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Rearrangement Approaches to Cyclic Skeletons. III. Practical Route to *cis*-Bicyclo[4.3.0]non-4-en-7-ones Based on Photochemical [1,3] Acyl Migration of Bicyclo[3.2.2]non-6-en-2-ones[1]

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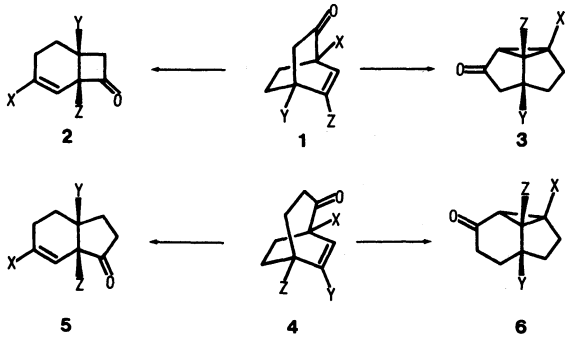
1-Methoxybicyclo[3.2.2]non-6-en-2-ones and the related compounds were derived I) from the Diels-Alder type 1,4-addition products of tropones with ethylene by selective reduction of the α,β-unsaturated carbonyl part (hydrosilylation followed by hydrolysis) and/or II) from bicyclo[2.2.2]oct-5-en-2-ones a) by the ring-enlargement utilizing Tieffeneau-Demjanov type conditions (1, TMS-CN; 2, $LiAlH_4$; 3, $NaNO_2$-AcOH) and/or b) by the related ring-expansion using trimethylsilyldiazomethane and boron trifluoride etherate. These bridged compounds were transformed into the respective [1,3] acyl migration products, *cis*-bicyclo[4.3.0]non-4-en-7-ones, in practical yields by direct irradiation through a Pyrex filter.

The photochemical behavior of tricyclo[2.2.2]oct-5-en-2-ones (**1**) has been investigated extensively.[3] The triplet-sensitized oxa-di-π-methane rearrangement of them into tricyclo[3.3.0.$0^{2,8}$]octan-3-ones (**3**) is particularly noticeable as a key reaction of syntheses of bi- and tricyclopentanoid natural products. On the other hand, there are only a few studies on the photochemical reaction of the higher homologs, bicyclo[3.2.2]non-6-en-2-ones (**4**).[4] As a part of our program to develop methods for stereoselective syntheses of [*m*–*n*] fused-ring natural products from bicyclic systems, we were interested in photochemical reactions of **4**.

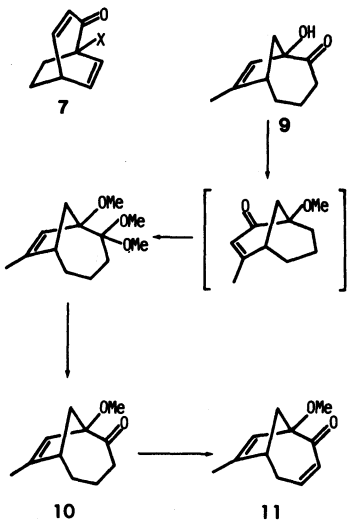
As is analogized from those reactions of **1**, the expected products from ketones **4** are the [5—6] fused-ring compounds (**5**) and/or the related tricyclic ketones (**6**). The C_2–C_9 bond of **6** will be cleaved to give the [5—6] fused-ring compounds which are different from **5**. Thus, whichever photochemical rearrangement is predominant we can get [5—6] fused-ring compounds.



	X	Y	Z
a	H	H	H
b	Me	H	H
c	OMe	H	H
d	OMe	Me	H
e	OMe	H	Me
f	OMe	Me	Me

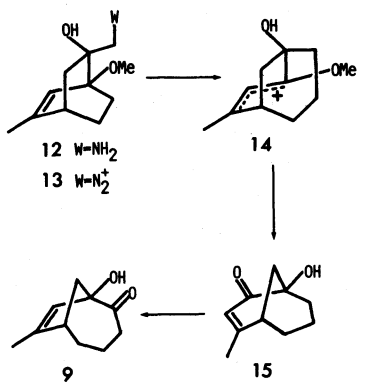
Results and Discussion

Syntheses of Bicyclo[3.2.2]non-6-en-2-ones. Already, we have reported that photochemical transformation of bicyclo[3.2.2]nona-3,6-dien-2-ones (**7**) into the C_7-disubstituted bicyclo[4.1.0]hept-2-enes is a practical synthetic method for [3—6] fused-ring sesquiterpenes such as sesquicarene[5] and isosesquicarene.[2] Bicyclononadienones **7a** and **7c** are the products of Diels-Alder reaction of tropones and ethylene.[6] Hydrosilylation of **7a** and **7c** with triethylsilane in the presence of Wilkinson's complex followed by hydrolysis[7] gave bicyclo[3.2.2]non-6-en-2-ones **4a** and **4c** in 47 and 84% yields, respectively. Another route to **4c** is sequential treatment of bicyclo[2.2.2]oct-5-en-2-one **1c**[8] with 1) cyanotrimethylsilane in the presence of a catalytic amount of zinc iodide, 2) lithium aluminium hydride, and 3) sodium nitrite in aqueous acetic acid (method A in Table 1). This Tieffeneau-Demjanov ring expansion[9] is useful to prepare the C_5-bridgehead methyl derivative (**4d**) from **1d**.[8] When 1-methylbicyclo[2.2.2]octenone **1b**[10] was treated similarly, the desired ketone (**4b**) was obtained along with a small amount of the regioisomer, 1-methylbicyclo-[3.2.2]non-6-en-3-one (**8**).[11]



However, a similar treatment of **1e**[12] gave the unexpected compound, 1-hydroxybicyclo[4.2.1]non-7-en-2-one (**9**), instead of **4e**. Treatment of **9** with trimethyl orthoformate in the presence of TsOH gave the trimethoxy derivative. Acetal exchange of the product with acetone yielded **10**. The enone was transformed into the α,β-unsaturated ketone (**11**) by palladium-catalyzed oxidation[13] of the enol trimethylsilyl ether of **10**. Proton-NMR spectra of **11** suggest this compound consists of the four-, two-, and one- carbon bridges.

Hydroxy ketone **9** is derived presumably from the hydroxylamine **12** which should give diazonium ion **13**. The 1,3-shift of the ethano bridge of **13** is not extravagant because of the additional stabilization of the resulting carbonium ion (**14**) with its methyl group. It is reasonable that ketone **9** is thermodynamically more stable than the valence isomer (**15**) since we can convert the former into **10**.



Ring enlargement of **1e** was accomplished by utilizing of trimethylsilyldiazomethane and BF_3-etherate (below −72°C) to give **4e** on desilylation with potassium carbonate in methanol[14] (method B in table 1). Table 1 shows this Tiffeneau-Demjanov type homologation is a general method to obtain bicyclo[3.2.2]non-6-en-2-ones from respective bicyclo[2.2.2]oct-5-en-2-ones. As observed in monocyclic systems,[14] the methylene carbon migrates in preference to the other in this bridged bicyclic system.

Photochemical Reactions of Bicyclo[3.2.2]non-6-en-2-ones. Table 2 shows the conditions and the results of these photoreactions. As reported previously,[4] direct irradiation of **4a** through a Pyrex filter gave mainly the [1,3] acyl migration product (**5a**). The minor products of the reaction were undefined aldehydes. Formation of these is presumably due to the hydrogen abstraction process of the diradical which mainly turns into **5a**. When acetone was used as the solvent, the product (**6a**) via the oxa-di-π-methane rearrangement was obtained competitively with **5a**. The tricyclic structure of **6a** is supported by its spectral characteristics which clearly show the presence of the six-membered ring ketone conjugated with a three-membered ring: IR (CCl_4) 1690 (C=O) cm^{-1}.

The photochemical behavior of the bridgehead methyl derivative (**4b**) is very similar to that of **4a**.

Table 1. Tieffeneau-Demjanov Ring Enlargements of Bicyclo[2.2.2]oct-6-en-2-ones

Substrate	Method[a]	Product	Yield/%
1b	A	**4b**[b]	49
1c	A	**4c**	64
1c	B	**4c**	73
1d	A	**4d**	64
1d	B	**4d**	80
1e	A	**9**	40
1e	B	**4e**	73
1f	B	**4f**	71

a) Described in the text. b) With 4.5% of **8**.

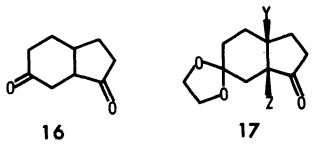
Table 2. Photochemical Rearrangement of Bicyclo[3.2.2]non-6-en-2-ones

Substrate	Solvent	Concentration	Time	Products
		mol dm^{-3}	h	%
4a	Hexane	0.012	2	**5a** (53)
4a	Acetone	0.039	5.5	**5a** (18), **6a** (18)[a]
4b	Hexane	0.025	3.5	**5b** (55)
4b	Acetone	0.020	3.5	**5b** (28), **6b** (23)[b]
4c	THF	0.010	4	**5c** (55)
4c	Acetone	0.031	4	**16** (64)
4d	Hexane	0.018	6	**5d** (56)
4d	THF	0.010	4	**5d** (56)
4d	Acetone	0.023	6.5	**5d** (41)
4e	THF	0.010	4	**5e** (47)
4f	THF	0.010	4	**5f** (50)

a) Ketone **4a**, 37%, was recovered. b) With 18% of recovery of **4b**.

In contrast with these, only the respective [1,3] acyl migration products (**5d—f**) were obtained from the substrates (**4d—f**) possessing a methoxyl group at the bridgehead position by irradiation in acetone. When the reaction of **4c** was carried out in acetone, a mixture of the isomeric diketones (**16**) was obtained. However, the HPLC analysis of the irradiated acetone solutions indicated that the primary product derived from **4c** is the [1,3] acyl migration product (**5c**).

The respective [1,3] acyl migration products (**5c—f**) are obtained in practical yields by direct irradiation of the bridged ketones (**4c—f**) in hexane or THF. As is analogized from the reactivity of **4c** in acetone, these enol methyl ethers are less stable compounds. However, the ethylene acetals (**17e—f**) derived selectively by acetal exchange are remarkably stable compounds.



Thus, the most useful process among the photochemical conversions of bicyclo[3.2.2]non-6-en-2-ones is the [1,3] acyl rearrangement to give bicyclo[4.3.0]non-4-en-7-ones. The products derived from the substrates having a methoxyl group at the bridgehead

position are synthetically versatile compounds because that they have a masked ketone in the six-membered ring and a carbonyl group itself in the five-membered ring. An application of this [1,3] acyl migration to a natural product synthesis has already been reported.[1]

In contrast with the cases of bicyclo[2.2.2]oct-5-en-2-ones,[3] the oxa-di-π-methane rearrangement dose not predominate over the [1,3] acyl migration when acetone was used as the solvent. The [1,2] migration process disappears when the irradiation of the substrate having a methoxyl group at the bridgehead was carried out in acetone.

In order to understand the photochemistry of these homoconjugated systems generally, the chemistry of an additional bridged system, bicyclo[3.2.1]oct-6-en-2-ones, is under investigation. Preliminary results indicate that 1) the processes via S_1 (n-π*), T (π-π*), and T (n-π*) give the products due to hydrogen abstraction, oxa-di-π-methane rearrangement, and [1,3] acyl migration, respectively, and 2) the energy difference between T (π-π*) and T (n-π*) is not large.[15] These results and the mechanistic studies of the reactions described in this paper will be reported in due course.

Experimental

General. Melting and boiling points are uncorrected. UV (in cyclohexane) and IR spectra (in CCl_4, unless otherwise mentioned) were recorded on Hitachi Model 323 and 215 spectrometers, respectively. ^1H NMR spectra (in CCl_4, unless otherwise noted) were obtained on JEOL JNM-PMX60, Varian EM-390 90 MHz, or Varian XL-200 NMR spectrometers, using tetramethylsilane as an internal standared. ^{13}C NMR spectra (in $CDCl_3$) were recorded on a JEOL FX 90Q NMR spectrometer. The mass spectral studies were conducted using a Hitachi M-52 spectrometer. Tetrahydrofuran and ether were distilled from benzophenone ketyl under argon, immediately prior to use. Dichloromethane was distilled from P_2O_5 and stored on 4A molecular sieves. Wilkinson's complex[16] and *N*-nitroso-*N*-trimethylsilylmethylurea[17] were prepared by using literature procedures. All reactions were monitored by analytical TLC using E. Merck precoated silica gel $60F_{254}$ plates. Column chromatography was carried out with E. Merck silica gel 60 (70—230 mesh ASTM). Analytical HPLC was performed on a Warters Associates Model R-401 liquid chromatograph using a 25 cm×4 mm stainless-steel column packed with Lichrosorb SI 100. Analytical VPC was carried out using a Hitachi 663-50 gas chromatograph, outfitted with a 3 m×3 mm stainless-steel column packed with 10% FFAP on 60/80 Uniport B.

Preparation of Bicyclo[3.2.2]non-6-en-2-one (4a). A flask containing of a mixture of 2.65 g (19.8 mmol) of bicyclo-[3.2.2]nona-3,6-dien-2-one (**7a**), ca. 10 mg of Wilkinson's complex, and 3.47 ml (21.7 mmol) of triethylsilane, was heated at 60 °C under argon for 4 d with stirring. The mixture was diluted with 20 ml of pentane, and filtered through a Celite layer. After removal of the solvent, the remaining oil (5.38 g) was treated with 0.6 g of K_2CO_3 in a mixture of 15 ml each of acetone, methanol, and water for 1 h. The solution was diluted with water, and extracted with ether. The extracts were combined, washed with two portions of water and with saturated brine, and then dried over $MgSO_4$. Removal of the volatiles by Kugelrohr distillation (100 °C/23—30 Torr (1 Torr=133.322 Pa)) gave 1.25 g (47%) of **4a** as colorless oil. **4a**: UV 289 (sh, ε 82), 298 (88), and 308 nm (72); IR 1700 (s) cm^{-1}. The 2,4-DNP derivative of **4a**: mp 149.5—150.5 °C (decomp). Found: C, 57.19; H, 5.08; N, 17.89%. Cacld for $C_{15}H_{16}N_4O_4$: C, 56.91; H, 5.10; N, 17.71%.

Preparation of 1-Methoxybicyclo[3.2.2]non-6-en-2-one (4c). a) Reduction of 1-Methoxybicyclo[3.2.2]nona-3,6-dien-2-one (7c). A mixture of 2.08 g (12.69 mmol) of **7c**, ca. 10 mg of $[Rh(PPh_3]Cl$, and 3.04 ml (19.0 mmol) of triethylsilane was heated at 60 °C overnight under argon. A similar workup to that employed for the synthesis of **4a** gave 3.37 g of a colorless oil. Chromatography (70 g of silica gel, 10:1—5:1 hexane, ethyl acetate) of the oil gave 1.78 g (84%) of **4c**: Colorless oil; UV 302 nm (ε103); IR 1715 (s) cm^{-1}. ^1H NMR δ=6.20 (H_6, dd, J=9.3, and 7.2 Hz), 5.87 (H_7, broad d, J=9.3 Hz), 3.22 (3H, s), 2.68 (H_5, m), 2.5—2.0 (2H, m), and 2.0—1.5 (6H, m); ^{13}C NMR δ=205.0 (s), 135.7 (d), 131.1 (d), 83.7 (s), 51.6 (q), 39.1 (t), 31.9 (t), 30.8 (d), 28.9 (t), and 22.7 (t); MS (13.5 eV) *m/z* (rel intensity) 166 (M^+, 55) and 110 (100). Found: C, 71.97; H, 8.65%. Calcd for $C_{10}H_{14}O_2$: C, 72.25; H, 8.49%.

b) Ring Enlargement of 1-Methoxybicyclo[2.2.2]oct-5-en-2-one (1c). (As a General Procedure for Method A). To a mixture of 2.40 g (15.77 mmol) of **1c** and ca. 10 mg of zinc iodide was added 2.3 ml (16.56 mmol)of cyanotrimethylsilane (TMSCN) at 0 °C, under argon, and the mixture was allowed to stand overnight at room temperature. After recognition of the end of the reaction from the disappearance of **1c**, the reaction mixture was diluted with 10 ml of dry ether, and the solution was added via a canula into a suspension of 0.9 g (23.66 mmol) of $LiAlH_4$ in 40 ml of dry ether at 0 °C. After stirring overnight at room tempetrature, this reaction mixture was treated successively with 0.9 ml of water, 0.9 ml of 15% aqueous NaOH, and 2.7 ml of water. A granular precipitate was filtered with K_2CO_3, and the filtrate was concentrated in vacuo to give 3.34 g of a pale yellow oil. To a solution of this oil in aqueous acetic acid, prepared from 4.7 ml of AcOH and 24 ml water, was added a solution of 1.63 g (23.64 mmol) of sodium nitrite in 7.9 ml of water over a period of 3 h using an Eyela Model MP-101 micro tube pump. After stirring overnight, the reaction mixture was diluted with water and extracted with three portions of ether. The extracts were combined, washed successively with saturated aqueous Na_2CO_3 and NaCl solutions, and dried over $MgSO_4$. Evaporation of the solvent gave 1.98 g of a yellow oil. Chromatography of the oil using 80 g of silica gel (10:1 hexane, ethyl acetate) gave 1.67 g (64%) of pure **4c**.

c) Ring Enlargement of 1-Methoxybicyclo[2.2.2]oct-5-en-2-one (1c) Using $TMSCHN_2$ and BF_3 Etherate. (As General Procedure for Method B). In a flask equipped with a Dry Ice condenser and a efficient magnetic stirrer were placed 4.59g (25.67 mmol) of *N*-nitroso-*N*-trimethylsilylmethylurea and 20 ml of pentane. To the mixture was added 8.8 ml of 20% aqueous potassium hydroxide solution at 0 °C. After 1.5 h stirring at 0 °C, the organic layer was diluted with pentane, separated, washed with water, and dried over Na_2SO_4. This solution was concentrated carefully to ca. 15 ml, and diluted with 30 ml of dichloromethane. To a solution of 1.56 g (10.3 mmol) of **1c** in 38 ml dichloromethane

was added 1.96 ml (15.34 mmol) of BF_3–etherate at −78 °C under argon and the mixture was stirred for 5 min. To this reaction mixture was added that $TMSCHN_2$ solution over a period of 1.5 h below −73 °C. After 30 min stirring, to the solution was added 40 ml of saturated aqueous $NaHCO_3$ solution. The mixture was allowed to warm to room temperature with stirring, and the organic layer was separated, washed with saturated brine, dried over $MgSO_4$, and concentrated in vacuo. Chromatography (40 g of silica gel, 8:1 hexane, ethyl acetate) of the remaining oil (2.2 g) gave 1.24 g (73%) of pure **4c**.

1-Methylbicyclo[3.2.2]non-6-en-2-one (4b): Colorless oil; UV 240 (sh,ε 62), 288 (sh, 91), 297 (102), and 303 nm (sh, 91); IR 1710 (s) cm^{-1}. ^1H NMR δ=6.21 (H_6, dd, J=8.9 and 7.5 Hz), 5.64 (H_7, d, J=8.9 Hz), 2.8—2.3 (3H, m), 2.0—1.2 (6H, m), and 1.11 (3H, s); MS (25 eV) m/z (rel intensity) 150 (M^+, 81) and 106 (100). The 2,4-DNP derivative of **4b**: Mp 138—139 °C. Found: C, 58.13; H, 5.46; N, 16.87%. Calcd for $C_{16}H_{18}N_4O_4$: C, 58 17; H, 5.49; N, 16.96%.

1-Methoxy-6-methylbicyclo[3.2.2]non-6-en-2-one (4d): Colorless oil; UV 293 (sh, ε 100), 301.5 (177), 311 (100), and 322 nm (sh, 65); IR 1715 (s) cm^{-1}. ^1H NMR δ=5.84 (1H, d, J=9.0 Hz), 5.76 (1H, dd, J=9.0 and<1.0 Hz), 3.18 (3H, s), 2.6—2.1 (3H, m), 2.0—1.3 (5H, m), and 1.16 (3H, s): ^{13}C NMR δ=204.6 (s), 140.7 (d), 130.2 (d), 83.5 (s), 51.6 (q), 39.7 (t), 39.3 (t), 34.9 (s), 30.9 (t), 29.0 (t), and 29.0 (q); MS (25 eV) m/z (rel intensity) 180(M^+, 14) and 124 (100). The 2,4-DNP derivative of **4d**: Mp 156—156.5 °C. Found: C, 56.82; H, 5.74; N, 15.50%. Calcd for $C_{17}H_{20}N_4O_5$: C, 56.66; H, 5.59; N, 15.55%.

1-Methoxy-5-methylbicyclo[3.2.2]non-6-en-2-one (4e): Mp 38.5—39.5 °C; UV 292 (sh, ε 141), 320 (174), 311 (169), and 323 nm (sh, 98); IR 1715 (s) cm^{-1}; ^1H NMR δ=5.45 (1H, s), 3.19 (3H, s), 2.6—2.1 (4H, m), 1.83 (3H, d, J=1.5 Hz), and 2.0—1.5 (5H, m); ^{13}C NMR δ=205.5 (s), 145.1 (s), 123.7 (d), 83.8 (s), 51.5 (q); MS (25 eV) m/z (rel intensity) 194 (M^+, 4) and 138 (100). DNP derivative of **4e**: Mp 131.5—132.5 °C. Found: C, 56.63; H, 5.65; N, 15.52%. Calcd for $C_{17}H_{20}N_4O_5$: C, 56.66; H, 5.59; N, 15.55%.

1-Methoxy-5,6-dimethylbicyclo[3.2.2]non-6-en-2-one (4f): Colorless oil; UV 292 (sh, ε 141), 302 (179), 312 (174), and 323 nm (sh, 102); IR 1710 (s) cm^{-1}; ^1H NMR δ=5.49 (1H, broad s), 3.18 (3H, s), 1.79 (3H, d, J=1.5 Hz), 2.5—1.3 (8H, m), and 1.12 (3H,s); ^{13}C NMR δ=205.4 (s), 146.5 (s), 124.7 (d), 83.8 (s), 51.4 (q), 39.1 (t), 39.0 (t), 37.3 (s), 31.7 (t), 26.3 (q), and 19.1 (q); MS (25 eV) m/z (rel intensity) 194 (M^+, 4) and 138 (100). Found: C, 74.10; H, 9.46%. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34%.

1-Methylbicyclo[3.2.2]non-6-en-3-one (8): Colorless oil; IR 1695 (s) cm^{-1}; ^1H NMR δ=6.14 (1H, dd, J=9.0 and 7.1 Hz), 5.95 (1H, d, J=9.0 Hz), 2.57 (1H, m), 2.4—2.25 (4H, m), 1.9—1.6 (4H, m), and 1.13 (3H, m); MS (13.5 eV) m/z (rel intensity) 150 (M^+, 81), 108 (100), and 93 (71). The 2,4-DNP derivative of **8**: Mp 140—141 °C. Found: C, 58.36; H, 5.68; N, 16.95%. Calcd for $C_{16}H_{18}N_4O_4$: C, 58.17; H, 5.49; N, 16.96%.

1-Hydroxy-7-methylbicyclo[4.2.1]non-7-en-2-one (9): Mp 71—72 °C; IR 1695 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ=5.14 (1H, broad s), 4.07 (1H, broad s), 1.74 (3H, d, J=1.5 Hz), 3.3—1.3 (9H, m); ^{13}C NMR δ=212.7 (s), 147.9 (s), 127.9 (d), 88.8 (d), 46.9 (d), 44.3 (t), 40.5 (t), 30.6 (t), 20.6 (t), and 15.1 (q); MS (25 eV) m/z (rel intensity) 116 (M^+, 34) and 109 (100). Found: C, 42.56; H, 8.64%. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49%.

Preparation of 1-Methoxy-7-methylbicyclo[4.2.1]non-7-en-2-one (10): To a solution of 280.4 mg (1.68 mmol) of **9** and 1.8 ml (16.4 mmol) of trimethyl orthoformate in dry dichloromethane was added a catalytic amount of TsOH at room temperature under argon. The resulting deep blue solution was allowed to stand overnight, and diluted with 20 ml of ether. The solution was successively washed with saturated aqueous $NaHCO_3$ solution, water, and saturated brine, and dried over $MgSO_4$. Evaporation of the solvents gave 373.6 mg of a yellow oil. To a solution of this oil in 5 ml of acetone was added a catalytic amount of TsOH, and the resulting deep blue solution was allowed to stand for 40 min. A similar workup to that used previously gave 291.5 mg of a yellow oil. Purification by chromatography (12 g of silica gel, 5:1 hexane, ethyl acetate) gave 232.5 mg (77%) of **10**: Colorless oil; IR 1710 (s) cm^{-1}. ^1H NMR δ=5.15 (1H, m), 3.11 (3H, s), 2.98 (1H, m), 2.5—2.2 (2H, m), 2.2—2.0 (2H, m), 1.70 (3H, d, J=1.5 Hz), 2.0—1.2 (4H, m); ^{13}C NMR δ=209.8 (s), 148.4 (s), 126.3 (d), 95.0 (s), 51.9 (q), 47.2 (d), 42.8 (t), 40.5 (t),31.0 (t), 21.2 (t), and 15.1 (q). The 2,4-DNP derivatve of **10**: Mp 172—172.5 °C. Found: C, 56.38; H, 5.75; N, 15.43%. Calcd for $C_{17}H_{20}N_4O_5$: C, 56.66; H, 5.59; N, 11.55%.

Preparation of 1-Methoxy-7-methylbicyclo[4.2.1]nona-3,7-dien-2-one (11). The enol trimethylsilyl ether of **10** was prepared by treating with LDA and then with TMSCl at −78 °C. To a mixture of 87.9 mg of palladium acetate (0.39 mmol), 43 mg (0.39 mmol) of p-benzoquinone, and 1 ml of acetonitrile, prepared under argon, was added a solution of 195.2 mg (0.78 mmol) of the enol ether in 2 ml of acetonitrile at room temperature. After stirring overnight, the reaction mixture was poured in 0.5 M hydrochloric acid (1 M=1 mol dm^{-3}) and extracted with ether. The combined extracts were washed successively with saturated aqueous $NaHCO_3$ solution, water, and saturated brine, and dried over $MgSO_4$. Concentration followed by chromatography (8 g of silica gel, 5:1 hexane, ethyl acetate) gave 55.8 mg (40%) of **11**: Colorless oil; IR 1680 (s) cm^{-1}. ^1H NMR δ=5.87 (H_4, dtd, $J_{4,3}$=13.5, $J_{4,5}$=3.0, and $J_{4,6}$=0.7 Hz), 5.62 (H_3, ddd, $J_{3,4}$=13.5, $J_{3,5}$=2.3, and 1.5 Hz), 5.34 (H_8, q, J=1.5 Hz), 3.21 (OCH_3, s), 3.00 (H_6, m), 2.58 (H_5, 2H, m), 2.21 (H_9, 1H, d, $J_{9,6}$=1.5 Hz), 2.17 (H_9, 1H, s), and 1.73 (CH_3, dd, $J_{,8}$=1.5 and $J_{,6}$=0.75 Hz); MS (25 eV) m/z (rel intensity) 178 (M^+, 14) and 110 (100).

Photoreaction of 4a (General Procedure). A solution of 156.9 mg (1.15 mmol) of **4a** in 100 ml of hexane was placed in an immersion well equipped with a Pyrex filter and degassed by sonication. Irradiation of the solution under nitrogen using a 100-W Rikou high pressure Hg lamp for 2 h resulted in more than 95% conversion. From the crude photolysate (126.9 mg), 83.0 mg (53%) of **5a** was isolated by column chromatography (4 g of SiO_2, 15:1 hexane, ether).

***cis*-Bicyclo[4.3.0]non-4-en-7-one (5a):** Colorless oil; UV 236 (ε 631), 292 (49), 302 (56), 312.5 (47), and 325 nm (22); IR 1740 (s) cm^{-1}. ^1H NMR δ=5.8—5.5 (2H, m) and 2.7—1.2 (10H, m); MS (13.5 eV) m/z (rel intensity) 136 (M^+, 88), 118 (100), and 92 (55). The 2,4-DNP derivative of **5a**: Mp 150—152 °C. Found C, 56.98; H, 5.15; N, 17.66%. Calcd for $C_{15}H_{16}N_4O_4$: C, 56.96; H, 5.10; 17.71%.

4-Methyl-*cis*-bicyclo[4.3.0]non-4-en-7-one (5b): Colorless oil; IR 1740 (s) cm^{-1}; ^1H NMR δ=5.3 (1H, m), 1.70 (3H, broad s), and 2.7—1.1 (10H, m); MS (25 eV) m/z 150 (100), 132 (54), 106 (92), and 94 (96). The 2,4-DNP derivative of **6a**; Mp 142—164 °C (decomp). Found; C, 58.08; H, 5.54; N, 16.90%. Calcd for $C_{16}H_{18}N_4O_4$: C, 58.17; H, 5.49; N, 16.96%.

4-Methoxy-*cis*-bicyclo[4.3.0]non-4-en-7-one (5c): Colorless oil; IR 1745 (s) and 1665 (m) cm^{-1}; ^1H NMR δ=4.49 (1H,

broad d, J=4.5 Hz), 3.19 (3H, s), 2.8—1.3 (10H, m); MS (25 eV) m/z (rel intensity) 166 (M^+, 56) and 110 (100).

4-Methoxy-1-methyl-*cis*-bicyclo[4.3.0]non-4-en-7-one (5d): Colorless oil; UV 240 (sh,ε 1050), 270 (sh, 1050), 280 (1380), 292 (1200), and 315 (sh, 200); IR 1740 (s) cm^{-1}; ^1H NMR δ=4.48 (1H, d, J=4.5 Hz), 3.49 (3H, s), 2.3—1.3 (9H, m), and 1.13 (3H, s); MS (25 eV) m/z (rel intensity) 180 (M^+, 43) and 124 (100).

4-Methoxy-6-methyl-*cis*-bicyclo[4.3.0]non-4-en-7-one (5e): Mp 50.5—52 °C; IR 1745 (s) and 1665 (m) cm^{-1}; ^1H NMR δ=4.15 (1H, broad s), 3.43 (3H, s), 2.4—1.5 (9H, m), and 1.04 (3H, s): ^{13}C NMR δ=221.7 (s), 156.2 (s), 95.3 (d), 54.1 (q), 49.3 (s), 41.8 (d), 36.0 (t), 24.0 (t), 22.7 (t), and 22.4 (t); MS (25 eV) m/z (rel intensity) 180 (M^+, 32) and 124 (100).

4-Methoxy-1,6-dimethyl-*cis*-bicyclo[4.3.0]non-4-en-7-one (5f): Colorless oil; IR 1735 (s) and 1660 (w) cm^{-1}; ^1H NMR δ=4.09 (1H, broad s), 3.45 (3H, s), 2.3—1.8 (5H, m), 0.95 (3H, s), and 0.91 (3H, s); MS (25 eV) m/z (rel intensity) 194 (M^+, 94) and 148 (100).

Tricyclo[4.3.1.$0^{2,9}$]nonan-3-one (6a): Colorless oil; UV 206.5 (ε 20300), 274 (sh, 26), 281.5 (28), and 291 nm (sh, 24); IR 1690 (s) cm^{-1}; ^1H NMR δ=2.9—0.8 (m); MS (25 eV) m/z (rel intensity) 136 (M^+, 30), 118 (37), 108 (35), 92 (64), 80 (60), and 79 (100). The 2,4-DNP derivative of **6a**: Mp 156—161 °C (decomp). Found: C, 56.93; H, 5.05; N, 17.76%. Calcd for $C_{14}H_{16}N_4O_4$: C, 56.96; H, 5.10; N, 17.71%.

9-Methyltricyclo[4.3.1.$0^{2,9}$]nonan-3-one (6d): Colorless oil; IR 1680 (s) cm^{-1}; ^1H NMR δ=2.8—1.4 (11H, m) and 1.30 (3H, s); ^{13}C NMR δ=210.1 (s), 42.8 (s), 40.5 (d), 40.1 (d), 36.2 (t), 35.8 (t), 34.6 (t), 34.3 (d), 31.9 (t), and 24.2 (q); MS (25 eV) m/z (rel intansity) 150 (M^+, 49) and 79 (100). The 2,4-DNP derivative of **6b**: Mp 167—169 °C. Found: C, 57.86; H, 5.49; N, 16.86%. Calcd for $C_{16}H_{18}N_4O_4$: C, 58.17; H, 5.49; N, 16.96%.

Bicyclo[4.3.0]nona-3,9-diones (16m and 16n).
16m: Colorless oil; IR 1745 (s) and 1720 (s) cm^{-1}; ^{13}C NMR δ=215.0 (s), 209.1 (s), 54.6 (d), 41.6 (d), 40.9 (t), 40.6 (t), 38.3 (t), 29.9 (t), and 26.7 (t); MS (25 eV) m/z (rel intensity) 152 (M^+, 100).

16n: Colorless oil; IR 1745 (s) and 1720 (s) cm^{-1}; ^{13}C NMR δ=217.3 (s), 209.3 (s), 49.2 (d), 39.3 (t), 36.7 (t), 34.9 (d), 34.5 (t), 29.9 (t), 27.6 (t), and 25.5 (t); MS (25 eV) m/z (rel intensity) 152 (M^+, 100).

Pereparation of 1-Methylspiro[bicyclo[4.3.0]nonane-3,2'-[1,3]dioxolan]-9-one (17e). To a solution of 55.4 mg (0.31 mmol) of **5e** in 0.5 ml each of 2-ethyl-2-methyl-1,3-dioxolane and benzene was added 3 mg of TsOH, and the mixture was allowed to stand for 2 d at room temperature. This mixture was diluted with ether, washed successively with saturated aqueous $NaHCO_3$ and NaCl solutions, and dried over $MgSO_4$. Concentration followed by chromatography (10 g of SiO_2, 10:1 hexane, ethyl acetate) gave 42.3 mg (65%) of **17e** as colorless prisms. **17e:** Mp 71—73 °C; IR (KBr) 1730 (s) cm^{-1}; ^1H NMR δ=4.0—3.6 (4H, m), 3.4—1.4 (10H, m), 1.20 (1H, d, J=14.3 Hz), and 0.97 (3H, s); MS (13.5 eV) m/z (rel intensity) 210 (M^+, 48), 182(16), and 99 (100). Found: C, 68.31; H, 8.92%. Calcd for $C_{12}H_{18}O_3$: C, 68.55; H, 8.62%.

Preparation of 1,6-Dimethylspiro[bicyclo[4.3.0]nonane-3,2'-[1,3]dioxolan]-9-one (17f). A similar procedure to that was used for the synthesis of **17e** gave 56.6 mg (76%) of **17f** starting from 64.2 mg (0.33 mmol) of **4f**. **17f:** Mp 58—60 °C; IR (KBr) 1728 (s) cm^{-1}; ^1H NMR δ=4.0—3.65 (4H, m), 3.4—1.3 (9H,m), 1.15 (d, J=14.3 Hz), 1.02 (3H, s), and 0.81 (3H, s); MS (25 eV) m/z (rel intensity) 224 (M^+, 17) and 99 (100). Found: C, 69.61; H, 8.98%. Calcd for $C_{13}H_{20}O_3$: C, 69.82; H, 9.08%.

References

1) A portion of this work has been published as a preliminary communication: T. Uyehara, Y. Kabasawa, T. Kato, and T. Furuta, *Tetrahedron Lett.*, **26**, 2343 (1985). Part II in this series is Ref. 2.

2) T. Uyehara, J. Yamada, T. Kato, and F. Bohlmann, *Bull. Chem. Soc. Jpn.*, **58**, 861 (1985).

3) M. Demuth and K. Schaffner, *Angew. Chem., Internat. Ed. Engl.*, **21**, 820 (1982).

4) L. A. Paquette, R. P. Henzel, and R. F. Eizenber, *J. Org. Chem.*, **38**, 3257 (1973).

5) T. Uyehara, J. Yamada, K. Ogata, and T. Kato, *Bull. Chem. Soc. Jpn.*, **58**, 211 (1985); *J. Chem. Soc., Chem. Commun.*, **1983**, 17.

6) T. Uyehara and Y. Kitahara, *Chem. Ind. (London)*, **1971**, 354; *Bull. Chem. Soc. Jpn.*, **52**, 3355 (1979).

7) I. Ojima, T. Kogure, M. Nihonyanagi, and Y. Nagai, *Bull. Chem. Soc. Jpn.*, **45**, 3506 (1972).

8) D. A. Evans, W. L. Scott, and L. K. Truesdale, *Tetrahedron Lett.*, **1972**, 121.

9) P. A. S. Smith and D. R. Baer, *Organic Reaction*, **11**, 157 (1960).

10) R. P. Gregson and R. N. Mirrington, *Aust. J. Chem.*, **29**, 2037 (1976).

11) L. G. Kozar, R. D. Clark, and C. H. Heathcock, *J. Org. Chem.*, **42**, 1386 (1977).

12) S. A. Monti, S. C. Chen, Y. L. Yang, S. S. Yuan, and O. P. Bourgeois, *J. Org. Chem.*, **43**, 4062 (1978).

13) Y. Ito, T. Hirao, and T. Saegusa, *J. Org. Chem.*, **43**, 1011 (1978).

14) N. Hashimoto, T. Aoyama, and T. Shioiri, *Chem. Pharm. Bull.*, **30**, 119 (1982).

15) T. Uyehara, T. Matsuoka, Y. Kabasawa, M. Akamatsu, and T. Kato, 50th National Meeting of the Chemical Society of Japan, Tokyo, April 1985, Abstr., No. 3038.

16) J. A.Osborn and G. Wilkinson, *Inorganic Synth.*, **10**, 67 (1967).

17) D. Seyferth, H. Menzel, A. W. Dow, and T. C. Flood, *J. Organomet. Chem.*, **44**, 279 (1972).