Tetrahedron Vol. 40, No. 24, pp. 5235 to 5242, 1984
Printed in the U.S.A.

0040-4020/84 \$3.00 + .00

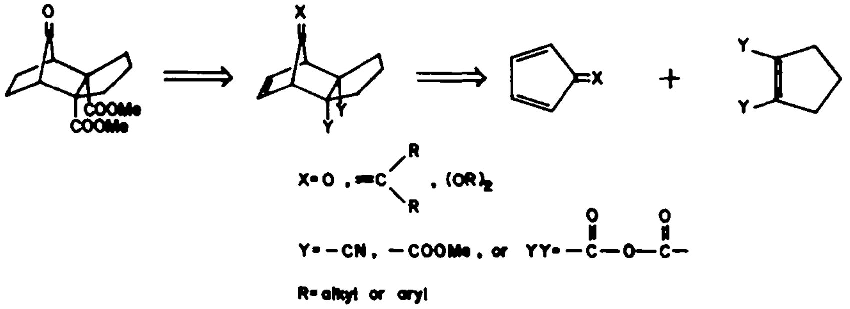
A STUDY OF THE DIELS–ALDER REACTION OF 3-OXABICYCLO[3.3.0]OCT-1(5)-ENE-2,4-DIONE WITH CYCLOPENTADIENE AND SOME RELATED DIENES†

P. CAMPS*
Departamento de Química Orgánica, Facultad de Farmacia, Universidad de Valencia, Valencia, Spain
J. CASTAÑÉ
Departamento de Investigación, Menadiona S. A., Palafolls, Barcelona, Spain
M. FELIZ
Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad de Barcelona, Barcelona, Spain
and
M. FIGUEREDO
Departamento de Química Orgánica, Facultad de Ciencias, Universidad Autónoma de Barcelona, Bellaterra, Barcelona, Spain

(*Received in UK* 20 *December* 1983)

Abstract—The reaction of 3-oxabicyclo[3.3.0]oct-1(5)-ene-2,4-dione, **2**, with cyclopentadiene, **3**, 5,5-diethoxycyclopentadiene, **4**, and 6,6-dimethylfulvene, **5**, is studied. Reaction of **2** and **3** yields the expected *endo*-adduct, while reaction of **2** and **5** gives a mixture of the *endo*- and *exo*-adducts whose ratio is slightly dependent on the reaction conditions. Attractive electrostatic interactions in the transition state leading to the *exo*-adduct can explain the absence of endo stereoselectivity in the last reaction. Steric factors seem to be responsible for the absence of reaction between **2** and **4**. The analysis of the ^{13}C NMR spectra of these adducts and some derived compounds confirms the tentative configuration assignment carried out on the basis of PMR data. Also, the synthesis of dimethyl(1*R*,2*S*,6*R*,7*S*)-10-oxotricyclo[5.2.1.0^{2,6}]decane-2,6-dicarboxylate, **1**, from the *endo*-adduct of the reaction of **2** and **5**, is described.

In connection with our work on the synthesis of poliquinanes we needed a method to prepare dimethyl(1*R*,2*S*,6*R*,7*S*)-10-oxotricyclo-[5.2.1.0^{2,6}]decane-2,6-dicarboxylate, **1**, on a fairly large scale. The retrosynthetic analysis of this compound shows that it could be synthesized, among other procedures, through a Diels–Alder reaction between an appropriate cyclopentadiene derivative and a synthon equivalent to a cyclopent-1-ene-1,2-dicarboxylic acid (Scheme 1).



Scheme 1.

Since cyclopentadienone, the most obvious diene, is a very unstable compound that rapidly dimerizes,[1] other dienes, such as a 5,5-dialkoxycyclopentadiene or a fulvene, in which the ketonic function of cyclopentadienone is masked, would be required. Among the easily accessible 5,5-dialkoxycyclopentadienes, the 5,5-diethoxy-derivative is advantageous over the 5,5-dimethoxy- or 5,5-ethylenedioxy-derivatives because of its greater stability towards dimerization.[2] Among fulvenes, those 6,6-disubstituted

---

†Dedicated to Mr. C. Cosin for his kindness in making possible this work.

with equivalent alkyl[3] or aryl[4] groups are easily prepared, quite stable towards dimerization, and generally react as dienes in the Diels–Alder reaction. As the active dienophile, possessing the carbon skeleton of cyclopent-1-ene-1,2-dicarboxylic acid, we chose 3-oxabicyclo[3.3.0]oct-1(5)-ene-2,4-dione, **2**, which can be easily prepared[5] in a large scale, and discarded cyclopent-1-ene-1,2-dicarbonitrile because it does not offer advantages over **2** as dienophile, and its low yield preparation[6] is very tedious. Thus we have studied the Diels–Alder reaction between anhydride **2** and cyclopentadiene, **3**, 5,5-diethoxycyclopentadiene, **4**, and 6,6-dimethylfulvene, **5**, the first one as reference reaction.

The reaction of anhydride **2** with cyclopentadiene, in CH_2Cl_2 at room temperature for 32 h, gave a single compound, m.p. 153–5° (ether), in 88.0% yield, that was tentatively characterized as the *endo*-adduct **6**, through the comparison of the PMR spectra of its derived compounds, anhydride **7** and diester **10**, prepared by standard methods as described in the experimental (see Fig. 1).

Using double irradiation experiments, the chemical shifts for the $H_{8(9)endo}$ and $H_{8(9)exo}$ protons of anhydride **7** and diester **10** were obtained from the corresponding 200 MHz PMR spectra, on the basis that, according to the Karplus equation, the coupling constant $J_{H8(9)exo\text{-}H7(1)}$ must be clearly greater than $J_{H8(9)endo\text{-}H7(1)}$. Although the values for these coupling constants could not be determined, irradiation of the $H_{8(9)exo}$ protons made the adsorption of the $H_{1(7)}$ protons to become sharper, while irradiation of the $H_{H8(9)endo}$ protons left this absorption practically unchanged. The chemical shifts for the $H_{8(9)endo}$ protons of **7** and **10** among those of other related compounds are collected in Table 1.

As can be seen, the change of the rigid anhydride function of compound **7** by the freely rotating methoxycarbonyl groups of diester **10**, deshields the $H_{8(9)endo}$ protons by *ca.* 0.3 ppm, a fact that points to

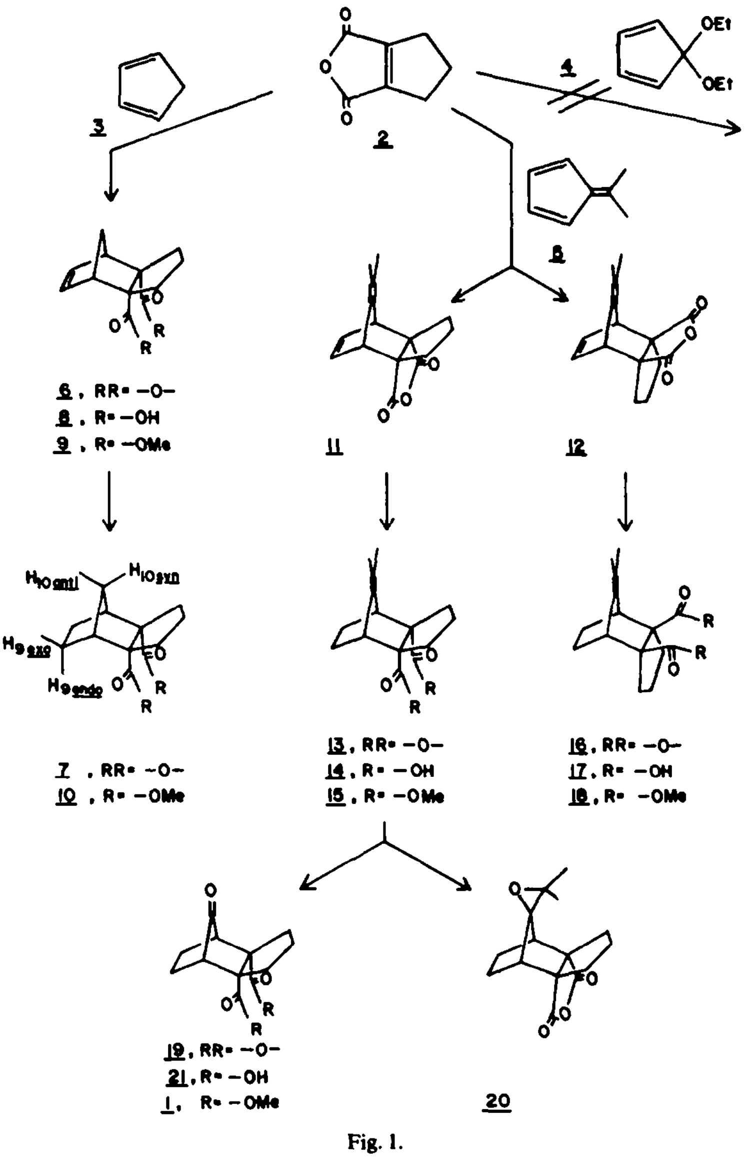


Fig. 1.

Table 1. Chemical shifts for the $H_{8(9)endo}$ protons of anhydrides **7**, **13** and **16** and their corresponding dimethyl esters **10**, **15** and **18**, respectively

Compound	**7**	**10**	**13**	**15**	**16**	**18**
$\delta H_{8(9)endo}$	1.38	1.66	1.42	1.74	1.60	1.62

the *endo*-configuration for these compounds, the contribution of conformations of diester **10** in which the carbonyl oxygen atoms are close to the $H_{8(9)endo}$ protons accounting for the observed effect.[7] Consequently, compound **6** must also have *endo*-configuration. This was later confirmed through the analysis of the ^{13}C NMR data.

Reaction of anhydride **2** with 5,5-diethoxycyclopentadiene,[2] **4**, in an ether/pentane: 1/5 mixture at room temperature for 6 h, did not yield the desired Diels–Alder adduct, instead, the starting anhydride **2** was recovered unchanged by crystallization from the reaction mixture. The oily residue obtained by evaporation of the mother liquors of crystallization must correspond to the Diels–Alder dimer of **4**, because its PMR spectrum closely resembles that of the product obtained by evaporation of the solvent from a pentane solution of diene **4** that has been allowed to stand at room temperature for 24 h.[2] Since, in our hands, diene **4** gave a Diels–Alder adduct with N-phenylmaleimide, under similar reaction conditions in 77% yield (lit.[8] 54%), the failure of the former reaction must be due to the severe steric interactions that must exist in both of the transition states leading to the *exo*- or *endo*-adducts, between one of the ethoxy groups of diene **4** and the furanic or cyclopentenic ring of anhydride **2**, respectively, making the dimerization of diene **4** the preferred reaction. Such an interaction is not present in the transition state leading to the *endo*-adduct of diene **4** and *N*-phenylmaleimide.

Reaction of 6,6-dimethylfulvene, **5**, with anhydride **2**, in xylene at 130° for 1 h, gave a mixture of the *endo*- and *exo*-adducts, **11** and **12**, respectively, in which one of them slightly predominated (92.1% isolated yield). Fractional crystallization from xylene led to a high yield separation of a compound, m.p. 172–4°, that was characterized as the *exo*-adduct **12**, and another compound, m.p. 134–5°, that was characterized as the *endo*-adduct **11**. The assignment of the configuration to these adducts was carried out as described for compound **6**, through the preparation of anhydride **13** and diester **15**, from adduct **11**, and anhydride **16** and diester **18**, from adduct **12** (see Experimental).

The comparison of the chemical shifts for the $H_{8(9)endo}$ protons of compounds **13**, **15**, **16**, and **18** (see Table 1) shows a deshielding effect of approximately 0.3 ppm in going from anhydride **13** to diester **15**, while no similar situation is found in going from **16** to **18**. As described before for compound **6**, these facts let us tentatively assign the *exo*-configuration to **12** and the *endo*-configuration to **11**, and this was later confirmed through the analysis of the ^{13}C NMR data.

A study on the effect of the reaction conditions on the stereoisomeric ratio in the reaction of 6,6-dimethylfulvene and anhydride **2** (see Table 2) showed that under kinetic control a mixture **11**/**12** in the approximate ratio 1/1 was formed, while under thermodynamic control the ratio **11**/**12** was 9/11. Heating the *exo*-adduct **12** without solvent in a nitrogen atmosphere at 180° for 10 min, a mixture **11**/**12** in the ratio 9/11 was obtained in high yield. Formation of 6,6-dimethylfulvene in this reaction was shown by the reflux of a yellow liquid. This fact shows that the equilibrium must be attained, at least partially, by cycloreversion[3a] of the adducts to the components. Degradation of the adducts can be explained by cycloreversion and oligomerization of the fulvene component.[9]

The results herein described about the reaction of 6,6-dimethylfulvene and anhydride **2**, closely parallel those described by Craig[3b] and Alder[3c] about the reaction of the same fulvene and maleic anhydride, since under kinetic control a mixture of both adducts,

Table 2. Stereoisomeric ratio in the reaction of anhydride **2** and diene **5** under various reaction conditions, and some related processes. [a]Adducts yield *ca.* 90%. [b]Most of the starting products remained unchanged. [c]Partial degradation of the adducts and formation of other by-products was observed. [d]Total degradation of the adducts took place. [e]High yield if carried out in an inert atmosphere

Starting products	Solvent	Temperature	Reaction time	**11/12** ratio
	Benzene	Reflux	1 h	1/1[a]
	Benzene	Reflux	3 h	1/1[a]
	Toluene	Reflux	1 h	1/1[a]
2+**5**	Toluene	Reflux	3 h	1/1[a]
	Xylene	Reflux	1 h	9/11[a]
	Xylene	Reflux	3 h	9/11[a]
	Benzene	20°C	7 days	1/1[a]
	Benzene	−20°C	10 days	1/1[b]
11/12	Xylene	Reflux	24 h	9/11[c]
1/1 ratio	Xylene	Reflux	72 h	—[d]
12	None	180°C	10 min	9/11[e]

in which the *endo*-adduct slightly predominated, was obtained. Under equilibration conditions the mixture contained the *endo*- and *exo*-adducts in the ratio 1/7[3b] (1/8.9).[3c] In this case, however, the relative stability of the *exo*-adduct seems to be greater than in our case, and consequently, its formation under equilibration conditions more preferred. Other fulvene derivatives, such as 6,6-diphenylfulvene[4] and 6,6-pentamethylenefulvene[3a] gave *endo*-adducts on reaction with maleic anhydride under kinetic control, that easily rearrange to give mainly the more stable *exo*-adducts under equilibration conditions. The absence of *endo*-stereoselectivity in the reaction of 6,6-dimethylfulvene and maleic anhydride was taken by Craig[3b] as a probe for a step wise ionic mechanism. However, the same type of mechanism could be operative in the reactions of diphenylfulvene or pentamethylenefulvene with maleic anhydride where the rule of *endo*-stereoselectivity does apply. The appropriate balance among the secondary orbital interactions[10] favouring the formation of the *endo*-adduct and the electrostatic interactions[11] favouring the formation of the *exo*-adduct (Fig. 2) in the transition states of these reactions must account for the observed kinetic stereoselectivity, since steric factors in these transition states should be slight due to the trigonal hybridization of the fulvene carbon atoms.[12]

As mentioned before, the analysis of the ^{13}C NMR spectra of the compounds (anhydrides and dimethyl esters) prepared in this work let us assign clearly their configuration. The chemical shift for the carbon atoms of these compounds, together with the reference compounds *endo*- and *exo*-tricyclo[5.2.1.0^{2,6}]-decane, **22** and **23**, respectively, isodihydroalbene, **24**, and dihydroalbene, **25**, are collected in Table 3 (see also Fig. 3).

The assignment of the ^{13}C NMR signals was carried out on the basis of their multiplicity and intensity, and by comparison with the values reported for related compounds.[13,14] Since the spectra of these compounds were all obtained using $CDCl_3$ as solvent, while those of the acids **8**, **14**, and **17**, using DMSO-d_6, the values of these acids have not been considered, although the discussion that follows could be extrapolated to them.

The comparison of the chemical shifts for the different carbon atoms of the reference compounds **22** and **23** shows that the greater differences correspond to $C_{10}(\Delta\delta_{22\rightarrow23} = -11.1$ ppm), $C_{3(5)}$ ($\Delta\delta_{22\rightarrow23} = +5.6$ ppm), and $C_{8(9)}$ ($\Delta\delta_{22\rightarrow23} = +5.8$ ppm). These differences can be easily explained because in the *endo*-compound 22, the steric interaction between the pairs of methylene groups at the 3–9 and 5–8 positions (γ-effect) shields the $C_{3(5)}$ and $C_{8(9)}$ atoms compared with **23**. Moreover, in the *exo*-compound **23**, such a type of interaction but small in magnitude[14] exists between the methylene groups at the 3–10 and 5–10 positions, shielding the C_{10} atom with respect to **22**. A similar situation is found in the compounds **24** and **25**. In this case, however, the chemical shift difference for the $C_{8(9)}$ atoms is smaller ($\Delta\delta_{24\rightarrow25} = -1.9$ ppm) and of opposite sign. The steric interaction between the methylene groups at the 3–9 and 5–8 positions in the *endo*-compound **24** is replaced in the *exo*-compound **25** by a similar or even greater interaction between the methylene at the 8 and 9 positions and the methyl groups. In accord with these facts, the $C_{3(5)}$ atoms are shielded by 5.1 ppm, while the methyl carbon atoms are deshielded by 5.1 ppm, in going from **25** to **24**.

On similar grounds, the comparison of the chemical shifts for the carbon atoms of anhydrides **13** and **16** and their dimethyl esters **15** and **18** clearly shows that **13** and **15** are related to **23** and **25**, while **16** and **18** are related to **22** and **24**, thus confirming the assigned configuration. The chemical shift differences for all the carbon atoms of **11** and **12** are equal or less than 1.6 ppm. The greatest difference corresponds to the shielding that the $C_{3(5)}$ atoms experience in going from **11** to **12**, thus showing that the introduction of the C_8–C_9 double bond drastically reduces the steric interaction between the groups at the 3–9 and 5–8 positions.

Since we have only one stereoisomer, to assign the configuration to **6** and derived compounds, we can compare their chemical shifts with those predicted starting from **11**, **12**, or their corresponding derived compounds, by introducing a correction for the change of the isopropylidene substituent at C_{10} by two hydrogen atoms. Since in benzonorbornene and 9-isopropylidenebenzonorbornene,[15] the chemical shifts for the common carbon atoms, except C_9, differ by 0.4 ppm or less, we can effect a direct comparison. Thus, comparing the chemical shifts for the annular carbon atoms, except C_{10}, of **6** with those of **11** and **12**, although the differences are not too large the better correlation between **6** and **11**, points to the *endo*-configuration for **6**. In the same way, the better correlation between **7** and **13** as compared with **7** and **16** confirms clearly the assigned configuration to **7**. Similar results are obtained by comparing **10** with **15** and **18**. Thus, compounds **6**, **7**, **9**, and **10**, must all have *endo*-configuration.

Having established the configuration of the anhydrides and dimethyl esters collected in Table 3, it is noteworthy the shielding effect observed for the C_4 atoms of the compounds derived from the *endo*-compounds **6**, **9**, and **11**, on saturation of the C_8–C_9 double bond ($\Delta\delta_{6\rightarrow7} = -4.0$ ppm, $\Delta\delta_{9\rightarrow10} =$

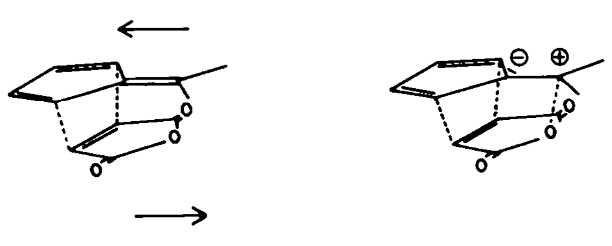


Fig. 2.

Table 3. Chemical shifts for the carbon atoms of compounds containing the tricyclo[5.2.1.$0^{2,6}$]decane skeleton. [a]Taken from Ref. 13; [b]Taken from ref. 14. In all cases the solvent was $CDCl_3$ and the chemical shifts are given in ppm with reference to internal TMS, except for compound **25** where the reference is $CDCl_3$ ($\delta = 77.02$)

	Carbon atom										
Compound	1(7)	2(6)	3(5)	4	8(9)	10	C=O	O$\underset{\cdot}{C}H_3$	$=\underset{\cdot}{C}Me_2$	$=C(\underset{\cdot}{C}H_3)_2$	$-\overset{\vert}{\underset{\vert}{C}}-\underset{\cdot}{C}H_3$
6	48.5	67.4	34.6	29.6	137.4	48.9	175.0				
7	43.7	66.3	36.1	25.6	25.0	37.8	175.7				
9	51.4	68.5	38.0	29.0	136.6	45.2	175.7	51.6			
10	46.8	64.2	39.5	25.9	24.5	35.6	175.6	51.3			
11	48.9	66.5	33.9	29.5	137.4	145.6	174.6		116.3	19.8	
12	49.2	67.8	32.3	28.7	137.3	145.8	175.5		115.3	19.2	
13	43.7	64.7	35.9	25.3	24.2	138.3	175.6		122.4	20.8	
15	47.0	63.2	39.3	25.6	23.6	139.8	175.4	51.3	118.2	20.6	
16	43.3	63.9	29.3	29.2	21.7	139.5	176.8		121.3	20.4	
18	45.3	65.1	33.2	28.2	23.0	143.1	176.3	51.8	116.1	20.5	
22[a]	41.5	45.5	27.0	28.7	23.1	43.3					
23[a]	40.8	48.4	32.6	27.4	28.9	32.2					
24[b]	50.7	50.9	38.5	26.2	24.9	39.5					25.7
25[b]	47.8	48.9	43.6	23.0	23.0	34.1					20.6

-3.1 ppm, and $\Delta\delta_{11\to 13} = -4.2$ ppm). This effect seems to be independent on the nature of the carboxyl functions (anhydride or dimethyl esters), and is absent in the compounds derived from the *exo*-adduct **12**. Since molecular mechanics calculations[16] show that for the compounds **6**, **7**, and **11**, the envelope conformation for the C_2 to C_6 cyclopentanic ring in which the C_4 atom is as far as possible from C_{10}, is clearly preferred, this shielding effect cannot be attributable to a conformational change due to the saturation of the C_8–C_9 double bond. On the other hand, since this bond is too far from C_4, its saturation cannot be responsible for such a large effect in a direct manner. A possible partial explanation might be related to the greater interaction that must exist between the methylene group at the 4 position and the substituents at C_2 and C_6, as a consequence of the greater interaction between these substituents and the methylenes at the 8 and 9 positions, in a sort of buttressing effect.

Knowing the configuration of the Diels–Alder adducts in the reaction of 6,6-dimethylfulvene and anhydride **2**, the synthesis of oxodiester **1** could be achieved in a straightforward manner. Ozonolysis of anhydride **13** gave a 2/1 mixture of oxoanhydride **19** and epoxyanhydride **20**, from which **19** was separated by crystallization. Alkaline hydrolysis of **19** followed by esterification of the corresponding diacid with ethereal solution of diazomethane gave oxodiester **1**. The epoxyanhydride **20** was shown to be identical (GLC) to the unique epoxide obtained by reaction of anhydride **13** with perbenzoic acid. The configuration shown for this epoxyanhydride was assumed on the basis that epoxidation takes place by the less hindered carbon–carbon double bond face. Work is in progress to develop an alternative synthesis of oxodiester **1**, by an entirely different approach, to overcome the experimental drawbacks found in the separation of the mixtures **11**/**12** and **19**/**20** of the synthesis herein described, when it is carried out on a large scale.

22, R=H
24, R=Me

23, R=H
25, R=Me

Fig. 3.

EXPERIMENTAL

Infrared spectra were recorded on a Perkin–Elmer, model 1310 spectrometer. The PMR and ^{13}C NMR spectra, unless otherwise stated, were taken at 200 and 50 MHz, respectively, on a Varian XL 200 spectrometer, while 80 MHz PMR and 20 MHz ^{13}C NMR spectra were recorded on a Bruker, model WP80SY. Chemical shifts are given in ppm relative to internal TMS (δ scale). GLC analyses were carried out on a Perkin–Elmer, model Sigma 3B, chromatograph using a 2 m × 1/8" ϕ OV-1 column, oven temperature: 160°, 25 ml N_2/min as eluent, and FID detection. Melting points were determined on a Kofler hot-stage and are corrected. For medium pressure hydrogenations, a Parr apparatus, model 3911, was used. Calculations were carried out at the Computing Center of Hokkaido University, Sapporo, Japan, on a HITAC M-200H system.

(1*R*, 2*S*, 6*R*, 7*S*)-*Tricyclo*[5.2.1.$0^{2,6}$]*dec - 8 - ene- 2,6 - dicarboxylic anhydride* **6**. A mixture of 10.0 g anhydride **2** (72 mmol) and 11 g freshly distilled cyclopentadiene (166 mmol) in 200 ml CH_2Cl_2 was stirred at room temperature for 10 min and allowed to stand at this temperature for 32 h. Evaporation of the volatile products left 16.3 g of a solid that crystallized from diethyl ether gave 13.0 g of **6**, m.p. 153–5°, 88.0% yield. IR(KBr), 1850 (m), 1820 (m), 1775(s) cm^{-1}; PMR($CDCl_3$), 1.60–1.90 (m, 3H), 1.93 (m, 2H, H_{10syn} and H_{10anti}), 2.10 (m, 1H), 2.36–2.50 (m, 2H), 3.11 (m, 2H, $H_{1(7)}$), 6.35 (t, J = 1.8 Hz, 2H, $H_{8(9)}$); ^{13}C NMR($CDCl_3$), 29.6 (t, C_4), 34.6 (t, $C_{3(5)}$), 48.5 (d, $C_{1(7)}$), 48.9 (t, C_{10}), 67.4 (s, $C_{2(6)}$), 137.4 (d, $C_{8(9)}$), 175.0 (s, $-\underset{\cdot}{C}OO-$). Found: C, 70.44; H, 6.15. $C_{12}H_{12}O_3$ requires: C, 70.58; H, 5.92%.

(1*R*, 2*R*, 6*S*, 7*S*)-*Tricyclo*[5.2.1.$0^{2,6}$]*decane - 2,6 - dicarboxylic anhydride* **7**. A mixture of 1.00 g anhydride **6** (4.9 mmol), 100 mg 10% Pd on charcoal, and 20 ml ethyl acetate was hydrogenated in a medium pressure hydrogenation apparatus at 4.2 atm for 30 min. Filtration of the mixture and evaporation of the solvent from the filtrate left

1.00 g anhydride **7**, m.p. 140–2° (ethyl acetate), 99.0% yield. IR(KBr), 1860 (m), 1820 (m), 1775 (s) cm^{-1}; PMR($CDCl_3$), 1.22–1.93 (m, 10 H), 2.38–2.52 (m, 2 H), 2.56 (m, 2 H, $H_{1(7)}$); ^{13}C NMR($CDCl_3$), 25.0 (t, $C_{8(9)}$), 25.6 (t, C_4), 36.1 (t, $C_{3(5)}$), 37.8 (t, C_{10}), 43.7 (d, $C_{1(7)}$), 66.3 (s, $C_{2(6)}$), 175.7 (s, –ÇOO–). Found: C, 69.99; H, 7.07. $C_{12}H_{14}O_3$ requires: C, 69.89; H, 6.84%.

(1*R*, 2*S*, 6*R*, 7*S*) - *Tricyclo*[5.2.1.$0^{2,6}$]*dec - 8 - ene* - 2,6 - *dicarboxylic acid*, **8**. A mixture of 4.0 g NaOH (0.1 mol), 8.16 g anhydride **6** (0.04 mol) and 30 ml water was heated under reflux for 4 h. While the starting **6** was coming into solution another solid precipitated. The mixture was cooled to 5° and 10 ml concentrated HCl (0.12 mol) was added. The voluminous white precipitate that appeared when the medium became acidic was filtered and dried in vacuum (0.05 Torr) to give 8.23 g of **8**, m.p. 173–5° (dec.)(water), 92.7% yield. IR(KBr), 1690 cm^{-1}; 80 MHz PMR(DMSO-d_6), 1.2–2.4 (m, 8 H), 2.7 (broad s, 2 H, $H_{1(7)}$), 6.1 (broad s, 2 H, $H_{8(9)}$), 11.8 (broad absorption, 2 H); 20 MHz ^{13}C NMR(DMSO-d_6), 28.3 (C_4), 37.9 ($C_{3(5)}$), 44.7 (C_{10}), 50.7 ($C_{1(7)}$), 67.6 ($C_{2(6)}$), 136.2 ($C_{8(9)}$). Found: C, 64.73; H, 6.29. $C_{12}H_{14}O_4$ requires: C, 64.85; H, 6.35%.

Dimethyl (1*R*, 2*S*, 6*R*, 7*S*) - *tricyclo*[5.2.1.$0^{2,6}$]*dec - 8 - ene* - 2,6 - *dicarboxylate*, **9**. An ethereal solution of diazomethane, prepared from 10.3 g *N*-nitroso-*N*-methylurea (0.1 mol), 30 ml of 50% aqueous KOH and 250 ml ether, was distilled over a mixture of 5.0 g diacid **8** (22.5 mmol) and 250 ml ether kept at 0° with an ice bath, and allowed to stand at this temperature for 2 h. Evaporation of the solvent gave 5.76 g of crude product that was crystallized from 25 ml ether to give 5.56 g of **9** as a white solid, m.p. 59–60°, 98.7% yield. IR(KBr), 1722 cm^{-1}; PMR($CDCl_3$), 1.52 (dt, J = 9.5 Hz, J′ = 1.7 Hz, 1 H, H_{10syn}), 1.58–1.70 (m, 2 H), 1.80 (broad d, J = 9.5 Hz, 1 H, H_{10anti}), 1.85–2.02 (m, 1 H), 2.03–2.27 (m, 1 H), 2.33–2.47 (m, 2 H), 2.81 (m, 2 H, $H_{1(7)}$), 3.59 (s, 6 H), 6.26 (t, J = 1.6 Hz, 2 H, $H_{8(9)}$); ^{13}C NMR($CDCl_3$), 29.0 (t, C_4), 38.0 (t, $C_{3(5)}$), 45.2 (t, C_{10}), 51.4 (d, $C_{1(7)}$), 51.6 (c, –OÇH_3), 68.5 (s, $C_{2(6)}$), 136.6 (d, $C_{8(9)}$), 175.7 (s, –ÇOOMe). Found: C, 67.16; H, 7.19. $C_{14}H_{18}O_4$ requires: C, 67.18; H, 7.25%.

Dimethyl (1*R*, 2*R*, 6*S*, 7*S*) - *tricyclo*[5.2.1.$0^{2,6}$]*decane* - 2,6- *dicarboxylate*, **10**. A mixture of 3.00 g diester **9** (12 mmol), 0.41 g 10% Pd on charcoal, and 50 ml ethyl acetate was placed in a 100 ml flask that was connected to an atmospheric pressure hydrogenation apparatus. After filling it with hydrogen, the mixture was magnetically stirred until hydrogen uptake ceased (60 min). The mixture was filtered and the filtrate evaporated to give 2.96 g of **10**, m.p. 63–5° (ethyl acetate), 97.9% yield. IR(KBr), 1725 cm^{-1}; PMR($CDCl_3$), 1.18 (dt, J = 10.0 Hz, J′ = 1.6 Hz, 1 H, H_{10anti}), 1.34–1.94 (m, 9 H), 2.24 (m, 2 H, $H_{1(7)}$), 2.28–2.42 (m, 2 H), 3.62 (s, 6 H); ^{13}C NMR($CDCl_3$), 24.5 (t, $C_{8(9)}$), 25.9 (t, C_4), 35.6 (t, C_{10}), 39.5 (t, $C_{3(5)}$), 46.8 (d, $C_{1(7)}$), 51.3 (s, –OÇH_3), 64.2 (s, $C_{2(6)}$), 175.6 (s, –ÇOOMe). Found: C, 66.79; H, 7.92. $C_{14}H_{20}O_4$ requires: C, 66.65; H, 7.99%.

(1*R*, 2*R*, 6*S*, 7*S*)- *and* (1*R*, 2*S*, 6*R*, 7*S*) - 10 - *isopropylidenetricyclo*[5.2.1.$0^{2,6}$]*dec - 8 - ene* - 2,6 - *dicarboxylic anhydride*, **11** *and* **12**. A mixture of 45 g anhydride **2** (326 mmol), 35 g freshly distilled 6,6-dimethylfulvene, **5**, (330 mmol), and 600 ml xylene was heated under reflux for 1 h. Evaporation of a sample of this solution at reduced pressure (20 Torr) gave a residue consisting essentially of a 9/11 mixture of the corresponding *endo*- and *exo*-adducts (PMR). The solution was kept at 0° for 48 h and filtered to give 32 g prismatic crystals, m.p. 172–4°, corresponding to the *exo*-adduct **12**. By cooling the filtrate at −78° for 2 h, more product crystallized. Filtration of the mixture gave 28.2 g of a white solid, m.p. 133–5°, corresponding to *endo*-adduct **11**. The filtrate was concentrated at reduced pressure (20 Torr) to a volume of 200 ml, cooled at −78° for 1 h, and filtered to give 10.3 g of a product, m.p. 112–5°, consisting of a mixture of **11** and **12** in the approximate ratio 3/1. By addition of 300 ml pentane to the filtrate and cooling at −78° for 1 h, 2.8 g of **12**, slightly contaminated with **11** (m.p. 168–70°) was precipitated. Evaporation of the filtrate gave an oily residue that was discarded. The total yield of isolated adducts was 92.1% (45.1% yield of **11** and 47.0% yield of **12**).

Analytical and spectroscopic data of **12**. GLC, r.t. 6.54 min; 7.02 min; IR(KBr), 1845 (m), 1820 (m), 1782 (s) cm^{-1}; PMR($CDCl_3$), 1.30–1.56 (m, 2 H), 1.56–1.84 (m, 1.65 (s), total 7 H), 1.88–2.04 (m, 1 H), 2.32–2.42 (m, 2 H), 3.57 (t, J = 2 Hz, 2 H, $H_{1(7)}$), 6.47 (t, J = 2 Hz, 2 H, $H_{8(9)}$); ^{13}C NMR($CDCl_3$), 19.8 (c, –ÇH_3), 29.5 (t, C_4), 33.9 (t, $C_{3(5)}$), 48.9 (d, $C_{1(7)}$), 66.5 (s, $C_{2(6)}$), 116.3 (s, =Ç$(CH_3)_2$), 137.4 (d, $C_{8(9)}$), 145.6 (s, C_{10}), 174.6 (s, –ÇOO–). Found: C, 73.78; H, 6.60. $C_{15}H_{16}O_3$ requires: C, 73.75; H, 6.60%.

Analytical and spectroscopic data of **12**. GLC, r.t. 6.54 min; IR(KBr), 1826 (m), 1765 (s) cm^{-1}; PMR($CDCl_3$), 1.18–1.44 (m, 2 H), 1.50–1.75 (m, 1.55 (s), total 7 H), 1.75–1.92 (m, 1 H), 2.14–2.28 (m, 2 H), 3.72 (t, J = 2 Hz, 2 H, $H_{1(7)}$), 6.48 (t, J = 2 Hz, 2 H, $H_{8(9)}$); ^{13}C NMR($CDCl_3$), 19.2 (–ÇH_3), 28.7 (C_4), 32.3 ($C_{3(5)}$), 49.2 ($C_{1(7)}$), 67.8 ($C_{2(6)}$), 115.3 (=Ç$(CH_3)_2$), 137.3 ($C_{8(9)}$), 145.8 (C_{10}), 175.5 (–ÇOO–). Found: C, 73.52; H, 6.88. $C_{15}H_{16}O_3$ requires: C, 73.75; H, 6.60%.

Pyrolysis of the exo-*adduct* **12**. In a 1 liter flask fitted with a reflux condenser, 34.8 g of **12** was placed without solvent, and the flask immersed in an oil bath at 180° for 10 min keeping the reaction mixture in a nitrogen atmosphere. The cold residue was crystallized from 100 ml isopropanol to give 30.1 g of a product, m.p. 105–7°, consisting of a mixture approximately 9/11 of **11** and **12**, respectively (PMR). Evaporation of the filtrate left a residue consisting majorly of degradation products (PMR).

(1*R*, 2*R*, 6*S*, 7*S*) - 10 - *Isopropylidenetricyclo*-[5.2.1.$0^{2,6}$]*decane* - 2,6 - *dicarboxylic anhydride*, **13**. A mixture of 3.9 g adduct **11** (16 mmol), 0.39 g 10% Pd on charcoal, and 50 ml ethyl acetate was hydrogenated at atmospheric pressure in 45 min, being most of the hydrogen consumed in the first 15 min. The suspension was filtered and the solvent evaporated from the filtrate to give 3.95 g of **13**, as a solid, m.p. 140–2° (ethyl acetate), quantitative yield. IR(KBr), 1850 (m), 1818 (m), 1770 (s) cm^{-1}; PMR($CDCl_3$), 1.28–1.50 (m, 5 H), 1.54–1.77 (m, 1.71 (s), total 9 H), 2.34–2.47 (m, 2 H), 2.95 (m, 2 H, $H_{1(7)}$); ^{13}C NMR($CDCl_3$), 20.8 (c, –ÇH_3), 24.2 (t, $C_{8(9)}$), 25.3 (t, C_4), 35.9 (t, $C_{3(5)}$), 43.7 (d, $C_{1(7)}$), 64.7 (s, $C_{2(6)}$), 122.4 (s, =Ç$(CH_3)_2$), 138.3 (s, C_{10}), 175.6(s, –ÇOO–). Found: C, 73.13; H, 7.34. $C_{15}H_{18}O_3$ requires: C, 73.15; H, 7.37%.

(1*R*, 2*R*, 6*S*, 7*S*) - 10 - *Isopropylidenetricyclo*-[5.2.1.$0^{2,6}$]*decane* - 2,6 - *dicarboxylic acid*, **14**. A mixture of 1.43 g anhydride **13** (5.81 mmol) 2 g NaOH (0.05 mol), and 25 ml water was heated under reflux for 3 h. While the starting product was coming into solution another solid precipitated. The solution was cooled to 5° and 4.9 ml concentrated HCl was added. A voluminous white precipitate appeared when the solution became acidic. The mixture was cooled at 0° for 30 min and filtered. The solid was washed with a small volume of cold water and dried in vacuum (0.05 Torr) giving rise to 1.53 g of diacid **14**, m.p. 192–5° (dec.)(water), 99.7% yield. IR(KBr), 3400 (m), 3200 (m), 1720 (s), 1690 (s) cm^{-1}; 80 MHz PMR(DMSO-d_6), 1.1–1.9 (m, 1.6 (s), total 14 H), 2.1–2.3 (m, 2 H), 2.5 (m, 2 H, $H_{1(7)}$), 11.9 (broad absorption, 2 H); 20 MHz ^{13}C NMR(DMSO-d_6), 20.2 (–ÇH_3), 23.2 ($C_{8(9)}$), 24.9 (C_4), 39.0 ($C_{3(5)}$), 46.3 ($C_{1(7)}$), 62.2 ($C_{2(6)}$), 116.6 (=Ç$(CH_3)_2$), 140.2 (C_{10}), 175.4 (–ÇOO–). Found: C, 68.56; H, 7.18. $C_{15}H_{20}O_4$ requires: C, 68.16; H, 7.63%.

Dimethyl(1*R*, 2*R*, 6*S*, 7*S*) - 10 - *isopropylidenetricyclo*-[5.2.1.$0^{2,6}$]*decane* - 2,6 - *dicarboxylate*, **15**. An ethereal solution of diazomethane, prepared from 5.0 g *N*-nitroso-*N*-methylurea (48.5 mmol), 4 ml 50% aqueous NaOH, and 100 ml ether, was distilled over a mixture of 1.53 g diacid **14** (5.8 mmol) and 150 ml ether kept at 0° with an ice bath, and allowed to stand at this temperature for 2 h. Evaporation of the solvent gave 1.68 g of crude product that was dissolved in methanol, decolorized with active charcoal, and crystallized to give 1.31 g of prismatic crystals, m.p. 50–51°

(methanol). Evaporation of the solvent from the filtrate gave 0.34 g more product. Total yield 97.5%. IR(KBr), 1720 cm^{-1}; PMR($CDCl_3$), 1.35–1.80 (m, 1.70 (s), total 14 H), 2.24–2.37 (m, 2 H), 2.70 (m, 2 H, $H_{1(7)}$), 3.64 (s, 6 H); ^{13}C NMR($CDCl_3$), 20.6 (c, $=C(\underset{|}{C}H_3)_2$), 23.6 (t, $C_{8(9)}$), 25.6 (t, C_4), 39.3 (t, $C_{3(5)}$), 47.0 (d, $C_{1(7)}$), 51.3 (c, $-O\underset{|}{C}H_3$), 63.2 (s, $C_{2(6)}$), 118.2 (s, $=\underset{|}{C}(CH_3)_2$), 139.8 (s, C_{10}), 175.4 (s, $-\underset{|}{C}OOMe$). Found: C, 70.07; H, 8.31. $C_{17}H_{24}O_4$ requires: C, 69.84; H, 8.27%.

(1*R*, 2*S*, 6*R*, 7*S*) - 10 - *Isopropylidenetricyclo-*[5.2.1.0^{2,6}]*decane* - 2,6 - *dicarboxylic anhydride*, **16**. A mixture of 1.00 g anhydride **12** (4.1 mmol), 0.1 g 10% Pd on charcoal, and 50 ml ethyl acetate was hydrogenated at 4.2 atm in 30 min. After the appropriate working up, 0.96 g of **16** was obtained, m.p. 200–202° (isopropanol), 95.2% yield. IR(KBr), 1840 (m), 1812 (m), 1770 (s) cm^{-1}; PMR($CDCl_3$), 1.50–1.70 (m, 1.63 (s), total 10 H), 1.72–2.04 (m, 6 H), 3.03 (m, 2 H, $H_{1(7)}$); ^{13}C NMR($CDCl_3$), 20.4 (c, $-\underset{|}{C}H_3$), 21.7 (t, $C_{8(9)}$), 29.2 (t, C_4), 29.3 (t, $C_{3(5)}$), 43.3 (d, $C_{1(7)}$), 63.9 (s, $C_{2(6)}$), 121.3 (s, $=\underset{|}{C}(CH_3)_2$), 139.5 (s, C_{10}), 176.8 (s, $-\underset{|}{C}OO-$). Found: C, 73.08; H, 7.10. $C_{15}H_{18}O_3$ requires: C, 73.15; H, 7.37%.

(1*R*, 2*S*, 6*R*, 7*S*) - 10 - *Isopropylidenetricyclo-*[5.2.1.0^{2,6}]*decane* - 2,6 - *dicarboxylic acid*, **17**. A mixture of 3.0 g anhydride **16** (12.2 mmol), 4.0 g NaOH (0.1 mol), and 50 ml water was heated under reflux for 3 h. The solution was cooled at 5°, acidified with 10 ml concentrated HCl, and allowed to stand at 0° for 30 min. The voluminous white precipitate was filtered, washed with 10 ml cold water, and dried in vacuum (0.05 Torr) giving rise to 3.21 g of **17**, m.p. 160–163° (dec.)(water), 99.7% yield. IR(KBr), 3220 (s), 1725 (s), 1695 (m) cm^{-1}; PMR(DMSO-d_6), 1.2–2.0 (m, 1.59 (s), total 14 H), 2.0–2.3 (m, 2 H), 2.85 (m, 2 H, $H_{1(7)}$), 11.6 (broad absorption, 2 H), ^{13}C NMR(DMSO-d_6), 20.8 (c, $-\underset{|}{C}H_3$), 22.9 (t, $C_{8(9)}$), 28.0 (t, C_4), 33.3 (t, $C_{3(5)}$), 45.1 (d, $C_{1(7)}$), 64.2 (s, $C_{2(6)}$), 114.1 (s, $=\underset{|}{C}(CH_3)_2$), 144.2 (s, C_{10}), 176.8 (s, $-\underset{|}{C}OO-$). Found: C, 67.96; H, 7.91. $C_{15}H_{20}O_4$ requires: C, 68.16; H, 7.63%.

Dimethyl(1*R*, 2*S*, 6*R*, 7*S*) - 10 - *isopropylidenetricyclo-*[5.2.1.0^{2,6}]*decane* - 2,6 - *dicarboxylate*, **18**. An ethereal solution of diazomethane, prepared from 10 g *N*-nitroso-*N*-methylurea (97 mmol), 80 ml 50% aqueous NaOH, and 200 ml ether, was distilled over a mixture of diacid **17** (3.20 g, 12.1 mmol) and 300 ml ether kept at 0° with an ice bath, and allowed to stand at this temperature for 2 h. Evaporation of the solvent gave 3.55 g of crude product that was dissolved in methanol, decolorized with active charcoal, and crystallized to give 3.10 g of **18**, m.p. 57–8° (methanol). Evaporation of the solvent from the filtrate gave 0.44 g more product, quantitative yield. IR(KBr), 1734 (s), 1720 (s) cm^{-1}; PMR($CDCl_3$), 1.38–1.50 (m, 2 H, $H_{8(9)exo}$), 1.56–1.68 (m, 1.66 (s), total 8 H, $2-C\underline{H}_3$ and $H_{8(9)endo}$), 1.78–2.04 (m, 4 H), 2.10–2.32 (m, 2 H), 2.88 (m, 2 H, $H_{1(7)}$), 3.56 (s, 6 H); ^{13}C NMR($CDCl_3$), 20.5 (c, $=C(\underset{|}{C}H_3)_2$), 23.0 (t, $C_{8(9)}$), 28.2 (t, C_4), 33.2 (t, $C_{3(5)}$), 45.3 (d, $C_{1(7)}$), 51.8 (c, $-O\underset{|}{C}H_3$), 65.1 (s, $C_{2(6)}$), 116.1 (s, $=\underset{|}{C}(CH_3)_2$), 143.1 (s, C_{10}), 176.3 (s, $-\underset{|}{C}OOMe$). Found: C, 69.81; H, 8.34. $C_{17}H_{24}O_4$ requires: C, 69.84; H, 8.27%.

(1*R*, 2*S*, 6*R*, 7*S*) - 10 - *oxotricyclo*[5.2.1.0^{2,6}]*decane* - 2,6-*dicarboxylic anhydride*, **19**. Through a solution of anhydride **13** (5.0 g, 20.3 mmol) in 250 ml CH_2Cl_2 at −78° (acetone-CO_2 bath), an ozone stream (generated as described in *Org. Synth.*,[17] using a flow of 0.25 l/min oxygen and 85 V, what approximately corresponds to an ozone concentration of 3.4%) was bubbled. After 3.5 h the solution became blue-violet (ozone in solution). The solution was poured in a 500 ml flask containing 5 g powdered Zn and 50 ml glacial acetic acid, and the mixture was magnetically stirred at room temperature for 3 h. The material corresponding to six batches like the one described was combined, the mixture was filtered, and the solid was washed with CH_2Cl_2. Evaporation of the volatile products from the filtrate at reduced pressure (first at 20 Torr and then at 0.1 Torr) left 26.3 g of a white solid, whose GLC analysis showed to be a mixture of **19** and epoxyanhydride **20** in the approximate 2/1 weight ratio (65% yield for the conversion **13**→**19**). Crystallization from benzene (50 ml) gave 10.35 g of pure **19**, m.p. 178–80° (isopropanol). IR(KBr), 1865 (m), 1775 (vs) cm^{-1}; PMR($CDCl_3$), 1.32–1.68 (m, 5 H), 1.78–1.92 (m, 1 H), 1.96–2.10 (m, 2 H), 2.45 (m, 2 H, $H_{1(7)}$), 2.52–2.61 (m, 2 H); ^{13}C NMR($CDCl_3$), 19.0 (t, $C_{8(9)}$), 24.8 (t, C_4), 36.1 (t, $C_{3(5)}$), 46.0 (d, $C_{1(7)}$), 58.6 (s, $C_{2(6)}$), 173.6 (s, $-\underset{|}{C}OO-$), 206.6 (s, C_{10}). Found: C, 65.36, H, 5.45. $C_{12}H_{12}O_4$ requires: C, 65.45; H, 5.49%.

(1*R*, 2*S*, 6*R*, 7*S*, 10*S*) - 3′,3′ - *Dimethylspiro*[*tricyclo-*[5.2.1.0^{2,6}]*decane* - 10,2′ - *oxirane*] - 2,6 - *dicarboxylic anhydride*, **20**. One gram of anhydride 13 (4.06 mmol) was added over 10 ml of a cold (0°) chloroform solution containing 0.7 g (5 mmol) of perbenzoic acid. The mixture was stirred at this temperature for 30 min and allowed to stand in the refrigerator for 12 h. The solution was washed with aqueous NaOH, water, and dried over anhydrous Na_2SO_4. Evaporation of the solvent gave 0.98 g of epoxide **20**, m.p. 158–60° (isopropanol), 92% yield. IR(KBr), 1870 (m), 1855 (m), 1830 (m), 1775 (s) cm^{-1}; PMR($CDCl_3$), 1.30–1.74 (m, 1.43(s), total 11 H), 1.82–1.94 (m, 1 H), 2.00–2.14 (m, 2 H), 2.22 (dd, J = 3 Hz, J′ = 2 Hz, 2 H, $H_{1(7)}$), 2.42–2.54 (m, 2 H); ^{13}C NMR($CDCl_3$), 23.0 (c, $-\underset{|}{C}H_3$), 23.8 (t, $C_{8(9)}$), 25.4 (t, C_4), 35.4 (t, $C_{3(5)}$), 43.0 (d, $C_{1(7)}$), 62.9 (s, $C_{2(6)}$), 63.8 (s, $-\overset{|}{\underset{|}{C}}(CH_3)_2$), 81.7 (s, C_{10}), 174.8 (s, $-\underset{|}{C}OO-$). Found: C, 68.69; H, 6.88. $C_{15}H_{18}O_4$ requires: C, 68.69; H, 6.92%.

(1*R*, 2*S*, 6*R*, 7*S*) - 10 - *oxotricyclo*[5.2.1.0^{2,6}]*decane* - 2,6-*dicarboxylic acid*, **21**. A mixture of 4.4 g anhydride **19** (20 mmol), 2 g NaOH (50 mmol), and 20 ml water was heated under reflux for 3 h. The solution was cooled to 0°, acidified with concentrated HCl to pH 1, and kept at 0° for 1 h. The precipitate was filtered and dried in vacuum (0.05 Torr) to give 4.48 g of **24**, m.p. 192–4° (dec.)(water), 94.1% yield. IR(KBr), 3160 (s), 1750 (s), 1700 (s) cm^{-1}; 80 MHz PMR(DMSO-d_6), 1.3–2.4 (m). 20 MHz ^{13}C NMR (DMSO-d_6), 18.0 (t, $C_{8(9)}$), 24.0 (t, C_4), 38.8 (t, $C_{3(5)}$), 49.3 (d, $C_{1(7)}$), 58.1 (s, $C_{2(6)}$), 173.9 (s, $-\underset{|}{C}OO-$), 212.1 (s, C_{10}). Found: C, 60.46; H, 6.14. $C_{12}H_{14}O_5$ requires: C, 60.50; H, 5.92%.

Dimethyl(1*R*, 2*S*, 6*R*, 7*S*) - 10 - *oxotricyclo-*[5.2.1.0^{2,6}]*decane* - 2,6 - *dicarboxylate*, **1**. An ethereal solution of diazomethane, prepared from 9.1 g *N*-nitroso-*N*-methylurea (88 mmol), 7.2 ml 50% aqueous NaOH, and 160 ml ether, was distilled over a mixture of 2.32 g diacid **21** (10 mmol) and 240 ml ether kept at 0° with an ice bath, and the mixture was allowed to stand at this temperature for 2 h. Evaporation of the volatile products gave 2.65 g of crude product, that was crystallized from methanol to give 2.55 g of pure **1** as white crystals, m.p. 82–4°, 95.9% yield. IR(KBr), 1770 (s), 1725 (s) cm^{-1}; PMR($CDCl_3$), 1.62–1.93 (m, 6 H), 1.94–2.08 (m, 2 H, $H_{8(9)endo}$), 2.13 (m, 2 H, $H_{1(7)}$), 2.32–2.52 (m, 2 H), 3.70 (s, 6 H); ^{13}C NMR($CDCl_3$), 18.5 (t, $C_{8(9)}$), 24.7 (t, C_4), 39.0 (t, $C_{3(5)}$), 49.9 (d, $C_{1(7)}$), 51.9 (c, $-O\underset{|}{C}H_3$), 59.1 (s, $C_{2(6)}$), 173.5 (s, $-\underset{|}{C}OO-$), 212.1 (s, C_{10}). Found: C, 63.35; H, 7.05. $C_{14}H_{18}O_5$ requires: C, 63.15; H, 6.81%.

Acknowledgements—We gratefully thank M. Guerra from Instituto de Química Bio-orgánica (C.S.I.C., Barcelona, Spain) for carrying out the elemental analyses, Dr. F. Pujol from the same Institute for ozonizing anhydride 13, and Dr. F. Sánchez-Ferrando from the Universidad Autónoma de Barcelona, for running the 80 MHz PMR and 20 MHz ^{13}C NMR spectra. We are indebted with Dr. C. Jaime for carrying out the molecular mechanics calculations and with Prof. E. Ōsawa from the Hokkaido University (Sapporo, Japan) for facilities to effect such calculations.

REFERENCES

[1] C. H. De Puy, M. Isaks, K. L. Eilers and G. F. Morris, *J. Org. Chem.* **29**, 3503 (1964).

[2] P. E. Eaton and R. A. Hudson, *J. Am. Chem. Soc.* **87**, 2769 (1965).

[3a] R. B. Woodward and H. J. Baer, *Ibid.* **66**, 645 (1944); [b]D. Craig, J. J. Shipman, J. Kiehl, F. Widmer, R. Fowler and A. Hawthorne, *Ibid.* **76**, 4573 (1954); [c]K. Alder and R. Rühmann, *Ann. Chem.* **566**, 1 (1950).

[4] K. Alder, F. W. Chambers and W. Trimborn, *Ann. Chem.* **566**, 27 (1950).

[5] R. E. Wingard, Jr., R. K. Russell and L. A. Paquette, *J. Am. Chem. Soc.* **96**, 7474 (1974).

[6] D. Belluš, K. von Bredow, H. Sauter and C. D. Weis, *Helv. Chim. Acta* **56**, 3004 (1973).

[7] L. M. Jackman and S. Sternhell, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd Edn, p. 89. Pergamon Press, Oxford (1969).

[8] P. J. Garratt and F. Hollowood, *J. Org. Chem.* **47**, 68 (1982).

[9] B. Vebersax, M. Neuenschwander and P. Engel, *Helv. Chim. Acta* **65**, 89 (1982).

[10] R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.* **87**, 4388 (1965); K. N. Houk, *Tetrahedron Letters* 2621 (1970); K. N. Houk and L. J. Luskus, *J. Am. Chem. Soc.* **93**, 4606 (1971).

[11] J. A. Berson, Z. Hamlet and W. A. Mueller, *J. Am. Chem. Soc.* **84**, 297 (1962); P. B. Sargent, *Ibid.* **91**, 3061 (1969); K. L. Williamson, Y. L. Hsu, R. Lacko and C. H. Youn, *Ibid.* **91**, 6129 (1969); E. W. Garbisch, Jr. and R. F. Sprecher, *Ibid.* **91**, 6785 (1969); K. L. Williamson and Y. L. Hsu, *Ibid.* **92**, 7385 (1970); P. L. Watson and R. N. Warrener, *Aust. J. Chem.* **26**, 1725 (1973).

[12] J. G. Martin and R. K. Hill, *Chem. Rev.* **61**, 537 (1961).

[13] K. Nakagawa, S. Iwase, Y. Ishh, S. Hamanaka and M. Ogawa, *Bull. Chem. Soc. Japan* **50**, 2391 (1977).

[14] W. Kreiser, L. Janitschke and L. Ernst, *Tetrahedron* **34**, 131 (1978).

[15] K. Tori, M. Ueyama, T. Tsuji, H. Matsumura, H. Tanida, H. Iwamura, K. Kushida, T. Nishida and S. Satoh, *Tetrahedron Letters* 327 (1974).

[16] Calculations were carried out using a modified MM2 program, C. Jaime and E. Ōsawa, *Tetrahedron* **39**, 2769 (1983).

[17] L. I. Smith, F. L. Greenwood and O. Hudrlik, *Org. Synth. Coll.* **III**, 673 (1953).