Heptafulvenone, Vinylketene, Butadienylketene, and Allenylketene – Facile Generation, Observation, and Radical Reaction with TEMPO

Thomas T. Tidwell*[a] and Michael H. Fenwick[a]

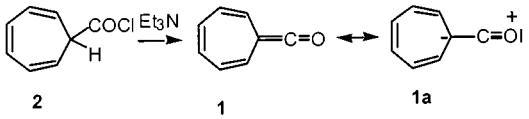
Dedicated to the memory of Tetsuo Nozoe (1902-1995)[+]

Keywords: Ketenes / Radicals / Radical reactions / Allenes / Dienes

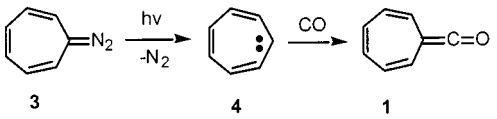
Heptafulvenone (**1**), vinylketene (**11**), 1,3-butadienylketene [(*E*)-**15**], and allenylketene (**21**) have been prepared by reaction of the corresponding acyl chlorides with 1,8-bis(dimethylamino)naphthalene as long-lived species in solution at room temperature, and their ketenyl IR bands observed under these conditions for the first time, at 2101, 2118, 2111, 2117 cm^{-1}, respectively. These unsaturated ketenes react with tetramethylpiperidinyloxyl (TEMPO, TO·) with initial attack at the carbonyl carbon giving delocalized radicals which give from **1** a mixture of the ring contracted *o*-, *m*-, and *p*-formylbenzoates O=CHC$_6$H$_4$CO$_2$T (**6**) and the bis(cycloheptatrienyl) dimer **7**. The products from **11**, (*E*)-**15**, and **21** are the bis(TEMPO) adducts (*E,Z*)-TOCH$_2$CH=CHCO$_2$T (**12**), (*E,E*)-TOCH$_2$CH=CHCH=CHCO$_2$T (**17**), and (*E,Z*)-CH$_2$=C(OT)CH=CHCO$_2$T (**22**), respectively.

Introduction

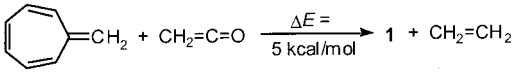
In 1972 Asao, Morita, and Kitahara[1a] reported the formation of heptafulvenone (**1**) from the reaction of the acyl chloride **2** with Et_3N [Equation (1)]. This ketene was not isolated, but was trapped by reactions with dienes, alkenes, and ketones, and also formed dimers.[1a–1c] The triplet carbene **4** formed by photolysis of diazocycloheptatriene (**3**) in an argon matrix containing carbon monoxide was found to react at 35 K to give a product with an IR band at 2103 cm^{-1} attributed to **1** [Equation (2)].[1d,1e] Isodesmic calculations suggest ketene **1** would suffer from a destabilization of about 5 kcal/mol [Equation (3)] due to the antiaromatic 8π-electron character indicated by the resonance structure **1a**.[2]



2 **1** **1a** (1)



3 **4** **1** (2)



(3)

Because of the structural interest in **1** and also because of our recent development of the reactions of ketenes with nitroxyl radicals,[3] we have undertaken further studies of **1** and other alkenylketenes, and their reactions with aminoxyl radicals. Radical addition to **1** also presents the opportunity to provide a new route to an open shell non-Hückel cycloheptatrienyl radical.[3f]

Results and Discussion

Reaction of the acyl chloride **2**[4] with 1,8-bis(dimethylamino)naphthalene (**5**) catalyzed by Et_3N according to the recently published procedure of Lectka, et al.[5] gave a yellow solution with an IR band at 2101 cm^{-1} assigned to **1** (Scheme 1). Addition of tetramethylpiperidinyloxyl (TEMPO, TO·) gave after chromatographic separation the three isomeric *N*-piperidinyl *o*-, *m*-, and *p*-formylbenzoates **6** (total 19%) and the bis(cycloheptatrienyl) derivative **7** in 24% yield (Scheme 2). The *o*-isomer of **6** (9%) was cleanly separated, while the *m*- and *p*-isomers were obtained as a mixture (10%, 1:5 ratio), although the structural assignments were very clear, especially from the characteristic aldehydic and aryl ^{1}H NMR signals, and the IR absorption. The dimer **7** was positively identified by comparison of the NMR spectra with the published spectrum of the corresponding dimethyl ester, for which the structure was proved by X-ray crystallography.[6a] As in this previous investigation,[6a] we could not obtain the dimeric ester in a pure form, and other product(s), possibly isomeric, were detected by NMR spectroscopy.[7]

[a] Department of Chemistry, University of Toronto
Toronto, Ontario, M5S 3H6 Canada
Fax: (internat.) +1-416/287-7279
E-mail: ttidwell@chem.utoronto.ca

[+] Pioneer in cycloheptatriene and tropolone chemistry, on the upcoming centenary of his birth.

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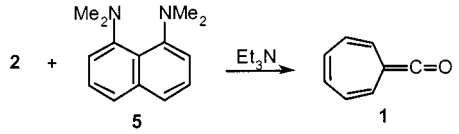
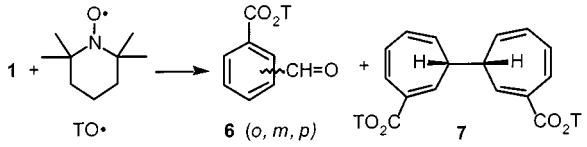
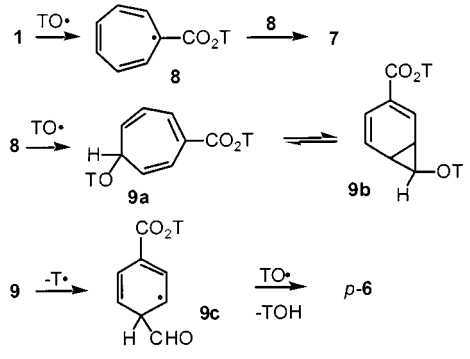


Scheme 1



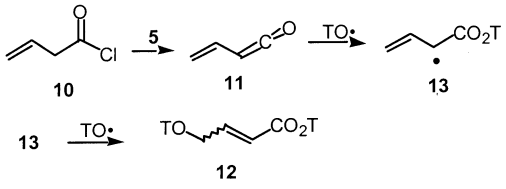
Scheme 2

Aminoxyl radical additions to ketenes have been shown to occur by initial radical attack at the carbonyl carbon of the ketenyl group.[3] A mechanism for the formation of **6** and **7** involves TEMPO attack on **1** giving the intermediate cycloheptatrienyl radical **8** (Scheme 3). The dimerization of **8** gives **7**, while addition of TEMPO to **8** would give the unobserved **9a** and a companion norcaradiene **9b**, which could lose tetramethylpiperidinyl radical T· forming **9c**, which then forms *p*-**6** by hydrogen abstraction. The isomeric compounds *o*- and *m*-**6** could form by similar routes. The ^{1}H NMR spectra of various isomeric cyclohexatrienyl and norcaradienyl structures analogous to **9a,b** have been reported previously,[6b,6c] and in some cases equilibrate rapidly; whether the unobserved intermediates **9a,b** in the present case are distinct entities was not established. There is precedent for the N−O cleavage in TEMPO adducts forming carbonyl groups as shown in Scheme 3.[3a]



Scheme 3

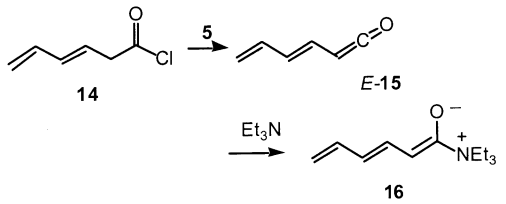
This procedure was extended to the preparation of some other unsaturated ketenes of structural and synthetic interest. The reaction of 3-butenoyl chloride (**10**) with **5** without catalytic Et_3N gave a yellow solution displaying an IR band at 2118 cm^{-1} assigned to vinylketene (**11**), and addition of TEMPO gave (*E*)- and (*Z*)-**12** (44 and 5%, respectively), evidently through the intermediate radical **13** [Equation (4)].[7] Ketene **11** has previously been prepared and captured by high temperature pyrolyses of crotonic acids[8a] or anhydrides,[8b] or vinylacetic acid,[8a] by dehydrochlorination with in situ capture by cyclopentadiene,[8c] and recently was captured by electrophilic chlorine using hexachloro-2,4-cyclohexadienone (C_6Cl_6O) to give $CH_3CH{=}CClCO_2C_6Cl_5$ in 65% yield.[5b] The ^{1}H NMR spectrum of **11** was measured at −70 °C,[8b] the photoelectron spectrum measured in the gas phase,[8a] and the structure has been studied theoretically.[8d,8e]



(4)

Qualitatively, the formation of **11** and the other unsaturated ketenes described below is significantly easier than the formation of heptafulvenone **1**. This is consistent with the antiaromatic character expected for a cycloheptatrienyl anion derived from **2**,[3f] and for the ketene **1**.[2]

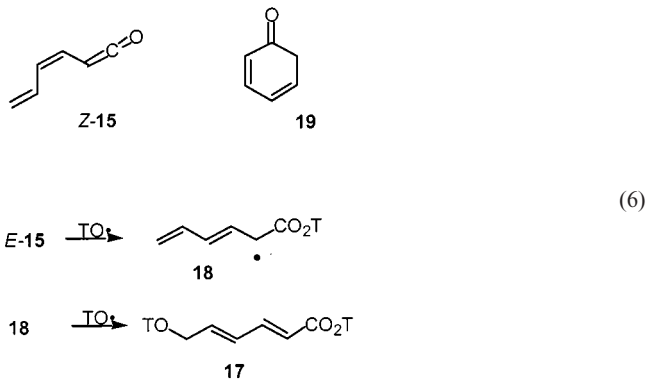
Treatment of (*E*)-3,5-hexadienoyl chloride (**14**)[9] with **5** at −78 °C without catalytic Et_3N gave rapid formation of a yellow solution with an IR absorption at 2111 cm^{-1} assigned to (*E*)-1,3,5-hexatrienone (**15**). Addition of Et_3N to the yellow solution of **15** at −78 °C resulted in the formation of a brilliant red color, which rapidly disappeared. This red color could be due to the formation of the highly conjugated zwitterion **16** [Equation (5)], which could react further by oligomerization with residual **15**. Such zwitterionic ketene adducts have been observed to form with pyridine under matrix isolation conditions,[10a−10c] or in solution with various amines.[10d] Ketenes are frequently prepared using Et_3N, but adducts between the two are seldom observed, although products resulting from the reaction of such species with $Ph_2C{=}C{=}O$ have been found.[10e] The ketene **15** generated in situ has found applications in synthesis.[9,10f,10g]



(5)

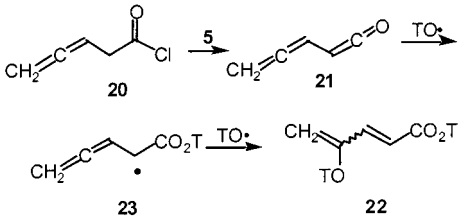
Addition of TEMPO to the solution of (*E*)-**15** gave the diaddition product (*E,E*)-**17** (44%) derived from the dienyl radical **18** [Equation (6)]. Ketene (*E*)-**15** has previously been proposed as an unobserved intermediate that was trapped by alcohols or in cycloaddition reactions,[9,10f,10g] and is of particular interest because of its relation to the isomer (*Z*)-**15**, which is formed by the photolysis of cyclohexadienone **19**, and has been implicated as an intermediate in the

photooxidation of benzene.[11] We have calculated that (*E*)-**15** is more stable than (*Z*)-**15** by 1.4 kcal/mol, and that (*Z*)-**15** is predicted to have a barrier of only 9.1 kcal/mol for ring closure back to cyclohexadienone,[3c] in agreement with the observed facility of this reaction. The formation and reactivity of substituted derivatives of (*Z*)-**15** formed by the photolysis of substituted cyclohexadienones (Barton−Quinkert reaction) have also been extensively investigated.[12]



(6)

Allenylketenes have been of interest,[13] but only silyl-stabilized examples have been readily observable.[13a−13c] However, the reaction of 3,4-pentadienoyl chloride (**20**)[13g] with **5** gave allenylketene (**21**), identified by the IR band at 2117 cm^{-1}, close to the reported value for **21** (2127 cm^{-1}) when generated by pyrolysis of **20** and trapped in a matrix.[13e] The addition of TEMPO to **21** gave the adducts (*E*)-**22** (60%) and (*Z*)-**22** (3%) derived from the allene-substituted radical **23** [Equation (7)].



(7)

Conclusion

In summary, the highly reactive conjugated ketenes **1**, **11**, (*E*)-**15**, and **21** are readily available in solution as observable intermediates from the dehydrochlorination of acyl chlorides, and show high reactivity towards TEMPO. The elucidation of the reactivity of these multifunctional, and hitherto elusive, ketenes is the subject of continued interest in this laboratory.

Experimental Section

General: Reactions were carried out under an atmosphere of argon or nitrogen. ^{1}H NMR spectra were obtained at 200 MHz (Varian Gemini), 300 MHz (Varian Gemini or Mercury) or 400 MHz (Varian Unity). ^{13}C NMR spectra were obtained at 100 MHz or 125 MHz (Varian Unity). IR spectra were obtained on a Perkin−Elmer FT-IR Spectrum 1000 spectrometer.

Synthesis of 6 and 7: 1,3,5-Cycloheptatriene-7-carbonyl chloride (**2**, 78 mg, 0.51 mmol) and 1,8-bis(dimethylamino)naphthalene (**5**, 120 mg, 0.56 mmol) were stirred in 3 mL of dry toluene at 0 °C for 30 min. Triethylamine (3 mg, 0.03 mmol) was then added, and the solution immediately turned red. TEMPO (800 mg, 5.12 mmol) was added, and the solution was stirred for 18 h. The mixture was then filtered through Celite, the solvent evaporated, and excess TEMPO removed by sublimation. Chromatography (10% EtOAc/hexane) gave first the *o*-formyl benzoate (*o*-**6**, 13 mg, 0.046 mmol, 9%), then a mixture of the *m*- and *p*-formyl benzoates (*m*,*p*-**6**, 15 mg, 0.051 mmol, 10%) in a 1:5 ratio and finally the dimer **7** (34 mg, 0.062 mmol, 24%, slightly impure). The structures of **6** and **7** were confirmed by COSY, TOCSY, ROSY, HSQC, and HSBC spectroscopy.

***o*-6:** ^{1}H NMR ($CDCl_3$): δ = 1.21 (s, 6 H, $2CH_3$), 1.30 (s, 6 H, $2CH_3$), 1.4−1.8 (m, 6 H, 3 CH_2), 7.69−7.72 (m, 2 H, Ar), 7.99−8.04 (m, 2 H, Ar), 10.7 (s, 1 H, CHO). − ^{13}C NMR ($CDCl_3$): δ = 17.2, 20.9, 32.1, 38.5, 60.9, 128.4 (Ar), 129.8 (Ar), 132.4 (Ar), 132.5 (Ar), 137.5 (Ar), 166.2 (CO_2T), 192.0 (CHO). − IR ($CDCl_3$): $\tilde{\nu}$ = 1742, 1697 cm^{-1}. − EIMS: *m*/*z* (%) = 290 (0.1) [MH^+], 156 (100) [TO], 133 (51) [M^+ − TO]. − HREIMS *m*/*z* calcd. for $C_{17}H_{24}NO_3$ 290.1756, found 290.1762.

***m*-6:** ^{1}H NMR ($CDCl_3$): δ = 1.13 (s, 6 H, $2CH_3$), 1.29 (s, 6 H, $2CH_3$), 1.4−1.9 (m, 6 H, 3 CH_2), 7.61−7.78 (m, 1 H, Ar), 8.11 (dt, *J* = 10.4, 2 Hz, 1 H, Ar), 8.33 (dt, *J* = 10.4, 2 Hz, 1 H, Ar), 8.54 (t, *J* = 2.4 Hz, 1 H, Ar), 10.1 (s, 1 H, CHO). − ^{13}C NMR ($CDCl_3$): δ = 17.2, 21.1, 32.2, 39.4, 60.9, 129.5, 131.5, 133.3, 135.4, 165.6 (CO_2T), 191.6 (CHO).

***p*-6:** ^{1}H NMR ($CDCl_3$): δ = 1.13 (s, 6 H, $2CH_3$), 1.29 (s, 6 H, $2CH_3$), 1.4−1.9 (m, 6 H, 3 CH_2), 7.96−7.99 (dm, 2 H, Ar), 8.21−8.24 (dm, 2 H, Ar), 10.1 (s, 1 H, CHO). − ^{13}C NMR ($CDCl_3$): δ = 17.2, 21.1, 32.3, 39.4, 60.9, 129.9 (Ar), 130.4 (Ar), 135.1 (Ar), 139.4 (Ar), 165.7 (CO_2T), 191.9 (CHO). − IR ($CDCl_3$): $\tilde{\nu}$ = 1745, 1706 cm^{-1}. − EIMS: *m*/*z* (%) = 290 (6) [MH^+], 289 (3) [M^+], 274 (84) [MH^+ − O], 156 (39) [TO], 133 (100) [M^+ −TO]. − HREIMS *m*/*z* calcd. for $C_{17}H_{23}NO_3$ 289.1678, found 289.1680. (IR and MS taken of mixture of *m, p* isomers)

7: ^{1}H NMR ($CDCl_3$): δ = 1.0−1.3 (m, 24 H, $8CH_3$), 1.4−1.8 (m, 12 H, 6 CH_2), 2.0−2.16 (m, 2 H), 5.3−5.4 (m), 5.55−5.65 (m), 6.3−6.4 (m), 6.8−6.9 (m), 7.25−7.35 (m), 7.8 (d). − ^{13}C NMR ($CDCl_3$): δ = 14.4, 17.2, 20.9, 21.1, 31.8, 32.1, 39.3, 42.0, 60.6, 124.8, 127.5, 128.7, 132.0, 132.4, 166.6. − IR ($CDCl_3$): $\tilde{\nu}$ = 1735 cm^{-1}. − EIMS: *m*/*z* (%) = 549 (0.2) [MH^+], 392 (5) [M^+ − TO], 274 (27) [M^+/2], 156 (25) [TO], 140 (100) [T]. − HREIMS *m*/*z* calcd. for $C_{34}H_{49}N_2O_4$ 549.3692, found 549.3690. − Further NMR signals ascribed to unidentified isomers of **7** were also present.

Synthesis of 12: 3-Butenoyl chloride (69 mg, 0.66 mmol) and **5** (158 mg, 0.74 mmol) were added to 3 mL of dry toluene at 0 °C immediately turning the solution a dark orange. TEMPO (262 mg, 1.7 mmol) was then added and the solution stirred for 20 h, after

which time it was filtered through Celite, concentrated, and chromatographed (1:9 EtOAc/hexane) yielding first (*Z*)-**12** as a colorless oil (12 mg, 0.032 mmol, 5%) and then (*E*)-**12** (110 mg, 0.29 mmol, 44%) as pale white needles (mp 110−111 °C).

(*Z*)-12: ^{1}H NMR ($CDCl_3$): δ = 1.0−1.2 (m, 24 H, 8 CH_3), 1.2−1.8 (m, 12 H, 6 CH_2), 4.89 (dd, *J* = 6.8, 3.2 Hz, 2 H, $TOCH_2$), 5.81 (br. d, *J* = 12.8 Hz, 1 H, C=$CHCO_2T$), 6.42 (m, 1 H, $TOCH_2CH$=). − ^{13}C NMR ($CDCl_3$): δ = 17.2, 17.4, 20.3, 20.9, 21.1, 29.9, 32.1, 33.3, 39.3, 39.8, 39.9, 59.8, 60.1, 60.3, 76.3 ($TOCH_2$), 117.4 (C=*C*CO_2T), 147.9 ($TOCH_2C$=C), 167.6 (CO_2T). − IR ($CDCl_3$): $\tilde{\nu}$ = 1741 cm^{-1}. − EIMS: *m*/*z* (%) = 381 (0.1) [MH^+], 224 (1) [M^+ − TO], 156 (100) [TO], 140 (58) [T]. − HREIMS *m*/*z* calcd. for $C_{22}H_{41}N_2O_3$ 381.3117, found 381.3109.

(*E*)-12: ^{1}H NMR ($CDCl_3$): δ = 1.06 (s, 6 H, $2CH_3$), 1.13 (s, 12 H, $4CH_3$), 1.17 (s, 6 H, $2CH_3$), 1.2−1.8 (m, 12 H, 6 CH_2), 4.47 (dd, 2 H, $TOCH_2$), 6.10 (br. d, *J* =15.7 Hz, 1 H, C=$CHCO_2T$), 6.95 (dt, *J* = 15.9, 3.8 Hz, 1 H, $TOCH_2CH$=). − ^{13}C NMR ($CDCl_3$): δ = 17.0, 17.1, 20.2, 20.6, 31.9, 32.9, 39.1, 39.7, 60.0, 60.2, 75.9 ($TOCH_2$), 118.8 (C=*C*CO_2T), 144.3 ($TOCH_2C$=C), 166.6 (CO_2T). − IR ($CDCl_3$): $\tilde{\nu}$ = 1732, 1658 cm^{-1}. − EIMS: *m*/*z* (%) = 380 (0.01) [M^+], 240 (1) [M^+ − T], 224 (1) [M^+ − TO], 156 (100) [TO]. − HREIMS *m*/*z* calcd. for $C_{22}H_{41}N_2O_3$ 381.3117, found 381.3113.

Synthesis of 17: (*E*)-**14** (30 mg, 0.23 mmol) and **5** (57 mg, 0.29 mmol) were added to 1 mL of dry toluene at 0 °C. After stirring for 30 min. TEMPO (111 mg, 0.71 mmol) was added and the solution stirred for 16 h. The mixture was then filtered through Celite, the solvent evaporated and the residue chromatographed (1:9 EtOAc/hexane) to give (*E,E*)-**17** (44 mg, 0.11 mmol, 47%) as a pale yellow solid (mp 114−117 °C). − ^{1}H NMR ($CDCl_3$): δ = 1.06 (s, 6 H, $2CH_3$), 1.12 (s, 6 H, $2CH_3$), 1.15 (s, 6 H, $2CH_3$), 1.17 (s, 6 H, $2CH_3$), 1.3−1.8 (m, 12 H, 6 CH_2), 4.41 (m, 2 H, $TOCH_2$), 5.93 (d, *J* = 15.0 Hz, 1 H, C=C*H*-CO_2T), 6.14 (dt, *J* = 15.0, 4.1 Hz, 1 H, $TOCH_2CH$=), 6.35−6.50 (m, 1 H, $TOCH_2CH$=C*H*), 7.34 (dd, *J* = 15.0, 4.1 Hz, 1 H, C*H*=$CHCO_2T$). − ^{13}C NMR ($CDCl_3$): δ = 17.2, 17.3, 20.4, 20.8, 32.1, 33.1, 39.2, 39.8, 60.1, 60.3, 77.0 ($TOCH_2$), 119.7 (C=*C*CO_2T), 128.4 ($TOCH_2C$=*C*), 138.7 ($TOCH_2C$=C), 144.8 (*C*=CCO_2T), 167.3 (CO_2T). − IR ($CDCl_3$): $\tilde{\nu}$ = 1730, 1644, 1617 cm^{-1}. − EIMS: *m*/*z* (%) = 407 (1) [MH^+], 251 (2) [MH^+ − TO], 156 (100) [TO], 140 (35) [T]. − HREIMS *m*/*z* calcd. for $C_{24}H_{43}N_2O_3$ 407.3274, found 407.3287.

Synthesis of 22: 3,4-Pentadiene-1-carbonyl chloride (60 mg, 0.52 mmol), TEMPO (805 mg, 5.2 mmol), **5** (134 mg, 0.63 mmol) and triethylamine (5.0 mg, 0.049 mmol) were stirred in 5 mL of dry toluene at 0 °C. The solution was allowed to warm slowly to room temperature and stirred for 16 h. It was then filtered through Celite, the solvent was evaporated and excess TEMPO sublimed. The residue was chromatographed (5% EtOAc/hexane) eluting first (*Z*)-**22** (6 mg, 0.014 mmol, 3%) as an orange oil, and then (*E*)-**22** (122 mg, 0.31 mmol, 60%) as colorless crystals (mp 168−170 °C).

(*Z*)-22: ^{1}H NMR ($CDCl_3$): δ = 0.9−1.8 (m, 36 H, TEMPO), 4.75 (s, 1 H, CH*H*=C), 5.22 (s, 1 H, *CH*H=C), 5.86 (d, *J* = 12.4 Hz, 1 H, $CHCO_2T$), 6.20 (d, *J* = 13.2 Hz, 1 H, CH=$CHCO_2T$). − ^{13}C NMR ($CDCl_3$): δ = 17.2, 17.3, 20.8, 21.0, 32.3, 32.6, 39.3, 40.1, 60.3, 60.6, 95.6 (*C*H=C), 118.6 (H*C*=$CHCO_2T$), 135.9 (HC=*C*(OT), 159.3 (HC=*C*HCO_2T). − IR (CH_2Cl_2): $\tilde{\nu}$ = 1732, 1637, 1560 cm^{-1}. − EIMS: *m*/*z* (%) = 392 (6) [M^+], 236 (28) [M^+ − TO], 156 (34) [TO], 140 (100) [T]. − HREIMS *m*/*z* calcd. for $C_{23}H_{40}N_2O_3$ 392.3039, found 392.3034.

(*E*)-22: ^{1}H NMR ($CDCl_3$): δ1.03 (s, 6 H, $2CH_3$), 1.08 (s, 6 H, $2CH_3$), 1.20 (s, 12 H, $4CH_3$), 1.36−1.8 (m, 12 H, 6 CH_2), 4.54 (s, 1 H, CH*H*=C), 5.24 (s, 1 H, C*H*H=C), 6.20 (br. d, *J* = 14.8 Hz, 1 H, $CHCO_2T$), 7.02 (d, *J* = 16.5 Hz, 1 H, CH=$CHCO_2T$). − ^{13}C NMR ($CDCl_3$): δ = 16.9, 20.6, 20.7, 31.9, 32.2, 39.0, 39.6, 60.2, 60.5, 98.6 (CH_2=C), 115.8 (*C*H=$CHCO_2T$), 139.2 (HC=*C*(OT), 159.1 (HC=*C*HCO_2T), 167.1 (CO_2T). − IR (CH_2Cl_2): $\tilde{\nu}$ = 1732, 1637, 1597 cm^{-1}. − EIMS: *m*/*z* (%) = 392 (6) [M^+], 236 (28) [M^+ − TO], 156 (34) [TO], 140 (100) [T]. − HREIMS *m*/*z* calcd. for $C_{23}H_{40}N_2O_3$ 392.3039, found 392.3034.

Acknowledgments

This work was supported by the Natural Sciences and Engineering Research Council of Canada. Grateful acknowledgment is made to Professor Jörg Daub (Universität Regensburg) for copies of spectra of analogues of **7**.

[1] [1a] T. Asao, N. Morita, Y. Kitahara, *J. Am. Chem. Soc.* **1972**, *94*, 3655−3657. − [1b] Y. Kitahara, *Pure Appl. Chem.* **1975**, *44*, 833−859. − [1c] T. Asao, N. Morita, J. Ojima, M. Fujiyoshi, K. Wada, S. Hamai, *Bull. Chem. Soc. Jpn* **1986**, *59*, 1713−1721. − [1d] R. J. McMahon, O. L. Chapman, *J. Am. Chem. Soc.* **1986**, *108*, 1713−1714. − [1e] R. J. McMahon, C. J. Abelt, O. L. Chapman, J. W. Johnson, C. L. Kreil, J.-P. LeRoux, A. M. Mooring, P. R. West, *J. Am. Chem. Soc.* **1987**, *109*, 2456−2469. −

[2] M. A. McAllister, T. T. Tidwell, *J. Am. Chem. Soc.* **1992**, *114*, 5362−5368.

[3] [3a] W. Huang, H. Henry-Riyad, T. T. Tidwell, *J. Am. Chem. Soc.* **1999**, *121*, 3939−3943. − [3b] A. D. Allen, B. Cheng, M. H. Fenwick, W. Huang, S. Missiha, D. Tahmassebi, T. T. Tidwell, *Organic Lett.* **1999**, *1*, 693−696. − [3c] A. D. Allen, B. Cheng, M. H. Fenwick, B. Givehchi, H. Henry-Riyad, V. A. Nikolaev, E. A. Shikova, D. Tahmassebi, T. T. Tidwell, S. Wang, *J. Org. Chem.* **2001**, *66*, 2611−2617. − [3d] J. Carter, M. H. Fenwick, W. Huang, V. V. Popik, T. T. Tidwell, *Can. J. Chem.* **1999**, *77*, 806−809. − [3e] K. Sung, T. T. Tidwell, *J. Org. Chem.* **1998**, *63*, 9690−9697. − [3f] T. T. Tidwell, *Chem. Rev.* **2001**, *101*, 1333−1348.

[4] 1,3,5-Cycloheptatrienyl-7-carboxylic acid was prepared by hydrolysis of the ethyl ester made by the rhodium trifluoroacetate-catalyzed reaction of N_2CHCO_2Et in benzene as described by E. R. Johnston, J. S. Barber, M. Jacomet, J. C. Barborak, *J. Org. Chem.* **1981**, *46*, 873−876.

[5] [5a] A. E. Taggi, A. M. Hafez, H. Wack, B. Young, W. J. Drury, III, T. Lectka, *J. Am. Chem. Soc.* **2000**, *122*, 7813−7832. − [5b] H. Wack, A. E. Taggi, A. M. Hafez, W. J. Drury, III, T. Lectka, *J. Am. Chem. Soc.* **2001**, *123*, 1531−1532. −

[6] [6a] W. Bauer, J. Daub, E. Eibler, A. Gieren, V. Lamm, H. Lotter, *Chem. Ber.* **1984**, *117*, 809−826. − [6b] G. E. Hall, J. D. Roberts, *J. Am. Chem. Soc.* **1971**, *93*, 2203−2207. − [6c] E. Ciganek, *J. Am. Chem. Soc.* **1971**, *93*, 2207−2212.

[7] The structures and stereochemistry of **7**, **12**, **17**, and **22** were confirmed by 2D NMR techniques.

[8] [8a] S. Mohmand, T. Hirabayashi, H. Bock, *Chem. Ber.* **1981**, *114*, 2609−2621. − [8b] W. S. Trahanovsky, B. W. Surber, M. C. Wilkes, M. M. Preckel, *J. Am. Chem. Soc.* **1982**, *104*, 6779−6781. − [8c] D. A. Jackson, M. Rey, A. S. Dreiding, *Helv. Chim. Acta* **1983**, *66*, 2330−2341. − [8d] M. T. Nguyen, T. K. Ha, R. A. More O'Ferrall, *J. Org. Chem.* **1990**, *55*, 3251−3256. − [8e] M. A. McAllister, T. T. Tidwell, *J. Am. Chem. Soc.* **1994**, *116*, 7233−7238.

[9] T. R. Hoye, A. S. Magee, W. S. Trumper, *Synth Commun.* **1982**, *12*, 183−187.

[10] [10a] G. C. Qiao, J. Andraos, C. Wentrup, *J. Am. Chem. Soc.* **1996**, *118*, 5634−5638. − [10b] P. Visser, R. Zuhse, M. W. Wong, C. Wentrup, *J. Am. Chem. Soc.* **1996**, *118*, 12598−12602. − [10c] A. Fiksdahl, C. Plüg, C. Wentrup, *J. Chem. Soc., Perkin Trans. 2* **2000**, 1841−1845. − [10d] B. D. Wagner, B. Arnold, G. S. Brown, J. Lusztyk, *J. Am. Chem. Soc.* **1998**, *120*, 1827−1834. − [10e] N. Abe, I. Osaki, S. Kojima, H. Matsuda, Y. Sugihara, A. Kakehi, *J. Chem. Soc., Perkin Trans. 1* **1996**, 2351−2356. − [10f] A. K. Sharma, R. S. Kumar, M. P. Mahajan, *Heterocycles* **2000**, *52*, 603−609. −[10g] A. K. Sharma, S. N. Mazumdar, M. P. Mahajan, *J. Org. Chem.* **1996**, *61*, 5506−5509.

[11] [11a] D. M. Jerina, B. Witkop, C. L. McIntosh, O. L. Chapman, *J. Am Chem. Soc.* **1974**, *96*, 5578−5580. − [11b] M. Capponi, I. Gut, J. Wirz, *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 344−345. − [11c] J. K. Parker, S. R. Davis, *J. Am. Chem. Soc.* **1999**, *121*, 4271−4277. − [11d] E. V. Dehmlow, M. Slopianka, *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 170.

[12] [12a] D. H. R. Barton, G. Quinkert, *J. Chem. Soc.* **1960**, 1−9. − [12b] G. Quinkert, E. Kleiner, B.-J. Freitag, J. Glenneberg, U. Billhardt, F. Cech, K. R. Schmeider, C. Schudok, H.-C. Steinmetzer, J. W. Bats, G. Zimmermann, G. Dürner, D. Rehm, E. F. Paulus, *Helv. Chim. Acta* **1986**, *69*, 469−535.

[13] [13a] W. Huang, D. Fang, K. Temple, T. T. Tidwell, *J. Am. Chem. Soc.* **1997**, *119*, 2832−2838. − [13b] W. Huang, T. T. Tidwell, *Synthesis* **2000**, 457−470. − [13c] G. Maier, H. W. Lage, H. P. Reisenauer, *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 976−977. − [13d] O. L. Chapman, C. J. Abelt, *J. Org. Chem.* **1987**, *52*, 1218−1221. − [13e] J.-P. Aycard, A. Allouche, M. Cossu, M. Hillebrand, *J. Phys. Chem. A* **1999**, *103*, 9013−9021. − [13f] W. S. Trahanovsky, M. Park, *J. Am Chem. Soc.* **1973**, *95*, 5412. − [13g] T. A. Price, T. E. Patten, *J. Chem. Ed.* **1991**, *68*, 256−257.

Received June 1, 2001
[O01262]