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Abnormal Nazarov Reaction. A New Synthetic Approach to 2,3-Disubstituted 2-Cyclopentenones

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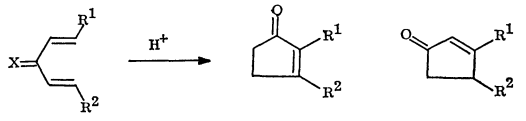
Acid-catalyzed reaction of β,β′-disubstituted cross conjugated dienones or the corresponding ethylene acetals gives mainly 2,3-disubstituted 2-cyclopentenones in stead of the simple Nazarov cyclization products, 3,4-disubstituted 2-cyclopentenones. This transformation is explained in terms of electrocyclic ring-closure, addition of hydroxylic solvent(s), tautomerization of the resulting 2-hydroxycyclopentanone intermediates, followed by solvolysis and isomerization. Based on this working hypothesis a new route to jasmonoids is disclosed which involves acid-treatment of the acyloin disilyl ethers derived from substituted glutarates.

Conjugated cyclopentenones[1] are the key compounds for the synthesis of natural products such as jasmonoids,[2] prostanoids,[3] and muscone[4] as well as of [*n*]-metacyclophanes.[5] Among various kinds of approach[1] to 2-cyclopentenones the Nazarov reaction[6] seemed attractive with respect to its simple operation, ready availability of the starting material and also to the mechanistic view point. We have studied the acid-catalyzed cyclization of β,β′-disubstituted cross-conjugated dienones or their ethylene acetals and observed the cyclization accompanied by transposition of the carbonyl group.[7] This unusual Nazarov reaction led us to explore an additional route to 2,3-disubstituted 2-cyclopentenones from 2-hydroxycyclopentanones or their enol disilyl ethers.

Acid-catalyzed Cyclization of Cross-conjugated Dienones ***1*** *or Their Ethylene Acetals* ***2*** *to 2-Cyclopentenones* ***3***. The starting dienones **1a**, **1b**, **1d** were prepared by usual hydrolysis of the corresponding ethylene acetals **2**[8] obtained by dibromination[9] and duplicated dehydrobromination of the saturated ketone acetals. Upon exposure to acidic conditions either **1** or **2**[10] afforded 2,3-dialkyl-2-cyclopentenones **3** in good yield (Scheme 1). Two acid systems, namely (A) phosphoric acid–formic acid (1:1) and (B) hydrobromic acid–acetic acid (1:3), were studied and the results are summarized in Table 1. Depending on the conditions and the substrates the Nazarov products, 3,4-dialkyl-2-cyclopentenones **4**, were produced to some extent, whose formation is understood by deprotonation of the oxyallyl cation **6** (Scheme 2) which is derived from the oxypentadienyl cation **5**[11] by electrocyclic conrotatory ring closure. The formal "shift" of the carbonyl group in the production of **3** is rationalized by assuming the attack of the hydroxylic solvents, such as water or carboxylic acids, onto **6** to yield **7**, which is subsequently converted to acyloin (and/or equivalents) **8** by tautomerization. Elimination of hydroxyl group

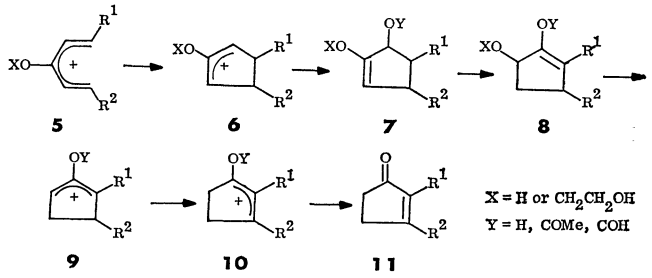


1, X=O
2, X=OCH_2CH_2O

3 **4**

a, $R^1=R^2=Et$
b, $R^1=R^2=-(CH_2)_7-$
c, $R^1=R^2=-(CH_2)_5-$
d, $R^1=n\text{-}C_5H_{11}$, $R^2=H$

Scheme 1.



5 **6** **7** **8**

9 **10** **11**

X = H or CH_2CH_2OH
Y = H, COMe, COH

Scheme 2.

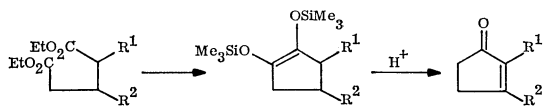
Table 1. 2-Cyclopentenones *via* acid-catalyzed cyclization of cross-conjugated dienones and the corresponding ethylene acetals

Starting material	Procedure[a]	Product (yield/%)[b]	
		3a	**4a**
1a (X = O)	A	77	–
	B	55 (41)[c]	15 (11)[c]
2a (X = OCH_2CH_2O)	A	67	–
	B	43	9
		3b	**4b**
1b (X = O)	B	41[c]	5[c]
2b (X = OCH_2CH_2O)	A	67 (63)[c]	–
	B	55	6
		3c	**4c**
2c (X = OCH_2CH_2O)	A	58	6
	B	47	37
		3d	**4d**
1d (X = O)	A[d]	18	2
2d (X = OCH_2CH_2O)	A	14	1

a) Details are in the experimental part. b) Estimated by GLC unless otherwise stated. c) Isolation yield. d) Treatment of **1d** with phosphoric acid gave **3d** (22%) and **4d** (13%).

and isomerization of the resulting oxyallyl cation **9** afford the most stable one **10**, deprotonation of which should give **3**. The driving force of this cyclopentenone formation is ascribed to the thermal cyclization of pentadienyl cation **5** to cyclopentenyl cation **6** and the subsequent isomerization to the most stable allylic cation **10**. Notably, when the reaction was carried out in less nucleophilic solvent or procedure B, the yield of the by-product **4** increased considerably. Hereby deprotonation of **6** is probably competing with the solvent attack. Previous study on the Nazarov reaction[6] has dealt only with α,β-disubstituted cross-conjugated dienone system wherein the cyclized form **6** is easily deprotonated to give a thermodynamically most favorable dienone of type **4**. The β,β'-disubstituted dienones studied here appear to have never been subjected to the acidic conditions before.[12] The proposed mechanism has been confirmed by the regioselective dehydration of alternatively synthesized **8** affording **3** as described below.

Regioselective Synthesis of 2-Cyclopentenones **3** via *Acid-catalyzed Dehydration of 2-Hydroxycyclopentanones.* In general, acyloins are hardly dehydrated to the corresponding α,β-enones. However, the proposed mechanism shown in Scheme 2 involves dehydration of the acyloin (and/or equivalents) **8**. In order to verify this 2,3-dialkylglutarates **11** were transformed to enediol disilyl ethers **12**, which were exposed to phosphoric acid. Both hydrolysis and dehydration[14] took place in one pot to give 2,3-dialkyl-2-cyclopentenones **3**. The results are summarized in Table 2. Disilyl ethers **12d** and **12e** were preferentially transformed to **3d** and **3e** respectively and their regioisomers **4d**, **4e**, were not isolated (entry 1, 2). This process gives dihydrojasmone (**3f**) in good yields. The substrates having olefinic appendage turned out rather unstable under these conditions and gave allethrone (**3g**) and *cis*-jasmone (**3h**) in somewhat lower yields.[15]



11 **12** **3**

d: $R^1=n\text{-}C_5H_{11}$, $R^2=H$
e: $R^1=Me$, $R^2=H$
f: $R^1=n\text{-}C_5H_{11}$, $R^2=Me$
g: $R^1=CH_2{=}CHCH_2$, $R^2=Me$
h: $R^1=cis$-2-pentenyl, $R^2=Me$

Scheme 3.

Experimental

All the temperatures are uncorrected. PMR spectra were taken on a JEOL JNM-PMX 60 or Varian EM 390 spectrometer and chemical shifts are recorded in ppm unit. IR spectra were recorded on a Shimadzu IR-27G spectrometer, and MS on a Hitachi RMU-6L spectrometer with 70 eV.

Dibromination of Ketone Ethylene Acetals. A General Procedure. Bromine (100 mmol) was added dropwise to a solution of the saturated ketone acetal (50 mmol) in dry ether (100 ml) under cooling with water bath. The mixture was neutralized with monosodium ethylene glycolate (prepared from sodium (2.5 g) and ethylene glycol (100 ml)) and worked up as usual. The yield and physical properties of α,α'-dibromo ketone ethylene acetals are given in the following order: R^1, R^2 of $R^1CHBrC(O_2C_2H_2)CHBrCH_2R^2$, yield(%), bp or mp, IR, PMR, elemental analysis. $R^1=R^2=Et$ (see Ref. 9). R^1, $R^2=-(CH_2)_7-$, 99%, mp 133—134 °C (ethyl acetate), IR (Nujol): 1185, 1047, 957 cm^{-1}, PMR ($CDCl_3$): δ 1.1—2.2 (m, 18H), 4.35 (s, 4H), 4.48 (t, 2H), (Found: C, 43.8; H, 6.4%. Calcd for $C_{14}H_{24}Br_2O_2$: C, 43.8; H, 6.3%). R^1, $R^2=-(CH_2)_5-$, 100%, mp 76—77.5 °C (ethyl acetate), IR (Nujol): 1045, 949 cm^{-1}, PMR ($CDCl_3$): 1.3—1.9 (m, 10H), 2.0—2.5 (m, 4H), 4.4 (s, 4H), 4.70 (t, $J=6$ Hz, 2H), (Found: C, 40.3; H, 5.7%. Calcd for $C_{12}H_{20}Br_2O_2$: C; 40.5; H, 5.7%). $R^1=n\text{-}C_5H_{11}$, $R^2=H$, *ca.* 96%, bp 135 °C/0.08 Torr, IR (neat): 1198, 1076, 954 cm^{-1}, PMR (CCl_4): 0.7—1.1 (m, 3H), 1.70 (d, $J=6.5$ Hz, 3H), 1.1—2.0 (m, 10H), 4.25 (s, 4H), 4.0—4.7 (m, 2H), (Found: C, 40.0; H, 6.5%. Calcd for $C_{12}H_{22}Br_2O_2$: C, 40.3; H, 6.2%).

Cross-conjugated Dienone Ethylene Acetals **2**. A solution of α,α'-dibromo acetal (30 mmol) dissolved in dry DMSO (120 ml) was admixed with finely powdered potassium *t*-butoxide (100 mmol) and the mixture stirred for 3 h at room temperature for acyclic bromides or at 50 °C for cyclic ones. The resulting dark-brown mixture was treated with water (200 ml) and the product extracted with benzene. Product, yield (%) were as follows: **2a**, 88; **2b**, 97; **2c**, 91; **2d**, 85 (based on the acetal). Physical properties of these are listed in Table 3.

Cross-conjugated Dienones **1**. Dienone acetal **2** (5 mmol) dissolved in THF (30 ml) was vigorously shaken with 10% sulfuric acid at room temperature for 2 h. The resulting mixture was saturated with sodium chloride and the product was extracted with ether. Product, yield (%): **1a**, 97; **1b**, 96; **1d**, 62. Physical properties are summarized in Table 3.

Acid-catalyzed Cyclization of Cross-conjugated Dienones **1** *or Their Ethylene Acetals* **2** *into 2-Cyclopentenones* **3**. *Procedure A*: A mixture of dienone **1** or its ethylene acetal **2** (1.0 mmol), 85% phosphoric acid (2.5 ml), and 90% formic acid (2.5 ml) was stirred at 90 °C for 2—3 h under a nitrogen atmosphere. The resulting brown solution was quenched with water (15 ml) and stirred for additional 0.5 h. After extraction with benzene the extract was washed with water, aq sodium hydrogencarbonate solution and brine, then dried over sodium sulfate. Preparative TLC on silica gel or GLC (SE 30 or Dowfax 9N9 on Chromosorb) gave pure **3** and **4** (Table 1). The structural assignment is based upon either comparison with the respective authentic samples or spectrometric analysis (see Table 4).

TABLE 2. 2-CYCLOPENTENONES *via* DEHYDRATION OF 2-HYDROXYCYCLOPENTANONE DERIVATIVES

Entry	Glutarate	2-Hydroxycyclopentanone enol disilyl ether Yield/%[a]	2-Cyclopentenone Yield/%[a]
1	**11d**	**12d**, 80	**3d**, 64
2	**11e**	**12e**, 87	**3e**, 73[b]
3	**11f**	**12f**, 85	**3f**, 74
4	**11g**	**12g**, 81	**3g**, 46
5	**11h**	**12h**, 81	**3h**, 39[c]

a) Isolation yield. b) The dehydration was carried out by simple distillation. c) This was prepared by the acid hydrolysis and the subsequent treatment of the resulting acyloin with *p*-toluenesulfonic acid in *N,N*-dimethylformamide at 60 °C for 20 h.

Table 3. Physical properties of dienones **1** and their ethylene acetals **2**

Compound	Bp (°C/Torr)	IR (cm^{-1})[a]	PMR (δ)[b]
1a[c]	100/14	1669, 1640, 1617 1199, 980	1.12 (t, J=7 Hz, 6H), 2.27 (td, J=7, 1 Hz, 4H), 6.22 (dt, J=15, 1 Hz, 2H), 6.88 (dt, J=15, 6 Hz, 2H)
1b[d]	110/0.4	1657, 1224, 992 744	0.9—1.9 (m, 10H), 1.9—2.7 (m, 4H), 5.45—6.37 (m, 2H), 6.13 (dd, J=16, *ca.* 1 Hz, 1H), 6.89 (dt, J=16, 6.5 Hz, 2H)
1d[e]	80/3.5	1668, 1635, 1614 1216, 986	0.7—1.1 (m, 3H), 1.1—1.7 (m, 6H), 2.2—2.5 (m, 2H), 5.6—7.1 (m, 5H)
2a[f]	95/13	1671, 1037, 968	1.0 (t, J=6.5 Hz, 6H), 1.6—2.35 (m, 4H), 3.65 (s, 4H), 4.8—5.7 (m, 4H)
2b[g]	125/5	3024, 1036, 978	1.0—1.8 (m, 10H), 1.8—2.7 (m, 4H) 3.84 (m, 4H), 5.2—6.2 (m, 4H)
2c[h]	150/5	1177, 1043, 979, 729	0.9—2.8 (m, 10H), 3.90 (s, 4H), 5.1—6.1 (m, 4H)
2d[i]	90/5	1672, 1057, 939	0.7—1.1 (m, 3H), 1.0—1.6 (m, 6H), 1.8—2.3 (m, 2H), 3.80 (s, 4H), 5.0—6.0 (m, 5H)

a) Neat liquid film. b) Recorded in CCl_4 solution. c) MS *m/e* (rel intensity): 139 (M^+, 9), 83 (100). Found: C, 78.3; H, 10.0%. Calcd for $C_9H_{14}O$: C, 78.2; H, 10.2%. d) MS *m/e* (rel intensity): 178 (M^+, 12), 107 (100), 81 (98). Found: C, 80.9; H, 9.9%. Calcd for $C_{12}H_{18}O$: C, 80.9; H, 10.2%. e) MS *m/e* (rel intensity): 152 (M^+, 1), 55 (100). Found: C, 78.7; H, 10.4%. Calcd for $C_{10}H_{16}O$: C, 78.9; H, 10.6%. f) MS *m/e* (rel intensity): 182 (M^+, 1), 127 (100), 83 (53). Found: C, 72.4; H, 9.8%. Calcd for $C_{11}H_{18}O_2$: C, 72.5; H, 10.0%. g) MS *m/e* (rel intensity): 222 (M^+, 23), 125 (100), 91 (68). Found: C, 75.8; H, 9.8%. Calcd for $C_{14}H_{22}O_2$: C, 75.6; H, 10.0%. h) MS *m/e* (rel intensity): 194 (M^+, 25), 125 (81), 112 (100). Found: C, 74.1; H, 9.4%. Calcd for $C_{12}H_{18}O_2$: C, 74.2; H, 9.3%. i) MS *m/e* (rel intensity): 196 (M^+, 1), 169 (36), 139 (72), 99 (100). Found: C, 73.6; H, 10.5%. Calcd for $C_{12}H_{20}O_2$: C, 73.4; H, 10.3%.

Table 4. Physical properties of cyclopentenones **3** and **4**

Compound	IR (cm^{-1})[a]	PMR (δ)[b]
3a[c]	1698, 1644, 1175, 936	0.97 (t, J=7.5 Hz, 3H), 1.15 (t, J=7.5 Hz, 3H), 1.9—2.7 (m, 8H)
3b[d]	1696, 1646, 1298, 1155 1070	1.2—2.0 (m, 10H), 2.0—2.7 (m, 8H)
3c[e]	1695, 1646, 1286, 1064 990, 816	1.3—2.1 (m, 6H), 2.1—2.7 (m, 8H)
3d[f]	1705, 1633, 1000, 788	0.7—1.1 (t, 3H), 1.0—1.8 (m, 6H), 1.8—2.7 (m, 6H), 7.15 (br s, 1H)
3e[g]	1702, 1640, 1067, 791	1.74 (m, 3H), 2.1—2.7 (m, 4H), 7.3 (m, 1H)
3f[h]	1701, 1640, 1178, 1075	0.90 (t, 3H), 1.0—1.8 (m, 6H), 1.9—2.6 (m+s (δ 2.03), 9H)
3g[i]	1695, 1640	2.00 (s, 3H), 2.1—2.6 (m, 4H), 2.90 (d, J=6.5 Hz, 2H), 4.7—5.1 (m, 2H), 5.3—6.0 (m, 1H)
3h[j]	1700, 1647, 1177, 1070	0.98 (t, J=7.0 Hz, 3H), 2.03 (s, 3H), 1.9—2.65 (m, 6H), 2.85 (d, 2H), 4.9—5.55 (m, 2H)
4a[k]	1685, 1613, 858[l]	0.7—1.4 (m, 6H), 1.5—2.9 (m, 7H), 5.9 (m, 1H)
4b[m]	1682, 1610, 854[l]	1.1—2.0 (m, 12H), 2.0—3.1 (m, 5H), 5.95 (br s, 1H)
4c[n]	1680, 1603, 910,[l] 853	1.1—2.3 (m, 18H), 2.3—3.1 (m, 5H), 5.80 (br s, 1H)
4d[o]	1707, 1677, 1616, 1181 864, 840	0.7—1.1 (m, 3H, 3H), 1.1—1.7 (m, 6H), 2.1—2.7 (m, 6H), 5.8 (m, 1H)

a) Neat liquid film unless otherwise stated. b) Recorded in CCl_4 solution. c) MS *m/e* (rel intensity): 138 (M^+, 100), 123 (69), 109 (74), 95 (38), 81 (72). Found: C, 77.9; H, 10.0%. Calcd for $C_9H_{14}O$: C, 78.2; H, 10.2%. d) Bp 95 °C/2 Torr, MS *m/e* (rel intensity): 178 (M^+, 51), 149 (33), 135 (100); see Ref. 5. e) Bp 104 °C/4 Torr; MS *m/e* (rel intensity): 150 (M^+, 73), 122 (100), 79 (52). Found: C, 79.8; H, 9.3%. Calcd for $C_{10}H_{14}O$; C, 80.0; H, 9.4%. f) Bp 115 °C/3.5 Torr; MS *m/e* (rel intensity): 152 (M^+, 65), 123 (88), 97 (100), see Ref. 2d. g) Bp 135 °C/95 Torr; MS *m/e* (rel intensity): 96 (M^+, 96), 67 (100), see Ref. 11d. h) MS *m/e* (rel intensity): 166 (M^+, 16), 151 (57), 110 (100), see Ref. 2. i) MS *m/e* (rel intensity): 136 (M^+, 100), 121 (88), see Ref. 2d. j) MS *m/e* (rel intensity): 164 (M^+, 67), 149 (52), 110 (59), 79 (73), 55 (100), see Refs. 2a—d. k) MS *m/e* (rel intensity): 138 (M^+, 35), 110 (100), 95 (53). Found: C, 78.3; H, 10.0%. Calcd for $C_9H_{14}O$: C, 78.2; H, 10.2%. l) Determined in $CHCl_3$. m) Bp 150 °C/5 Torr; MS *m/e* (rel intensity): 178 (M^+, 72), 135 (84), 79 (100). Found: C, 80.7; H, 10.0%. Calcd for $C_{12}H_{18}O$: C, 80.9; H, 10.2%. n) MS *m/e* (rel intensity): 150 (M^+, 100), 107 (94). Found: C, 79.7; H, 9.2%. Calcd for $C_{10}H_{14}O$: C, 80.0; H, 9.4%. o) MS *m/e* (rel intensity): 152 (M^+, 24), 96 (100), see P. M. McCurry, Jr., and R. K. Singh, *J. Org. Chem.*, **39**, 2317 (1974).

TABLE 5. PHYSYCAL PROPERTIES OF GLUTARATES **11** AND 1,2-BIS(TRIMETHYLSILYLOXY)CYCLOPENTENES **12**

Compound	Bp (°C/Torr)	IR (cm^{-1})[a]	PMR (δ)[b]
11c	78—80/0.009	1732	0.85 (t, 3H), 0.92 (t, J=6.5 Hz, 6H), 1.0—2.4 (m, 13H), 4.00 (q, J=6.5 Hz, 4H)
11f[d]	140—145/0.2	1736, 1177, 1030	1.27 (t, J=7 Hz, 6H), 0.7—2.5 (m, 18H), 4.08 (q, J=7 Hz, 4H)
11g[e]	145/20	1735, 1643	0.95 (m, 3H), 1.25 (t, J=7 Hz, 6H), 1.8—2.6 (m, 6H), 4.10 (q, J=7 Hz, 4H), 4.8—5.3 (m, 2H), 5.3—6.1 (m, 1H)
11h[f]	115—120/0.07	1737, 1176, 1095 1030	0.9—1.1 (m+t (δ 0.96, J=7.5 Hz), 6H), 1.25 (t, J=7 Hz, 6H), 1.3—2.7 (m, 8H), 4.10 (q, J=7 Hz, 4H), 4.8—5.6 (m, 2H)
12d[g]	95—120/0.15	1702, 1250, 840	0.10 (s, 18H), 0.90 (t, 3H), 1.1—1.9 (m, 10H), 2.0—2.5 (m, 3H)
12e[h]	108/25	1700, 1249, 840	0.15 (s, 18H), 0.95 (d, J=6 Hz, 3H), 1.0—1.4 (m, 1H), 1.8—2.5 (m, 4H)
12f[i]	120/0.2	1704, 1252, 914 843, 754	0.15 (s, 18H), 0.7—2.7 (m, 18H, main peaks at δ 2.2, 1.8, 1.3, 1.1, 0.97, 0.90)
12g[j]	75/4	1697, 1635	0.15 (s, 18H), 1.0 (m, 3H), 1.4—2.8 (m, 6H), 4.8—5.3 m, 2H), 5.3—6.1 (m, 1H)
12h[k]	115—120/0.07	3007, 1703, 1251 841, 753	0.15 (s, 18H), 0.7—2.9 (m, 14H), 5.2—5.7 (m, 2H)

a) Neat liquid film. b) Recorded in carbon tetrachloride solution. c) MS *m/e* 213 (M^+-OEt). Found: C, 64.9; H, 10.2%. Calcd for $C_{14}H_{26}O_4$: C, 65.1; H, 10.1%. d) MS *m/e* (rel intensity): 227 (M^+-OEt, 35), 69 (100). Found: C, 66.0; H, 10.4%. Calcd for $C_{15}H_{28}O_4$: C, 66.1; H, 10.4%. e) MS *m/e* 197 (M^+-OEt). Found: C, 64.2; H, 9.1%. Calcd for $C_{13}H_{22}O_4$: C, 64.4; H, 9.2%. f) MS *m/e* (rel intensity): 225 (M^+-OEt, 46), 196 (80), 109 (100). Found: C, 66.5; H, 9.9%. Calcd for $C_{15}H_{26}O_4$: C, 66.6; H, 9.7%. g) MS *m/e* (rel intensity): 314 (M^+, 13), 293 (55), 91 (100). h) MS *m/e* 258 (M^+). i) MS *m/e* (rel intensity): 328 (M^+, 18), 257 (100). j) MS *m/e* (rel intensity): 298 (M^+, 6), 256 (79), 73 (100). k) MS *m/e* (rel intensity): 326 (M^+, 11), 257 (100).

Procedure B: Dienone **1** or its ethylene acetal **2** (1.0 mmol) was cyclized by treatment with a mixture of 47% hydrobromic acid (2 ml) and acetic acid (6 ml) at 80—90 °C for 2 to 3 h. Work-up and product analysis were carried out as described above.

*2-Cyclopentenone **3** from 2-Hydroxycyclopentanone Enol Disilyl Ether **12**.* A mixture of acyloin disilyl ether **12** (1.0 mmol) and 57% phosphoric acid (4.5 ml) was stirred at 50—60 °C for 1.5—3 h under a nitrogen atmosphere. Work-up followed by preparative TLC on silica gel gave analytically pure **3** (Tables 2 and 4).

Diethyl 2-Alkyl-2-ethoxycarbonyl-3-methylglutarate. Introduction of Allylic Group: Into a suspension of sodium hydride (22 mmol) in dry 1,2-dimethoxyethane (20 ml) diethyl 2-ethoxycarbonyl-3-methylglutarate[16] (5.48 g, 20 mmol) dissolved in the same solvent (10 ml) was added over a period of 10 min under cooling with a water bath. After 1 h allyl bromide or *cis*-2-pentenyl bromide (22 mmol) was added and the mixture was stirred overnight. Work-up gave the desired products: diethyl 2-allyl-2-ethoxycarbonyl-3-methylglutarate, 79% yield, bp 135 °C/5 Torr; IR (neat): 1739, 1635 cm^{-1}; MS *m/e* 269 (M^+-OEt); (Found: C, 61.1; H, 8.5%. Calcd for $C_{16}H_{26}O_6$: C, 61.1; H, 8.3%); diethyl 2-ethoxycarbonyl-3-methyl-2-(*cis*-2-pentenyl)glutarate, 86% yield, bp 130—135 °C/0.07 Torr, IR (neat): 1739, 1728, 1187, 860 cm^{-1}, MS *m/e* 297 (M^+-OEt). (Found: C, 63.2; H, 9.0%. Calcd for $C_{18}H_{30}O_6$: C, 63.1; H, 8.8%).

Reaction with 1-Iodopentane: The anion of the triester was prepared as above and to the anion solution hexamethylphosphoric triamide (30 ml) and successively 1-iodopentane (22 mmol) were added. Work-up gave diethyl 2-pentyl-2-ethoxycarbonyl-3-methylglutarate in 82% yield. Bp 150—160 °C/0.17 Torr; IR (neat): 1735, 1240, 1218, 1189, 1033 cm^{-1}; MS *m/e* 299 (M^+-OEt). Found: C, 62.6; H, 9.4%. Calcd for $C_{18}H_{32}O_6$: C, 62.8; H, 9.4%.

*Diethyl 2-Alkyl-3-methylglutarate (**11**).* A mixture of the above triester (10 mmol) and aqueous sodium hydroxide (50 mmol in 30 ml of water) was vigorously stirred at 100 °C for 10 h, the resulting clear solution being acidified (pH *ca.* 5) with 4 mol dm^{-3} hydrochloric acid and then subjected to thermal decarboxylation at bath temperature as high as 150—160 °C for 3—4 h under a nitrogen atmosphere. The reaction mixture was treated with 6 mol dm^{-3} hydrochloric acid and the separated free dicarboxylic acid was extracted with ether. The crude acid was esterified by treating with refluxing ethanol (50 ml) and benzene (60 ml) in the presence of a catalytic amount of *p*-toluenesulfonic acid under continuous removal of water with molecular sieves (3A). Product, % yield were as follows: **11f**, 84; **11g**, 85; **11h**, 81%. Physical properties of these are listed in Table 5.

*Diethyl 2-Pentylglutarate (**11d**).* Diethyl pentylmalonate[17] (400 mg, 2.0 mmol) was added to sodium hydride (3 mmol) suspended in dimethoxyethane (4 ml) and the resulting mixture was stirred for 30 min. Ethyl acrylate (300 mg, 3 mmol) dissolved in dimethoxyethane (2 ml) was added and the mixture stirred for an additional 30 min. Work-up followed by distillation afforded the recovered malonate (20 mg) and diethyl 2-pentyl-2-ethoxycarbonylglutarate (501 mg, 76% yield based on the consumed starting malonate), bp 120—122 °C/0.01 Torr, IR (neat): 1712 cm^{-1}. Found: C, 61.8; H, 9.3%. Calcd for $C_{17}H_{30}O_6$: C, 61.8; H, 9.2%. Decarboxylation of the triester to **11d** was performed as described above in 67% yield (see Table 5).

*3,4-Dialkyl-1,2-bis(trimethylsilyloxy)cyclopentene (**12**).* To sodium dispersion (276 mg, 12 mmol) stirred vigorously in dry toluene (25 ml) a mixture of glutarate **11** (2.0 mmol), chlorotrimethylsilane (1.30 g, 12 mmol) and toluene (10 ml) was added dropwise over a period of 20 min at 110 °C under an argon atmosphere. After 30 min the insoluble material was filtered off and solvent was evaporated *in vacuo*. Distillation gave the product listed in Table 5.

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