References and Notes

(1) Presented in part at the 172nd National Meeting of the American Chemical Society, San Francisco, 1976.
(2) (a) Robert A. Welch Postgraduate Fellow; (b) taken in part from the Master's Thesis of D.M.C., Trinity University, 1970.
(3) (a) NSF Undergraduate Research Participant; (b) Robert A. Welch Undergraduate Scholar.
(4) The interesting photochemical properties of acenaphthylene may be found in references in the following papers: (a) W. I. Ferree, Jr., B. F. Plummer, and W. W. Schloman, Jr., *J. Am. Chem. Soc.*, **96**, 7741 (1974). (b) D. O. Cowan and J. Koziar, *ibid.*, **98**, 1001 (1976).
(5) J. R. Erdman and H. E. Simmons *J. Org. Chem.*, **33**, 3808 (1968).
(6) It has not escaped our attention that compound **3** offers potential for the storage of solar energy[7] and we are continuing our efforts to find suitable photochemical conditions for its transformation.
(7) (a) G. Jones and B. R. Ramachandran, *J. Org. Chem.*, **41**, 798 (1976). (b) D. P. Schwendeman and C. Kutal, *Inorg. Chem.*, **16**, 719 (1977).
(8) (a) D. R. Adams and D. I. Davies, *J. Chem. Soc., Perkin Trans. 1*, 2012, (1974); (b) *ibid.*, 1237, (1972).
(9) D. C. Morrison, *J. Org. Chem.*, **25**, 1665 (1960).
(10) The assignment of endo orientation to **1** is based upon the classical Alder Rule[11] and the theoretical framework of Woodward–Hoffmann formalism.[12]
(11) K. Alder and G. Stein, *Angew. Chem.* **50**, 514 (1937).
(12) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Academic Press, New York, N.Y., 1970.
(13) J. H. Beynon, "Mass Spectrometry and Its Applications to Organic Chemistry", Elsevier, Amsterdam, 1960.
(14) J. Michl, *J. Am. Chem. Soc.*, **98**, 4546 (1976).
(15) A full spectrum was not reported so that the extent of the perturbation of the K band is unknown: K. Yamamotao, M. Morioka, and I. Murata, *Tetrahedron Lett.* 3009 (1975).
(16) M. N. Paddon-Row, D. N. Butter, and R. N. Warrener, *J. Chem. Soc., Chem. Commun.* 741 (1976).
(17) The diagrams we have chosen for illustration are arbitrarily illustrated with the alkoxy group in the exo position for clarity of presentation. We shall attempt to identify the correct geometry for these adducts when subsequent studies are finished.
(18) (a) M. Akhtar, D. M. Bratby, J. C. Chadwick, and G. I. Fray, *Tetrahedron*, **32**, 2265 (1976). (b) L. S. Besford, R. C. Cookson, and J. Cooper, *J. Chem. Soc. C*, 1385 (1967).
(19) R. Baker and T. J. Mason, *J. Chem. Soc. C*, 596 (1970).
(20) K. L. Williamson, Y. Hsu, and E. I. Young, *Tetrahedron*, **24**, 6007 (1968).
(21) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed, Pergamon, New York, N.Y., 1969, p 334–344.
(22) Melting points were taken on a Fisher-Johns apparatus and are uncorrected. Infrared spectra were recorded in KBr pellets on a Perkin-Elmer 337 or 283. NMR spectra were obtained in dilute solutions of $CDCl_3$ or CCl_4 with internal Me_4Si on a Varian T-60. UV–visible spectra were obtained on a Cary 118C. GLC analyses were run on a Varian Hy-Fl 2400 with a flame-ionization detector and a 5 ft × 0.125 in. column of 1.5% OV-101 on Chromosorb G. Mass spectra were recorded on a Finnegan 1015 C system/150 Quadrupole spectrometer at 70 eV. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Versatile Allene and Carbon Dioxide Equivalents for the Diels–Alder Reaction

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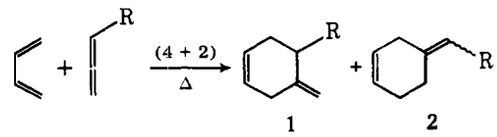
The Diels–Alder cycloaddition of vinyltriphenylphosphonium bromide (**4**) with a variety of 1,3-dienes generated the unsaturated cyclic phosphonium salts **3** in excellent yield. Wittig condensation of the ylides of **3** with aldehydes afforded the alkylidene derivatives. In addition, the known Diels–Alder adducts **13** were prepared from diethyl ketomalonate (**12**) and 1,3-dienes. These dihydropyrans could be transformed, via diacids **14**, to β,γ-unsaturated valerolactones **15** by either lead tetraacetate mediated oxidative decarboxylation or by the Curtius degradation.

The Diels–Alder reaction figures prominently in the arsenal of organosynthetic reactions, and a wealth of knowledge exists concerning reactivity profiles, regioselectivity, and stereochemistry of the 4 + 2 cycloaddition reaction.[2] In recent years the construction of synthetic equivalents for unreactive dienophiles such as ketene[3] and allene[4] has extended the scope of this cyclization reaction to the production of cyclohexene systems not normally generated by this thermal process. This report relates the development of two such Diels–Alder equivalents: an allene equivalent[5] capable of introducing the $-CH_2C(=CHR)-$ group in a Diels–Alder sense, and a carbon dioxide equivalent[6] which places the $-OC(=O)-$ group into the cycloadduct.

Results and Discussion

General Allene Equivalent. Two isomeric Diels–Alder products may be realized from the 4 + 2 cyclization between alkyl-substituted allenes and 1,3-dienes (eq 1).[7] It was felt that

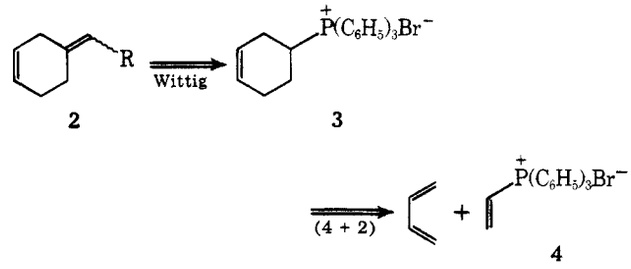


(1)

1 2

an allene equivalent capable of producing the alkylidene moiety in **2** might be obtained from the intermediate **3** via a Wittig transformation (Scheme I). Cycloadduct **3** might then be obtained using the Diels–Alder transform, thus requiring a 1,3-diene and vinyltriphenylphosphonium bromide (**4**) as starting materials.

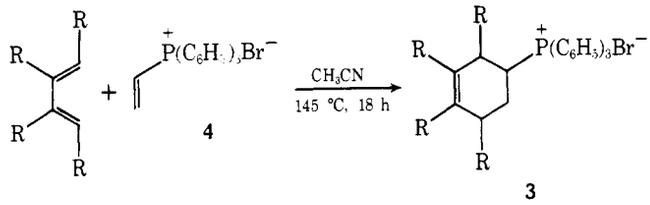
Scheme I



2 3 4

Indeed, vinyltriphenylphosphonium bromide[8] underwent smooth Diels–Alder reaction with a number of dienes at elevated temperatures to afford the desired adducts in excellent yield as shown in Table I. Cycloadducts **3a–e** were recovered as powders after recrystallization. These new phosphonium salts could be readily converted to the ylides by treatment with lithium diisopropylamide at −78 °C in tetrahydrofuran. Addition of a slight excess of aldehyde at 0 °C followed by warming to room temperature afforded the alkylidene derivatives as shown in Table II. Formaldehyde, aliphatic and aromatic aldehydes, and α,β-unsaturated aldehydes underwent condensation and the desired olefins were obtained in good yield although, in some cases, product volatility con-

Table I. Diels-Alder Adducts of 4 with 1,3-Dienes



Registry no.	Diene	Adduct	Yield,[a] %
106-99-0	1,3-Butadiene	3a	93
78-79-5	Isoprene	3b	90[b]
513-81-5	2,3-Dimethyl-1,3-butadiene	3c	92
542-92-7	Cyclopentadiene	3d	90[c]
592-57-4	1,3-Cyclohexadiene	3e	96[c]

[a] Yields are reported after recrystallization from $CHCl_3$-Et_2O. [b] The para isomer was found in greater than 90% excess over the meta isomer. See ref 14. [c] Both ^1H and ^{31}P NMR methods failed to allow analysis of endo:exo isomer ratio. ^{13}C NMR spectrometry did reveal a ratio of approximately 80:20; however, exact structure assignment was not possible.

tributed to substantial decreases in the actual quantity isolated.

It is well documented that allenes possessing electron-withdrawing groups undergo Diels–Alder reactions in generally good yield across the α,β portion of the allenic π-bond system.[7b] Condensation of the ylide of the bicyclic phosphonium salt **3d** with glyoxal monodiethyl acetal[9] led to isolation of a mixture of *Z* and *E* isomers of the conjugated aldehyde **6** (required for another study) following treatment of the crude acetal Wittig product with silica gel in pentane (eq 3). Mild

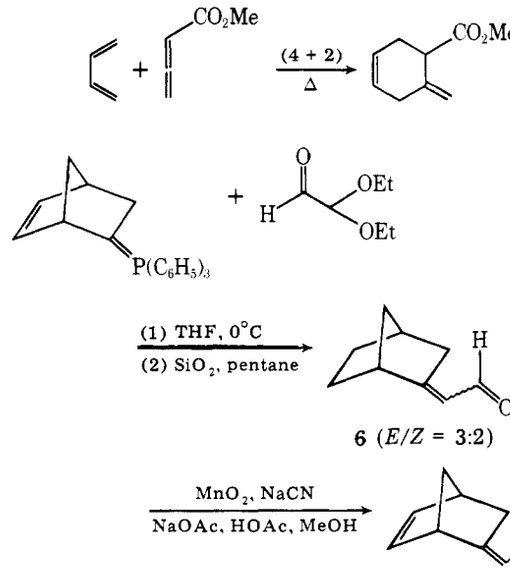
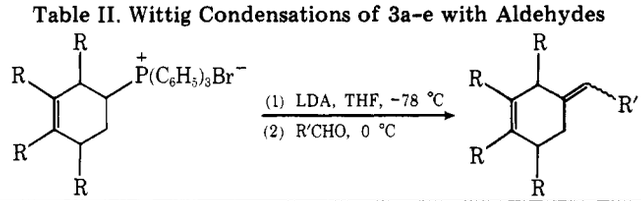


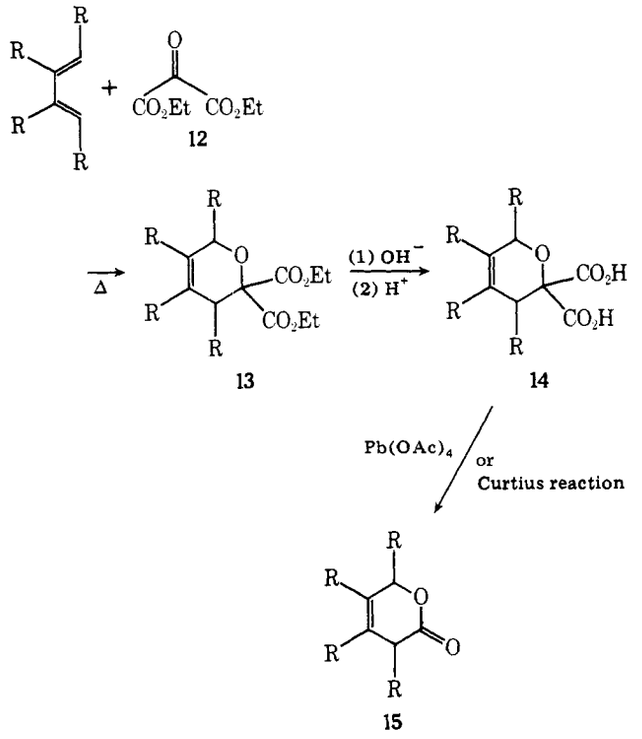
Table II. Wittig Condensations of 3a–e with Aldehydes



Registry no.	Phosphonium salt	Registry no.	Aldehyde	Product[a]	Yield,[b] %
63797-62-6	3a	100-52-7	C_6H_5CHO	5a	78
63797-63-7	3b		C_6H_5CHO	5b	80
54222-64-9	3c		C_6H_5CHO	5c	75
	3d		C_6H_5CHO	5d	81
	3d	5344-23-0	$(C_2H_5O)_2CHCHO$	6 (E) = 60% + (Z) = 40%	35
	3e		C_6H_5CHO	5e	85
	3e	50-00-0	CH_2O(g) or $(CH_2O)_n$	7	50
	3e	111-71-7	n-$C_6H_{13}CHO$	8	63
	3e	4170-30-3	$CH_3CH{=}CHCHO$	9	30

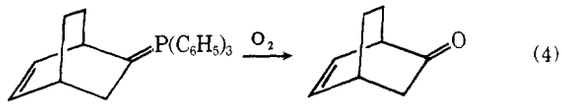
[a] Amounts of *Z* and *E* isomers were not determined except in **6**. [b] Yields are reported after chromatographic purification.

Scheme II



oxidation of this aldehyde using activated manganese dioxide and sodium cyanide[10] afforded the methyl ester in excellent yield.

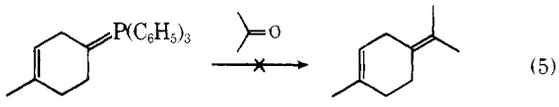
Furthermore, vinyltriphenylphosphonium bromide may also be considered as a ketene equivalent as demonstrated below using **3e** (eq 4). By bubbling a stream of oxygen through



(4)

a solution of the ylide at room temperature,[11] the bicyclic ketone **10** could be generated.

One particular limitation of the Wittig reaction is its failure to allow formation of tetrasubstituted olefins.[12] For example,



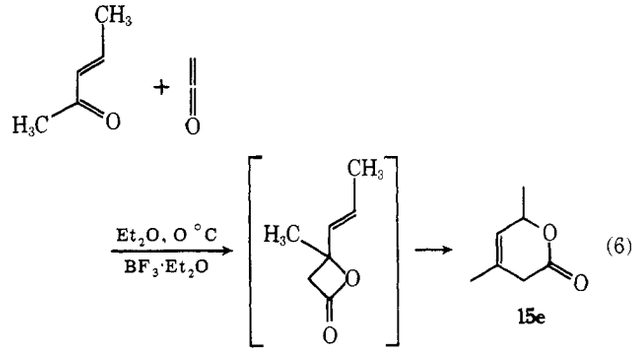
(5)

an attempt at the synthesis of the natural product terpinolene[13] **11** by condensation of acetone with the ylide of **3b** led to recovery of starting material after 24 h.

Carbon Dioxide Equivalent. To complete the triad of Diels–Alder equivalents for carbon and oxygen cumulated systems, a study was undertaken to develop a method for the introduction of the –OC(=O)– group into the 4 + 2 cycloadduct. Of the myriads of known carbonyl compounds, only a few have been shown to act as dienophiles in the Diels–Alder reaction.[15] Diethyl ketomalonate[8] (**12**) is one such species, and its Diels–Alder adducts with a variety of 1,3-dienes have been well characterized.[16]

As can be seen in Scheme II, we envisioned the conversion of the biscarboethoxy group of cycloadduct **13** to the lactone carbonyl of **15** to proceed by either lead tetraacetate mediated oxidative decarboxylation[17] of diacid **14** or by the classical Curtius degradation[18] of the same intermediate.

Although a number of syntheses of β,γ-unsaturated valerolactones are known,[19] one in particular is capable of generating only dialkyl-substituted species such as **15e** in high yield (eq 6). This method involves the addition of ketene to γ-alkyl-α,β-unsaturated ketones.[19a]

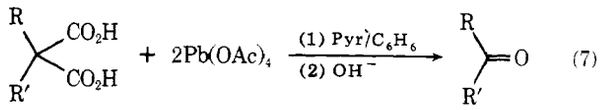


(6)

Diels–Alder Adducts of Diethyl Ketomalonate (12). The 4 + 2 cycloaddition products were made by dissolving **12** and an excess of the 1,3-diene in acetonitrile and heating the solution at 130–135 °C for the designated period of time in a sealed tube (Table III). The diesters **13a–f** were then hydrolyzed to the biscarboxylic acids **14a–f** in good overall yield based on diethyl ketomalonate.

Conspicuously absent from Table III is the cyclopentadiene adduct. Cycloaddition of this normally reactive diene had been reportedly unsuccessful.[16a] We also attempted the cyclization of monomeric cyclopentadiene with **12** at various temperatures ranging from −20 to 135 °C, but we were unable to isolate the cycloadduct. Apparently, if the adduct is formed, thermodynamic instability results in facile cycloreversion. Anthracene also failed to form a product with the carbonyl substrate.

Lactone Carbonyl Release. Lead Tetraacetate Method. Alkyl-substituted malonic acids undergo oxidative decarboxylation to form aldehydes or ketones upon treatment with lead tetraacetate,[20] LTA (eq 7). When similarly applied to



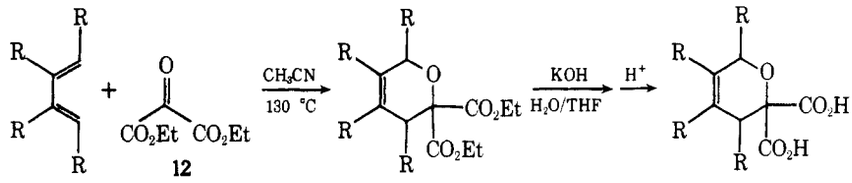
(7)

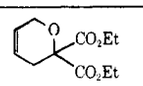
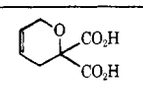
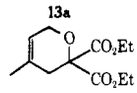
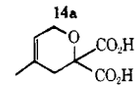
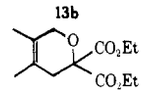
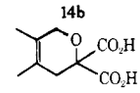
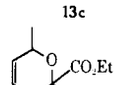
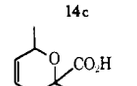
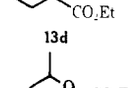
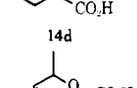
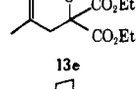
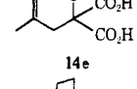
diacid **14c** (see Table IV), this procedure allowed isolation of the desired lactone in 20% yield after aqueous workup. Following numerous attempts to improve the yield of valerolactone **15c**, the best conditions were found to be a variation of a procedure developed by Cope and co-workers[21] utilizing sodium acetate to facilitate carboxyl ligand transfer to Pb^{IV}, a prerequisite for successful oxidation.[17] (Pyridine also functions in this manner.) However, due to limited success in generation of other valerolactones with lead tetraacetate, the Curtius degradation was explored.

Trimethylsilyl Azide Method. The essential feature of the Curtius degradation of carboxylic acids is the thermal rearrangement of an acyl azide to the isocyanate, and numerous approaches to the synthesis of acyl azides are known.[22] One procedure which has been developed recently is the one-pot conversion of an acid chloride to the isocyanate using trimethylsilyl azide (TMSA).[23] (See Scheme III.)

Upon treatment of a warm cyclohexane solution[24] of the bisacid chloride of **14c** with an excess of TMSA, the bisacyl azide was rapidly formed as evidenced by infrared spectroscopy (λ_{max} 4.67 and 5.80 μm). On further warming, stepwise rearrangement to the bisisocyanate apparently occurred. Within 15 min strong isocyanate infrared absorptions (λ_{max} 4.40 and 4.46 μm) were seen which were equal in intensity to those of the acyl azide. After about 30 min of heating, no acyl azide remained. Removal of solvent, followed by mild hydrolysis of a tetrahydrofuran solution of the bisisocyanate with either aqueous acetic acid or aqueous oxalic acid generated

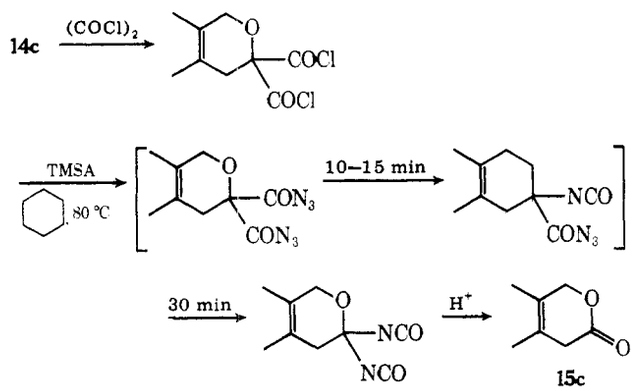
Table III. Diels-Alder Adducts of 12 and 1,3-Dienes



Registry no.	Diene[a]	Diester (%)[b,g]	Diacid (%)[c]	Mp, °C
	1,3-Butadiene (16 h)	 13a (78)	 14a (63)	Oil
	Isoprene (4 h)	 13b (80)[d]	 14b (64)	Oil
	2,3-Dimethyl-1,3-butadiene (4 h)	 13c (86)	 14c (70)	138-140
504-60-9	Piperylene (4 h)	 13d (85)[e]	 14d (66)	124-126
1118-58-7	2-Methyl-1,3-pentadiene (1.5 h)	 13e (95)[f]	 14e (90)	146-147
	1,3-Cyclohexadiene (4 h)	 13f (84)	 14f (74)	128-130

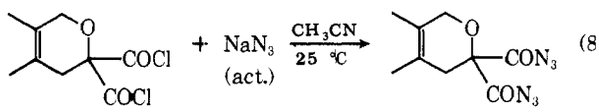
[a] Reaction time in parentheses. [b] Yields reported after distillation. [c] Overall yield based on 12. [d] NMR analysis revealed 11:1 ratio of para:meta isomers. [e] NMR analysis revealed 95% ortho isomer. [f] No meta isomer detected by NMR analysis. [g] Registry no.: 13c, 24588-60-1; 13d, 36749-08-3; 13e, 63797-64-8; 13f, 24588-62-3.

Scheme III



valerolactone **15c** in 55% yield after distillation. Similar treatment of diacid **14b** produced **15b** in only 30% yield.

Sodium Azide Method. Alternatively, excellent conversion of the acid chloride to the acyl azide could be accomplished under mild conditions by stirring an acetonitrile solution of the acid chloride with an excess of activated sodium azide[25] at room temperature (eq 8). Within 40 min substitution was



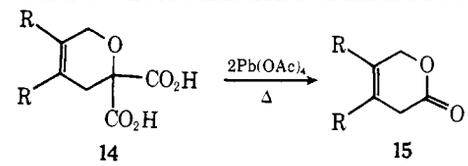
(8)

complete and filtration of the reaction mixture to remove insoluble sodium salts, followed by thorough concentration at room temperature, generated the viscous product (λ_{max} 4.67 μm).

Without further purification, careful addition of cyclohexane to the potentially explosive acyl azide followed by rapid stirring at 80 °C for 40 min resulted in formation of the insoluble isocyanate. Hydrolysis of this material as before led to isolation of **15c** in 72% yield (Table V) based on diacid. Extension of this method to other diacids resulted in improved yields of the desired valerolactones.

However, when the sodium azide method was applied to the bisacid chlorides of **14d** and **14e**, the dienoic acids **16d** and **16e** were recovered along with the lactone in the case of the latter material. Perhaps stabilization of an incipient cation by the allylic methyl group allows this rearrangement to take place during isocyanate hydrolysis (eq 9 and 10).

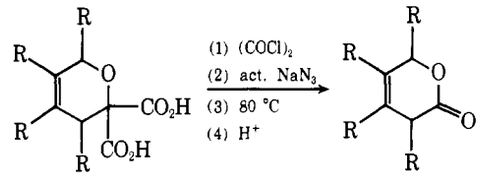
Table IV. LTA Oxidation of Diacids 14a-c



Diacid	Method	Lactone (%)[a]
14c	2 equiv of Pyr, C_6H_6, 80 °C, 3 h[b]	15c (20)
14c	NaOAc, HOAc, C_6H_6, 40 °C, 1 h[c]	15c (63)
14b	NaOAc, HOAc, C_6H_6, 40 °C, 1 h[c]	15b (40)
14a	NaOAc, HOAc, C_6H_6, 40 °C, 1 h[c]	15a (0)

[a] Yields reported after distillation. [b] Tufariello and Kissel, ref 20. [c] Cope, Park, and Scheiner, ref 21.

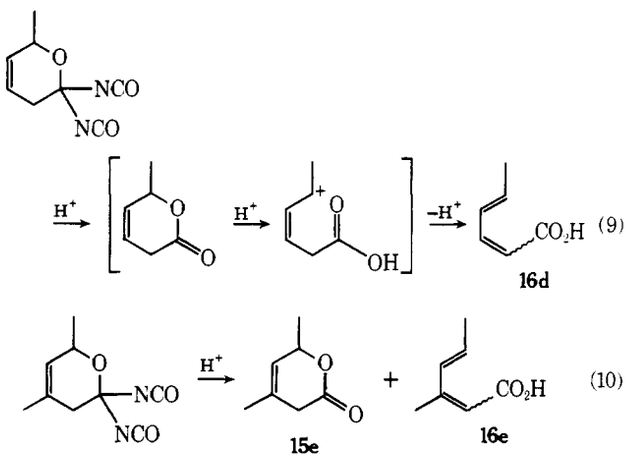
Table V. Lactone Formation by the Sodium Azide Method



14 15

Registry no.	Diacid	Hydrolysis method[a]	Time, min	Lactone (%)[b]	Other products (%)
57668-92-5	14a	A	40	15a (52)	.....
57668-93-6	14b	A	50	15b (60)	.....
57668-94-7	14c	A	60	15c (72)	.....
828-50-2	14d	B	60	.....	16d (55)
63797-65-9	14e	A	40	15e (30)	16e (34)
61779-36-0	14f	C		15f (7)	.....

[a] Method A: aqueous oxalic acid/THF/25 °C; method B: hydrolysis was run under a variety of conditions ranging from mildly acidic to mildly basic ($NaHCO_3$); method C: 5% aquous $NaHCO_3$/THF/25 °C/18 h followed by acidification to pH 2. [b] Yields are reported after distillation and are based on diacid.



Synthetic Transformations of Lactone 15c. The synthetic versatility of these lactones is outlined in Scheme IV where lactone **15c** was subjected to a variety of chemical manipulations.

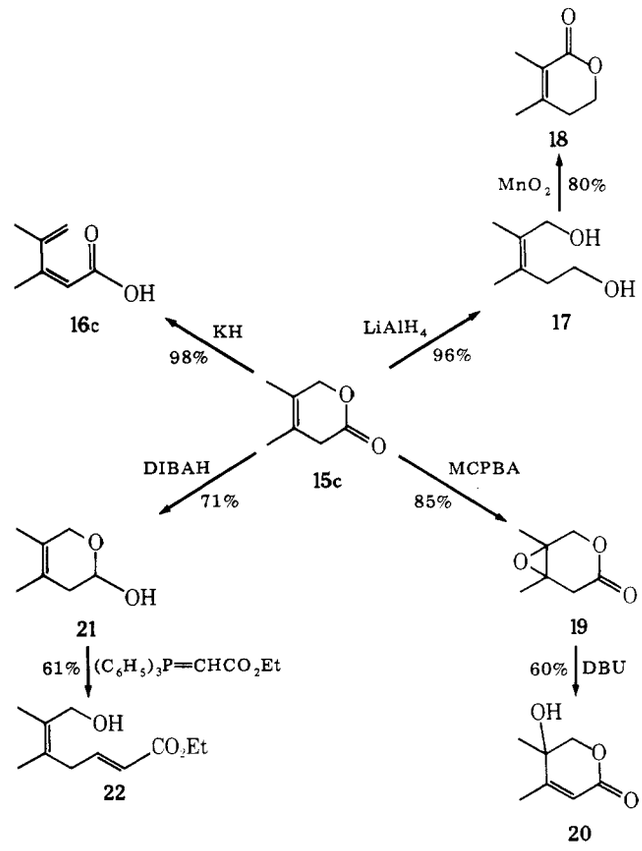
Production of 3,4-dimethyl-2(*Z*),4-pentadienoic acid (**16c**) was cleanly accomplished by treatment of the lactone with 1 equiv of potassium hydride in THF at 0 °C.

Lithium aluminum hydride reduction of the lactone in THF at room temperature afforded diol **17** in excellent yield. This product could be transformed to the α,β-unsaturated valerolactone **18** upon selective oxidation of the allylic alcohol using activated manganese dioxide.[26]

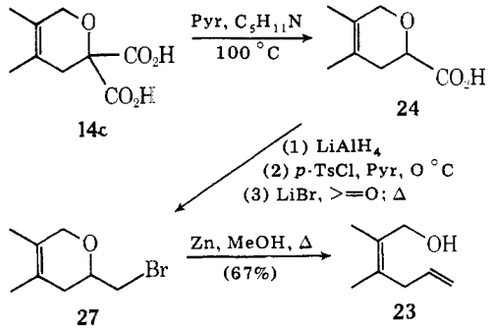
Epoxylactone **19** was prepared by oxidation of **15c** with *m*-chloroperbenzoic acid in dichloromethane at 0 °C. Treatment of the crystalline epoxide with diazabicyclo[5.4.0]-undec-5-ene (DBU) in THF generated the rearranged alcohol **20** in good yield.[27]

Reduction of **15c** to the cyclic hemiacetal **21** was achieved at −20 °C in ether using diisobutylaluminum hydride (DIBAH). Wittig condensation of the weakly basic stabilized ylide carboethoxyethylidene triphenylphosphorane with **21** generated the 1,4-diene **22** in 61% yield. Attempted Wittig reaction of **21** with the unstabilized ylide methylene tri-

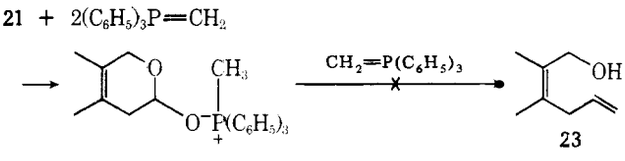
Scheme IV



Scheme V



phenylphosphorane led to recovery of starting material (eq 11). Diene **23** could be obtained by a different route starting



(11)

with the diacid **14c**. This compound could be monodecarboxylated using pyridine and a few equivalents of piperidine at 100 °C as shown in Scheme V. The new carboxylic acid **24** was then reduced to the alcohol **25** using LAH in ether. Conversion to the *p*-toluenesulfonate **26** was accomplished using standard procedures, and displacement by lithium bromide in refluxing acetone then generated the primary bromide in 70% overall yield from **25**. Zinc-mediated fragmentation of the bromide was performed in refluxing methanol to afford the desired product.

Experimental Section

Reactions were carried out under a nitrogen atmosphere unless otherwise noted. Melting points were taken on a Fisher-Johns hot stage apparatus and are uncorrected. IR spectra were determined on a Perkin-Elmer 137 spectrophotometer. NMR spectra were taken on either Varian T-60 or A-60A spectrometers with tetramethylsilane as an internal standard. In describing NMR chemical shifts, peaks are reported by indicating the center of the pattern. The multiplicity of the peak is abbreviated as s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. Mass spectra were obtained using a Hitachi Perkin-Elmer Model RMU-7E spectrometer. Elemental analyses were determined by Robertson Laboratory, Florham Park, N.J. Micro thin-layer chromatography was performed on Eastman Chromatogram Sheets No. 960 precoated with silica gel and fluorescent indicator. Preparative thick-layer chromatography was done on precoated Silica Gel G-200 plates with fluorescent indicator as supplied by Brinkman Instruments, Inc. Column chromatography was conducted with Grace silica gel, grade 923, 100–200 mesh.

All chemicals were commercial samples unless reference is given to their preparation. They were used as received unless otherwise noted. Anhydrous solvents were obtained by distillation from the specified substances: acetonitrile, chloroform, and dichloromethane from P_2O_5; benzene and methanol from calcium hydride; cyclohexane from sulfuric acid; ether and tetrahydrofuran (THF) from sodium benzophenone ketyl.

General Procedure for Cycloaddition of Vinyltriphenylphosphonium Bromide with 1,3-Dienes. A solution of an excess of freshly distilled 1,3-butadiene (precooled to −78 °C), vinyltriphenylphsophonium bromide (2.50 g, 7 mmol), and a trace of hydroquinone in 5 mL of acetonitrile was heated in a sealed tube at 145 °C. After 20 h the tube was opened and the contents were removed with CH_2Cl_2. Following concentration at reduced pressure, the gummy residue was dissolved in a minimal volume of $CHCl_3$ and triturated with Et_2O to afford, after drying under vacuum, 2.90 g (93%) of cyclohex-3-enyltriphenylphosphonium bromide (**3a**): mp 240–241 °C dec; NMR ($CDCl_3$) δ 5.70 (br s, 2 H), 5.00–5.50 (br m, 1 H), 1.90–3.00 (complex m, 6 H). Anal. Calcd for $C_{24}H_{24}BrP$: C, 68.09; H, 5.71. Found: C, 67.66; H, 5.26.

In a similar fashion, the following phosphonium salts were prepared.

Table VI. Spectral and Analytical Data

Compound	NMR (δ)[a]	Analysis,[b] mol wt
5a	5.70–6.0 (m, 3 H)	Calcd: 170.2588 Found: 170.2610
5b	6.15 (br s, 1 H), 5.70 (br s, 1 H), 1.75 (br s, 3 H)	Calcd: 183.2796 Found: 183.2808
5c	6.20 (br s, 1 H), 1.70 (br s, 6 H)	Calcd: 198.1401 Found: 198.1392
5d	6.30 (br s, 1 H), 6.02 (ABq, J = 2 Hz, 2 H)	Calcd: 182.1093 Found: 182.1102
5e	6.10–6.25 (m, 3 H), 3.09 (br s, 1 H), 2.71 (br s, 1 H)	Calcd: 196.1262 Found: 196.1279
7	6.20–6.35 (m, J = 3.5 Hz, 2 H), 4.55, 4.70 (2m, 2 H)	Calcd: 120.1963 Found: 120.1982
8	6.24 (m, J = 4 Hz, 2 H), 5.15 (br t, 1 H)	Calcd: 204.3571 Found: 204.3558
9	6.25 (m, J = 4 Hz, 2 H), 5.13–6.05 (m, 3 H), 1.75 (d, J = 6 Hz, 3 H)	Calcd: 160.2689 Found: 160.2702
10	6.40 (q, 2 H), 3.02 (br m, 2 H), 1.95 (d, J = 3 Hz, 2 H), 0.95–1.85 (complex m, 2 H)	Calcd: 122.0731 Found: 122.0720

[a] Spectra taken in CCl_4. [b] By mass spectral analysis.

4-Methylcyclohex-3-enyltriphenylphosphonium bromide (3b): mp 232–235 °C dec; NMR ($CDCl_3$) δ 5.30–5.60 (br s, 1 H), 4.40–4.95 (br m, 1 H), 2.00–3.00 (br m, 6 H), 1.65 (br s, 3 H). Anal. Calcd for $C_{25}H_{26}BrP$: C, 68.65; H, 5.99. Found: C, 68.04; H, 5.16.

3,4-Dimethylcyclohex-3-enyltriphenylphosphonium bromide (3c): mp 114–115 °C dec; NMR ($CDCl_3$) δ 6.23 (s, 1 H), 2.90 (br s, 2 H), 1.90–2.56 (br m, 4 H), 1.55 (s, 6 H). anal. Calcd for $C_{26}H_{28}BrP$: C, 69.18; H, 6.25. Found: C, 70.04; H, 5.98.

Bicyclo[2.2.1]hept-5-enyl-2-triphenylphosphonium bromide (3d): mp 220–223 °C dec; NMR ($CDCl_3$) δ 5.10–5.95 (br m, 3 H). Anal. Calcd for $C_{25}H_{24}BrP$: C, 68.97; H, 5.55. Found: C, 69.10; H, 5.93.

Bicyclo[2.2.2]oct-5-enyltriphenylphosphonium bromide (3e): mp 263–266 °C; NMR ($CDCl_3$) δ 5.10–6.03 (br m, 3 H). Anal. Calcd for $C_{26}H_{26}BrP$: C, 69.49; H, 5.83. Found: C, 70.05; H, 6.18.

General Procedure for Wittig Condensation. To a cooled solution (0 °C) of the phosphorane of **3e** (0.442 g, 1 mmol) in 10 mL of THF (prepared by addition of 1.1 mmol of lithium diisopropylamide in THF to a suspension of phosphonium salt in the same solvent at −78 °C) was added 0.127 g (1.2 mmol) of benzaldehyde. After stirring overnight at 25 °C, the product was diluted with pentane and the organic layer was washed many times with water, dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The pure olefin was obtained by column chromatographic purification over silica gel using hexane as eluent. Thus, 2-benzylidenebicyclo[2.2.2]oct-5-ene (**5e**) was obtained (0.166 g, 85%) as a colorless oil. Anal. Calcd for $C_{15}H_{16}$: mol wt, 196.1279. Found: mol wt (MS), 196.1262.

Table VI contains spectral and analytical data for Wittig products **5a–d**, **7**, **8**, **9**, and **10**.

Bicyclo[2.2.2]oct-5-en-2-one (10). Phosphorane **3e** (0.442 g, 1 mmol) was prepared as above. Oxygen was bubbled into the stirring suspension until the characteristic deep red color of the ylide disappeared. After 24 h, the resulting mixture was directly filtered through silica gel to afford 0.024 g (20%) of ketone **10**: IR (hexane) 5.78, 6.2 μm.

Bicyclic Aldehyde (6). To a cooled solution (0 °C) of the ylide of phosphonium salt **3d** (1.254 g, 3 mmol) in 50 mL of THF was added glyoxal monodiethyl acetal[9] (0.53 g, 4 mmol). After stirring overnight, the product was diluted with pentane and the organic layer was repeatedly washed with water and dried over $MgSO_4$. The crude diethyl acetal was obtained by removal of solvent by distillation at atmospheric pressure. The volatile product was redissolved in pentane and stirred overnight with 3 g of silica gel at room temperature. After filtration and concentration at atmospheric pressure, the crude aldehyde was purified by thick-layer chromatography using 4:1 hexane–ether

as developing solvent and obtained as a colorless volatile liquid (0.14 g, 35%, a mixture of *Z* and *E* isomers); IR (CH_2Cl_2) 5.97, 6.07, and 6.17 μm; NMR ($CDCl_3$) δ 9.80 (d, *J* = 8.5 Hz, *CHO*, *Z* isomer): 9.60 (d, *J* = 8.5 Hz, *CHO*, *E* isomer), 4.22 (m, doubly allylic methine *Z* isomer), 3.42 (m, doubly allylic methine *E* isomer); mp (semicarbazide) 207–208 °C dec. Anal. Calcd for $C_{10}H_{13}N_3O$: mol wt, 191.2258. Found: mol wt, 191.2284.

General Procedure for Cycloaddition of Diethyl Ketomalonate with 1,3-Dienes. Freshly distilled 1,3-butadiene (an excess) was condensed into a Carius tube containing a trace of hydroquinone, diethyl ketomalonate (1.82 mL, 12 mmol) and 4 mL of acetonitrile. The tube was sealed and after heating at 135 °C for 16 h, the product was isolated with CH_2Cl_2. After concentration, approximately 50 mL of 95% EtOH was added to precipitate polymeric material and the resulting white suspension was vacuum-filtered through Celite and then concentrated. Evaporative distillation produced diethyl 3,6-dihydropyran-2,2-biscarboxylate (**13a**) (2.17 g, 78%) as a colorless liquid; bp 100 °C (0.8 mm); IR (neat) 5.71 μm; NMR (CCl_4) δ 5.79 (s, 2 H), 4.23 (q and buried s, 6 H), 2.65 (m, 2 H) and 1.27 (t, 6 H). Anal. Calcd for $C_{13}H_{20}O_5$: mol wt, 256.1317. Found: mol wt, 256.1320.

In a similar fashion the following known compounds were prepared.

Diethyl 4-Methyl-3,6-dihydropyran-2,2-biscarboxylate (13b). Isoprene (2.7 mL, 27 mmol) and diethyl ketomalonate (1.82 mL, 12 mmol) were treated as above. After 4 h of heating, identical workup afforded **13b** as a colorless liquid after distillation (2.4 g, 80%). Para:meta isomer ratio was 11:1 as determined by NMR analysis: bp 110 °C (1.0 mm); IR (neat) 5.70 μm; NMR (CCl_4) δ 5.38 (s, 1 H), 4.23 (q and buried s, 6 H), 2.50 (s, 2 H), 1.76 (s, *p*-CH_3), 1.65 (s, *m*-CH_3).

Diethyl 4,5-Dimethyl-3,6-dihydropyran-2,2-biscarboxylate (13c). 2,3-Dimethyl-1,3-butadiene (2.7 mL, 25 mmol) and diethyl ketomalonate (1.82 mL, 12 mmol) were treated as above. After 4 h heating, similar workup afforded **13c** (2.64 g, 86%): bp 120 °C (1.0 mm); IR (neat) 5.72 μm; NMR (CCl_4) δ 4.20 (q and buried s), 2.46 (s, 2 H), 1.68 and 1.52 (2s, 6 H).

Diethyl 6-Methyl-3,6-dihydropyran-2,2-biscarboxylate (13d). Piperylene (2.7 mL, 27 mmol) and diethyl ketomalonate (1.55 mL, 10.2 mmol) were treated as above to afford **13d** (2.19 g, 85%): bp 105 °C (1.5 mm); IR (neat) 5.73 μm; NMR (CCl_4) δ 5.62 (m, 2 H), 4.20 (q and buried m, 5 H), 2.58 (m, 2 H) and 1.30 (m, 9 H). No 3-methyl isomer was detected by NMR analysis.

Diethyl 4,6-Dimethyl-3,6-dihydropyran-2,2-biscarboxylate (13e). 2-Methyl-1,3-pentadiene (4 mL, 40 mmol) and diethyl ketomalonate (2.7 mL, 18 mmol) were treated as above to produce, after 90 min heating, adduct **13e** (4.50 g, 95%): bp 112 °C (1.0 mm); IR (neat) 5.73 μm; NMR (CCl_4) δ 5.38 (m, 1 H), 4.33 (q and buried m, 5 H), 2.58 (m, 2 H), 1.78 (s, 3 H). No 4,6-dimethyl isomer was detected by NMR analysis.

2-Oxa-3,3-dicarboethoxybicyclo[2.2.2]oct-5-ene (13f). 1,3-Cyclohexadiene (2.7 mL, 27 mmol) and diethyl ketomalonate (1.82 ml, 12 mmol) were treated as above. After 4 h heating, similar workup afforded **13f** (2.86 g, 84%): bp 120 °C (0.8 mm); IR (neat) 5.72 μm; NMR (CCl_4) δ 6.43 (m, 2 H), 4.50 (br m, 1 H), 4.15 (m, 4 H), 3.30 (br m, 1 H), 1.6–2.5 (complex m, 4 H).

General Procedure for Hydrolysis of Diester 13 to Diacid 14. To a solution of diester **13a** (0.821 g, 3.4 mmol) in 30 mL of THF was added 30 mL of 10 N KOH and the resulting mixture was stirred at room temperature for 30 h. Acidification to pH 1 with 2 N HCl was followed by thorough extraction with Et_2O and the combined organic extracts were dried over Na_2SO_4. Complete removal of solvent afforded 3,6-dihydropyran-2,2-biscarboxylic acid (**14a**) as a golden viscous oil (0.50 g, 80%) (dry by NMR analysis) which resisted numerous crystallization attempts: IR (Et_2O) 5.78 μm; NMR ($CDCl_3$) δ 5.78 (s, 2 H), 4.42 (s, 2 H) and 2.78 (s, 2 H).

4-Methyl-3,6-dihydropyran-2,2-biscarboxylic Acid (14b). Diester **13b** (0.968 g, 4 mmol) was treated as above. The resulting diacid **14b** was also obtained as a golden viscous oil (0.670 g, 85%): IR (neat) 5.75 μm; NMR ($CDCl_3$) δ 5.57 (s, 1 H), 4.53 (s, 2 H), 2.78 (s, 2 H), 1.90 (s, *p*-vinyl CH_3) and 1.88 (*m*-vinyl CH_3).

4,5-Dimethyl-3,6-dihydropyran-2,2-biscarboxylic Acid (14c). Diester **13c** (2.640 g, 10.3 mmol) was treated as above. Diacid **14c** was isolated as crystals and recrystallization from Et_2O–petroleum ether afforded 1.80 g (87%) of product: IR (CH_2Cl_2) 5.75 μm; NMR ($CDCl_3$) δ 4.25 (s, 2 H), 2.63 (s, 2 H) and 1.70, 1.55 (2s, 6 H).

6-Methyl-3,6-dihydropyran-2,2-biscarboxylic Acid (14d). Diester **13d** (2.187 g, 9.5 mmol) was treated as above. Diacid **14d** was obtained as a powdery solid after recrystallization (1.38 g, 78%): NMR ($CDCl_3$) δ 5.75 (m, 2 H), 4.67 (br m, 1 H), 2.72 (ABq, J_{AB} = 15 Hz, 2 H) and 1.33 (d, *J* = 6 Hz, 3 H).

4,6-Dimethyl-3,6-dihydropyran-2,2-biscarboxylic Acid (14e). Diester **13e** (4.50 g, 16.9 mmol) was treated as above to afford diacid **14e** (3.24 g, 90%) as a powder: NMR ($CDCl_3$) δ 5.35 (m, 1 H), 4.58 (br m, 1 H), 2.65 (ABq, J_{AB} = 18 Hz, 2 H), 1.78 (s, 3 H) and 1.30 (d, *J* = 6 Hz, 3 H).

2-Oxa-3,3-dicarboxybicyclo[2.2.2]oct-5-ene (14f). Diester **13f** (2.50 g, 8.8 mmol) was treated as above to generate diacid **14f** (1.78 g, 90%) as a powder: IR (CH_2Cl_2) 5.68 μm; NMR ($CDCl_3$) δ 6.10 (complex m, 2 H), 5.17 (br m, 1 H), 2.7 (br m, 1 H).

Lactone Carbonyl Release—Representative Procedures. 3,4-Dimethyl-3,4-dehydrovalerolactone (15c). Lead Tetraacetate Oxidation. Lead tetraacetate (1.00 g, 2 mmol, 90% in acetic acid) was added to a flask containing a suspension of excess anhydrous NaOAc in 2 mL of dry benzene and 1 mL of glacial HOAc. The mixture was then heated to 65 °C. Diacid **14c** (0.10 g, 0.5 mmol) was dissolved in 2 mL of glacial HOAc and then introduced into the preheated mixture. Immediate CO_2 evolution was observed and the oxidation was allowed to proceed for 1 h.

Upon cooling, the resulting white suspension was extracted with Et_2O and washed with water, neutralized with aqueous $NaHCO_3$, washed with brine, and dried over $MgSO_4$. After concentration and Kugelrohr distillation of the residue, lactone **15c** was recovered in 63% yield (0.040 g, yield based on diacid): bp 105 °C (1.0 mm); IR (neat) 5.75, 5.98 μm; NMR (CCl_4) δ 4.60 (s, 2 H), 2.85 (s, 2 H) and 1.70 (s, 6 H); *m/e* 126, 110, 108, 82, 69, 67, 55, 54, 53. Anal. Calcd for $C_7H_{10}O_2$: mol wt, 126.0681. Found: mol wt, 126.0667.

Trimethylsilyl Azide Method. To a stirring suspension of diacid **14c** (0.1 g, 0.5 mmol) in 25 mL of benzene containing a catalytic amount of pyridine was added 0.254 g (2 mmol) of oxalyl chloride. The reaction mixture was heated at reflux temperature until formation of acid chloride was complete, i.e., 2 h (IR, 5.59 μm). After removal of solvent and traces of oxalyl chloride, the acid chloride was dissolved in cyclohexane and heated to reflux. A solution of trimethylsilyl azide (0.180 g, 1.5 mmol) in 5 mL of cyclohexane was then added. Isocyanate formation was accomplished in about 40–50 min (IR, 4.40 and 4.46 μm).

After the product was allowed to cool, 10 mL of a 2:1 HOAc–H_2O solution was added and the mixture was stirred for 1 h at 25 °C. Following thorough Et_2O extraction, the combined organic portions were washed with water, neutralized with aqueous $NaHCO_3$, washed with brine, and dried over $MgSO_4$. Concentration afforded lactone **15c** in 57% yield (0.035 g, based on diacid).

Sodium Azide Method. (These bisacyl azides are potentially explosive and should be handled behind a safety shield.) The bisacid chloride of diacid **14c** (0.189 g, 0.95 mmol) was prepared as above using 0.30 g (2.3 mmol) of oxalyl chloride. After isolation of the crude product, the resulting oil was redissolved in dry acetonitrile (25 mL) and activated sodium azide[25] (0.25 g, 3.8 mmol) was added. The suspension was stirred at room temperature for 45 min (IR 4.67, 5.81, and 5.85 μm).

The reaction mixture was quickly filtered and then concentrated at room temperature under reduced pressure to afford a gummy golden residue of the bisacyl azide. (CAUTION! The bisacyl azide is shock sensitive. Cover with solvent before introduction of magnetic stirring bar.)

Curtius rearrangement was effected as before by vigorously stirring the insoluble residue in dry cyclohexane at reflux temperature. Formation of the insoluble bisisocyanate normally required 45–50 min (IR 4.40 and 4.46 μm). After concentration and redissolution in THF, hydrolysis was accomplished using 3 mL of 5% aqueous oxalic acid and stirring at 25 °C for 1 h.

Isolation of lactone **15c** was performed according to the same procedure as above generating 0.086 g (72%, based on diacid) of the desired compound.

3,4-Dehydrovalerolactone (15a). The sodium azide method was employed as above. Diacid **14a** (0.5 g, 2.8 mmol) afforded 0.120 g (52%) of the desired lactone **15a**. Hydrolysis time was shortened to 40 min: bp 97–100 °C (0.8 mm); IR (neat) 5.69 μm; NMR (CCl_4) δ 5.88 (s, 2 H), 4.83 (m, 2 H), and 2.98 (m, 2 H); *m/e* 98, 70, 54, 43, 39. Anal. Calcd for $C_5H_6O_2$: mol wt, 98.0368. Found: mol wt, 98.0404.

3-Methyl-3,4-dehydrovalerolactone (15b). The sodium azide method was employed as above. Diacid **14b** (0.130 g, 0.7 mmol) generated 0.042 g, (60%) of the desired lactone **15b**. Hydrolysis time was 50 min: bp 100–102 °C (1.0 mm); IR (neat) 5.76 μm; NMR (CCl_4) δ 5.60 (s, 1 H), 4.79 (s, 2 H), 2.91 (s, 2 H) and 1.80 (s, 3 H); *m/e* 112, 84, 82, 69, 55, 41. Anal. Calcd for $C_6H_8O_2$: mol wt, 112.0524. Found: mol wt, 112.0518.

3,5-Dimethyl-3,4-dehydrovalerolactone. (15e). The sodium azide method was employed as above. Diacid **14e** (0.2 g, 1 mmol) afforded 0.034 g (30%) of the desired lactone **15e**. Hydrolysis time was

45 min: bp 98–101 °C (1.0 mm); IR (neat) 5.74 μm; NMR (CCl_4) δ 5.58 (m, 1 H), 5.10 (m, 1 H), 2.98 (m, 2 H), 1.80 (s, 3 H) and 1.45 (d, 3 H); *m/e* 126, 110, 98, 83, 67, 55, 43. Anal. Calcd for $C_7H_{10}O_2$: mol wt, 126.0681. Found: mol wt, 126.0674.

3-Methylhexa-2,4-dienoic Acid (16e). Upon concentration of the crude parent lactone **15e** during the isolation procedure above, a solid appeared. Following addition of 5 mL of Et_2O, the supernatant containing the lactone was removed. Recrystallization of the solid from $CHCl_3$–Et_2O produced the dienoic acid **16e** (0.036 g, 34%): mp 119–121 °C; IR (CH_2Cl_2) 5.87 μm; NMR ($CDCl_3$) δ 7.58 (m, 1 H),[28] 6.60–5.46 (m, 3 H, vinyl H and OH) and 1.97 (m, 6 H). Anal. Calcd for $C_7H_9O_2$: (M − 1)/*e*, 125.0602. Found: (M − 1)/*e*, 125.0586.

Hexa-2,4-dienoic Acid (16d). The sodium azide method was employed as above using diacid **14d** (0.186 g, 1 mmol). Following hydrolysis, extraction and isolation afforded the dienoic acid **16d**, presumably a mixture of isomers, after recrystallization from $CHCl_3$–Et_2O (0.061 g, 55%). No lactone precursor was found: mp 115–117 °C; NMR ($CDCl_3$) δ 7.43 (m, 1H),[28] 6.60–5.50 (complex m, 4 H, vinyl H and OH), and 1.82 (d, 3 H); *m/e* 112, 111, 92, 67, 41, 29. Anal. Calcd for $C_6H_8O_2$: mol wt, 112.0524. Found: mol wt, 112.0514.

Bicyclic Lactone (15f). The sodium azide method was used as shown above. Diacid **14f** (0.35 g, 1.7 mmol) afforded the bisacid chloride (5.58 μm) after 24 h at reflux, then the bisacyl azide (4.63 and 5.81 μm) and the bisisocyanate (4.39 and 4.43 μm). Lactone carbonyl release was effected by dissolution of the bisisocyanate in 20 mL of THF followed by addition of 10 mL of 5% aqueous $NaHCO_3$. After stirring at 25 °C overnight, the biphasic mixture was acidified to pH 2 and thoroughly extracted into Et_2O. Drying (Na_2SO_4) and concentration led to recovery of a golden oil. Evaporative distillation afforded the lactone **15f** as a colorless liquid (0.015 g, 7% from diacid): IR (neat) 5.71, 6.20, 11.48 μm; NMR (CCl_4) δ 6.50 (m, 2 H), 5.10 (br m, 1 H), 3.40 (br m, 1 H) and 1.35–2.30 (complex m, 4 H); *m/e* 124, 96, 80, 79, 78, 77, 68. Anal. Calcd for $C_7H_8O_2$: mol wt, 124.0524. Found: mol wt, 12.0558.

***cis*-2,3-Dimethylpent-2-ene-1,5-diol (17).** To a suspension of lithium aluminum hydride (0.046 g, 1.2 mmol) in 40 mL of dry THF at 25 °C was slowly added a THF solution of lactone **15c** (0.126 g, 1 mmol). The reduction was allowed to proceed overnight. After addition of 2 mL of 10% aqueous NaOH, followed by stirring for 10 min, the contents were repeatedly extracted into Et_2O. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated to afford diol **17** (0.114 g, 96%) as a colorless oil which needed no further purification: IR (neat) 3.0 and 6.04 μm; NMR (CCl_4) δ 4.47 (s, 2 H), 3.93 (s, 1 H), 3.57 (t, 2 H), 2.29 (t, 2 H), 1.76 and 1.70 (2s, 6 H); *m/e* 130, 112, 97, 84, 82, 67, 55. Anal. Calcd for $C_7H_{14}O_2$: mol wt, 130.0994. Found: mol wt, 130.0982.

2,3-Dimethyl-2,3-dehydrovalerolactone (18). A solution of diol **17** (0.038 g, 0.29 mmol) in 6 mL of CH_2Cl_2 was stirred at room temperature. Excess activated manganese dioxide (0.35 g, 4 mmol) was slowly added and the mixture was stirred overnight. Isolation of lactone **18** was accomplished by dilution of the suspension with 10 mL of CH_2Cl_2 and then filtration through Celite. After removal of solvent, the product was obtained in 80% yield (0.029 g): IR (neat) 5.83 μm; NMR (CCl_4) δ 4.27 (t, 2 H), 2.38 (t, 2 H), 1.96 and 1.86 (2s, 6 H); *m/e* 126, 96, 81, 68, 67, 53, 41. Anal. Calcd for $C_7H_{10}O_2$: mol wt, 126.0681. Found: mol wt, 126.0678.

3,4-Dimethyl-2(*Z*),4-pentadienoic Acid (16c). Potassium hydride (0.03 g, 1 mmol, 24% in oil) was washed three times with petroleum ether and then suspended in 10 mL of THF. A solution of lactone **15c** (0.063 g, 0.5 mmol) was added to the stirring mixture with immediate evolution of H_2 accompanied by formation of a pale yellow solid. Following acidification with dilute HCl, the contents were extracted with Et_2O and the organic layer was washed with water and brine and then dried over Na_2SO_4. After removal of solvent, feathery white crystals were isolated. Recrystallization from $CHCl_3$–Et_2O afforded the *cis*-dienoic acid **16c** in 98% yield (0.062 g): mp 54.5–56 °C; IR (CH_2Cl_2) 5.89, 6.05, and 6.08 μm; NMR ($CDCl_3$) δ 5.68 (m, 1 H), 4.88 (m, 1 H), 4.70 (m, 1 H), and 1.98 (m, 6 H); *m/e* 126, 125, 111, 79, 55, 53. Anal. Calcd for $C_7H_{10}O_2$: mol wt, 126.0681. Found: mol wt, 126.0677.

3,4-Dimethyl-3,4-epoxyvalerolactone (19). A solution of lactone **15c** (0.126 g, 1 mmol) in 20 mL of CH_2Cl_2 was cooled to 0 °C; 100% *m*-chloroperbenzoic acid[29] (0.344 g, 2 mmol) was then added as a solution in CH_2Cl_2. After 4 h, excess oxidizing agent was destroyed with 10 mL of saturated $NaHSO_3$ solution. Isolation was accomplished with CH_2Cl_2 extraction. After neutralization of the organic extract with aqueous $NaHCO_3$ and drying over $MgSO_4$, the solvent was removed to afford white needle crystals (0.120 g, 85%) of epoxide **19**: mp 49–51 °C; NMR (CCl_4) δ 4.28 (ABq, J_{AB} = 12 Hz, 2 H), 2.76 (s, 2 H) and 1.22 (s, 6 H); *m/e* 112, 99, 83, 69, 43. Anal. Calcd for $C_6H_8O_2$ (M − 30): 112.0524. Found: 112.0532. Loss of CH_2O produces the major fragment.

3,4-Dimethyl-4-hydroxy-2-dehydrovalerolactone (20). Epoxide **19** (0.044 g, 0.35 mmol) was dissolved in 10 mL of THF. 1,5-Diazabicyclo[5.4.0]undec-5-ene (DBU) (0.053 g, 0.35 mmol) was introduced into the solution and the reaction was allowed to proceed at 25 °C for 3 h. Dilute HCl (5 mL) was added and the contents of the flask were extracted into CH_2Cl_2. After the organic layer was washed with water and dried over Na_2SO_4, concentration led to recovery of 0.032 g (60%) of hydroxylactone **20** as a colorless liquid: IR (neat) 2.98 and 5.80 μm; NMR ($CDCl_3$) δ 5.74 (m, J_{AX} = 0.7 Hz, 1 H, vinyl H), 4.17 (s, 2 H), 2.74 (br s, 1 H), 2.01 (d, J_{AX} = 0.7 Hz, 3 H, vinyl CH_3) and 1.37 (s, 3 H). Anal. Calcd for $C_7H_{10}O_3$: mol wt, 142.1523. Found: mol wt, 142.1514.

3,4-Dimethyl-3,4-dehydrovalerolactol (21). Lactone **15c** (0.252 g, 2 mmol) was dissolved in 10 mL of dry Et_2O and cooled to −20 °C. Diisobutylaluminum hydride (4 mL, 5.2 mmol, 20% in hexane) was slowly added by syringe to the precooled solution and after 30 min, 2 mL of MeOH was introduced. The mixture was stirred overnight and, after dilution with Et_2O, the organic layer was washed with brine, dried over $MgSO_4$, and filtered through Celite. Concentration led to recovery of the crude product. Purification was accomplished by column chromatographic separation over silica gel. Lactol **21** was eluted with Et_2O and obtained as a colorless liquid (0.18 g, 71%): IR (neat) 2.90 μm; NMR ($CDCl_3$) δ 5.01 (t, 1 H), 3.99 (br s, 2 H), 2.10 (br s, 2 H) and 1.58 (d, 6 H); *m/e* 110, 95, 82, 77, 64, 51, 41. Anal. Calcd for $C_7H_{10}O$: (M − 18), 110.0732. Found: 110.0737. Loss of H_2O produces the major fragment.

Ethyl 5,6-Dimethyl-7-hydroxyhepta-2 (*E*),5(*Z*)-dienoate (22). Lactol **21** (0.064 g, 0.5 mmol) was dissolved in 15 mL of benzene contained in a 25-mL two-neck flask fitted with a reflux condenser. A benzene solution of carboethoxyethylidene triphenylphosphorane was then added to the reaction flask and heated to reflux. After 20 h, the mixture was cooled and then diluted with H_2O. Following extraction with Et_2O and drying over Na_2SO_4, the organic extract was concentrated to furnish the crude product. Preparative thick layer chromatography on silica gel afforded, after development with 1:1 hexane–Et_2O, diene **22** as a colorless liquid (0.058 g, 61%); IR (neat) 2.90, 5.80 and 5.85 μm; NMR ($CDCl_3$) δ 6.95 (d of t, J_{AB} = 14 Hz, J_{AC} = 7 Hz, 1 H), 5.80 (d, 1 H), 3.0 (d, 2 H), 4.20 (m, 5 H), 1.75 (d, 6 H), 1.22 (t, 3 H). Anal. Calcd for $C_{11}H_{18}O_3$: mol wt. 198.2620. Found: mol wt, 198.2603.

Production of Monocarboxylic Acid 24. A solution of diacid **14c** (1.40 g, 7.0 mmol) in 40 mL of dry pyridine containing 1 mL of piperidine was heated at 100 °C for 5 h. After the reaction mixture was allowed to cool, it was diluted with Et_2O and thoroughly extracted with dilute HCl to remove traces of base. The remaining Et_2O layer was washed with H_2O, then with brine, and dried over Na_2SO_4. Removal of solvent led to recovery of the monocarboxylic acid **24** as white crystals (0.940 g, 86%): mp 84.5–85 °C; IR (CH_2Cl_2) 5.72 μm; NMR ($CDCl_3$) δ 4.27 (partially buried t, 1 H), 4.13 (br s, 2 H), 2.30 (br d, 2 H), 1.68 and 1.53 (2s, 6 H); *m/e* 156, 138, 111, 110, 109, 96, 95, 83, 67, 55. Anal. Calcd for $C_8H_{12}O_3$: mol wt, 156.0796. Found: mol wt, 156.0812.

LAH Reduction of 24. LAH (0.5 g, 5 mmol) was suspended in Et_2O and the mixture was stirred at 0 °C for 20 min. An ethereal solution of carboxylic acid **24** (1.1 g, 5.5 mmol) was added dropwise to the hydride suspension and the mixture was then stirred for 2 h at 25 °C. Excess hydride was quenched by cautious addition of H_2O, followed by 10 mL of 0.1 N NaOH. After stirring for 30 min, the contents were extracted with Et_2O. The organic layer was washed with H_2O, then with brine, and dried over $MgSO_4$. Concentration and evaporative distillation led to recovery of 0.58 g (74%) of alcohol **25** as a colorless liquid: bp 105 °C (2 mm); IR (neat) 2.90 μm; NMR (CCl_4) δ 3.94 (br s, 2 H), 3.48 (br s and buried m, 4 H), 1.8–1.96 (br m, 2 H), 1.54 and 1.65 (2s, 6 H). Anal. Calcd for $C_8H_{14}O_2$: mol wt, 142.0998. Found: mol wt, 142.1013.

Preparation of Tosylate 26 and Bromide 27. To a solution of alcohol **25** (0.46 g, 3.2 mmol) in 10 mL of pyridine cooled to 0 °C was added 1.25 g (6.5 mmol) of *p*-toluenesulfonyl chloride. After 8 h at 0 °C, ice chips were added to destroy excess *p*-tosyl chloride, and the product was isolated with Et_2O. Yield of crude tosylate **26**, 0.81 g (83%); IR (CH_2Cl_2) 8.39 and 8.47 μm; NMR (CCl_4) δ 7.23 and 7.67 (centers of 2d of ABq, J_{AB} = 8 Hz, 4 H), 2.40 (s, 3 H).

The crude tosylate (0.81 g, 2.74 mmol) was then dissolved in 30 mL of anhydrous acetone. Lithium bromide (0.952 g, 11 mmol) was added and the solution was heated at reflux for 20 h. The solution was allowed to cool and, after removal of acetone, the residue was extracted with Et_2O. After drying over Na_2SO_4, the organic extract was concentrated to a brown liquid. Filtration through silica gel and Celite

afforded bromide **27** (0.475 g, 85%): IR (CCl_4) 7.98 and 8.08 μm; NMR (CCl_4) δ 3.95 (br s, 2 H), 3.61 (m, 1 H), 3.20–3.30 (m, 2 H), 2.0 (br m, 2 H), and 1.62 and 1.50 (2s, 6 H).

1-Hydroxy-2,3-dimethylhexa-2(*Z*),5-diene (23). Bromide **27** (0.40 g, 1.94 mmol) was dissolved in 25 mL of dry methanol. Activated zinc (2.80 g, prepared by stirring zinc dust for 5 min in glacial HOAc and then washing with several portions of methanol) was then added to the solution and stirred at reflux temperature for 20 h. After the reaction mixture had cooled, it was filtered through Celite to remove the zinc. The product (0.160 g, 67%) was obtained after Et_2O extraction and distillation (bp 92 °C (2 mm)) using a Kugelrohr apparatus: IR (CH_2Cl_2) 2.89, 6.00, and 6.10 μm; NMR (CCl_4) δ 5.37–6.03, 5.0, and 4.79 (3 m, 3 H), 3.96 (s, 2 H), 3.43 (s, 1 H), 2.80 (d, J = 6 Hz, 2 H) and 1.63 and 1.70 (2d, 6 H). Anal. Calcd for $C_8H_{14}O$: mol wt, 126.1045. Found: mol wt, 126.1034.

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Registry No.—*exo*-**3d,** 63797-66-0; *endo*-**3d,** 63797-67-1; *exo*-**3e,** 63864-73-3; *endo*-**3e,** 63864-74-4; **4,** 5044-52-0; (*E*)-**5a,** 63797-68-2; (*Z*)-**5a,** 63797-69-3; (*E*)-**5b,** 63797-70-6; (*Z*)-**5b,** 63797-71-7; (*E*)-**5c,** 63797-72-8; (*Z*)-**5c,** 63797-73-9; (*E*)-**5d,** 28764-49-0; (*Z*)-**5d,** 28764-48-9; (*E*)-**5e,** 63797-74-0; (*Z*)-**5e,** 63797-75-1; (*E*)-**6,** 63797-76-2; (*Z*)-**6,** 63797-77-3; 6 semicarbazide, 63797-78-4; **7,** 19386-05-1; (*E*)-**8,** 63797-79-5; (*Z*)-**8,** 63797-80-8; **9,** 54222-72-9; **10,** 2220-40-8; **12,** 609-09-6; **13a,** 24588-58-7; **13b,** 24588-59-8; **15a,** 26677-08-7; **15b,** 10021-22-4; **15c,** 22937-02-6; **15e,** 22936-96-5; **16c,** 63797-81-9; (*E*)-**16d,** 110-44-1; (*Z*)-**16d,** 5309-57-9; (*E*)-**16e,** 63797-82-0; (*Z*)-**16e,** 26050-06-6; **17,** 63797-83-1; **18,** 57668-96-9; **19,** 63797-84-2; **20,** 63797-85-3; **21,** 63797-86-4; **22,** 63797-87-5; **23,** 63797-88-6; **24,** 27944-71-4; **25,** 63797-89-7; **26,** 63797-90-0; **27,** 63797-91-1; carboethoxyethylidenetriphenylphosphorane, 1099-45-2; diethyl 5-methyl-3,6-dihydropyran-2,2-biscarboxylate, 63797-92-2.

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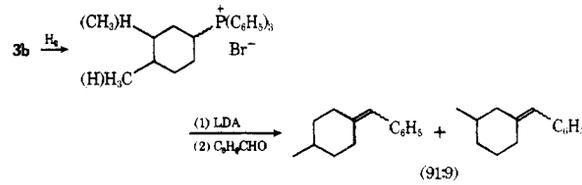

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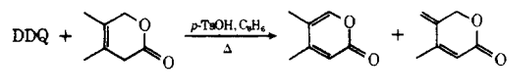

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