and 1.068 g (10.0 mmol) of 2,6-lutidine in 150 ml of 80% acetone–water was heated at 100° for 48 hr (*ca.* 10 half-lives). Work-up gave 1.319 g of a pale yellow oil. Column chromatography separated the residue into three fractions. The minor fraction (138 mg) was a pale yellow solid. The middle fraction (352 mg) was shown by glpc retention times and ir spectra to consist of *anti*-**16**-OH (88%), *trans*-**18**-OH (12%), and *trans,trans*-**19**-OH (1%). The remainder of the sample was 2,6-lutidine.

Recrystallization of the minor fraction from petroleum ether (*trans*-**18**-OPNB) gave 124 mg of a pale yellow solid: mp 54–55°; ir (CS_2) 3020, 2920, 2860, 1720, 1605, 1340, 1270, 1110, 1100, 1015, 980, 870, and 720 cm^{-1}; nmr ($CDCl_3$) 1.2–2.9 (14, m, H at C_3 and C_5–C_{10}), 5.2 (1, m, H at C_4), 5.6 (2, m, H at C_1 and C_2), and 8.16 ppm (4, s, aromatic H).

Anal. Calcd for $C_{17}H_{21}NO_4$: C, 67.31; H, 6.98; N, 4.62. Found: C, 67.22; H, 6.89; N, 4.47.

Analytical Product Solvolyses. Solutions 0.01 *M* in *p*-nitrobenzoate or *p*-bromobenzenesulfonate and 0.02 *M* in 2,6-lutidine were heated at the appropriate temperature for 10 half-lives. Acetone–water (80%) was used in all of the studies. Glpc analyses at 80 and 160° were carried out without prior work-up. The products were identified by glpc retention times, and the results are summarized in Schemes III and IV. Mixtures of 1 equiv of the product alcohols, 1 equiv of *p*-nitrobenzoic acid, and 2 equiv of 2,6-lutidine were heated for the same time periods required for solvolysis of the precursor *p*-nitrobenzoate. Comparison of glpc traces before and after heating established that the products were stable to the reaction conditions.

Studies in Mass Spectrometry. XIII.[1] Stereospecific Electron Impact Induced Fragmentation Processes in Some Tricyclic Diesters

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Contribution from the Department of Chemistry, Israel Institute of Technology, Haifa, Israel. *Received December 1, 1969*

Abstract: *endo*-Dimethyl esters **1a**, **2a**, **3a**, and **4a** undergo elimination of methanol under electron impact through a seven-centered transition state. Stereoisomeric *exo* diesters **1b**, **2b**, **3b**, and **4b** do not appreciably eliminate methanol. Loss of methoxyl radical from the molecular ion has been observed instead. *trans*-Diesters **1c**, **2c**, **3c**, and **4c** eliminate methanol under electron impact through a five-centered transition state. An additional stereospecific hydrogen migration accompanying retro-Diels–Alder fragmentation has been observed in the *endo* isomers.

The effect of stereochemical factors on the behavior of organic ions produced in the ion source of a mass spectrometer has been of considerable interest since mass spectrometry became a widely used tool in organic structural analysis.[3] Differences in the abundance of certain ions obtained from stereoisomers under electron impact (or photoionization) have been observed in many cases, and attempts have been made to relate these differences to distinctive features of the parent compounds.

One possible argument for the difference in the abundance of certain fragment ions originating from different stereoisomeric parent ions is the existence of sterically controlled fragmentation processes which may be preferred in one of the isomers. This is usually the explanation for the difference in the abundance of the products of rearrangement processes which are believed to occur *via* cyclic transition states.[4] Stereoisomers in which such cyclic transition states are possible without the occurrence of prior skeletal rearrangements can be expected to give rise to more abundant rearrangement ions than those isomers, in which a different group may migrate or skeletal rearrangements must be postulated to enable attainment of a cyclic transition state. Relatively few cases have been reported in which radical difference exists between the mass spectra of stereoisomers.[3]

In the course of our study of the specific double hydrogen migration in the adducts of bi-1-cycloalken-1-yls and *p*-benzoquinone[5] we examined the mass spectra of the three isomeric methyl esters of *endo*-, *exo*-, and *trans*-1,2,3,3a,4,5,5a,6,7,8-decahydroindacen-4,5-dicarboxylic acids, **1a**, **1b**, and **1c**[6] (Figure 1). The mass spectra differed very much in the high mass range in the fragmentation of the carbomethoxy group. While in the case of the *exo* isomer **1b** methoxyl radical CH_3O was lost from the molecular ion (*m/e* 247 ion a_{1b}, abundance ratio $a_{1b}/M^+ = 0.81$), methanol elimination gave rise to very abundant ions in the case of the *endo* (*m/e* 246 ion b_{1a}, abundance ratio $b_{1a}/M^+ = 2.1$) and *trans* (*m/e* 246 ion b_{1c}, abundance ratio $b_{1c}/M^+ = 2.3$) isomers **1a** and **1c** (see Figure 1). Elimination of methanol gave rise to a very low peak in the mass spectrum of the *exo* isomer **1b**. The same was true for the loss of a methoxyl radical from the molecular ion of **1a** and **1c** (see Figure 1).

This different behavior under electron impact was found to be general for the three isomeric forms of homologous diesters **1**–**4** having various rings A and C. All *exo* isomers (series b) exhibit M − 31 ions (M − 32

(1) Part XII: M. Solomon and A. Mandelbaum, *Chem. Commun.*, 890 (1969).

(2) Based in part on the D.Sc. and M.Sc. Theses of J. Deutsch.

(3) K. Biemann, "Mass Spectrometry, Organic Chemical Applications," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 144; S. Meyerson and A. W. Weitkamp, *Org. Mass. Spectrom.*, **1**, 659 (1968), and references cited therein; M. M. Green, R. J. Cook, J. M. Schwab, and R. B. Roy, *J. Amer. Chem. Soc.*, **92**, 3076 (1970).

(4) F. W. McLafferty in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963, p 331; R. G. Cooks, *Org. Mass Spectrom.*, 2, 481 (1969), and references cited therein.

(5) J. Deutsch and A. Mandelbaum, *J. Amer. Chem. Soc.*, 91, 4809 (1969).

(6) H. Christol and M. Levy, *Bull. Soc. Chim. Fr.*, 3046 (1964).

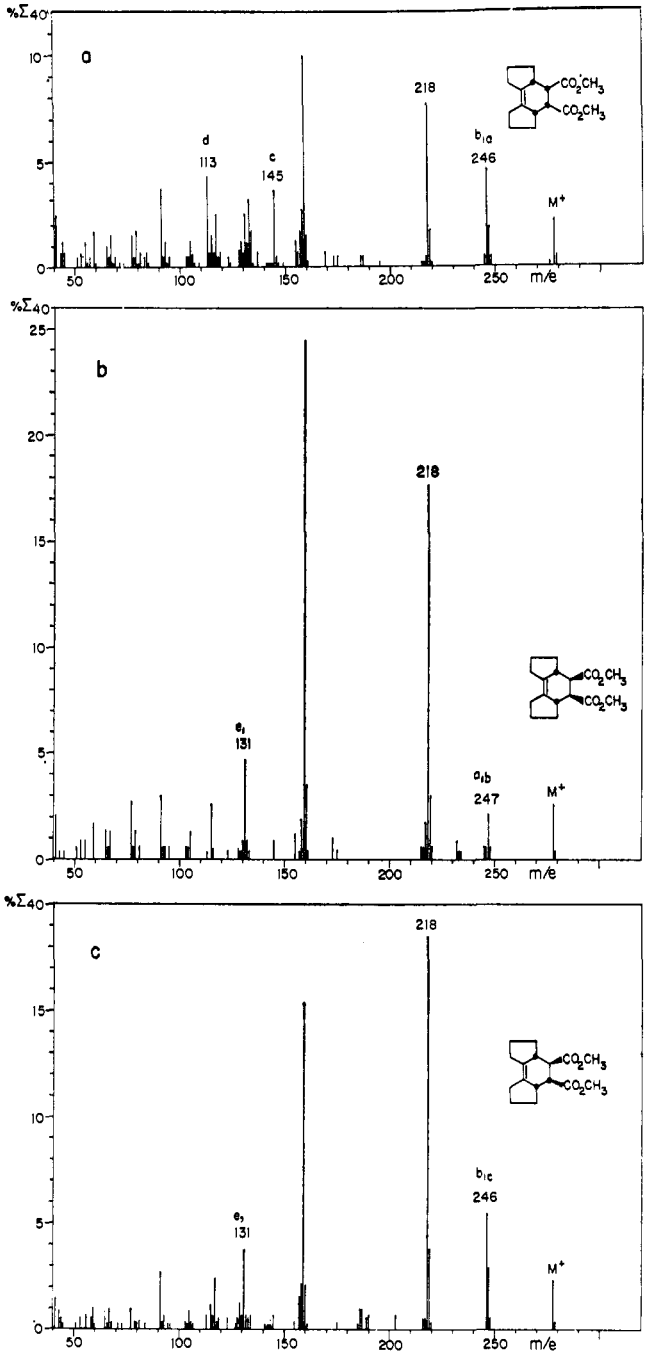
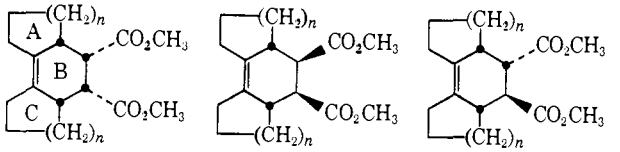


Figure 1. Mass spectra of the dimethyl esters of (a) *endo*-, (b) *exo*-, and (c) *trans*-1,2,3,3a,4,5,5a,6,7,8-decahydroindacene-4,5-dicarboxylic acids.

ions due to elimination of methanol are of very low abundance), while *endo* and *trans* isomers (series a and c)



1a, $n=1$	**1b**, $n=1$	**1c**, $n=1$
2a, $n=2$	**2b**, $n=2$	**2c**, $n=2$
3a, $n=3$	**3b**, $n=3$	**3c**, $n=3$
4a, $n=4$	**4b**, $n=4$	**4c**, $n=4$

give rise to abundant M − 32 ions (M − 31 ions of lower abundance). The abundances of these ions are

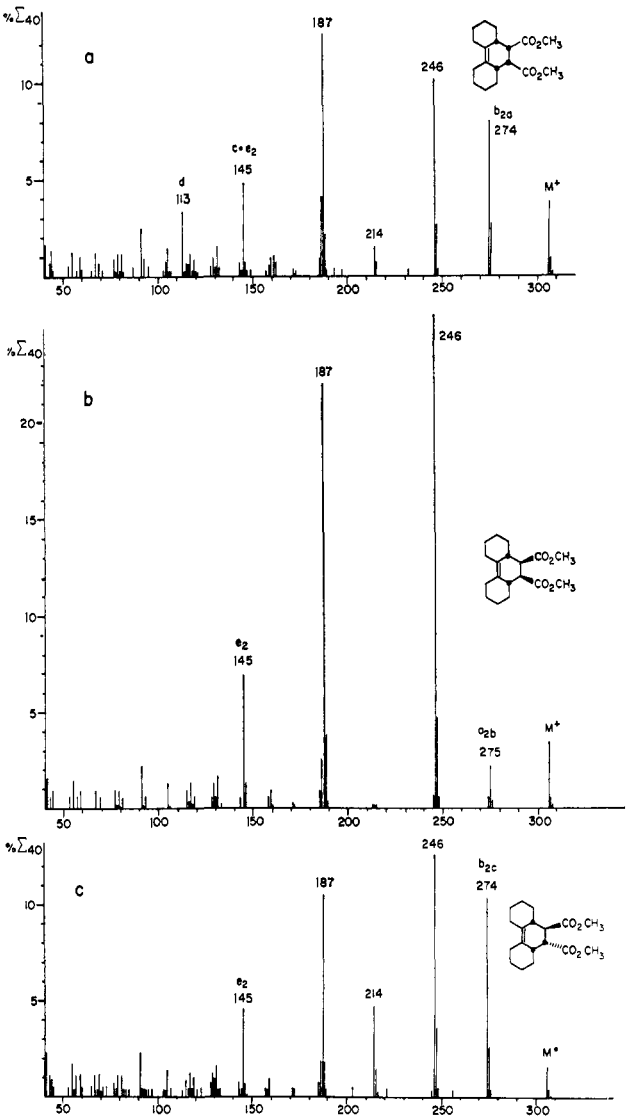


Figure 2. Mass spectra of the dimethyl esters of (a) *endo*-, (b) *exo*-, and (c) *trans*-1,2,3,4,5,6,7,8,8a,9,10,10a-dodecahydrophenanthrene-9,10-dicarboxylic acids.

listed in Table I and can be compared in Figures 1 and 2.

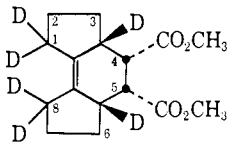
Large differences appeared in the mode of CH_3OH elimination from the molecular ions of the two stereoisomers **1a** and **1c** when 1,1,3a,5a,8,8-d_6 analogs were

Table I. Relative Abundance (% Σ_{40}) of Ions $[M - CH_3O]^+$ and $[M - CH_3OH]\cdot^+$ in the Mass Spectra of *endo*-, *exo*-, and *trans*-Diesters **1–4**

	endo (a)		*exo* (b)		*trans* (c)	
Compd	$[M - MeO]^+$	$[M - MeOH]\cdot^+$	$[M - MeO]^+$	$[M - MeOH]\cdot^+$	$[M - MeO]^+$	$[M - MeOH]\cdot^+$
1	1.1	4.6	2.1	0.4	2.0	5.5
2	1.1	8.0	2.2	0.6	0.5	10.4
3	0.8	6.7	1.4	0.3	1.2	12.2
4	1.3	7.1	0.9	0.2	1.7	12.1

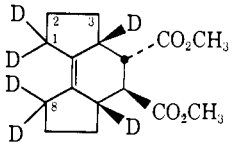
examined. The *endo*-d_6 analog **5a** eliminated CH_3OD giving rise to *m/e* 251 ion b_{5a}, while the *trans*-d_6 isomer **5c** eliminated only CH_3OH yielding *m/e* 252 ion b_{5c}.

The specific elimination of CH_3OD from **5a** shows that the hydrogen atom lost with one of the two meth-



$\xrightarrow{-e}$ [M − CH_3OD]$^+$ ion b_{5a}, *m/e* 251

5a

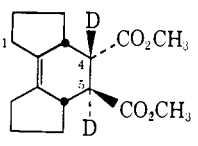


$\xrightarrow{-e}$ [M − CH_3OH]$^+$ ion b_{5c}, *m/e* 252

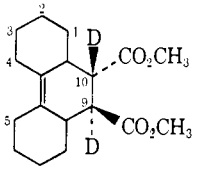
5c

oxyl groups originates at one of the four positions 1, 3a, 5a, or 8. Hydrogens at positions 3a and 5a are very far from both methoxyl groups in the *endo* isomer. Since molecular ions of the *exo* isomers do not eliminate CH_3OH to an appreciable extent it is not reasonable to assume the occurrence of a skeletal rearrangement of the molecular ion prior to the elimination process. Therefore, in analogy with the double hydrogen migration in the adducts of bi-1-cycloalken-1-yls and *p*-benzoquinone,[5] it may be assumed that the allylic hydrogen atom from position 1 (or 8) is abstracted with the methoxyl group of position 4 (or 5) through a seven-centered transition state.[7]

The hydrogen atom abstracted in the elimination of CH_3OH from the molecular ion of the *trans* isomer **1c** has been shown to originate from positions 4 or 5. In the mass spectra of **6** and **7** only [M − CH_3OD]$^{\cdot+}$ has been observed. Apparently the abstraction of the 4-methoxyl group with the 5-hydrogen atom from the molecular ion of **1c** *via* a five-centered transition state is preferred to its loss with a 1-H atom through a seven-membered ring transition state. When only the latter



6



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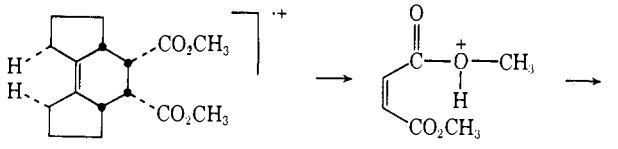
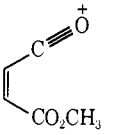
possibility exists (as in the *endo* isomer **1a**), 1-H is abstracted in the course of elimination of methanol from the molecular ion. However, when both possibilities are sterically possible (as in the *trans* isomer **1c**) only 5-H participates in the elimination process. It should be stated here that the high specificity strongly indicates the lack of rearrangement of the molecular ion prior to the methanol elimination process. The *exo* isomers do not eliminate methanol to an appreciable extent apparently also due to the lack of such rearrangement.

Another stereospecific fragmentation process was found in the lower mass range. A relatively abundant *m/e* 145 ion c has been detected in the mass spectrum of the *endo*-diester **1a** ($\%\Sigma_{40}$ 3.6) while in the mass spectra of the other two isomers **1b** and **1c** the corresponding peak was of very low intensity. An *m/e* 113 ion d was also detected in the mass spectrum of **1a** (but not in **1b** and **1c**) and the presence of a "metastable peak" at *m/e* 88.0 indicated that the *m/e* 113 ion d was formed by the elimination of CH_3OH from ion c. It appears that ion c has the structure of protonated dimethyl maleate formed by retro-Diels–Alder fragmentation accompanied by a hydrogen migration. In the mass spectrum of **5a** the *m/e* 145 peak is shifted to *m/e* 146 indicating that a hydrogen atom from position 1 participates specifically in this rearrangement process. This is an additional example of a hydrogen migration in this system through a seven-centered transition state presumably due to the allylic character of the migrating hydrogen and to the relative proximity of that hydrogen to the functional group in the *endo* isomer.[5]

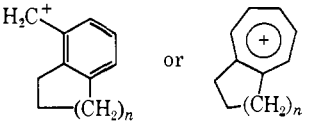


ion c, *m/e* 145



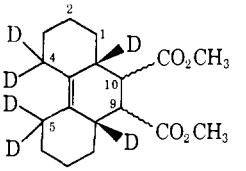
ion d, *m/e* 113

A similar process has also been found in the higher homolog **2a**. However in that case the difference between the stereoisomers was obscured (see Figure 2) by the presence of a different nonstereospecific fragmentation process leading to *m/e* 145 ion e_2 of composition $C_{11}H_{13}$.[8] Similar nonstereospecific processes led to corresponding ions in the cases of all isomers of **1** (*m/e* 131 ion e_1), **3** (*m/e* 159 ion e_3), and **4** (*m/e* 173 ion e_4) differing by one methylene group per added methylene group in ring A or C.



ion e

A difference between the stereoisomers of **2** appeared when the mass spectra of the d_6 analog **8a**, **8b**, and **8c** were measured. The *m/e* 145 peak was split in the mass spectrum of **8a** to *m/e* 146 corresponding to ion c (containing one deuterium atom which migrated from position 4 or 5[5]), and a group of peaks at *m/e* 148, 149, and 150 corresponding to ions e_2 of varying deuterium content. No significant shift to *m/e* 146 was detected in the mass spectra of **8b** and **8c**, indicating the high stereospecificity of the fragmentation process leading to ion c. It should be added that the *m/e* 113 ion d was of significant abundance only in the mass spectrum of



8a, *endo* isomer
8b, *exo* isomer
8c, *trans* isomer

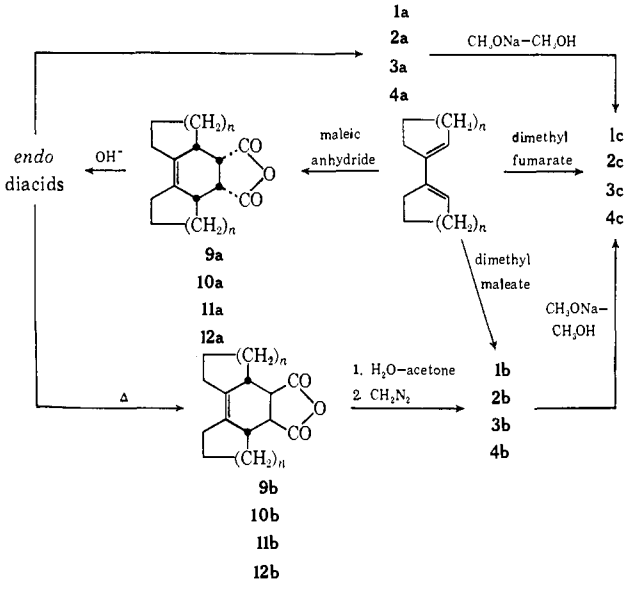
(7) (a) See footnotes 9 and 10 in ref 5; (b) N. E. Truce and L. W. Christensen, *J. Org. Chem.*, 33, 2261 (1968).

(8) The *m/e* 145 peak in the mass spectrum of **2a** was resolved into a doublet and the compositions of the two ions were confirmed by a high-resolution measurement on an MS 902 mass spectrometer at AEI, Manchester.

the *endo* isomer **2a**. It was not shifted in the case of the d_6 analog (m^* 87.5). The *m/e* 145 ion c is of much lower abundance in the higher homologs **3a** and **4a**. This distinct behavior of compounds having larger rings A and C will be dealt with elsewhere.

The stereoisomers were prepared according to the general procedure[6] outlined in Scheme I. The con-

Scheme I



figuration assignment has been done by the iodolactone reaction[9] which yielded immediately solid iodolactones when the *endo* diacids were tested, but failed to yield any precipitate with the *exo* diacids. Nmr spectra were also of aid in the stereochemical interrelation of the examined compounds and they will be dealt with elsewhere.

Experimental Section[10]

endo-**Diesters.** *endo*-Diesters **1a**,[6] **2a**,[6] and **4a**[11] have been described in the literature. **3a** (colorless crystals from ethanol, mp 49–50°), **5a** (d_3 5.7%, d_4 15.3%, d_5 35.0%, d_6 44.0%, no trace of less than d_3), and **8a** (d_3 2.8%, d_4 13.8%, d_5 34.2%, d_6 49.2%, no trace of less than d_3) were prepared by a similar route from the corresponding dienes.[5]

(9) C. S. Rondestvedt and C. D. Ver Nooy, *J. Amer. Chem. Soc.*, 77, 4878 (1955); J. Kallos and P. Deslongchamps, *Can. J. Chem.*, 44, 1239 (1966).

(10) Melting points (mp) are uncorrected. Mass spectra were measured with an Atlas CH4 mass spectrometer fitted with a TO-4 ion source and direct inlet system, operated without heating. The samples were heated externally, if necessary, until the ion current was sufficient to provide usable mass spectra. The ionization energy was maintained at 70 eV.

(11) J. Strumza and D. Ginsburg, *J. Chem. Soc.*, 1514 (1961).

Table II. *exo*-Anhydrides

Compd	Yield, %	Mp (solvent), °C	Anal, % Found C	Found H	Calcd C	Calcd H
9b	54[a]	103 (ether)				
10b	53[b]	87–90 (ether)				
11b	53	94–95 (hexane)	74.43	8.59	74.97	8.39
12b	28	128–130 (acetone–water)	75.42	8.91	75.92	8.91
9b-d_6[c]	21	100–103 (ether)				
10b-d_6	42	86–89 (ether–petroleum ether)				

[a] Reported[6] yield 30–50%, mp 104°. [b] Reported[6] yield 63%, mp 94°. [c] d_3 8.6%, d_4 14.6%, d_5 32.4%, d_6 44.4%. No trace of less than d_3 compound.

Table III. *exo*-Diesters

Compd	Yield, %	Mp (solvent), °C	Anal, % Found C	Found H	Calcd C	Calcd H
1b	85	Oil	69.22	8.01	69.04	7.97
2b	82	58–59[a] (pentane)				
3b	18	81–82 (ethanol)	71.49	9.33	71.82	9.04
4b	97	59–60 (methanol)	73.03	9.05	72.89	9.45
5b	14	Oil[b]				
8b	55	54–56[c] (pentane)				

[a] Reported[6] mp 57.5°. [b] d_3 8.6%, d_4 14.2%, d_5 34.3%, d_6 43.0%. [c] d_3 2.8%, d_4 13.8%, d_5 34.2%, d_6 49.2%.

Table IV. *trans*-Diesters

Compd	Yield, %	Mp (solvent), °C	Anal, % Found C	Found H	Calcd C	Calcd H
1c	85	72–74 (pentane)	69.14	7.79	69.04	7.97
2c	63[a]	108–109 (pentane)				
3c	88	62–63 (ethanol)	71.52	9.28	71.82	9.04
4c	32	85–87 (pentane)	72.52	9.15	72.89	9.45
5c[b]		72–74 (pentane)				

[a] Reported[6] mp 109°. [b] d_3 5.4%, d_4 13.8%, d_5 36.2%, d_6 44.6%.

exo-**Diesters.** *endo*-Anhydrides **9a**, **10a**, **11a**, **12a**, and the corresponding d_6 analogs were hydrolyzed in 5% aqueous NaOH, and the resulting diacids were heated for 1 hr at 280–300° *in vacuo* (25 Torr). The resulting recrystallized *exo*-anhydrides **9b**, **10b**, **11b**, and **12b** (see Table II) were hydrolyzed by boiling in acetone–water 1:1 solution, and methylated by diazomethane in ether solution (see Table III).

trans-**Diesters.** The best route to the *trans*-diesters **1c**, **2c**, **3c**, and **4c** was the addition of dimethyl fumarate and the corresponding dienes in boiling toluene for about 4 hr. For details see Table IV.

trans-d_2-Diesters **6** and **7** were obtained by a single equilibration of **1a** and **2a** in a boiling solution of CH_3ONa in CH_3OD; **6**, d_1, 23%; d_2, 77%; **7**, d_1, 23%; d_2, 77%.