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PREPARATION AND ALUMINUM TRICHLORIDE-INDUCED CATIONIC REARRANGEMENTS OF BICYCLO[2.2.0]HEXENE CARBOXYLIC ESTERS

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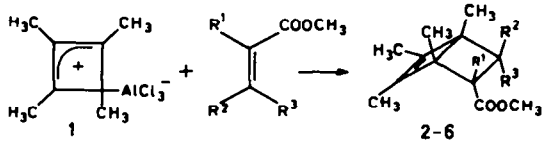
Abstract—Reaction between the tetramethyl[4]annulene aluminum trichloride σ-complex and α,β-alkenic esters gave the corresponding 1,4,5,6-tetramethylbicyclo[2.2.0]hex-5-ene-2-*endo*-carboxylic esters. $AlCl_3$-induced cationic rearrangements of these bicyclic esters yielded a number of bicyclo[3.1.0]hexene carboxylic esters and related lactones which were isolated and identified. The isomerization seems to proceed via stereospecific *endo* protonation and subsequent rearrangement to 2-methoxycarbonyl-1,4,5,6-*exo*-tetramethylbicyclo[3.1.0]hex-4-yl carbocations.

Reaction of tetramethyl[4]annulene[2] (tetramethylcyclobutadiene) aluminum trichloride complex[3-5] (1)—formed by cyclodimerization of 2-butyne in the presence of aluminum trichloride—with appropriate dienophiles constitutes a convenient route to carboxylic esters of tetramethylbicyclo[2.2.0]hexenes[3] and -hexadienes.[3,6,7] Two procedures have been reported:[3] Method A comprises addition of 1 to a solution of the dienophilic ester in the presence of dimethyl sulphoxide (DMSO). The transfer of aluminum trichloride to DMSO results in the liberation of tetramethyl[4]annulene and its subsequent Diels–Alder reaction. Method B involves direct addition of the dienophilic ester to a solution of 1. Superior yields have been reported for this procedure.[3] However, aluminum trichloride remains present in the product mixture, mainly as an ester complex, which is an obvious disadvantage with acid-sensitive bicyclic products.

In the present paper we report on the reaction of 1 with α,β-alkenic monoesters. The resulting bicyclo-[2.2.0] hex-5-ene-2-*endo*-carboxylic esters were rather prone to rearrange to isomeric bicyclic esters as well as to lactones under the conditions of method B. The structure of the products has been elucidated and provides a basis for the discussion of the mechanism of the rearrangements.

Preparation of bicyclo[2.2.0]hexene carboxylic esters

Reaction of 1 with a number of α,β-alkenic esters afforded the corresponding 2-*endo*-methoxycarbonyl-1,4,5,6-tetramethylbicyclo[2.2.0]hex-5-enes 2–6 (Scheme 1). The cycloaddition reactions of 1 seem to follow the *endo* rule for Diels–Alder reactions,[8] since no products with the ester group in *exo* position could be detected. Some further aspects are discussed below.

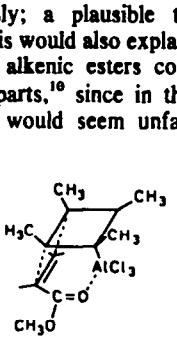


	2	3	4	5	6
R^1	H	H	H	CH_3	H
R^2	H	H	CH_3	H	C_6H_5
R^3	H	CH_3	H	H	H

Scheme 1.

Method A. The decomposition of 1 by DMSO in the presence of a dienophile will obviously lead to competition between reaction of the liberated tetramethyl[4]annulene with itself—yielding dimers and related products—and reaction with the dienophile. When the reaction temperature was raised the latter reaction became more competitive,[9] but the tendency of the product to isomerize was increased. Methyl acrylate was sufficiently reactive to give useful yields of the adduct 2 upon reaction at 0° (selected yields are tabulated in the Experimental). Higher reaction temperatures were advantageous for the less reactive alkenic esters; thus, the preparations of 4 and 6 were carried out in refluxing benzene.

Method B. The preparation of 3–5 according to method B required low temperatures (below −25°) in order to avoid the aluminum trichloride-induced isomerization of the products; 2 isomerized even under these conditions. However, the related compound 2-*endo*-cyano-1,4,5,6-tetramethylbicyclo[2.2.0]hex-5-ene (7) could be prepared with this procedure. The yields of 3–6 were consistently higher than the yields which could be obtained with method A. It would seem, therefore, that aluminum trichloride exerts a strongly activating effect on the dienophile. Addition of 1 to the dienophilic esters (reaction of 1 in the presence of an excess of dienophile) gave the same yields. We suggest that the abstraction of aluminum trichloride and the Diels–Alder reaction proceed simultaneously; a plausible transition state is depicted below. This would also explain the higher yields obtained with the alkenic esters compared with their acetylenic counterparts,[10] since in the latter case synchronous reaction would seem unfavourable for geometric reasons.



$AlCl_3$-Induced cationic rearrangements

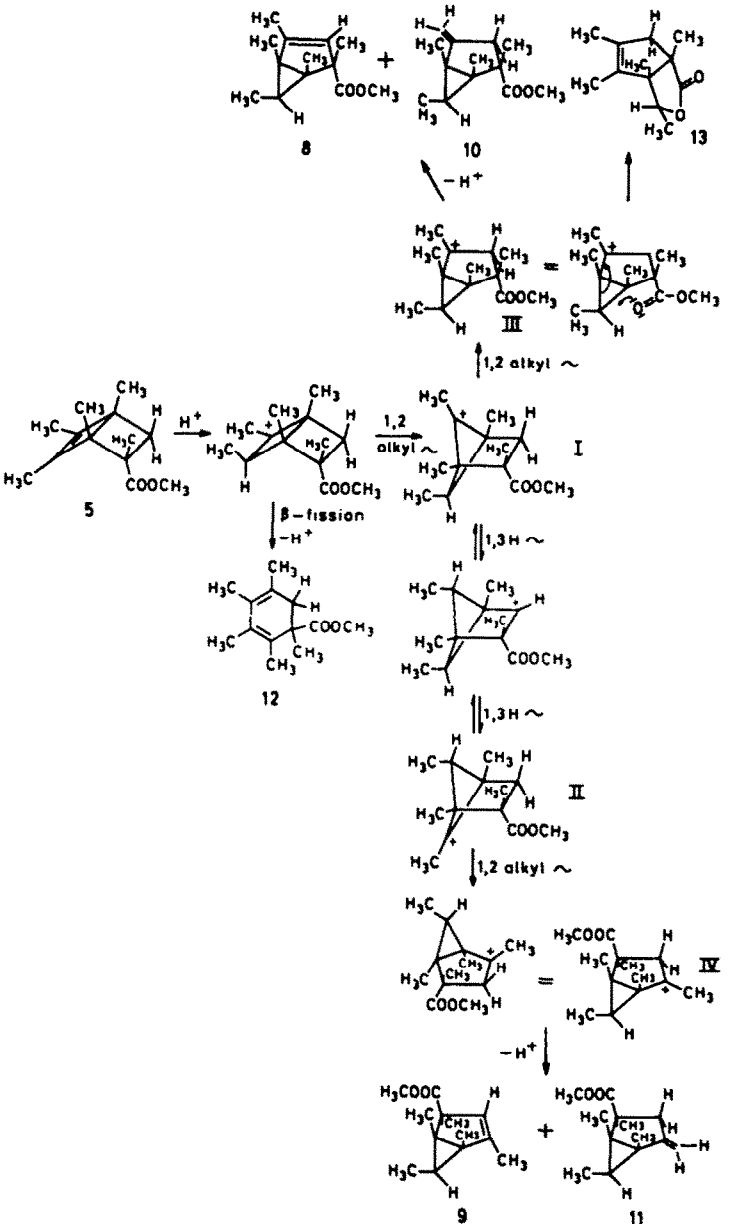
In the course of the preparation of compounds 2–5 according to method B, the tendency of these compounds to undergo cationic rearrangements became apparent, particularly upon prolonged reaction times at −15°. The rearrangements in the presence of "an-

hydrous" aluminum trichloride reflect a general sensitivity of 2–5 for strong proton acids as observed by us.[11] In the present paper, the discussion will be confined to the aluminum trichloride-induced reactions because of the obvious connection with the synthetic method. Moreover, the combined action of Lewis and proton acid as exerted by aluminum trichloride on the bicyclic system, results in a reaction pattern which is rather different from the one observed with proton acids; this latter subject will be discussed in a subsequent paper.[11]

Isomerization of 5. Compound 5 was selected for a more detailed study of the aluminum trichloride-induced isomerization reactions. Reaction of methyl propene-2-carboxylate with 1 at −15° resulted in a complex mixture, which contained only a small amount of 5. A number of rearranged compounds (8–13, see Scheme 2) were isolated from the product mixture. Reaction of 5 proper with aluminum trichloride gave a similar result. Some composition–time plots are given in the Experimental.

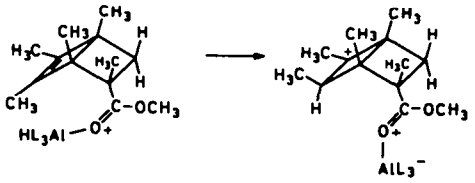
A plausible reaction mechanism, involving *endo* protonation of 5 at the 6-position and rearrangement to the epimeric 2-methoxycarbonyl-1,2,4,5,6-*exo*-pentamethylbicyclo[3.1.0]hex-4-yl carbocations (III and IV) is depicted in Scheme 2. Expulsion of a proton from III or IV gives the alkenic esters 8–11, whilst attack of the carbonyl oxygen at the 6-C atom of the 3-membered ring, and subsequent abstraction of the ester Me group, e.g. by chloride ion, would account for the formation of the lactone 13 from III. The sterically unattractive *exo* configuration of the Me groups is retained in 13; this indicates that the formation of the lactone proceeds concerted rather than via a secondary carbocation. Some aspects of the reaction mechanism will be discussed in detail.

The protons which initiate the rearrangement are

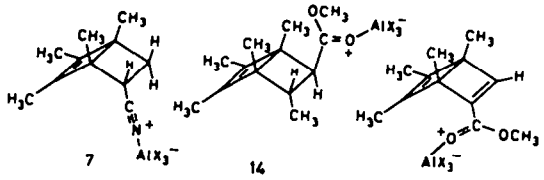


Scheme 2.

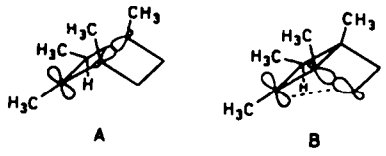
presumably generated from the traces of water which are reputedly[12] present in commercial "anhydrous" aluminum trichloride according to: $AlCl_3 + H_2O \rightarrow AlCl_2OH + HCl$.[13] It should be noted that hydrochloric acid in the absence of aluminum trichloride does not initiate the rearrangement at −15°. We conclude from the configuration of the isolated products that the protonation of 5 proceeds *endo* in the presence of aluminum trichloride[14] (treatment of 5 with strong acid in the absence of aluminum trichloride resulted in *exo* as well as *endo* protonation[11,15]). Trivalent aluminum is obviously present in the reaction mixture as an ester complex,[16] and we suggest that the initial step of the isomerization reaction is a *trans*-annular transfer of a proton from the aluminum complex to the alkenic bond.



Several additional experiments confirmed this mechanistic picture. Thus, reaction of 5 with 0.25 equivalent of "anhydrous" aluminum trichloride, or with 1 equivalent of freshly sublimed aluminum trichloride resulted in partial conversion. The reaction rate increased when dry hydrochloric acid was supplied. Addition of 1 equivalent of D_2O resulted in partial incorporation of deuterium (30% in 13, according to GC–MS).[17] The geometric requirements of the proton transfer step became apparent with the nitrile 7 and the *exo*-methoxycarbonyl compound 14, which were found to be stable for a considerable period in the presence of aluminum trichloride at −15°. Molecular models show that a similar geometric effect is operative, although less pronounced, in the case of bicyclo[2.2.0]hexadiene carboxylic esters. Accordingly, ester-substituted Dewarbenzenes have been prepared under method B conditions without isomerization.[3,6]



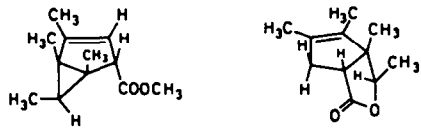
The formation of III from protonated 5 is accounted for by two successive 1,2 alkyl shifts. A direct rearrangement of protonated 5 to give III seems unlikely, because the orbitals involved are nearly perpendicular (A). The geometry of protonated 5 seems favourable for the formation of I; we estimate the inter-orbital angle at 25° (B). Likewise, the molecular geometry of I and II seems favourable for the 1,2 alkyl and 1,3 hydrogen shifts leading to III and IV. Only a small amount of the monocyclic product 12 was formed at −15°, so β-fission—which involves a much less favourable interaction (A)—seems to be a slow process compared with the other reactions. At 0° the order was reversed, and 12 became the main reaction product. This temperature effect indicates that the transition state connected with 12 is considerably more flexible than the transition state



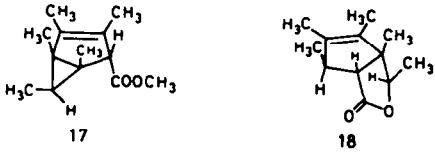
for alkyl migration, as would be expected. Formation of 12 through β-fission and deprotonation of III and IV cannot be excluded *a priori*, but for that case similar arguments apply.

It is pertinent to note that direct lactone formation—which is the main reaction upon treatment of 5 with Brønsted acids[11,18]—does not occur in the presence of aluminum trichloride. This may be due to the decreased electron density in the aluminum-coordinated CO group. The coordination equilibrium: $AlL_3 + RCOOCH_3 \rightleftharpoons AlL_3.RCOOCH_3$ is of course dependent on the concentration. Accordingly, *exo* protonation and subsequent lactone formation came to the fore when the concentration was decreased by an order of magnitude.

Isomerization of 2 *and* 4. The reaction pattern established for 5 under the conditions of method B (−15°) viz *endo* protonation, rearrangement and finally deprotonation and lactone formation, was also operative for 2 and 4. Compounds 15 and 16 were isolated from the product mixture of 2 as the main components. Compound 2 reacted much more rapidly than 5, probably because in protonated 2 the buttressing effect of the 2-*exo*-Me group is absent.



The isomerization of 4 proceeded rather sluggishly, therefore only small amounts of 17 and 18 could be isolated. Compound 17 was also present in the product resulting from reaction of 1 and methyl *cis*-crotonate (method B, −15°).



Structural assignments and spectral data

Bicyclo[2.2.0]*hexenes.* The ^1H and ^{13}C NMR spectral data of compounds 2–5 and 14 are compiled in Tables 1 and 2, respectively. Relative values[19] of the europium(III) induced shifts are given in parentheses for the proton resonances (the LIS of the methoxycarbonyl signal is taken as unity). Some structural details are confirmed by the LIS data. Thus, the LIS values of the

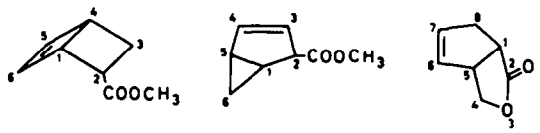


Fig. 1. Numbering system used in Tables 1–6.

Table 1. ^{1}H NMR data of the bicyclo[2.2.0]hex-5-enes[a]

Compound	1-CH_3	2-CH_3	3-CH_3	4-CH_3	5-CH_3	6-CH_3	2-H	3-H_{endo}	3-H_{exo}	$COOCH_3$
2	1.12 (0.32)			0.99 (0.16)	1.53;1.43 (0.20)	(0.47)	2.81[b] (0.92)	2.04[b] (0.81)	1.73[b] (0.43)	3.54 (1.00)
3[c]	1.03 (0.39)		d (0.84)	0.98 (0.25)	1.53 (0.24)	(0.57)	2.85[e] d		2.39[e] d	3.50 (1.00)
4	1.09 (0.36)		0.97 (0.19)	0.80 (0.21)	1.51;1.43 (0.22)	(0.53)	2.20 (1.08)			3.56 (1.00)
5	1.03 (0.41)	1.30 (0.62)		1.00 (0.22)	1.49 (0.20)	1.37 (0.55)		2.38[f] (1.06)	1.30[f] (0.48)	3.56 (1.00)
14	1.02 (0.71)		0.93 (0.23)	0.84 (0.28)	1.54 (0.15)	(0.24)	2.19[g] (1.02)		2.57[g] (1.30)	3.57 (1.00)

[a]Varian T-60; δ values from internal TMS; CCl_4 solution. In parentheses Eu(fod)$_3$ induced shifts relative to the methoxycarbonyl signal are given.
[b]$^3J(H_2H_{3n}) = 6.2$ Hz; $^3J(H_2H_{3x}) = 10.0$ Hz; $^2J(H_{3n}H_{3x}) = (-)12.0$ Hz.
[c]LIS for Eu(dpm)$_3$.
[d]Owing to overlap with other signals no further data can be given.
[e]$^3J(H_2H_3) = 10.7$ Hz.
[f]$^2J(H_{3n}H_{3x}) = (-)12.0$ Hz.
[g]$^3J(H_2H_{3x}) = 6.5$ Hz.

Table 2. ^{13}C NMR data of the bicyclo[2.2.0]hex-5-enes[a]

	$\underline{C}H_3$	$\underline{C}H_2$	$\underline{C}H$	C_{quat}	C = C	C = O
2	8.7; 9.4; 15.0; 16.1; 50.6	30.0	42.9	47.0; 52.8	138.1; 143.3	174.0
3	10.1; 11.0; 13.8; 14.6; 16.1; 50.4		40.1; 45.9	49.0; 50.4	140.6; 140.8	173.5
4	8.6; 9.2; 9.8; 17.0; 17.8; 50.6		35.6; 53.0	48.3; 50.7	138.6; 144.6	174.5
5	8.7; 9.1; 10.2; 15.8; 23.2; 50.9	40.0		45.1; 54.5	139.4; 143.9	176.8
14	8.5; 10.4; 11.0; 15.3; 16.7; 50.4		39.5; 48.6	47.2; 50.0	140.8; 142.4	174.5

[a]Varian XL-100 and CFT-20; δ values downfield from internal TMS; $CDCl_3$ solution.

1-Me signal of **2-5** are in the range 0.3-0.4, whilst for **14**, with the methoxycarbonyl group *exo*, a LIS of 0.71 was observed.

Bicyclo[3.1.0]*hexenes and -hexanes.* The presence of a 3-membered ring in compounds **8–11**, **15** and **17** becomes apparent from the shielding of the methine proton in **8**, **9** and **15**, as well as from the high-field position of two quaternary C atoms ($\delta = 30$–40) and one tertiary C atom ($\delta = 20$–31) in the ^{1}H and ^{13}C NMR spectra (Tables 3 and 4). The *endo* position of the methoxycarbonyl groups in **8**, **10**, **15** and **17** is required by the relative LIS of the bridgehead Me signals (0.4–0.5 and 0.1–0.2) compared with the *exo*-methoxycarbonyl compounds **9** and **11** (0.6–0.9 and 0.3).

The 6-*exo*-Me configuration of **8**, **10**, **15** and **17** is inferred from the LIS of the proton at the 6-position (0.7–1.0). The pattern in the ^{13}C NMR spectra of **8** and **10**, with three Me groups resonating at $\delta < 10$ is also observed in the spectra of the *exo*-methoxycarbonyl compounds **9** and **11**.[20] We conclude that compounds **9** and **11** also possess the 6-*exo*-Me configuration.

Lactones **13**, **16** *and* **18**. The ^{1}H and ^{13}C NMR spectral data are compiled in Tables 5 and 6. The presence of a 5-membered lactone ring becomes apparent from the IR frequencies of the CO moieties (1765–1774 cm^{-1}).[21] The presence of a carbocyclic 5-membered ring is indicated by the ^2J values of the methylene moieties in **13** and **16** ((−) 16 Hz).[22] Further configurational assignments are relatively straightforward. The ^{13}C NMR signals at $\delta = 9$–10 and 12–13 are assigned to the 6- and 7-Me groups. The signals at $\delta = 17.3$–19.5 indicate that the corresponding Me groups are *exo*.[23] The presence of three vicinal *cis-exo* Me groups in **13** should cause an upfield shift of the 5-Me carbon resonance.[20] Accordingly, one Me group resonates at $\delta = 14.4$.

EXPERIMENTAL

NMR spectra were recorded on Varian T-60, XL-100 and CFT-20 instruments. The shift reagents tris(hexafluorodimethyloctadionate)europium(III) (Eu(fod)$_3$) and tris(dipivalomethanato)europium(III) (Eu(dpm)$_3$) were supplied by Merck.

Preparation of tetramethyl[4]*annulene aluminum trichloride complex* (1)[3]

In dichloromethane. A soln of 2-butyne (Chemische Werke Hüls, Marl, G.F.R.) (108 g, 2 moles) in CH_2Cl_2 (100 ml) was added dropwise over 1 hr to a stirred suspension of powdered anhy $AlCl_3$ (J. T. Baker Chemicals) (133.5 g, 1 mole) in CH_2Cl_2 (150 ml). The temp was kept at −10°. The resulting deep red soln was stirred for an addnl 30 min, made up to 0.5 l with CH_2Cl_2 and stored at −10°. The complex was stable for several weeks.

In benzene. A soln of 2-butyne (27 g, 0.5 mole) in C_6H_6 (50 ml) was added dropwise to a stirred suspension of $AlCl_3$ (33.5 g, 0.25 mole) in C_6H_6 (150 ml) which was kept at +6°.

Preparation of the bicyclo[2.2.0]*hex-5-enes*

General procedures are described first, then the preparation of **2-7** is described according to the procedure which gave the best results.

Table 3. ^{1}H NMR data of the bicyclo[3.1.0]hexenes and -hexanes[a]

Compound	1-CH_3	2-CH_3	3-CH_3	4-CH_3	5-CH_3	6-CH_3	2-H	3-H_{endo}	3-H_{exo}	6-H	$=CH_2$	$COOCH_3$
8	1.06 (0.51)	1.21 (0.71)		1.67 (0.11)	0.78 (0.22)	0.91 (0.24)		4.89 (0.77)		0.38 (0.94)		3.58 (1.00)
9	1.14 (0.87)	0.84 (0.71)		1.70 (0.23)	0.98 (0.31)	0.91 (0.20)		4.65 (0.67)		0.42 (0.34)		3.56 (1.00)
10	1.01 (0.43)	1.13 (0.60)			1.01 (0.16)	1.00 (0.17)		2.69[c] (0.85)	1.85[c] (0.45)	b (0.67)	4.86 (0.05;0.12)	3.64 (1.00)
11	0.85 (0.58)	1.14 (0.76)			1.03 (0.33)	0.93 (0.20)		1.87[d] (0.49)	2.31[d] (0.80)	b (0.45)	4.59 (0.36;0.38)	3.56 (1.00)
15	1.12 (0.45)			1.67 (0.10)	0.97 (0.19)	0.92 (0.24)	3.34 (1.10)	4.80 (0.68)		0.51 (0.89)		3.58 (1.00)
17[e]	1.08 (0.49)		1.58 (0.53)	1.47 (0.20)	0.96 (0.22)	0.84 (0.17)	3.24 (1.24)			b (1.04)		3.60 (1.00)

[a]Varian T-60; δ values downfield from internal TMS; CCl_4 solution. In parentheses $Eu(fod)_3$ induced shifts relative to the methoxycarbonyl signal are given.
[b]Because of overlap with other signals, no further data can be given.
[c]$^2J(H_{3n}H_{3x}) = (-)16.4$ Hz.
[d]$^2J(H_{3n}H_{3x}) = (-)16.0$ Hz.
[e]LIS for $Eu(dpm)_3$.

Table 4. ^{13}C NMR data of the bicyclo[2.2.0]hexenes and -hexanes[a]

	$\underline{C}H_3$	$\underline{C}H_2$	$\underline{C}H$	C_{quat}	C = C	C = O
8	7.8; 8.2; 9.3; 14.2; 23.7; 51.2		31.2	33.4; 36.8; 59.4	124.7; 148.2	176.9
9	7.8; 8.7; 9.3; 14.2; 18.5; 51.2		29.3	34.3; 37.5; 60.1	124.7; 152.2	176.9
10	7.9; 9.1; 9.3; 21.9; 51.7	40.8	23.2	33.5; 38.6; 51.1	102.0; 155.5	185.5
11	8.4; 8.9; 9.2; 18.4; 51.4	41.7	21.7	35.3; 39.8; 52.3	100.6; 157.2	177.5
15	7.8; 8.9; 13.2; 14.4; 51.2		27.9; 58.4	29.7; 36.8	117.9; 151.3	174.2
17[b]	8.2; 8.9; 11.7; 12.4; 12.7		26.9; 62.3	29.8; 37.3	124.2; 143.5	180.4

[a]Varian XL-100; δ values downfield from internal TMS; $CDCl_3$ solution.
[b]Spectrum recorded with the carboxylic acid.

Table 5. ^{1}H NMR data of the bicyclic lactones[a]

Compound	1-CH_3	4-CH_3	5-CH_3	6-CH_3	7-CH_3	8-CH_3	1-H	4-H	8-H_{endo}	8-H_{exo}
13	1.20 (1.38)	1.25 (0.61)	0.96 (0.60)	1.59 (0.31)	(0.40)			4.39 (1.00)	2.66[b] (2.11)	2.10[b] (1.87)
16		1.22 (0.63)	1.08 (0.50)	1.57 (0.38)			2.54[c] (2.06)	4.45 (1.00)	2.54[b,c] (2.08)	(0.84)
18		1.25 (0.58)	1.19 (0.53)	1.58 (0.40)		1.15 (0.60)	2.27[d] (2.25)	4.38 (1.00)	2.76[d] (2.46)	

[a]Varian T-60; δ values downfield from internal TMS; CCl_4 solution. In parentheses $Eu(fod)_3$ induced shifts relative to the 4-H signal are given.
[b]$^2J(H_{8n}H_{8x}) = (-)16.0$ Hz.
[c]$^3J(H_{8x}H_1) = 7.6$ Hz.
[d]$^3J(H_1H_{8n}) = 1.4$ Hz.

Method A (CH_2Cl_2). A 2 M soln of 1 in CH_2Cl_2 (125 ml, 0.25 mole) was added over 30 min to a stirred soln of the dienophile (0.25 mole) and DMSO (20 ml, 0.25 mole or 40 ml, 0.5 mole, Table 7) in CH_2Cl_2 (100 ml). The mixture was poured into ice-water and extracted thrice with pentane. The combined extracts were washed (H_2O), dried ($MgSO_4$) and concentrated *in vacuo*.

Method A (C_6H_6). A 1 M soln of 1 in C_6H_6 (250 ml, 0.25 mole) was added dropwise to a stirred, refluxing soln of the dienophile (0.25 mole) and DMSO (40 ml, 0.5 mole) in C_6H_6 (100 ml). The work-up procedure was similar as given for CH_2Cl_2.

Selected yields obtained with method A are compiled in Table 7.

Table 6. ^{13}C NMR data of the bicyclic lactones

	$\underline{C}H_3$	$\underline{C}H_2$	$\underline{C}H$	C_{quat}	C = C	C = O
13	9.7; 13.7; 14.4; 18.1; 19.0	48.4	79.6	50.6; 57.9	131.1; 134.7	183.3
16	9.3; 13.9; 17.3; 18.6	38.9	47.3; 79.9	57.7	131.3; 134.3	180.3
18	9.5; 12.1; 18.5; 19.4; 19.6		47.3; 54.8; 80.0	56.9	133.2; 135.9	179.6

[a]Varian XL-100; δ values downfield from internal TMS; $CDCl_3$ solution.

Table 7. Results obtained with method A[a]

Reaction temperature		-15°	0°	+40°	+80°
Compound	solvent	CH_2Cl_2	CH_2Cl_2	CH_2Cl_2	C_6H_6
2		13	21		21[b]
4		0			18[b]
5		8			
6				10	30[b]

[a]Isolated yields in %.
[b]Reaction in the presence of 2 equivalents of DMSO.

Method B. A soln of the dienophilic ester (0.25 mole) in CH_2Cl_2 (50 ml) was added over 30 min to a stirred 2 M soln of 1 in CH_2Cl_2 (125 ml, 0.25 mole). After an addnl 15 min, a soln of DMSO[24] (20 ml, 0.25 mole) in CH_2Cl_2 (20 ml) was added cautiously. The aqueous work-up was carried out as described above.

2 - endo - *Methoxycarbonyl* - 1,4,5,6 - *tetramethylbicyclo*[2.2.0]*hex* - 5 - *ene* (2). Reaction of 1 (0.25 mole) with methyl acrylate (21 g, 0.25 mole) and DMSO (20 ml, 0.25 mole) according to method A (CH_2Cl_2, 0°) afforded after work-up and distillation (42–45°/0.15 mm) 10.3 g (21%) of 2. The acid was obtained by alkaline hydrolysis (10% methanolic KOH) and purified by repeated crystallization from hexane, m.p. 90.0–91.0°. (Found: C, 73.06; H, 9.03. Calc. for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95%).

2 - endo - *Methoxycarbonyl* - 1,3 - endo, 4,5,6 - *pentamethylbicyclo*[2.2.0] - *hex* - 5 - *ene* (3). Reaction of methyl (*Z*)-propene-1-carboxylate (10 g, 0.1 mole)(prepared from isocrotonic acid[25] by esterification[26]) (method B, −30°) gave after work-up and distillation (40–41°/0.15 mm) 8.3 g (40%) of 3. The acid was obtained by alkaline hydrolysis and purified by repeated crystallization from hexane, m.p. 98.5–100.5° (Found: C, 74.17; H, 9.30%. Calc. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34%).

2 - endo - *Methoxycarbonyl* - 1,3 - exo, 4,5,6 - *pentamethylbicyclo*[2.2.0]*hex* - 5 - *ene* (4). Reaction of methyl (*E*)-propene-1-carboxylate (25 g, 0.25 mole) with 1 (0.25 mole) (method B, −30°) gave after work-up and distillation (48–51°/0.15 mm) 20.4 g (39%) of 4. Alkaline hydrolysis and repeated cryst. from hexane afforded the acid, m.p. 104.0–106.0° (Found: C, 74.36; H, 9.35. Calc. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34%).

2 - endo - *Methoxycarbonyl* - 1,2 - exo, 4,5,6 - *pentamethylbicyclo*[2.2.0]*hex* - 5 - *ene* (5). Reaction of methyl propene-2-carboxylate (50 g, 0.5 mole) with 1 (0.5 mole) (method B, −30°) gave after work-up and distillation (43–48°/0.15 mm) 40.1 g (39%) of 5 which solidified upon standing. Repeated cryst. from hexane and sublimation afforded a pure sample, m.p. 33.0–35.7° (Found: C, 74.68; H, 9.76. Calc. for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68%).

Compound 5 resisted alkaline hydrolysis when the usual procedures were applied. To a stirred, refluxing soln of dicyclohexyl-18-crown-6[27] (*ex* Aldrich) (0.5 g, 1.2 mmoles) in 2 N aqueous KOH (70 ml), 5 (5.7 g, 27 mmoles) was added. After 2 days, the resulting mixture was extracted with hexane, acidified and extracted with ether. The ether layers were dried ($MgSO_4$) and concentrated *in vacuo*. The crude acid (3.6 g, 68%) was purified via the benzylamine salt and liberated by treatment with acid, m.p. 73.2–74.5°.

2 - endo - *Methoxycarbonyl* - 1,4,5,6 - *tetramethyl* - 3 - exo - *phenylbicyclo*[2.2.0]*hex* - 5 - *ene* (6). Reaction of ethyl (*E*)-phenylethene-1-carboxylate[28] (46.5 g, 0.25 mole) with 1 (0.25 mole) was carried out according to method B (−15°). The unconverted ethyl cinnamate was removed by distillation at 0.1 mm. The residue was treated with 10% ethanolic KOH (150 ml) for 3 days at room temp. After the usual work-up 21.7 g (34%) of the acid was obtained, which was purified by cryst. from AcOH. ^{13}C NMR ($CDCl_3$): δ = 8.6, 9.8, 10.5, 16.4 (primary C); 47.6, 48.7 (tert. C); 51.2, 51.8 (quaternary C); 126.2, 128.3, 128.4, 139.2, 140.4, 144.8 (olefinic and arom. C); 180.2 (CO). Cryst. from hexane and sublimation *in vacuo* afforded a pure sample of the acid, m.p. 136.6–138.6° (Found: C, 79.48; H, 7.88%. Calc. for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86%). Esterification with CH_2N_2 afforded 6, ^1H NMR (CCl_4): δ = 0.62 (s, 3H), 1.28 (s, 3H), 1.48 (q, 3H), 1.63 (q, 3H), 3.06 (d, 1H), 3.47 (d, 1H), 3.58 (s, 3H), 7.17 (br.s, 5H), m.p. 55.5–58.5°.

2 - endo - *Cyano* - 1,4,5,6 - *tetramethylbicyclo*[2.2.0]*hex* - 5 - *ene* (7). Reaction of acrylonitrile (13 g, 0.25 mole) with 1 (0.25 mole) (method B, −15°) gave after work-up and distillation (38–42°/0.5 mm) 22 g (55%) of crude 7. A small amount of a persistent impurity was removed by cryst. from pentane at −60°. ^1H NMR (CCl_4): δ = 1.00 (s, 3H), 1.11 (s, 3H), 1.61 (q, 3H), 1.70 (q, 3H), 1.9–2.3 (m, 2H), 2.75 (dd, 1H).

2 - exo - *Methoxycarbonyl* - 1,3 - endo, 4,5,6 - *pentamethylbicyclo*[2.2.0]*hex* - 5 - *ene* (14). Compound 3 (3 g, 15 mmoles) was epimerized in refluxing methanolic (30 ml) CH_3ONa (1.6 g, 30 mmoles) for 2 h. After aqueous work-up, the resulting mixture (GC: 3, 15% 14, 85%) was subjected to preparative GC (SE–30 column, 170°); the fractions containing 14 were collected.

Isomerization of 5

Time-composition measurements. Some plots are depicted in Fig. 2.

Isolation of 8–13. Reaction of 1 with methyl propene-2-carboxylate (25 g, 0.25 mole) (method B, −15°) for 1 hr afforded a mixture which was fractionated under reduced pressure. The fraction boiling at 56–76°/0.25 mm (10.4 g) was subjected to preparative GC (SE–30 column, 170°). A 2:1 mixture of 8 and 9 was collected in one fraction (4.2 g), compounds 10 (0.53 g) and 11 (0.84 g) were collected in separate fractions. From the fraction boiling above 77°/0.25 mm (4.4 g) compound 13 (1.5 g) was isolated by means of preparative GC (SE–30 column, 180°).

Reaction of methyl propene-2-carboxylate with 1 (method B, 0°) afforded a mixture from which 12 was separated by means of preparative GC. ^1H NMR (CCl_4): δ = 1.09 (s, 3H), 1.71 (br.s, 12H), 1.92 (br.d, 1H), 2.76 (br.d, 1H), 3.59 (s, 3H).

Isomerization of 2 *and* 4

Preparation of 15 *and* 16. Reaction of methyl acrylate (21.5 g, 0.25 mole) with 1 (0.25 mole) (method B, −15°) for 30 min followed by aqueous work-up afforded a mixture from which 15 (3.5 g, 7%) was isolated by means of fractionation under reduced pressure (b.p. 46°/1 mm). The fractions with boiling range 46–75°/1 mm (16 g) were treated with 10% methanolic KOH for 3 days at room temp. Water was added and the mixture was extracted with pentane. The aqueous layer was acidified and extracted with ether, the extracts were washed with aqueous

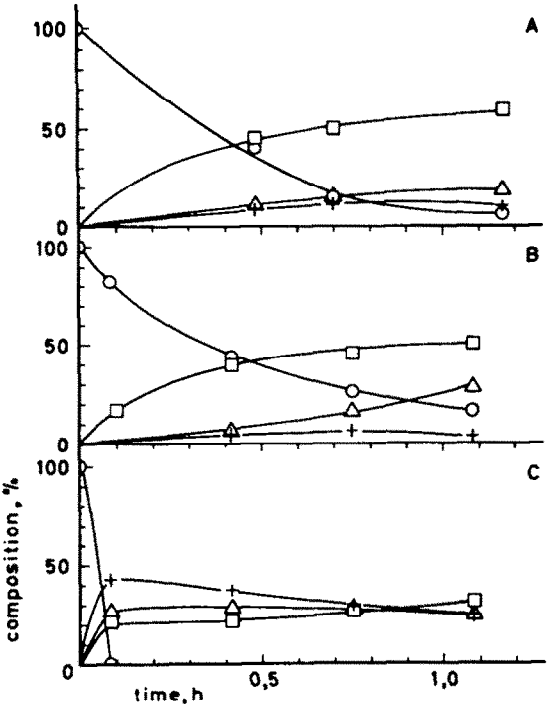


Fig. 2. Isomerization of 5 in the presence of $AlCl_3$. A: composition-time plot of the preparation of 5 according to method B at −15°; B: reaction of 5 (1.25 mmoles) with $AlCl_3$ (1.25 mmoles) in CH_2Cl_2 (1 ml) at −15°; C: ditto, at 0°. ○, 5; △, 8+9; +, 12; □, 13.

$NaHCO_3$ until free of acid, washed with H_2O and dried ($MgSO_4$) Removal of the solvent *in vacuo* afforded **16** (5.6 g 12.4%).

Preparation of **17** *and* **18**. Reaction of methyl (E)-propene-1-carboxylate (40 g, 0.4 mole) with 1 (0.4 mole) (method B, −15°, 1 hr) afforded after work-up and distillation at 0.1 mm a mixture which contained **4**, **17** and **18**. Preparative GC afforded **4** (18 g, 22%), compound **17** (1.5 g, 2%) and **18** (2 g, 3%). A sample of **17** was hydrolysed in methanolic KOH, the acid was repeatedly cryst. from hexane, m.p. 101.0–102.2° (Found: C, 74.38; H, 9.40. Calc. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34%).

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