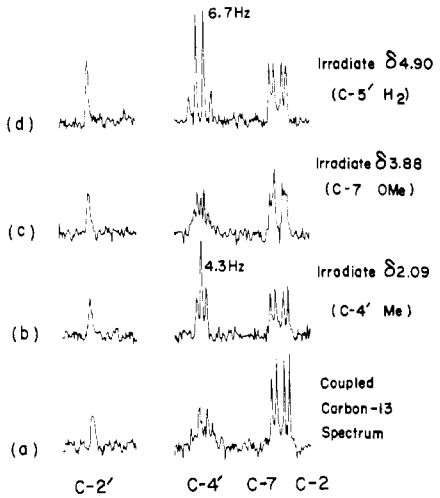

Figure 3. Low-power single frequency selective decoupling $^{13}C\{^1H\}$ spectra of microminutin (2), observation of low-field spectral region.

to a 2.5% NOE for the pattern due to the methylene protons. No appreciable NOE was observed when the methoxyl protons (δ 3.90) were similarly irradiated. The NOE observed for the methylene protons is much smaller than that observed for the aromatic CH because the dominant relaxation of each methylene proton is through its geminal neighbor. Nevertheless there are some contributions from the neighboring C–CH_3 protons that would only occur in structure **2**.

Low-power single frequency selective decoupling (LPSFSD) of the ^{13}C spectrum (25.05 MHz, 50 °C) gave complimentary results (Figure 3). Thus irradiation of the C–CH_3 protons caused the multiplet at δ 162.9 observed in the coupled ^{13}C spectrum to collapse to a triplet ($^3J_{CH}$ = 4.3 Hz). Conversely, irradiation of the methylene proton signal centered at δ 4.90 (100 MHz, ^1H) caused the signal at δ 162.9 to collapse to a quartet ($^3J_{CH}$ = 6.7 Hz). The observation that only *one* carbon signal is affected in these LPSFSD experiments argues in favor of both the methyl and the methylene groups being attached to the *same* sp^2 carbon atom; i.e., microminutin has the structure **2**.

Microminutin (**2**) is the first member of a new series of prenylated coumarins in which neither the "head" nor "tail" of the isoprene unit is attached either to a heteroatom or the coumarin nucleus, but rather an adjacent carbon forms the crucial bond.

Microminutin (NSC-324638) was found to be inactive in the KB cytotoxicity test but did show weak activity (ED_{50} 3.7 μg/mL) in the P-388 lymphocytic leukemia test system in vitro.[5]

Flindersine (**3**) was also obtained from the leaf extract and identified by direct comparison of the spectroscopic data with those of flindersine from *Geijera parviflora*[23] and *Haplophyllum perforatum*.[24] This alkaloid has also been isolated from *Atlantia roxburghiana*,[25] *Flindersia australis*,[26,27] *Haplophyllum tuberculatum*,[28] and *Zanthoxylum coco*.[29,30]

Experimental Section

Plant Material. The leaf material of *Micromelum minutum* (Forst. f). Seem. was collected at San Lam Waterfall, Saraburi Province, Thailand. It was identified by the Botany Section, Technical Division, Department of Agriculture, Ministry of Agriculture and Cooperatives, Thailand. A herbarium specimen is deposited in the herbarium of the Department of Pharmaceutical Botany, Faculty of Pharmaceutical Sciences, Chulalongkorn University, Bangkok, Thailand.

Extraction and Isolation of Microminutin. Dried powdered leaves (650 g) of *Micromelum minutin* were macerated with 95% EtOH (2 L) for 3 days. After evaporation of the eluent in vacuo (to 200 mL), distilled H_2O (300 mL) and saturated $Pb(OAc)_2$ solution (120 mL) were added, the mixture was centrifuged, filtered, extracted with $CHCl_3$ (3 L), and the $CHCl_3$ fraction was dried (Na_2SO_4). The residue after evaporation (8.5 g) was chromatographed on Si gel eluting with $CHCl_3$ and the main constituent crystallized from absolute EtOH to afford cream-colored rosettes of microminutin (**2**, 6.35 g, 0.98%): mp 154–155 °C; IR (KBr) υ_{max} 1740 (vs), 1675 (m), 1600 (s), 1560 (m), 1495 (m), 1440 (m), 1395 (m), 1285 (s), 1247 (s), 1142 (s), 1108 (s), 1090 (s), 1075 (m), 1060 (m), 1033 (s), 1003 (m), 928 (w), 890 (m), 830 (s), 760 (m), 720 (w), 640 (w), 610 (w), 460 (w), 390 (w) cm^{-1}; UV (EtOH) λ_{max} (log ε) 268 nm (3.59), 321 (4.23); ^1H NMR (360 MHz, $CDCl_3$) δ 2.02 (t, J = 0.8 Hz, 3 H, C_4–CH_3), 3.88 (s, 3 H, C_7–OCH_3), 4.87 (qd, J = 0.8, 17.4 Hz, 1 H, C_5–H), 4.95 (qd, J = 0.8, 17.4 Hz, 1 H, C_5–H), 6.25 (d, J = 9.5 Hz, 1 H, C_3–H), 6.93 (d, J = 8.8 Hz, 1 H, C_6–H), 7.50 (d, J = 8.8 Hz, 1 H, C_5–H), 7.68 (d, J = 9.5 Hz, 1 H, C_4–H); ^{13}C NMR (25.05 MHz, $CDCl_3$), see Figure 1; MS, m/e 272 (M^+, 7), 257 (57), 243 (12), 227 (42), 216 (15), 215 (100), 213 (27), 199 (25), 187 (16), 185 (14), 172 (16), 171 (16), 159 (16), 128 (22). Mass measurement: obsd, 272.0599; calcd for $C_{15}H_{12}O_5$, 272.0685.

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Registry No. Microminutin, 84041-46-3; flindersine, 523-64-8.

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Iodine-Induced Formation of Bicyclo[3.3.0]octane Derivatives from 1,5-Cyclooctadiene

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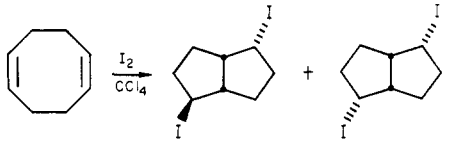
It has been known that the addition of various pseudohalogens IX (X = NCO, N_3, NO_3) to *cis,cis*-1,5-cyclooctadiene (COD) yields only 1,2-monocyclic adducts and does not give any bicyclic products via transannular π

Table I. Iodination of COD in Various Solvents[a]

COD, mmol	I_2, mmol	solvent, mL	additive, mmol	product (yield, %)[b]
46	70	CCl_4 (100)[c]		1 + 2 (77)
20	10	CCl_4 (15)		1 + 2 (61)
10	10	CCl_4 (15)		1 + 2 (58)
20	30	MeCN (50)[d]		1 + 2 (20), 3 + 4 (39)
20	30	MeCN (50)	HCl (20)	1 + 2 (10), 3 + 4 (24)
20	30	MeCN (50)	CF_3CO_2H (20)	1 + 2 (28), 3 + 4 (44)
20	30	MeCN (40)	H_2O (10 mL)	1 + 2 (38), 3 + 4 (15)
46	70	DMF (100)		5 (X = OCHO) (60)[e]
46	70	AcOH (100)		1 + 2 (67),[f] 5 (X = OAc) (7)[f]
46	70	MeOH (100)		6 (28)

[a] At 25 °C for 24 h. [b] Isolated yield. [c] Yields were over 70% when $CHCl_3$ or CH_2Cl_2 was used as solvent. [d] When the reaction was carried out at reflux for 1 h, only a mixture of 1 and 2 was obtained in a yield of 10%. [e] Small amounts of 1 and 2 were also formed. [f] Estimated by ^1H NMR.

Scheme I



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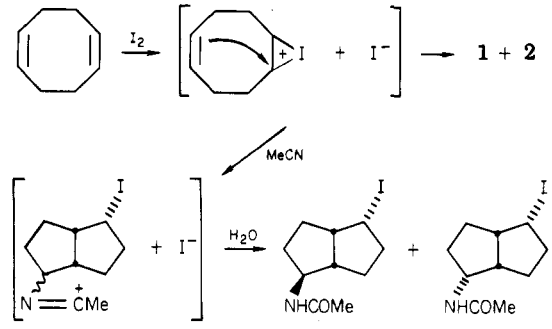
Scheme II



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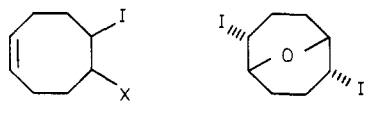
participation.[1,2] On the contrary, the treatment of IN_3 with C-9 and C-10 medium-ring dienes in acetonitrile results in a formation of a Ritter reaction intermediate of bicyclic compound that undergoes cycloaddition with azide ion to form a tetrazole derivative.[3] We have now found that a transannular cyclization of COD takes place smoothly when iodine (I_2) is used in place of IX in a suitable solvent and also that the mode of I_2 addition to COD according to solvent differs profoundly from that of Br_2 or Cl_2 addition. As one of a series of our studies on halogenation of olefins[4,5] we report here the details of these reactions, focusing especially on the effect of the solvents used upon the iodination products. It should be noted that iodocyclization of diene with I_2 has so far been reported in the cases of 4,4-dimethyl- and 4-ethyl-4-methyl-1,6-heptadienes[6] and 3-methylene-7-isopropylidenebicyclo-[3.3.1]*nonane*.[7]

When a solution of COD (1 equiv) and iodine (1.5 equiv) in CCl_4 was stirred at room temperature for 24 h, an isomeric mixture of 2,6-diiodobicyclo[3.3.0]octanes (*endo,exo*-1 and *endo,endo*-2) was obtained in a good yield together with small amounts of unidentified products, the ratio of 1/2 being 49–50/51–50 as determined by HPLC (Scheme I). Almost identical results were obtained by the use of $CHCl_3$ or CH_2Cl_2 as solvent. Each of 1 and 2 was separated by column chromatography and determined by ^1H and ^{13}C NMR spectra and by combustion analysis. The reaction proceeded as well by use of 0.5 or 1 equiv of iodine to give a mixture of 1 and 2 of nearly the same isomer ratio as the one above, but its yield was slightly lower.

When the reaction was carried out in acetonitrile as solvent under similar conditions, the formation of an isomeric mixture of 2-iodo-6-acetamidobicyclo[3.3.0]octanes (*endo,exo*-3 and *endo,endo*-4, 30–40% yield) was observed together with 1 and 2 (20–30% yield), the ratios of 3/4 and 1/2 being 50/50 and 46/54, respectively, as determined by HPLC. Although it is obvious from various spectral data and combustion analysis that 3 and 4 are stereoisomers, their assignments are still obscure. We tentatively assign 3 and 4 to *endo,exo* and *endo,endo* isomers, respectively, from ^1H NMR spectral data. Namely, the chemical shifts of the C_1 and C_5 (bridgehead) protons are very close to each other in 4 and the two multiplet peaks collapse, while those differ much in 3. Stereochemical environment to both protons should be more similar in the case of 4 than in the case of 3. The formation of 3 and 4 may be explained by iodocyclization followed by the capture of a carbonium ion with solvent acetonitrile to give a Ritter reaction intermediate that leads to the final products (Scheme II), as has been shown in the case of IN_3 addition to some nine- and ten-membered ring dienes in acetonitrile.[3] Several attempts to increase both the yield and the selectivity of 3 and 4, relative to 1 and 2, by adding water or some acids and by changing the reaction temperature were unsuccessful.

In *N,N*-dimethylformamide (DMF) as solvent, 3-formyl-6-iodocyclooctene (5, X = OCOH) was obtained as almost the sole product in an isolated yield of 60% together with small amounts of 1, 2, and several unidentified compounds. This compound may be produced by the hydrolysis of an intermediate (5, X = $OCH{=}^+NMe_2$) which is formed by the attack of carbonyl oxygen of DMF on an iodonium ion intermediate.



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When acetic acid was used as solvent, the main products were 1 and 2 (67% yield), but the formation of a small

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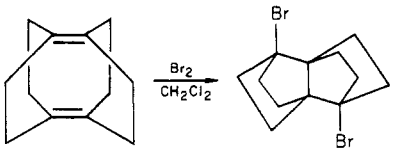
Table II. Solvent-Dependence of Products in the Halogenation of COD with Various Halogens

halogen	solvent	product: transannular	product: 1,2- and/or 1,4-addition	product: oxabridged	yield,[a] %
I_2	CCl_4, $CHCl_3$, CH_2Cl_2	1, 2			60-80
	MeCN	1-4			50-60
	DMF		5[b]		50-60
	AcOH	1, 2[c]			60-70
	MeOH			6	20-30
Br_2	CCl_4, $CHCl_3$, CH_2Cl_2, MeCN, DMF, AcOH MeOH		7, 8		40-80
Cl_2[d]	CH_2Cl_2		11[e]		67
	MeCN	12			90
	MeOH		11, 13	14	81

[a] The yield of several runs. [b] Small amounts of transannular products 1 and 2 were also formed. [c] 1,2-Addition product 5 (X = OAc) was also formed (5-10% yield). [d] The data are from ref 8. [e] Transannular products 12 (7% yield) and their dehydrochlorinated compounds (9% yield) were also formed.

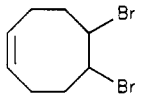
Scheme III



9 10

amount of 5-acetoxy-6-iodocyclooctene (5, X = OAc) was also detected by ^1H NMR (ca. 7% yield). Although the increase of the yield of the latter was expected by adding sodium acetate to the reaction system, the addition resulted only in lowering both the yield and the selectivity of 1 and 2, the amount of 5 (X = OAc) being unchanged. In methanol as solvent, only *endo,endo*-2,6-diiodo-9-oxabicyclo[3.3.1]nonane (6) was formed in a yield of 28% as has been reported by Labows and Swern,[2] with neither 1 nor 2 being detected by ^1H NMR and TLC. Typical results are shown in Table I.

As described above, the reaction products in the iodination of COD depend profoundly on the solvent used. On the contrary, the bromination of COD under similar conditions (COD/Br_2 = 1/1.5, at 25 °C for 24 h) afforded almost solely a mixture of 5,6-dibromocyclooctene (7) and



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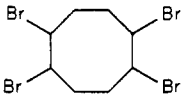

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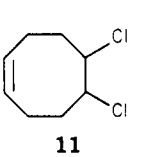
1,2,5,6-tetrabromocyclooctane (8; 40–80% yield, determined by ^1H NMR) in various solvents such as CCl_4, $CHCl_3$, MeCN, DMF, AcOH, and MeOH. It has also been reported that the bromination of COD in CH_2Cl_2 only gives 7 in a yield of 95%[8] and that the bromination in CCl_4 with excess bromine gives 8.[9] It is interesting to note that the reaction of tricyclo[4.2.2.2^{2,5}]dodeca-1,5-diene (9) with bromine in CH_2Cl_2 leads to a formation of a dibromide (10) where a transannular cyclization occurred solely (Scheme III).[10] In this case, the release of much strain energy may be accomplished by forming 10 rather than by giving an normal 1,2-addition product.

According to the literature,[8] the chlorination of COD with chlorine gas is also solvent dependent, but the situation differs profoundly from the case of iodination. Namely, in CH_2Cl_2 (at −30 °C) 5,6-dichlorocyclooctene (11,



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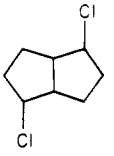

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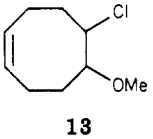

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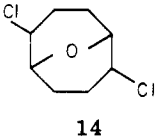

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67% yield) is formed as the main product together with some bicyclo[3.3.0]octane and bicyclo[3.3.0]octene derivatives, while in acetonitrile a transannular product, 2,6-dichlorobicyclo[3.3.0]octane (12), is the sole product (90% yield). On the other hand, in methanol (at −30 °C) the products are 5-chloro-6-methoxycyclooctene (13), 11, and dichloro-9-oxabicyclononane (14; ca. 3:1:1, 81% yield). We have also shown that the chlorination with chlorine gas in CH_2Cl_2 at −50 °C for 0.5 h gives a mixture of *trans*- and *cis*-11 (93:7).[5]

Although the exact reason for such solvent dependence of products in the halogenation of COD is not yet clear, we summarize all results together with the reported one in Table II in order to facilitate comparisons among various halogens.

Experimental Section

IR spectra were recorded with a Hitachi EPI-S2 spectrometer. ^1H NMR spectra were taken with Varian EM-360 and JEOLCO JNM-MH-100 instruments on solutions in $CDCl_3$ with Me_4Si as an internal standard. ^{13}C NMR spectra were taken at 25.1 MHz with a JEOLCO ^{13}C Fourier transform NMR system and were recorded on solutions in $CDCl_3$ after 250–1000 pulses with intervals of 2.7–2.8 s. Liquid chromatographic analyses were carried out with a Waters HPLC system equipped with a 6000A solvent delivery system and a Model 440 absorbance detector (at 254 nm) with a μPorasil (3.9 mm × 0.3 m) column (*n*-hexane for 1 and 2, 99:1 $CHCl_3$–*i*-PrOH for 3 and 4 as eluant). Mass spectra were measured on a JEOL JMS-DX 300 mass spectrometer, equipped with a JMA-3500 data processing system. The ionization voltage was 70 eV for all compounds. Melting points were determined with Shimadzu MM-2 micro melting point determination apparatus and were uncorrected.

Iodination of *cis,cis*-1,5-Cyclooctadiene (COD) in CCl_4. A solution of iodine (17.8 g, 70 mmol) and COD (5.04 g, 46.7 mmol) in CCl_4 (100 mL) was stirred at 25 °C for 24 h. The mixture was then washed with aqueous $Na_2S_2O_3$ to remove excess iodine, washed with brine, and dried over $MgSO_4$. Evaporation of the solvent in vacuo left a pale yellow solid, the HPLC analysis of which revealed the presence of 1 and 2 (1/2 = 49/51) and three

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minor unidentified products (no olefinic carbon was observed by ^{13}C NMR). This was then subjected to column chromatography (silica gel) to give a mixture of 1 and 2 (13.0 g, 35.8 mmol, 77% yield) (10:1 petroleum ether–ethyl acetate as eluant) as a white solid (mp 60–62 °C): IR (KBr disk) 2950, 2880, 1450, 1295, 1260, 1245, 1190, 1160, 1130, 1090, 1060, 1020, 930, 865, 820, 790, 740, 670 cm^{-1}; mass spectrum, *m/e* (relative intensity) 362 (M^+, $C_8H_{12}I_2$, 1), 235 ($M^+ - I$, 99), 107 ($M^+ - I_2 - H$, 100).

A mixture of 1 and 2 was subjected to column chromatography on a silica gel 60 prepacked column (Merck, size A) with petroleum ether as eluant to give each of pure 1 and 2, the former being eluted at first. 1: mp 79–80 °C (recrystallized from *n*-hexane); ^1H NMR ($CDCl_3$) δ 1.2–2.4 (m, 8 H), 2.5–3.1 (m, 2 H), 3.75–4.0 (m, 1 H), 4.1–4.35 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 30.6 (t), 31.1 (d, CI), 32.1 (d, CI), 34.3 (t), 36.9 (t), 39.8 (t), 47.8 (d, CH), 54.5 (d, CH). 2: mp 67–68 °C (recrystallized from *n*-hexane); ^1H NMR ($CDCl_3$) δ 1.80 (t, 4 H), 1.95–2.3 (m, 4 H), 2.5–2.85 (m, 2 H), 4.25–4.6 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 33.2 (d, CI), 33.4 (t), 38.1 (t), 47.6 (d, CH).

Anal. Calcd for $C_8H_{12}I_2$: C, 26.55; H, 3.34; I, 70.11. Found for 1: C, 26.51; H, 3.41; I, 69.85. Found for 2: C, 26.47; H, 3.38; I, 69.99.

Iodination of COD in Acetonitrile (MeCN). A solution of iodine (7.61 g, 30 mmol) and COD (2.16 g, 20 mmol) in MeCN (50 mL) was stirred at 25 °C for 24 h. The mixture was then added to aqueous NaCl (150 mL) and extracted with chloroform. The extract was treated as described above and the residue was subjected to column chromatography to give a mixture of 1 and 2 (1.45 g, 4.0 mmol, 20% yield; *n*-hexane as eluant) and a mixture of 3 and 4 (2.31 g, 7.88 mmol, 39% yield; ethyl acetate as eluant), both as solids. The HPLC analysis revealed the ratios of 1/2 and 3/4 to be 46/54 and 50/50, respectively. Mixture of 3 and 4: mp 65–85 °C; IR (KBr disk) 3400 (s), 3110, 2980 (s), 2900, 1640 (s), 1545 (s), 1450, 1370, 1305, 1185, 1170, 1130, 825, 695 cm^{-1}; mass spectrum, *m/e* (relative intensity) 293 (M^+, $C_{10}H_{16}INO$, 4), 234 (M^+ – NHCOMe – H, 3), 166 (M^+ – I, 78), 107 (M^+ – I – NHCOMe – H, 100).

A mixture of 3 and 4 was subjected to column chromatography on a silica gel 60 prepacked column (Merck, size A) with 1:1 benzene–hexane as eluant to give pure 3 and 4 each as a white solid, the latter being eluted at first. 3: mp 136–137 °C dec; ^1H NMR ($CDCl_3$) δ 1.0–2.30 (m, 9 H), 1.94 (s, 3 H), 2.64 (quintet, 1 H), 3.70–4.25 (m, 2 H), 5.60 (s, br, 1 H); ^{13}C NMR ($CDCl_3$) δ 23.4 (q), 30.7 (d), 30.8 (t), 32.9 (t), 33.4 (t), 36.5 (t), 47.4 (d), 48.6 (d), 58.8 (d), 169.8 (s). 4: mp 125–126 °C; ^1H NMR ($CDCl_3$) δ 1.25–2.24 (m, 8 H), 1.90 (s, 3 H), 2.36–2.84 (m, 2 H), 4.0–4.40 (m, 2 H), 5.88 (s, br, 1 H); ^{13}C NMR ($CDCl_3$) δ 23.2 (q), 25.7 (t), 31.8 (t), 31.8 (t), 35.9 (d), 39.3 (t), 44.6 (d), 48.0 (d), 53.9 (d), 169.8 (s).

Anal. Calcd for $C_{10}H_{16}INO$: C, 40.97; H, 5.50; N, 4.78; I, 43.29. Found for 3: C, 40.81; H, 5.58; N, 4.84; I, 43.08. Found for 4: C, 41.01; H, 5.59; N, 4.60; I, 43.32.

Iodination of COD in *N,N*-Dimethylformamide (DMF). The same scale reaction as in the case of CCl_4 was carried out with DMF as solvent at 25 °C for 24 h. After the usual workup procedure (addition of brine, washing with aqueous $Na_2S_2O_3$, extraction with benzene), evaporation of the solvent left a yellow-brown oil, which was passed through a short column of silica gel to remove resinous products. The eluent contained 5 (X = OCHO) and small amounts of 1 and 2, the former then being isolated by preparative TLC (10:1 petroleum ether–ethyl acetate; Merck silica gel 60 F-254 plate) as a pale yellow oil (7.84 g, 28 mmol, 60% yield): IR 3040, 2955, 1730 (s), 1485, 1430, 1175 (s), 1070, 1030, 990, 710, 655 cm^{-1}; mass spectrum, *m/e* (relative intensity) 280 (M^+, $C_9H_{13}IO_2$, 16), 251 (M^+ – CHO, 9), 153 (M^+ – I, 100); ^1H NMR ($CDCl_3$) δ 1.4–2.8 (m, 8 H), 4.62 (dt, 1 H), 5.40 (dt, 1 H), 5.44–5.88 (m, 2 H), 8.12 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 23.6 (t), 27.1 (t), 30.8 (t), 34.6 (d, CI), 36.7 (t), 77.3 (d, COCHO), 127.4 (d), 129.4 (d), 159.3 (d).

Anal. Calcd for $C_9H_{13}IO_2$: C, 38.59; H, 4.68. Found: C, 37.92; H, 4.70.

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Registry No. 1, 84064-77-7; 2, 84064-78-8; 3, 84064-79-9; 4, 84107-46-0; 5 (X = OCHO), 84064-80-2; 6, 29417-22-9; 7, 24165-06-8; 8, 3194-57-8; (*Z,Z*)-COD, 1552-12-1.

A Butatriene Cycloaddition Equivalent Approach to the Multiple Linear Homologation of Six-Membered Rings and the Synthesis of Benzocyclobutenes

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The construction of six-membered rings through Diels–Alder reactions is of immense importance in organic synthesis. It clearly would be desirable to have methodology available for the construction of linear polycyclic structures through repetitive [2 + 4] cycloadditions. We describe here a straightforward conceptual and experimental means of achieving this end, as well as its elaboration as a general and convenient route to benzocyclobutenes.

Diethyl Acetylenedicarboxylate (DEAD) as a Butatriene Cycloaddition Equivalent. In the course of work directed toward the synthesis of complex polycyclic hydrocarbons, we had need of a convenient approach to molecules of general structure 1.[1] Conceptually, at least, these may be obtained through repetitive 1,2,3-butatriene [2 + 4] cycloadditions, as shown in Scheme I. Cycloaddition of butatriene to a 1,3-diene can, in principle, yield a cycloadduct which contains an exocyclic 1,2-dimethylene unit. This can react with a second molecule of butatriene, and the sequence should be repeatable indefinitely. Unfortunately, direct use of butatriene in this reaction is not feasible due to its apparently weak dienophilicity[2] and its propensity toward oligomerization;[3] thus we perforce need some type of butatriene synthetic equivalent. The requirements for such a method are that it involve a good, readily available dienophile and that subsequent chemistry not involve strong acid, base, or high temperature, due to the sensitivity of polydehydro aromatic structures such as 1. Since this is a linear approach, good to excellent yields are a necessity.

In past years, a variety of reagents which may be considered butatriene synthetic equivalents have been reported, with the purpose of synthesis of the 1,2-dimethylene unit.[4] Most common is maleic anhydride, which usually is elaborated via acetate or amine oxide pyrolysis or via base-induced halide elimination. Such methods often are of moderate to good efficiency, but because of the pyrolytic step or strong base, these did not seem suitable for multiple homologations.

Our approach to this problem has been to use dimethyl or diethyl acetylenedicarboxylate (DMAD or DEAD) as butatriene synthetic equivalents; this is outlined in Scheme II. Several examples of the use of DMAD as a precursor

(1) Preliminary report: Angus, R. O., Jr.; Johnson, R. P. "Abstracts of Papers", 17th Midwest Regional Meeting of the Americal Chemical Society, Columbia, MO, 1981; American Chemical Society: Washington, DC, 1981.

(2) (a) Although the corresponding retro [2 + 4] reaction is well-known,[2b] successful [2 + 4] cycloadditions to the central bond of a butatriene are rare.[2c] (b) Ripoll, J. L.; Rouessac, A.; Rouessac, F. *Tetrahedron* **1978**, *34*, 19. (c) Reid, W.; Neidhardt, R. *Justus Liebigs Ann. Chem.* **1970**, *739*, 155.

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