylene iodide (80 g) with rigorous stirring at reflux for 1 hr. After stirring for 1 hr, a solution of 0.5 M HCl and ice was added. The usual work-up followed by distillation gave a mixture (10.2 g, 67—75°C/30 mmHg), which contained norbornen-7-one (8%), an unidentified product (16%), *exo*-tricyclo[3.2.1.$0^{2,4}$]octan-8-one (70%), and *exo*-8,8-dimethoxy-tricyclo[3.2.1.$0^{2,4}$]octane (6%). Mass m/e 168; IR (CCl_4 (liquid film) 3100 and 1020 cm^{-1} (cyclopropyl C–H); NMR (CCl_4) δ 3.03 (s, 6H), 2.06 (broad s, 2H), 1.7 (m, 2H), 1.30—1.15 (m, 4H), and 0.75 (m, 2H). Found: C, 71.28; H, 9.95%. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.95%. Further fine distillation gave pure *exo*-tricyclo[3.2.1.$0^{2,4}$]octan-8-one (bp 75 °C/30 mmHg) in 32% yield. Mass m/e 122; IR (liquid film) 1775 cm^{-1} (C=O); NMR (CCl_4) δ 1.98 (broad s, 2H), 1.77 (broad s, 4H), 1.16 (d-d, $J_{H^2H^3}$=3.4 Hz, $J_{H^2H^{3'}}$=6.9 0.50 (d-t, $J_{H^3H^{3'}}$=6,9 Hz, $J_{H^2H^{3'}}$=6.9 Hz, $H^{3'}$), and 0.14 (d-t, $J_{H^3H^{3'}}$=6.9 Hz, $J_{H^2H^3}$=3.4 Hz, H^3). Found: C, 78.68; H, 8.36%. Calcd for $C_8H_{12}O$: C, 78.65; H, 8.23%. *exo*-8,8-Dimethoxytricyclo[3.2.1.$0^{2,4}$]octane can be quantitatively converted into the ketone on treatment with a small amount of acetic acid at ambient temperature for 8 hr.

exo-*Tricyclo[3.2.1.$0^{2,4}$]octan-8-one* p-*Toluenesulfonylhydrazone (**12**).* *p*-Toluenesulfonylhydrazine (6 g, 32 mmol) was dissolved in a minimum amount of dry methanol, and *exo*-tricyclo[3.2.1.$0^{2,4}$]octan-8-one (4 g, 33 mmol) was added. The mixture was stirred under reflux for 30 hr. On standing, a precipitated colorless solid was collected by filtration. Recrystallization from methanol gave **12** (5 g, 53%). [Mp 165—166°; IR (Nujol mull) 3330 cm^{-1} (N–H); NMR (acetone-d_6) δ 7.88 (AX, J=9 Hz, 2H), 7.51 (AX, J=9 Hz, 2H), 3.2 (broad s, H), 2.45 (s, 3H), 2.3 (broad s, 2H), 1.6 (broad s, 4H), 1.05—0.95 (m,. 2H), 0.16 (d-t, $J_{H^2H^3}$=6.55 Hz, $J_{H^3H^{3'}}$=6.7 Hz, H^3), and —0.33 (d-t, $J_{H^3H^{3'}}$=6.7 Hz, $J_{H^2H^{3'}}$=3.5 Hz, $H^{3'}$). Found: C, 62.16; H, 6.13; N, 9.76; S, 11.21%. Calcd for $C_{15}H_{18}N_2O_2S$: C, 62.04; H, 6.25; N, 9.65; S, 11.04%].

*Pyrolysis of the Sodium Salt (**13**) of* exo-*Tricyclo[3.2.1.$0^{2,4}$]octan-8-one* p-*Touenesulfonylhydrazone (**12**).* Vacuum pyrolysis of salt **13** prepared from sodium hydride (0.7 g, 15 mmol) and **12** (3.2 g, 11 mmol) gave the pyrolysate (0.7 g, 60%) in a cold trap. Vpc analysis (KF-96, 20%, 2m, 80 °C) showed that three components were contained in the ratio 2.5 : 2.2 : 95.3. The first component was assigned to toluene, but the second component could not be identified. Preparative vpc (Ucon oil, 20%, 2m, 50 °C) gave an analytical sample of the extremely unstable third component, assigned to tricyclo[5.1.0^{2,5}.0^{1,7}]oct-5-ene (**14**) according to the following spectral data. Mass *m/e* 106, NMR(CCl_4) (at -20 °C) δ 5.20—5.08 (m, H), 3.00—2.40 (m, 3H), 2.30—1.50 (m, 4H), 1.03 (d-t, $J_{H^1H^8}=4.05$ Hz, $J_{H^8H^{8'}}=4.05$ Hz, H^8), and 0.44 (d-t, $J_{H^1H^8}=8.3$ Hz, $J_{H^8H^{8'}}=4.05$ Hz, $H^{8'}$)]. Hydrogenation **14** over palladium black at -30—20 °C in carbon tetrachloride gave tricyclo[5.1.0^{2,5}.0^{1,7}]octane (**15**), [Mass *m/e* 108; (CCl_4) 3080(m), 3045(m), 2950(s), 2875(s), 1730(w), 1460(m), 1380(w), 1338(w), 1300(w), 1250(w), 1120(w), 1080(w), 1030 (w), 1005(w), 980(w), 830(w), 810(m), 790(w), and 730(w); NMR (CCl_4) δ 2.93—1.14 (m, 10H), 0.43 (d-t, $J_{H^8H^{8'}}=$ 4.2 Hz, $J_{H^1H^8}=8.4$ Hz, H^8), and -0.34 (d-t, $J_{H^8H^{8'}}=4.2$ Hz, $J_{H^1H^{8'}}=4.2$•Hz, $H^{8'}$)], which was independently synthesized by hydrogenation of *trans*-tricyclo[5.1.0^{2,5}.0^{1,7}]oct-3-ene (98 mg) over palladium black in methanol.

7-Norbornenone p-*Toluenesulfonylhydrazone (**17**).* 7-Norbornenone was prepared by the method of Gassman and Rape[24] from 7,7-dimethoxybicyclo[2.2.1]hept-2-ene, [Bp 64.5—65.5 °C/30 mmHg, IR (liquid film) 1860, 1790, and 1780 cm^{-1} (C=O); NMR (CCl_4) δ 0.9—2.5 (m, 4H), 2.75 (q, 2H), 6.5(t, $J=2.5$ Hz, 2H)]. A solution of *p*-toluenesulfonylhydrazine (2.2 g, 12 mmol) and 7-norbornenone (1.3 g, 12 mmole) in methanol (30 ml) was stirred at ambient temperature for 1 hr. Precipitated white crystals were collected and recrystallized from methanol to give **11** (2.7 g, 82%). [Mp 159—160 °C (decomp); IR (Nujol mull) 3230 (N–H), 1720(s), 1600(s), 1460(s), 1330(s), 1290(m), 1170(s), 1090(s), 1018(s), and 930(s). NMR (acetone-d_6) δ 7.73 (AX, $J=8$ Hz, 2H), 7.35 (AX, $J=8$ Hz, 2H), 6.55 (t, $J=2$ Hz, 2H), 3.6(m, 1H), 2.65—2.8 (m, 2H), 2.38(s, 3H), 1.6—2.0 (m, 2H), and 1.0—1.3 (m, 2H). Found: C, 60.57; H, 5.96; N, 10.01%. Calcd for $C_{14}H_{16}N_2SO_2$: C, 60.85; H, 5.84; N, 10.13%].

*Pyrolysis of the Sodium Salt (**18**) of 7-Norbornenone* p-*Toluenesulfonylhydrazone (**17**).* Vacuum pyrolysis of salt **18** prepared from tosylhydrazone **17** (7.68 g, 28 mmol) and sodium hydride (0.16 g) gave volatile products (2 g) in the trap. Vpc analyses (di-*n*-decyl phthalate 2 m, column temp 60 °C, detecter temp 135 °C, injection temp 130 °C) showed that five components were contained in the reaction mixture in the ratio 1.0 : 2.2 : 19 : 1.5 : 3.3. The first component was assigned to 1,3-cyclohexadiene, the second to norbornadiene, and fourth to toluene. These compounds were collected by preparative vpc, and their structures were determined by comparison with those of authentic samples. The fifth component was assigned to spiro-[2.4]heptadiene-(**19**) which was identified by comparison of their NMR spec trum with that of an authentic sample. NMR (CCl_4) δ 7.45 (m, 2H), 6.05—5.75 (m, 2H), 1.52 (s, 4H); Mass *m/e* (species %) 92 (M^+, 100), 91 (M^+-1, 215), 65 ($M^++1-C_2H_4$, 37), 63($M^+-C_5H_5$, 15). For confirmation of the stractural assignment, **19** was converted into the TCNE adduct. To a solution of tetracyanoethylene (692 mg, 5.4 mmol) in THF (20 ml) was added **19** (500 mg, 5.4 mmol) with stirring. After being stirred for 1 hr, precipitated white crystals were collected by filtration. Recrystallization from THF gave the adduct **20** (1.1 g, 90%). [Mp 217 °C (decomp); NMR (acetone-d_6) δ 6.85 (t, $J=2.5$ Hz, 2H), 3.88 (t, $J=2.5$ Hz, 2H), and 1.05 (A_2X_2, $\Delta\nu/J$ 2, 4H). Mass *m/e* 220(M^+). Found: C, 70.61; H, 3.70; N, 25.50%. Calcd for $C_{13}H_{18}N_4$: C, 70.89; H, 3.66; N, 25.44%]. The fourth component, highly polymerizable even at -20 °C, was assigned to bicyclo[3.2.0]hept-1,6-diene (**21**) as follows. Hydrogenation of a sample collected by vpc palladium-sponge in ether at -30° gave rise to bicyclo[3.2.0]heptane. Mass *m/e* 96; NMR (CCl_4) δ 2.7 (m, 2H), 2.4—1.7 (m, 4H), and 1.6—1.2 (m, 6H). The NMR spectrum was identical with that of the sample prepared by hydrogenation of bicyclo[3.2.0]-hept-2,6-diene. Mass *m/e* (species, %) 92 (M^+, 100), 91(M^+-1, 360), 73(620), 72(1900), 71(1000), 58(400), and 57(2900); NMR (CS_2, -60 °C) δ 6.67 (d, $J=1.5$ Hz, H^7), 6.36 (t, $J=2$ Hz, H^6), 4.92 (q, H^2), 3.6—3.0 (m, H^5), and 3.0—1.0 (m, 4H). To a solution of the pyrolysate in THF was added a solution of TCNE in THF at -60°. White crystalline material precipitated was collected and recrystallized from THF and acetone to give pure 8,8,9,9-tetracyanotricyclo[5.2.0]oct-2-ene (**23**). [Mp 154—155°; IR (Nujol mull) 2260(m), 1310(m), 1305(s), 1280(m), 1195(m), 1150(m), 905(m), 800(m), 785(s), 760(s), and 700(m) cm^{-1}; NMR($CDCl_3$) δ 6.47 (d-d, $J_{H^1H^2}=3$ Hz, H^2), 6.21(d, H^1), 3.87(d, H^8), 3.63 (m, H^3), 2.55(m. H^4, H^5), and 2.30 and 1.89(m, H^6, H^7). Found: C, 70.70; H, 3.70%. Calcd for $C_{13}H_8N_4$: C, 70.89; H, 3.66%].

*Photolysis of the Sodium Salt (**18**) of* p-*Toluenesulfonylhydrazone (**17**).* A solution of sodium salt (**18**, 30 mg) in THF (10 ml) was irradiated at -78 °C with a high pressure mercury arc for various periods of time with and without Pyrex filter. Aliquots were withdrawn periodically and examined by vpc.

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