Acknowledgment. We wish to thank the Research Corporation and State University of New York at Binghamton (Biomedical Research Support Grant) for generous financial support. We also thank Jon Stickles and John Soderquist for technical assistance.

Registry No.—**1**, 2816-57-1; **2**, 61259-60-7; **3**, 61288-74-2; **4** (5-ene), 61259-61-8; **4** (6-ene), 61259-62-9; **5** (5-ene), 61259-63-0; **5** (6-ene), 61259-64-1; **6**, 59056-74-5; 1-iodooctane, 629-27-6; MeI, 74-88-4; Ac_2O, 108-24-7.

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A Facile Internal Dilactonization of 1,6-Dialkyl-7,8-diphenyltricyclo[4.2.1.$0^{2,5}$]non-7-en-9-one-*endo*-2,5-dicarboxylic Acids

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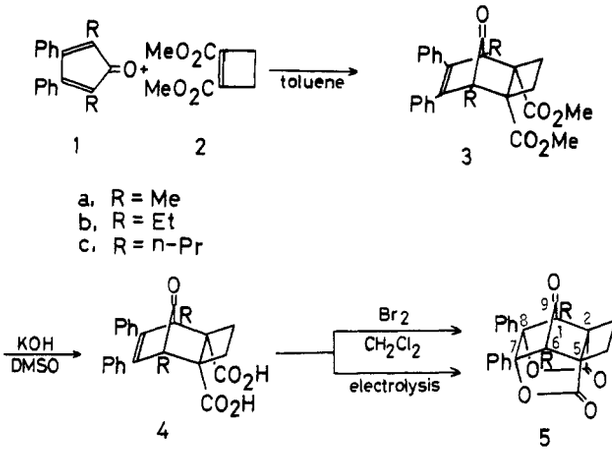
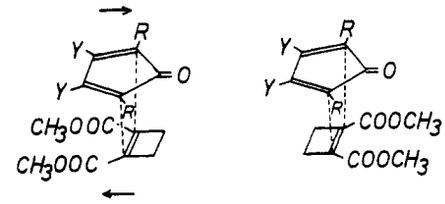
Although electrophile-induced monolactonization of 2-*endo*-norbornenecarboxylic acid and related compounds is well known,[1] examples involving formation of dilactone are rare.[2] The present note describe the facile formation of dilactones **5** from 1,6-dialkyl-7,8-diphenyltricyclo[4.2.1.$0^{2,5}$]-non-7-en-9-one-*endo*-2,5-dicarboxylic acids (**4**) which were obtained by Diels–Alder reactions[3] of 2,5-dialkyl-3,4-diphenylcyclopentadienones (**1**)[4] with dimethyl Δ^1-cyclobutene-1,2-dicarboxylate (**2**),[5] followed by hydrolysis.



Reaction of **1** with two equimolar amounts of **2** in refluxing toluene for 3–4 days produced the single products in 42–93% yields. The analytical and spectral data are compatible with the 1:1 adduct structure of **3** (see Tables I and II). The ^1H ester methyl resonances which appear at 3.61–3.62 ppm for these adducts are in accord with the *endo*-carbomethoxy assignment.[1c] The endo stereoselectivity can be predicted on the basis of the secondary orbital interactions[6] between carbomethoxy groups and diene systems, as well as the dipole–



dipole interactions[7] between reactants in the transition state of the [4 + 2] cycloaddition.

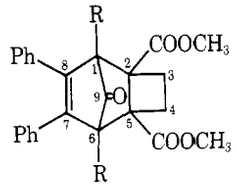
The dimethyl esters **3** were converted by alkaline hydrolysis in dimethyl sulfoxide at 80 °C to the corresponding dicarboxylic acids **4**, which, on treatment with excess bromine in dichloromethane at room temperature, afforded the corresponding dilactones **5** in 22–26% yields (from **3**). The struc-

Table I. Cycloadducts 3 Derived from Cyclopentadienones 1 and Dimethyl Δ^1-Cyclobutene-1,2-dicarboxylate (2)

Registry no.	Compd[b]	R	Time,[a] days	Yield, %	Mp, °C	IR (KBr), cm^{-1}, $\nu_{C=O}$	^1H NMR, δ ($CDCl_3$) $-COOCH_3$	^1H NMR, δ ($CDCl_3$) Others
61202-87-7	**3a**	Me	3	42	142–144.5	1726 1749 1778	3.62	1.33 (s, 6 H, CH_3) 1.66–2.87 (m, 4 H, $-CH_2CH_2-$) 6.88–7.19 (m, 10 H, aromatic)
61202-88-8	**3b**	Et	3.5	93	126–128.7	1724 1750 1773	3.61	0.77 (t, J = 8 Hz, 6 H, CH_3) 2.05 (q, J = 8 Hz, 4 H, $-CH_2-$) 1.95–2.72 (m, 4 H, $-CH_2CH_2-$) 6.89–7.20 (m, 10 H, aromatic)
61202-89-9	**3c**	*n*-Pr	4	59	120–122	1720 1742 1763	3.62	0.7–2.8 (m, 18 H, n-$CH_3CH_2CH_2-$) 6.63–7.37 (m, 10 H, aromatic)

[a] Time of disappearance of 1, monitored by TLC. [b] Satisfactory analytical data (±0.4% for C, H) for all compounds were submitted for review.

Table II. ^{13}C NMR Spectral Data of 3[a]



Compd	R	C-1, 6 (s)	C-2, 5[b] (s)	C-3, 4 (t)	C-7, 8 (s)	C-9 (s)	–CO– (s)	$-OCH_3$ (q)	CH_3- (q)	$-CH_2-$ (t)	$-CH_2-$ (t)
3a	Me	59.74	58.92	21.10	142.85	200.31	172.39	51.94	6.98		
3b	Et	62.98	59.09	21.75	142.60	201.12	172.72	51.78	9.74	16.07	
3c	*n*-Pr	62.82	59.09	21.75	142.52	221.25	172.72	51.78	15.10	18.34	25.49

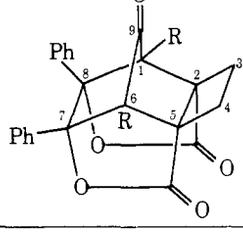
[a] In parts per million, from internal Me_4Si in $CDCl_3$. Parentheses indicate splitting patterns in the partial proton decoupling measurements. [b] Assigned from comparison with the corresponding ^{13}C chemical shifts of the adducts from 1 and dimethyl maleate and dimethyl fumarate.

Table III. 1,6-Dialkyl-7,8-diphenyltricyclo[4.2.1.$0^{2,5}$]nonan-9-one-2,8:5,7-dicarbolactone (5)

Registry no.	R[b] (no.)	Yield, % method[a] A	B	Mp, °C	M^+, *m/e*	$\nu_{C=O}$ (KBr disk), cm^{-1}		^1H NMR, δ, ppm (in $CDCl_3$)
61202-90-2	Me (**5a**)	26	21	284–285	400	1810	1783 1772	1.18 (s, 6 H, CH_3) 1.94–2.96 (m, 4 H, CH_2) 6.99 (s, 10 H, Ph)
61202-91-3	Et (**5b**)	23	58	264–266	428	1808	1781 1774	0.53 (t, 6 H, CH_3) 1.74–3.02 (m, 8 H, CH_2) 7.02 (s, 10 H, Ph)
61202-92-4	*n*-Pr (**5c**)	22	35	231–232	456	1803	1778 1769	0.58–1.24 (m, 14 H, *n*-Pr) 1.57–2.00 2.01–2.98 (m, 4 H, ring CH_2) 6.99 (s, 10 H, Ph)

[a] Method A: treatments of the dicarboxylic acids **4** with excess bromine in dichloromethane. Yields from the methyl ester **3**. Method B: electrolysis of the dicarboxylic acids **4** under Kolbe condition. Yields from **4**. [b] Satisfactory analytical data (±0.3% for C, H) for all compounds were submitted for review.

Table IV. ^{13}C NMR Spectral Data of 5[a]



R (no.)	C-2, 5 (s)	C-1, 6 (s)	C-3, 4 (t)	C-7, 8 (s)	–COO– (s)	C-9 (s)	CH_3- (q)	$-CH_2-$ (t)	$-CH_2-$ (t)
Me (**5a**)	55.84	59.57	16.56	92.69	170.93	207.29	6.17		
Et (**5b**)	54.87	63.11	16.49	92.26	170.00	207.90	7.92	15.26	
n-Pr (**5c**)	55.11	62.82	16.56	92.36	172.07	207.94	14.61	16.88	24.59

[a] In parts per million, from internal Me_4Si in $CDCl_3$. Parentheses indicate splitting patterns in the partial proton decoupling measurements.

tures of **5** were confirmed by NMR (^{13}C and ^1H), IR, mass spectra, and elemental analysis. The results are summarized in Tables III and IV.

Recently, benzocyclobutene derivatives have been prepared by the Diels–Alder addition of **2** to an appropriate diene and subsequent bisdecarboxylation and aromatization of the resulting six-membered ring.[8] An attempted decarbonylative bisdecarboxylation of **4** by electrolysis under Kolbe condition[1b,9] was unsuccessful, giving **5** in 21–58% yields (Table III). No benzocyclobutene derivatives or bisdecarboxylated compounds[1b,9] were detected. The other electrophilic reagents such as lead(IV) acetate and thallium(III) acetate were ineffective under usual conditions[1a,8a,10] so far in our hands.

The facile formation of dilactone may be ascribed to the close proximity of the double bond to the carboxyl groups.[2a,b]

Experimental Section

General. Melting points were taken on a Yanagimoto micromelting point apparatus and are uncorrected. Infrared spectra were obtained on a Jasco IR-G or a Hitachi EPI-G3 spectrometer. ^1H NMR spectra were measured on a JEOL C-60HL or a JEOL 4H-100 instrument and are reported in parts per million downfield from internal Me_4Si. ^{13}C NMR spectra were recorded on a JEOL FX-60 pulsed Fourier transform nuclear magnetic resonance spectrometer operating at 15.030 MHz. Samples were observed in 10-mm o.d. tubes, at 0.1–0.2 M solutions in chloroform-*d* at 30 °C. Chemical shifts are given in parts per million downfield from Me_4Si as zero. Partial proton decoupling was used to distinguish between individual carbon atoms. Mass spectra were obtained on a JEOL 01SG-2 mass spectrometer.

General Procedure for Reaction of 1 with 2. A stirred solution of **1** (3 mmol) and **2** (6 mmol) in dry toluene (25 ml) was refluxed under nitrogen until **1** was consumed. The reaction was followed by NMR and TLC. Toluene was evaporated from the solution and the residue was recrystallized from ethanol to afford colorless crystals of **3** (Tables I and II).

General Procedure for Hydrolysis and Dilactonization of 3. The dimethyl ester **3** (4 mmol) in 95% aqueous dimethyl sulfoxide (150 ml) containing potassium hydroxide (0.8 g) was stirred at 80 °C in a water bath for 5 h. The reaction mixture was poured into ice–water (ca. 1.5 l.) and acidified carefully with dilute hydrochloric acid. The white solid formed was filtered and dried. Without further purification, the hydrolysis product was treated with excess bromine (6 mmol) in dichloromethane (20 ml) with stirring at room temperature for 7 h, and the solution was concentrated under reduced pressure. The residue was recrystallized from ethanol, forming colorless prisms of **5** (Tables III and IV).

General Procedure for Electrolysis of 4. The diacid **4** (1 mmol) was dissolved in a solution of 90% aqueous pyridine (50 ml) and triethylamine (0.7 ml). This stirred mixture was electrolyzed under nitrogen between two platinium plate electrodes at 100–200 V (dc) with a current of 0.5 A for 7 h, during which time the mixture was cooled with an ice water bath. The dark brown mixture was concentrated under reduced pressure. To the residue was added 10% aqueous solution of sodium hydrogen carbonate and the mixture was extracted with benzene and ether, washed with water, and then dried ($MgSO_4$). After evaporation of the solvents, the residue was crystallized from ethanol to yield **5** (Table III).

Acknowledgment. We are grateful to Professor Kazuhiro Maruyama (Faculty of Science, Kyoto University) for his interest and encouragement. This work has been supported in part by a Research Grant (to K.M. and T.U.) from the Ministry of Education, Japan.

Registry No.—**1a,** 26307-17-5; **1b,** 51932-77-5; **1c,** 61202-93-5; **2,** 1128-10-5; **4a,** 61202-94-6; **4b,** 61202-95-7; **4c,** 61202-96-8.

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1-Methyl-1-dihalomethylcyclohexane Derivatives[1]

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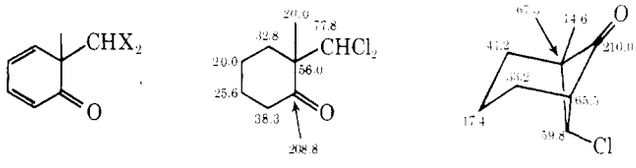
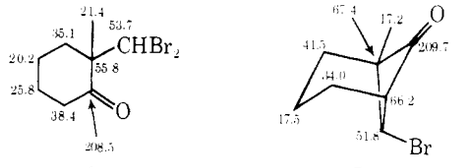
Two projects of terpene synthesis required the use of dihalomethylcyclohexadienones, derived from Reimer–Tiemann reactions of *o*- and *p*-cresols, as starting materials. In this connection it became important to determine the stereochemistry and conformation of the cyclohexanic substances encountered in early steps of the reaction sequences, a task accomplished in part by ^{13}C NMR spectroscopy.

Whereas dichloromethylcyclohexadienones are common Reimer–Tiemann products, their dibromomethyl equivalents have been reported only rarely.[2,3] Treatment of *o*-cresol with bromoform and base yielded dienone **1b**, whose hydrogenation produced ketone **4**. Dehydrobromination of the latter with potassium *tert*-butoxide led to bicycle **5**. These three reactions parallel the earlier **1a** → **2** → **3** sequence[4] and have the same



1a, X = Cl
b, X = Br

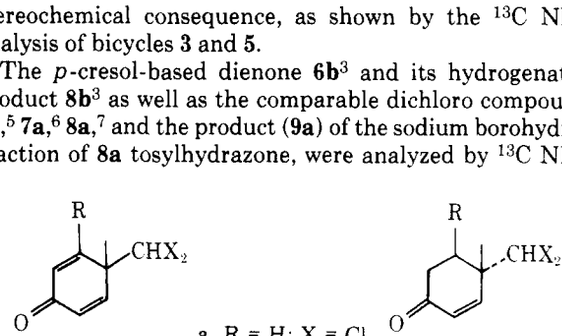
2 **3**



4 **5**

stereochemical consequence, as shown by the ^{13}C NMR analysis of bicycles **3** and **5**.

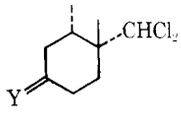
The *p*-cresol-based dienone **6b**[3] and its hydrogenation product **8b**[3] as well as the comparable dichloro compounds **6a**,[5] **7a**,[6] **8a**,[7] and the product (**9a**) of the sodium borohydride reaction of **8a** tosylhydrazone, were analyzed by ^{13}C NMR



6 **7**

a, R = H; X = Cl
b, R = H; X = Br
c, R = Me; X = Cl
d, R = Me; X = Br

8 **9**



10a, Y = O
b, Y = H_2