A portion (421.2 mg, 2.50 mmol) was dissolved in ether (10 mL), and chlorotrimethylsilane (0.38 mL) and triethylamine (0.42 mL) were added. The mixture was refluxed for 2 h and worked up as described for **4b**. The crude product was purified by flash chromatography over silica gel (2 × 18 cm) with hexane containing increasing amounts of ethyl acetate (1–20% v/v). Kugelrohr distillation [160 °C (10 mm)] gave **8b** as a mixture of isomers (200.5 mg, 33.2%) of better than 98% purity (VPC, DEGS, 115 °C): IR (film) 1252, 1085 cm^{-1}; NMR ($CDCl_3$, 200 MHz) δ 0.088, 0.079, 0.044, 0.041 (4 s, 9 H overall), 0.95–1.2 (series of 8 overlapping d, 6 H overall), 1.2–3.0 (m, 12 H), 4.75–5.00 (m, 1 H); exact mass 240.1907 (calcd for $C_{14}H_{28}OSi$ 240.1909). Anal. Calcd for $C_{14}H_{28}OSi$: C, 69.93; H, 11.74. Found: C, 70.18; H, 11.84.

The flash chromatography also afforded, after Kugelrohr distillation, the starting alcohol (240.9 mg, 57.2%) as an apparently homogeneous (TLC, silica, 1:4 ethyl acetate–hexane) oil.

(4aβ,8aβ)-(4a-Methyldecahydronaphth-2-ylidene)-2-propanol (9b). The procedure for **1b** was followed with **9** (148.2 mg, 0.771 mmol) in ether (1 mL plus 2 × 1 mL rinse) and ethereal MeLi (1.52 M, 0.75 mL, 1.156 mmol) in ether (10 mL). The workup, flash chromatography over silica gel (2 × 18 cm) with 1:8 ethyl acetate–hexane, and Kugelrohr distillation [160 °C (0.15 mm)] gave **9b** (124 mg, 77.2%) as an apparently homogeneous (TLC, silica, 1:8 ethyl acetate–hexane) oil of better than 98% purity (VPC, FFAP, 210 °C). The material was a mixture (NMR) of four diastereoisomers: IR (film) 3330, 1660, 1055 cm^{-1}; NMR ($CDCl_3$, 200 MHz) δ 0.9–2.5 (m, 22 H, incorporating 4 sharp d with J = 8 Hz at δ 1.240, 1.230, 1.222, and 1.220 and 2 s at δ 1.032 and 1.026, all of comparable intensity), 4.58 (m, 1 H), 5.11 (br d, J = 8 Hz, 0.5 H), 5.22 (br d, J = 8 Hz, 0.5 H); exact mass 208.1829 (calcd for $C_{14}H_{24}O$ 208.1827). Anal. Calcd for $C_{14}H_{24}O$: C, 80.70; H, 11.61. Found: C, 80.74; H, 11.54.

2,3,4-Trimethyl-3-penten-2-ol. Ethereal methyllithium (1.53 M, 3 mL, 4.59 mmol) was diluted with ether (10 mL) and treated at 0 °C with 3,4-dimethyl-3-penten-2-one (**12**;[79] 275.8 mg, 2.458 mmol) in ether (1 mL plus 2 × 1 mL rinse). After 1 h at 0 °C the mixture was poured onto a saturated aqueous solution of ammonium chloride and extracted with ether (2 × 30 mL). The organic extract was dried, and evaporation gave an oil that was purified by flash chromatography over silica gel (2 × 18 cm with 1:8 ethyl acetate–hexane. Kugelrohr distillation [110 °C (10 mm)] gave 2,3,4-trimethyl-3-penten-2-ol as a white solid: 236.9 mg (75%); mp 37–39 °C; better than 99% pure (VPC, DEGS, 95 °C); IR (film) 3345, 1650, 1143 cm^{-1}; NMR ($CDCl_3$, 200 MHz) δ 1.37 (s, 6 H), 1.66 (m, 6 H), 1.80 (br s, 1 H), 1.94 (m, 3 H); exact mass 128.1197 (calcd for $C_8H_{16}O$ 128.1201), 110.1096 [calcd for C_8H_{14} ($M^{+\cdot}$ – H_2O) 110.1096].

(79) House, H. O.; Chu, C.-Y.; Wilkins, J. M.; Umen, M. J. *J. Org. Chem.* **1975**, *40*, 1460.
(80) Crandall, J. K.; Banks, D. B.; Colyer, R. A.; Watkins, R. J.; Arrington, J. P. *J. Org. Chem.* **1968**, *33*, 423.

Acknowledgment for financial support is made to the Natural Sciences and Engineering Research Council of Canada and to the Alberta Heritage Foundation for Medical Research.

Registry No. **1**, 1713-63-9; **1a**, 79405-31-5; **1b**, 79405-36-0; (*E*)-**2**, 60934-89-6; (*Z*)-**2**, 60934-90-9; **2a**, 79405-32-6; **2a** 2,4-dinitrophenylhydrazone, 81535-49-1; (*E*)-**2b**, 81535-50-4; (*Z*)-**2b**, 81535-51-5; (*E*)-**3**, 74063-65-3; (*Z*)-**3**, 81535-52-6; **3a**, 17920-90-0; (*E*)-**3b**, 34562-09-9; (*Z*)-**3b**, 81535-53-7; (*E*)-**4**, 69625-48-5; (*Z*)-**4**, 81535-54-8; **4a**, 79405-33-7; (*E*)-**4b**, 81535-55-9; (*Z*)-**4b**, 81535-56-0; **5**, 7062-12-6; **5a**, 79405-34-8; **5b**, 79405-39-3; **6**, 76966-13-7; **6a**, 76966-34-2; **6b**, 76966-35-3; **6c**, 81535-57-1; **7**, 79405-30-4; **7** 2,4-dinitrophenylhydrazone, 81535-58-2; **7a**, 79405-35-9; **7a** 2,4-dinitrophenylhydrazone, 81535-59-3; **7b**, 79405-40-6; (*E*)-**8**, 81535-60-6; (*Z*)-**8**, 81535-61-7; (*E*)-**8** 2,4-dinitrophenylhydrazone, 81535-62-8; (*Z*)-**8** 2,4-dinitrophenylhydrazone, 81535-63-9; **8a** (isomer 1), 81535-64-0; **8a** (isomer 2), 81535-65-1; **8a** 2,4-dinitrophenylhydrazone, 81535-66-2; **8b**, 81535-67-3; (*E*)-**9**, 81535-68-4; (*Z*)-**9**, 81535-69-5; (*E*)-**9** 2,4-dinitrophenylhydrazone, 81535-70-8; (*Z*)-**9** 2,4-dinitrophenylhydrazone, 81600-21-7; **9a** (epimer 1), 81535-71-9; **9a** (epimer 2), 81535-72-0; **9a** (epimer 1) 2,4-dinitrophenylhydrazone, 81535-73-1; **9a** (epimer 2) 2,4-dinitrophenylhydrazone, 81535-74-2; **9b** (epimer 1), 81600-70-6; **9b** (epimer 2), 81535-75-3; **9b** (epimer 3), 81600-22-8; **9b** (epimer 4), 81600-23-9; **10**, 1210-39-5; **10b**, 15295-29-1; **12**, 684-94-6; (trimethylsilyl)acetaldehyde *tert*-butylimine, 73198-78-4; cycloheptanone, 502-42-1; 2-(trimethylsilyl)propionaldehyde *tert*-butylimine, 58707-01-0; 2-methylcyclohexanone, 583-60-8; (*Z*)-1-bromo-2-ethoxyethylene, 23521-49-5; *cis*-4a-methyloctahydro-2-naphthalenone, 938-06-7; (*E*)-3-methyl-3-decen-2-ol, 26560-10-1; (*Z*)-3-methyl-3-decen-2-ol, 81535-76-4; 3-cyclohexylidene-2-butanol, 69986-44-3; 3-(2-methylcyclohexylidene)-2-butanol, 81535-77-5; 2,3,4-trimethyl-3-penten-2-ol, 72486-21-6; $Me_5Cu_3Li_2$, 61701-36-8.

Dimerization of 3-Benzoyl-4-phenylisocrotonic Acid†

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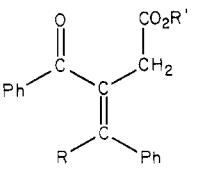
Department of Chemistry, Banaras Hindu University, Varanasi 5, India

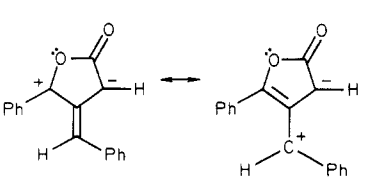
Received August 25, 1981

The acid-catalyzed self-condensation of acid **1a** formed the tricyclic pseudoacid dichloride **3a**, which on pyrolysis underwent a ring-expansion rearrangement to produce the dilactone **5a**. The structures and stereochemistries of these dimeric compounds are deduced by a study of their chemical transformations involving extensive use of deuterium incorporation.

In the course of the attempted synthesis of the zwitterionic species **2** from 3-benzoyl-4-phenylisocrotonic acid[2] (**1a**) for a study of its participation in 1,3 dipolar cycloaddition reactions, an interesting dimerization took place. The details of this investigation are described in this paper.[3]



1a, R′ = H; R = H
b, R′ = H; R = D
c, R′ = CH_3; R = H



2

Results and Discussion

The acid-catalyzed dehydration of the acid **1a** was carried out under a variety of conditions. Reaction with acetyl chloride produced the tricyclic pseudoacid chlorides **3a** (40% yield) and **4a** (5% yield).[4] The use of oxalyl

† Dedicated to Professor Gilbert Stork on his 60th birthday.

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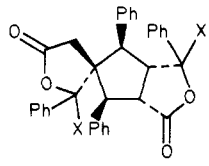
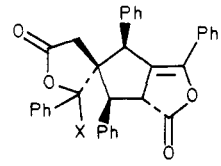
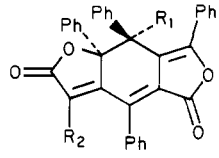


3a, X = Cl
b, X = OCH_3



4a, X = Cl
b, X = $OCOCF_3$



5a, $R_1 = R_2 = H$
b, $R_1 = D$; $R_2 = H$
c, $R_1 = H$; $R_2 = D$

chloride and thionyl chloride also formed the dimer **3a** in a small amount. No self-condensation of **1a** occurred with acetic anhydride at room temperature[5] or during thermal dehydration.[6] Refluxing with acetic anhydride in the presence of a catalytic quantity of sulfuric acid led to copious polymerization. However, after rigorous purification it was possible to isolate a novel highly crystalline orange compound which has been characterized (vide infra) as the dimeric dilactone **5a**. The dimerization was accomplished in high yield (60%) by treatment of the parent acid with trifluoroacetic anhydride in dry ether. In this case the only product isolated was the monotrifluoroacetoxy dilactone **4b**.

A study of the reactions and the degradation products of the dimer **3a** has revealed some interesting features of its chemistry. The tertiary benzylic halogen atom on the carbon next to C_3 was found to be more labile. When a sample was refluxed in anhydrous benzene the evolution of hydrogen chloride (1 molar equiv) was observed, resulting in the formation of the monochloro dilactone **4a**. The pseudoacid chloride nature of the halogen atoms was demonstrated by their replacement with methoxyl groups on refluxing with anhydrous methanol. The pseudo dimethyl ester **3b** was formed in quantitative yield. This transformation indirectly ascertained the presence of two halogen atoms in **3a**.

The dilactone functionality in **3a** readily undergoes hydrolysis with wet methylene chloride to form the dicarboxylic acid **9a** (Scheme I). The corresponding dimethyl ester **9b** was obtained by reaction with diazomethane. The acid **9a** on being refluxed with base (10% KOH), formed its more stable epimer **10a**, suggesting an inversion of the proton next to benzoyl function at C_3. This change could also be brought about by boiling **9a** with acetic acid in presence of hydrogen chloride. Esterification of the product with diazomethane gave the dimethyl ester **10b**. The latter was also formed directly from **9b** on exposure to sodium methoxide in anhydrous benzene. The hydrolysis of the pseudoester **3b** under acidic conditions furnished acid **9a**, whereas its cleavage in basic medium yielded the isomeric acid **10a**. As expected, the monochloro dilactone **4a** and trifluoroacetoxy dilactone **4b** on acid hydrolysis also furnished the dicarboxylic acid **9a**.

Table I. H^1 NMR Analysis of Deuterated Isomers of 10b

isotopomer	obsd chemical shift, δ	location of proton
10b	4.0-4.90 (m, 4 H)	C_2, C_3, C_4, C_5
10b-d_1	4.18 (d, J = 12 Hz, 1 H)	C_5
	4.38 (d, J = 12 Hz, 1 H)	C_4
	4.73 (s, 1 H)	C_2
10b-d_2	4.38 (d, J = 12 Hz, 1 H)	C_4
	4.67 (d, J = 12 Hz, 1 H)	C_3
10b-d_3	4.38 (s, 1 H)	C_4

In order to further elucidate the stereochemistry of the dimers, we synthesized various deuterated isomers of **10b**. Protons at C_2, C_3, and C_5 were easily replaced by deuterium. The epimerization reaction described above was exploited to introduce deuterium at the C_3 position. Thus the monodeuterated isotopomer of **10b** (D at C_3) was prepared by carrying out isomerization of **9a** with sodium methoxide in deuterium oxide followed by esterification of the acid. The two protons next to phenyl groups at C_2 and C_5 were successfully replaced by deuterium by the dimerization of the parent deuterated acid[7] **1b** followed by the conversion of this dimer to the dideuterated isotopomer of the ester **10b** (D at C_2 and C_5). Finally the trideuterated isotopomer of **10b** (D at C_2, C_3, and C_5) was made by carrying out inversion of the dideuterated isotopomer of **10b** by a method identical with the one described above. The results of the NMR studies of the three deuterated isomers of **10b** are summarized in Table I. This enabled assignment of the chemical shift values of each proton on the cyclopentane ring.

It appears that the coupling constant for adjacent protons at C_3, C_4 and C_4, C_5 is the same in both cases. In the heavily substituted five-membered ring system it is difficult to assign the stereochemistry of the substituents on the basis of the spin–spin coupling constants.[8] Nevertheless, the NMR analysis supported the regiochemistry of the five-membered carbocyclic ring of the dimer **3a**.

The cis–trans relationship of the esters **9b** and **10b** was unambiguously established by a careful examination of their behavior under conditions of catalytic hydrogenation. The acid **8a** was obtained on prolonged reduction of the ester **9b** over palladium/charcoal in methanol. Reaction of **8a** with diazomethane gave the ester **8b**. As illustrated in Scheme I, it is evident that the initial reduction of the two benzoyl carbonyls would form the dihydroxy ester **6** which may close to the dilactone **7**. The latter on hydrogenolysis will give rise to the acid **8a**. The transformation is a consequence of the cis projection of the benzoyl at C_3 and the carbomethoxyl group at C_4. This observation led us to reason that the direct hydrogenation of the dimer **3a** should also in principle produce the lactonic acid **8a**. This inference met an experimental confirmation. A solution of the dimer **3a** in anhydrous ethyl acetate was subjected to reduction in presence of palladium catalyst. The acid isolated after repeated crystallizations proved to

(1) To whom correspondance regarding this work may be addressed at The Squibb Institute for Medical Research, P.O. Box 4000, Princeton, NJ 08540

(2) W. Borsche, *Chem. Ber.*, **47**, 1108 (1914).

(3) A preliminary account of this work has been reported: J. Singh, K. P. Agarwal, and G. Singh, *Tetrahedron Lett.*, 3775 (1981).

(4) (a) A minor byproduct was isolated during some runs and has been characterized as an isomer of **4a** with a double bond in the C_3–C_4 position: mp, 220 °C dec; 2% yield. (b) Combustion analysis for carbon in pseudoacid chlorides **3a** and **4a** registered values higher by 0.59 and 1.00%, respectively. (c) **3a** was unstable and highly insoluble in organic solvents. In the mass spectrum (see Experimental Section) the parent molecular ion (M^+) was not observed. It was difficult to obtain a satisfactory NMR spectrum.

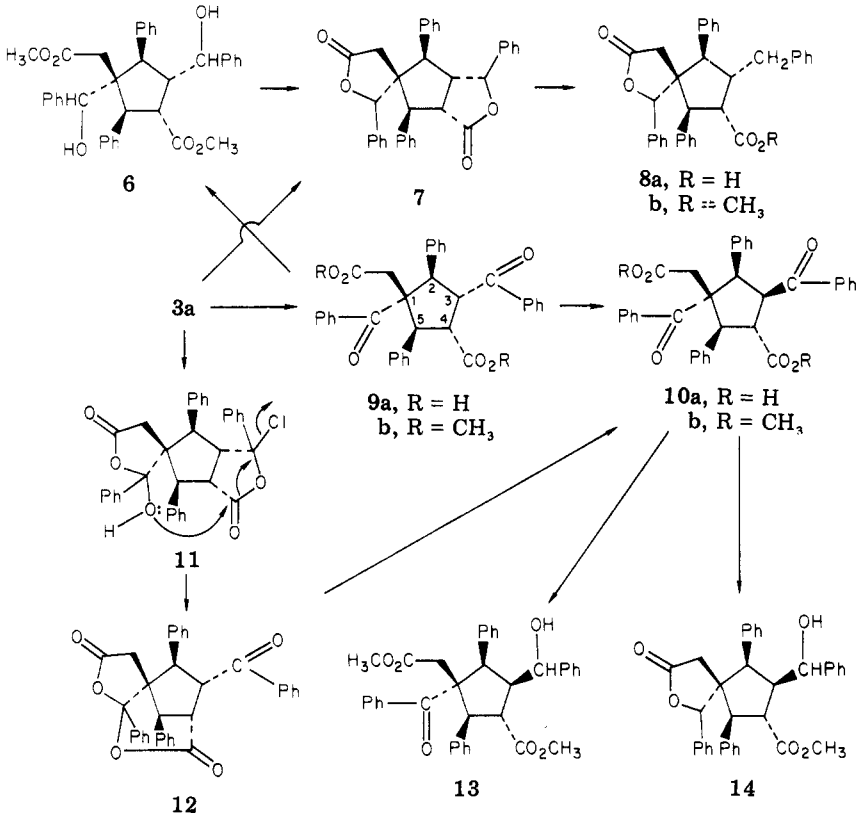
(5) W. Borche, *Chem. Ber.*, **47**, 113 (1914). This reaction gives 3-benzoyl-1-naphthol i and 4-benzoyl-3-phenylbutyrolactone ii.

(6) E. P. Kohler and J. B. Conant, *J. Am. Chem. Soc.*, **39**, 1404 (1917). These authors have described the formation of ii[5] on heating **1a** to 160 °C.

(7) The deuterated acid **1b** was prepared by the condensation[2] of β-benzoylpropionic acid with C_6H_5CDO (D. Seebach, B. W. Erickson, and G. Singh, *J. Org. Chem.*, 31, 4303 (1966). **1b** was used to prepare the deuterated dimeric products.

(8) L. E. Erickson, *J. Am. Chem. Soc.*, **87**, 1867, (1965).

Scheme I



be identical with **8a**. Once again the dilactone **7** appears to be the plausible intermediate, which in this instance is formed by hydrogenolysis of the two halogen atoms.[9]

On the other hand, the two hydrogenation products of the isomeric ester **10b** under similar conditions were the dimethyl ester **13** and the lactonic ester **14**. The trans orientation of the substituents at C_3 and C_4 in this case prevents the easy interaction of the secondary alcohol and the ester function. It may be of interest to note that the spirolactone portion in **8a** and **14** resisted hydrogenolysis even on exposure over an extended period of time to hydrogen in the presence of the catalyst. This is ascribed to the nonplanarity of the spirane ring system with the rest of the molecule, which renders its adsorption on the catalyst surface far more difficult.

The relative stereochemistry of the substituents at C_1 and C_4 in the dimer **3a** is assigned as cis on the basis of the following experimental observation. Treatment of **3a** with reagent grade pyridine furnished the spirodilactone **12**. Formation of this product may be rationalized through the involvement of the hydroxychloro lactone intermediate **11**, produced by replacement of the tertiary halogen atom in the spirolactone part of the molecule by a hydroxyl group. Further intramolecular interaction of the carbinol oxygen with the lactone carbonyl, culminating in the displacement of the second halogen atom, would yield **12**.

At this stage it was envisaged that if under certain conditions the active methylene next to the ester function at C_1 is induced to interact with the benzoyl group at C_3 it might be possible to develop a more rigid system to reveal further the details of the stereochemistry of the dimeric products. It was interesting to find that refluxing **9b** or **10b** with excess sodium methoxide in methanol resulted in cyclization to produce the bicyclic compound **17b** (Scheme II). In order to resolve the multiplet in the NMR

(9) A. R. Pinder, *Synthesis*, **6**, 425 (1980).

Scheme II

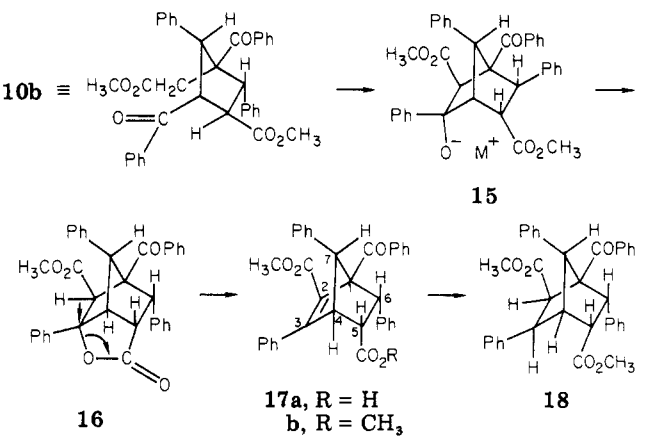


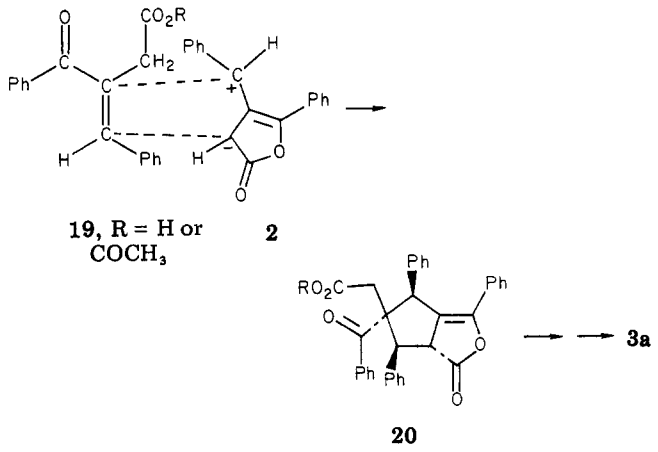
Table II. H^1 NMR Analysis of 17

proton	chemical shift, δ	coupling constant, Hz
H_5	3.78 (q)	$J_{4,5} = 3.5$, $J_{5,6} = 6.5$
H_6	4.13 (d)	$J_{5,6} = 6.5$
H_4	4.45 (d)	$J_{4,5} = 3.5$
H_7	4.52 (s)	

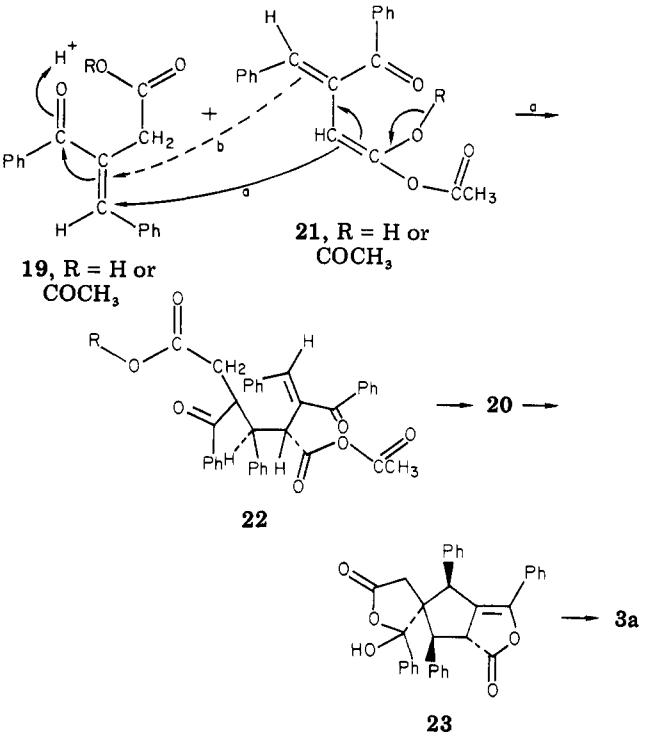
due to protons on the bicyclic ring we prepared the dideuterated isotopomer of **17** (D at C_6 and C_7) by the cyclization of the C_2, C_5 dideuterated ester **9b**. When the reaction of **9b** was carried out with sodium methoxide in deuteriomethanol, the corresponding d_2' isotopomer of **17** (D at C_4 and C_5) was obtained.

The chemical shift and the coupling constant values of the bicyclic ring protons in **17b** are summarized in Table II. A coupling constant of 3.5 Hz between the bridgehead proton at C_4 and the proton at C_5 established an exo configuration for the C_5 hydrogen atom. The corre-

Scheme III



Scheme IV



sponding value for an endo proton is known to be close to zero.[10,11] Further, since the proton at C_6 has displayed a coupling constant of 6.5 Hz with the C_5 hydrogen, these are considered to be cis to each other. These conclusions require the epimerization of the ester at C_4 in **10b**. It is postulated that this might happen by intramolecular interaction of the alkoxide ion at C_3 with the endo ester at C_5 (which is in equilibrium with the parent exo ester) in **15**, forming the intermediate **16**. A β-eliminative opening of the lactone **16** would then give the configurationally stable salt of the acid **17a**.[12]

The anti configuration of the proton in the remaining nonepimerizable center C_7 is corroborated by the observation that on reduction of the double bond in **17** this proton registered an upfield shift of 0.14 ppm (chemical shift determined by 100-MHz H^1 NMR, δ 4.38) in the norbornane system **18**. This inference is derived from the generalization that the presence of a double bond in bicyclic systems exercises a deshielding effect on the anti proton of the bridge which lies in the sp^2 bond plane. On the contrary, the syn proton, being located above the plane of the sp^2 bond, registers an upfield shift.[13-15]

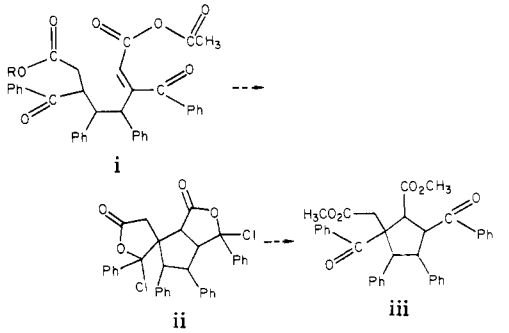
While we were rationalizing the mode of the dimerization reaction, it was believed that the originally conceived 1,3-dipole **2** might have been formed and reacted with **19** in the manner delineated in Scheme III.[16] The intermediate **20** would give rise to the dimeric products (vide infra). However, when the dimerization reaction was carried out in the presence of other dipolarophiles (dimethyl acetylenedicarboxylate, dimethyl maleate, dimethyl fumerate, or tetracyanoethylene) the presumed 1,3 dipole **2** was not trapped. Therefore, its intermediacy is regarded as less likely.

An alternative pathway, besides the one speculated earlier,[3] is assumed to involve the ketene acetal type intermediate **21** arising from the mixed anhydride **19** by enolization at the active methylene position (Scheme IV). The acid-catalyzed Michael reaction[17] of **21** with **19** (route a) would form **22**.[18] A second intramolecular reaction in **22** results in the formation of the five-membered carbocyclic system **20** in which the interaction of the carboxyl function with the benzoyl carbonyl would generate the hydroxy lactone **23**. Protonation of the tertiary benzylic hydroxyl under strongly acidic conditions and its displacement by the halide ion along with addition of the elements of hydrogen chloride in **23** would give rise to the dimer **3a**.

The stereoelectronic factors responsible for a stereoselective formation of the C_4–C_5 linkage are not clear. However, an examination of the molecular models suggests that, for the isomer **22**, in the transition state for the ring closure the carboxy function at C_4 and the phenyl at C_5 are in a less crowded trans relationship. We assume that the second isomer, if formed, either undergoes inversion at C_4 prior to cyclization or, faced with a high-energy transition state for ring closure, leads to intractable products.

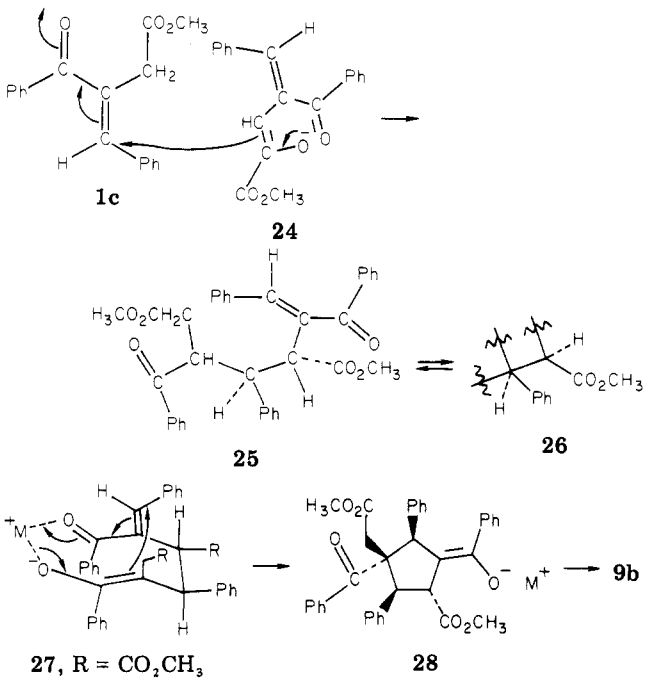
(10) P. M. Subramanian, M. T. Emerson, and N. A. LeBel, *J. Org. Chem.*, **30**, 2624, (1965).
(11) J. L. Marshall and S. R. Walter, *J. Am. Chem. Soc.*, **96**, 6358 (1974).
(12) The monoacid ester intermediate **17a** was not isolated.
(13) P. Laszlo and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1171 (1964).
(14) E. I. Snyder and B. F. Franzus, *J. Am. Chem. Soc.*, **86**, 1166 (1964).
(15) K. Tori, Y. Hata, R. Muneyuki, Y. Takano, T. Tsuji, and H. Tanida, *Can. J. Chem.*, **42**, 926 (1964).
(16) R. Huisgen, *Angew. Chem., Int. Ed. Engl.* **11**, 633 (1963).
(17) H. Rubinstein, *J. Org. Chem.*, **27**, 3886 (1962).

(18) An isomeric formulation (ii) for the dimer could be considered to arise from the intermediate i, which may be formed by the attachment



of C_4 in **21** to C_4 in **19** as shown by the dotted lines in Scheme IV. Degradation of ii in the manner described for **3a** would form the diester iii that is regioisomeric with **10b** and possesses the two phenyl rings on the adjacent carbon atoms of the cyclopentane ring. However, the ^1H NMR spectra of the deuterated isomers (Table I) has revealed that the two benzylic protons at δ 4.73 and 4.18 do not display spin–spin coupling with each other. This is expected only in the case of the assigned structure **10b** and is not likely in iii. This led us to unambiguously rule out the structure ii for the dimerization product.

Scheme V



Base-Catalyzed Dimerization of the Ester 1c. We next turned our attention to study the behavior of the methyl ester **1c** under base-catalyzed Michael reaction conditions.[19] Several attempts with different bases and solvents formed polymeric products. Incidentally the reaction with sodium hydride in dimethyl sulfoxide formed a dimeric product which was proved to be identical with the dimethyl ester **9b**. The reaction sequence is illustrated in Scheme V. Initial self-condensation of **1c** with its enolate **24** would lead to the intermediates **25** and **26**. Stork[20] has recently reported the control of stereochemistry at the vicinal carbon atoms in intramolecular Michael reactions. Considering analogous projections for the intermediates **25** and **26** in which the metal cation is held closer to the enolate oxygen and the oxygen atom of the developing enolate, we have infered that the transition state **27** is more favorable for the second stage of the conjugate addition. The second isomer **26**, if formed, either epimerizes at the position next to the ester function to produce **25**, which provides the less crowded transition state **27** for the cyclization, or leads to unidentifiable by products. The dimer **9b** will be obtained from the enolate intermediate **28** by a kinetic protonation process probably involving a transition state in which benzoyl enolate oxygen is in interaction with ester carbonyl. The isomeric dimethyl ester **10b** has not been isolated during this reaction.

Thermal Rearrangement of the Chloro Lactones. The chloro lactones **3a** and **4a** displayed a curious rearrangement reaction on pyrolysis at 200 °C, forming another dimeric dilactone devoid of the halogen atoms. It has been characterized as the orange lactone **5a** (60% yield) that has been mentioned above to be the product (<1% yield) of the direct dimerization of the parent acid **1a** with acetic anhydride. Thermolysis of the trifluoroacetoxy dilactone **4b** also gave **5a** in lower yields.

The molecule exhibited an exceedingly simple proton NMR spectrum. In the nonaromatic region two singlets appeared at δ 5.15 for benzylic and at δ 5.97 for the vinylic proton. These assignments were confirmed by the NMR analysis of the deuterated isomers. Thermal rearrangement of the deuterated **3a** (D at C_2 and C_5)[7] yielded d_1 isotopomer **5b**. In its NMR the absorption for the benzylic proton at δ 5.15 was missing. The synthesis of the d_1' isotopomer **5c** required replacement at a vinylic position. At this stage a reference may be made to the behavior of the orange lactone **5a** in alkaline medium. When **5a** was refluxed with 1 molar equiv of ethanolic sodium hydroxide for 0.5 h, a deep crimson solution was obtained. Acidification of the reaction mixture precipitated a pale yellow acid, **31a** (Scheme VI), which after crystallization melted at 180° dec. On being heated at 200 °C this acid was quantitatively converted to the orange lactone **5a**.

A scrutiny of the possible intermediates generated by opening of the two lactones and the migration of the double bonds during hydrolysis with base suggested involvement of a doubly vinylogous β-keto acid salt, **30**. The extended conjugation present in the tautomeric form **32** is probably responsible for the profound crimson color of the reaction mixture. In the intermediate **30** the enhanced activation of the methylene group may allow for its exchange with deuterium. As a matter of fact, this could be executed in practice.

When dimer **5a** was subjected to alkaline hydrolysis with anhydrous sodium methoxide in the presence of deuterium oxide in dioxane, the acid **31b** was obtained. Thermolysis of this product resulted in recyclization to create the monodeuterated orange lactone **5c**. In the NMR spectrum there was no absorption for the vinylic proton at δ 5.97.

Furthermore, it appeared possible to convert the orange lactone **5a** to a compound with a completely aromatic central ring by the dehydration of the dihydrobenzene intermediate **30**. This transformation was brought about under rigorous base hydrolysis conditions, which required refluxing with ethanolic potassium hydroxide for several hours. The dicarboxylic acid **33a** was formed, which on esterification with diazomethane gave the dimethyl ester **33b**. The corresponding dideuterated isomer **33c** was made by employing sodium methoxide in deuterium oxide in the above-described conversion. No incorporation of deuterium at the benzylic position of **33b** was observed on refluxing this ester with sodium methoxide in deuterium oxide. This observation provides an additional support to the correctness of the nature of the intermediates proposed in Scheme VI.

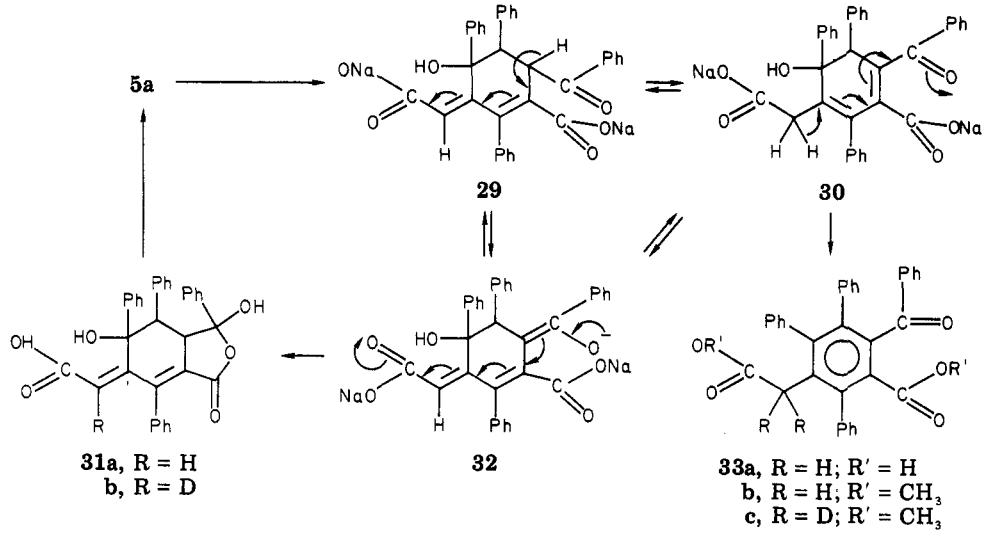
The results obtained during hydrogenation of **5a** are described in Scheme VII. Reaction with hydrogen in the presence of palladium/carbon in benzene for a short time formed the partially reduced yellow lactone **34** in which only one double bond had undergone saturation. However, chemical reduction with zinc/acetic acid gave rise to the colorless product **35**. On exhaustive hydrogenation with palladium–charcoal in ethyl acetate, the dicarboxylic acid **36a** was isolated in low yields after repeated crystallizations. During this operation the double bond that ended up between the two phenyl groups resisted further reduction in analogy with the behavior of stilbene.[21] Treatment of **36a** with diazomethane afforded the dimethyl ester **36b**. The stereochemistry of this product has not been determined.

Formation of the orange lactone **5a** undoubtedly involved a ring expansion of the five membered carbocyclic system in **3a**. The following mechanism (Scheme VIII) may be postulated.

Elimination of one molecule of hydrogen chloride along with thermal dissociation of the second halogen atom in

(19) A. T. Nielson and D. W. Moore, *J. Org. Chem.*, **34**, 444 (1969).
(20) G. Stork, C. S. Shiner, and J. D. Winkler, *J. Am. Chem. Soc.*, **104**, 310 (1982).
(21) W. H. Zartman and H. Adkins, *J. Am. Chem. Soc.*, **54**, 1668 (1932).

Scheme VI

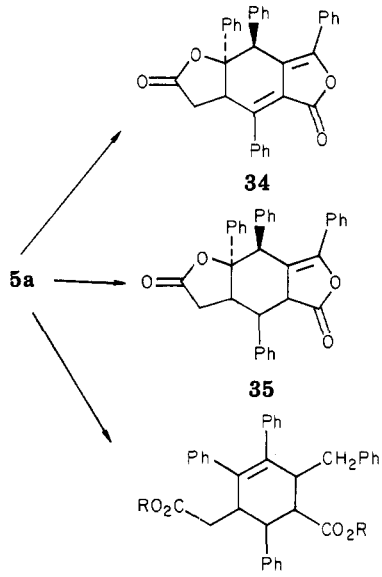


31a, R = H
b, R = D

32

33a, R = H; R′ = H
b, R = H; R′ = CH_3
c, R = D; R′ = CH_3

Scheme VII

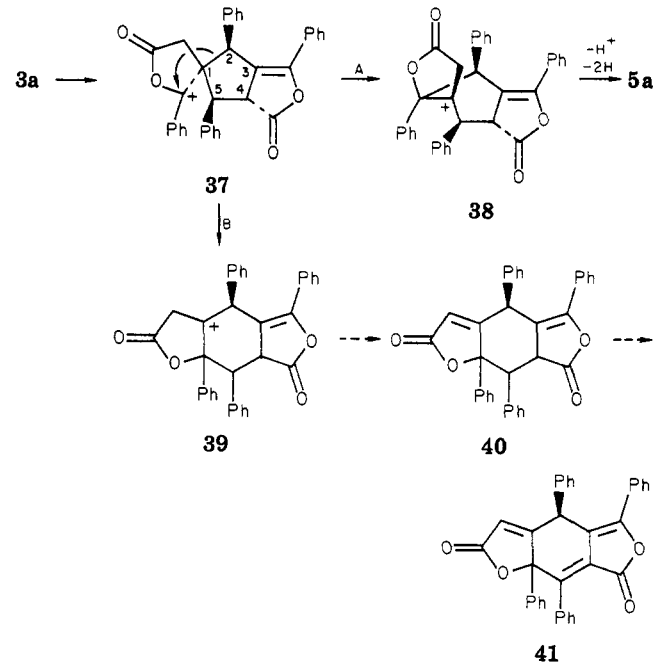


34

35

36a, R = H
b, R = CH_3

Scheme VIII



37

38

39

40

41

3a would produce the benzylic carbocation **37**. A 1,2-shift (path A; cf. Wagner–Meerwein rearrangement)[22] of the allylic carbon C_2 may form the cyclohexyl cation **38**. The final fully conjugated product **5a** would be created by a loss of a proton followed by elimination of a hydrogen molecule under pyrolytic conditions. The alternative mode of rearrangement involving rupture of the C_1–C_5 bond (path B) in **37** would form the cyclohexyl derivative **40** via the cation **39**. The structure **41** derived from **40** by removal of a hydrogen molecule is isomeric with **5a**. In view of the physical characteristics and the chemical behavior of the orange lactone **5a** (Scheme VI), which are attributed to the presence of extended conjugation in the intermediate **32**, the alternative structure **41** is considered less likely.

The stereochemistry of the two adjacent phenyl rings would be determined by the orientation of the substituent at C_2 in the dimer **3a**. It is evident from the transition state **37** that with a β configuration (vide supra) for the phenyl group at the migrating carbon, in the product it will develop a trans relationship with the phenyl ring at the adjacent carbon atom.

In conclusion, we have elucidated the structures of the dimerization products of 3-benzoyl-4-phenylisocrotonic acid (**1a**) by their interesting chemical transformations. The chemistry of the thermal ring-expansion product **5a** from the dimer **3a** is also described. The synthesis of the various deuterated isomers and the use of the spectroscopic methods helped in establishing the stereochemistry of the compounds. The dimerization of **1a** is proposed to proceed by (Scheme IV) an acid-catalized conjugate addition.

Experimental Section

H^1 NMR spectra were measured on a Varian A-60D spectrometer of $CDCl_3$ solutions with tetramethyl silane as the internal standard. Infrared spectra were traced by a Perkin-Elmer 237 IR spectrometer. Ultraviolet spectra were recorded with a Cary 14 UV spectrometer of samples in 95% ethanol. Mass spectral measurements were obtained from an AE/MS-9 double-focussing spectrometer. The analytical samples were purified by thick-layer chromatography over silica gel. Melting points were uncorrected. Acetyl chloride was purified by fractionation through a 30-in. glass-helix-packed, vacuum-jacketed, mirrored column.

(22) A. Nickon and R. C. Weglein, *J. Am. Chem. Soc.*, **97**, 1271 (1975), and references therein.

4-Carboxy-1,3-bis(α-chloro-α-hydroxybenzyl)-2,5-diphenylcyclopentaneacetic Acid Di-γ-lactone (3a). A mixture of powdered anhydrous **1a** (50.0 g, 188 mmol) was dissolved in acetyl chloride (450.0 ml) at room temperature. After 3 days the colorless crystalline dimer **3a** (18.5 g) was separated by decantation under an inert atmosphere, washed with dry benzene, and stored in a desiccator. A second crop (1.5 g) was isolated after 1 week: mp 180 °C dec; 40% yield; IR (CH_2Cl_2) ν_{max} 1818 cm^{-1}; MS (M^+ − Cl) m/e 533 and 535 (ratio 3:1).[3]

Isolation of Monochloro Dilactone (4a).[3] The mother liquor of the above reaction mixture was concentrated under low pressure to about one-third by volume and allowed to stand at room temperature for 1 week. A mixture of crystalline products was separated and washed with dry benzene and refluxed in a mixture of benzene and methylene chloride (200.0 mL, 9:1 by volume) until evolution of HCl ceased (20 h). On evaporation of the solvent, the crystalline monochloro dilactone **4a** was obtained: mp 205 °C dec; 2.5 g (5% yield); NMR δ 2.08, 2.41 (AB q, J = 17 Hz, 2 H), 4.07 (s, 1 H), 4.29, 4.49 (AB q, J = 9.5 Hz, 2 H), 6.7–7.7 (m, 20 H); IR (CH_2Cl_2) ν_{max} 1818, 1795 cm^{-1}; MS m/e 532 (M^+).

4-Carboxy-1,3-bis(α-methoxy-α-hydroxybenzyl)-2,5-diphenylcyclopentaneacetic Acid Di-γ-lactone (3b). Compound **3a** (0.7 g, 1.23 mmol) was refluxed with absolute methanol (200.0 mL) for 20 h. The reaction mixture was concentrated under diminished pressure. The product **3b** crystallized on cooling: 0.65 g (95% yield); mp 298–300 °C (C_6H_6–CH_3OH); NMR δ 2.18, 2.37 (AB q, J = 17 Hz, 2 H), 2.77 (m, 1 H), 2.97 (s, 3 H), 3.01 (s, 3 H), 3.70 (m, 2 H), 4.72 (m, 1 H), 6.52–7.92 (m, 20 H); IR (KBr) ν_{max} 1808, 1792 cm^{-1}; MS m/e 561 (M^+ + 1). Anal. Calcd for $C_{36}H_{32}O_6$: C, 77.14; H, 6.01. Found: C, 76.93, H, 5.72.

Formation of Trifluoroacetoxy Dilactone 4b. Finely powdered and dried **1a** (10.0 g, 37.6 mmol) was treated with trifluoroacetic anhydride (20.0 mL) in dry ether (50.0 mL) at 0 °C. Separation of the colorless crystalline material ensued in about 6 h. After 16 h the product **4b** was filtered and washed with dry ether: 6.1 g (60% yield); mp 145–47 °C dec; NMR δ 2.08, 2.26 (AB q, J = 17 Hz, 2 H), 4.16, 4.48 (AB q, J = 9.5 Hz, 2 H). 4.18 (s, 1 H), 6.65–8.05 (m, 20 H); IR ($CHCl_3$) ν_{max} 1825, 1808 cm^{-1}. Anal. Calcd for $C_{36}H_{25}F_3O_6$: C, 70.70; H, 4.25. Found: C, 70.79; H, 4.03.

1,3-Dibenzoyl-4-*cis*-carboxy-2,5-diphenylcyclopentaneacetic Acid (9a). Compound **3a** (5.0 g, 8.79 mmol) was vigorously stirred with water (20.0 mL) and methylene chloride (200.0 mL) at room temperature for 24 h. Organic solvent was removed under reduced pressure and the residue treated with $NaHCO_3$ solution (10%). Unhydrolyzed material was removed by filtration, and the filtrate was acidified with HCl (10%). The solid product was filtered, washed with water, and dried under vacuum. The dicarboxylic acid **9a** thus obtained (3.4 g, 73% yield) was crystallized from benzene and methanol and dried at 185 °C (0.001 mm): mp 283–285 °C; IR (KBr) ν_{max} 1770, 1718, 1692 cm^{-1}; MS m/e 532 (M^+). Anal. Calcd for $C_{34}H_{28}O_6$: C, 76.69; H, 5.26. Found: C, 76.65; H, 5.31.

Isomerization of 9a to 10a. A solution of **9a** (1.0 g, 1.88 mmol) was refluxed in aqueous solution of KOH (20.0 mL, 10%) for 2 h. The reaction mixture was cooled and acidified with HCl (10%). The white precipitate of **10a** thus obtained was washed with water and dried under vacuum: 0.80 g (80% yield); mp 318–320 °C (CH_3OH–CH_2Cl_2); IR (KBr) ν_{max} 1767, 1701, 1695 cm^{-1}; MS m/e 532 (M^+). Anal. Calcd for $C_{34}H_{28}O_6$: C, 76.69; H, 5.26. Found: C, 76.77; H, 5.53.

Dimethyl 1,3-Dibenzoyl-2,5-diphenylcyclopentane-*cis*-1,4-diacetate (9b). Compound **9a** (1.0 g, 1.88 mmol) was dissolved in methanol (20.0 mL) and treated with ethereal diazomethane at 0 °C. Removal of the solvent under diminished pressure furnished **9b**: mp 159–160 °C (needles from CH_3OH); 0.77 g (73% yield); NMR δ 2.91 (s, 3 H), 3.03 (s, 2 H), 3.12 (s, 3 H), 4.15–4.90 (m, 4 H), 7.15–8.0 (m, 20 H); IR (CCl_4) ν_{max} 1748, 1689 cm^{-1}; UV λ_{max} 245 nm (ε 22 400); MS m/e 560 (M^+). Anal. Calcd for $C_{36}H_{32}O_6$: C, 77.14; H, 6.01. Found: C, 77.22; H, 5.77.

Dimethyl 1,3-Dibenzoyl-2,5-diphenylcyclopentane-*trans*-1,4-diacetate (10b). Esterification of **10a** with diazomethane in the manner described above afforded the dimethyl ester **10b** in quantitative yield: mp 175–177 °C (white needles from CH_3OH); NMR δ 2.47, 2.63 (AB q, J = 18 Hz, 2 H), 3.0 (s, 3 H), 3.5 (s, 3 H), 4.0–4.9 (m, 4 H), 7.0–7.9 (m, 20 H); IR (CCl_4) ν_{max} 1748, 1689 cm^{-1}; UV λ_{max} 245 nm (ε 15 500); MS m/e 560 (M^+). Anal. Calcd for $C_{36}H_{32}O_6$: C, 77.14; H, 6.01. Found: C, 76.91; H, 5.72.

1-(α-Hydroxybenzyl)-3-benzyl-*cis*-4-carboxy-2,5-diphenylcyclopentaneacetic Acid γ-Lactone (8a). The suspension of dichloro lactone **3a** (1.0 g, 1.76 mmol) and palladium on charcoal (0.2 g, 10%) was hydrogenated in a Parr shaker at 40 psi of H_2 at room temperature. After 60 h the catalyst was filtered and washed with ethyl acetate. The solvent was distilled under reduced pressure and the residue treated with $NaHCO_3$ solution (10%). It was filtered and the filtrate acidified with HCl (10%). The precipitate was collected by filtration, washed with water, and dried to afford **8a**: 0.5 g (57% yield); mp 275–77 °C (CH_3OH); IR (CH_2Cl_2) λ_{max} 1790, 1745 cm^{-1}; MS m/e 502 (M^+). Anal. Calcd for $C_{34}H_{30}O_4$: C, 81.27; H, 5.97. Found: C, 80.88; H, 6.11.

Reduction of 9b to 8a. Hydrogenolysis of **9b** was carried out in methanol as above. Lactonic acid **8a** was isolated in moderate yield; mp 275–77 °C.

1-(α-Hydroxybenzyl)-3-benzyl-*cis*-4-(carbomethoxy)-2,5-diphenylcyclopentaneacetic Acid γ-Lactone (8b). The acid **8a** was esterified in methanol with ethereal diazomethane to afford **8b** quantitatively: mp 205–206 °C (CH_3OH–CH_3COCH_3); NMR δ 2.3–2.6 (m, 5 H), 3.08 (m, 1 H), 3.40 (s 3 H), 3.85–4.15 (m, 2 H), 5.50 (s, 1 H), 6.3–7.5 (m, 20 H); IR (CH_2Cl_2) ν_{max} 1785, 1739 cm^{-1}; MS m/e 516 (M^+). Anal. Calcd for $C_{35}H_{32}O_4$: C, 81.39; H, 6.20. Found: C, 81.28; H, 6.56.

Dimethyl 1-Benzoyl-3-(benzylhydroxy)-2,5-diphenylcyclopentane-*trans*-1,4-diacetate (13). Compound **10b** (2.0 g, 3.57 mmol) and palladium on charcoal (0.1 g, 10%) in methanol (100.0 mL) was hydrogenated at 60 psi of H_2 at room temperature for 60 h. The catalyst was filtered and washed with methanol, and the solvent was stripped off under low pressure. The residue on purification by thick-layer chromatography (silica gel; ethyl acetate–cyclohexane, 2:3) gave **13**: 0.55 g (27.5% yield); mp 172–174 °C (CH_3OH); NMR δ 2.15 (s, 1 H, exchanged with D_2O), 2.26, 2.64 (AB q, J = 18 Hz, 2 H), 2.95 (s, 3 H), 3.52 (s, 3 H), 3.5–4.5 (m, 5 H), 6.4–7.9 (m, 20 H); IR (CH_2Cl_2) ν_{max} 3650, 1742, 1684 cm^{-1}; MS m/e 562 (M^+). Anal. Calcd for $C_{36}H_{34}O_6$: C, 76.86; H, 6.05. Found: C, 76.55; H, 6.15.

1-(α-Hydroxybenzyl)-3-(benzylhydroxy)-*trans*-4-(carbomethoxy)-2,5-diphenylcyclopentaneacetic Acid γ-Lactone (14). Hydrogenation of **10b** (2.0 g, 3.57 mmol) with palladium on charcoal (2.0 g, 10%) as above for 5 days produced **14**: 1.40 g (70% yield); mp, 221–222 °C (CH_3OH); NMR δ 5.50 (s, 1 H, methine proton of spirolactone); IR (CH_2Cl_2) ν_{max} 3597, 1786, 1730 cm^{-1}; MS m/e 532 (M^+). Anal. Calcd for $C_{35}H_{32}O_5$: C, 78.94; H, 6.01. Found: C, 78.66; H, 6.10.

Formation of Spiro Dilactone 12. A solution of **3a** (0.5 g, 0.88 mmol) in reagent grade pyridine (50.0 mL) was allowed stand at room temperature for 7 days. Pyridine was removed under vacuum and the residue triturated with HCl (10%). The solid was filtered and washed with $NaHCO_3$ solution (10%) and water and dried to furnish **12**: 0.3 g (66% yield); mp 238–240 °C (CH_3OH–CH_2Cl_2); NMR δ 2.67 (s, 2 H), 3.85–4.25 (m, 1 H), 4.87–5.35 (m, 2 H), 4.08 (s, 1 H), 6.05–8.0 (m, 20 H); NMR of C_2, H_5 dideuterated isomer of **12**[7] δ 2.67 (s, 2 H), 3.96 (d, J = 6.0 Hz, 1 H), 5.03 (d, J = 6.0 Hz, 1 H), 6.05–8.0 (m, 20 H)); IR (CH_2Cl_2) ν_{max} 1808, 1783, 1684 cm^{-1}; UV λ_{max} 248 nm (ε 13 100); MS m/e 514 (M^+). Anal. Calcd for $C_{34}H_{26}O_5$: C, 79.38; H, 5.06. Found: C, 79.09; H, 5.13.

Base-Catalyzed Dimerization of 1c. Formation of 9b. Methyl ester **1c** (20.0 g, 71.4 mmol) was added to dimsylsodium (made from Na; 0.050 g, 2.17 mmol) in dry dimethyl sulfoxide (250.0 mL). The dark red reaction mixture was let stand at ambient temperature for 60 h. Solvent was distilled off under vacuum and the residue treated with crushed ice. The brown solid was filtered, washed with water, and dried. The material was chromatographed over neutral alumina (Woelm activity II, 200.0 g) and eluted with benzene. Evaporation of solvent gave a colorless solid which was further purified by thick-layer chromatography (silica gel, ethyl acetate–*n*-hexane, 2:3). **9b** was isolated: 20% yield; mp 159–160 °C.

1-Benzoyl-2,5-bis(carbomethoxy)-3,6,7-triphenylbicyclo[2.2.1]-2-heptene (17). Compound **9b** (0.5 g, 0.89 mmol) was refluxed with sodium methoxide (0.2 g, 0.37 mmol) in absolute methanol (150.0 mL) under nitrogen for 4 h, water (5.0 mL) was

added, and refluxing was continued for 1 h. Solvent was removed under low pressure, and the residue was treated with $NaHCO_3$ solution (10%) and filtered. The filtrate was acidified with HCl (10%), and the precipitate was washed with water and dried. Purification by thick-layer chromatography (silica gel; ethyl acetate–cyclohexane, 2:3) afforded **17**: 0.3 g (55% yield); mp 203–205 °C (CH_3OH–CH_2Cl_2); NMR δ 3.08 (s, 3 H), 3.44 (s, 3 H), 3.68–4.64 (m, 4 H), 6.32–8.28 (m, 20 H); IR (CH_2Cl_2) ν_{max} 1739, 1712, 1686 cm^{-1}; MS m/e 542 (M^+). Anal. Calcd for $C_{34}H_{24}O_4$: C, 79.70; H, 5.54. Found: C, 79.82; H, 5.62.

1-Benzoyl-2,5-bis(carbomethoxy)-3,6,7-triphenylbicyclo[2.2.1]heptane (18). To **17** (0.5 g, 0.92 mmol) in ethyl acetate (75.0 mL) was added palladium/charcoal (0.1 g, 10%), and the mixture was hydrogenated at 30 psi of H_2 at room temperature for 20 min. The catalyst was filtered and washed with ethyl acetate. The solid obtained on removal of solvent was purified by thick-layer chromatography (silica gel; ethyl acetate–cyclohexane, 2:3). Crystallization from CH_3OH–CH_2Cl_2 gave **18**: 0.4 g (80% yield); mp 227–229 °C; NMR δ 2.89 (s, 3 H), 3.45 (s, 3 H), 3.72 (m, 2 H), 4.16–4.43 (m, 3 H), 4.98 (d, J = 8.4 Hz, 1 H), 6.68–7.84 (m, 20 H); IR (CH_2Cl_2) ν_{max} 1740, 1689 cm^{-1}; MS m/e 544 (M^+). Anal. Calcd for $C_{36}H_{32}O_5$: C, 79.49; H, 5.88. Found: C, 79.04; H, 5.94.

***trans*-8,8a-Dihydro-4,7,8,8a-tetraphenylbenzo[1,2-*b*:4,5-*c*']difuran-2,5-dione (5a).** Anhydrous **3a** (0.5 g, 0.88 mmol) was melted under nitrogen in a sublimer at 220 °C. After the evolution of HCl had ceased (5 min), the material was sublimed under vacuum (0.001 mm). The temperature was gradually raised to 260 °C over 0.5 h. The sublimate on being washed with dry ether and crystallized from nitromethane furnished **5a** as shining orange needles: mp 303–305 °C; 0.265 g (60% yield); NMR δ 5.15 (s, 1 H), 5.97 (s, 1 H), 7.0–7.84 (m, 20 H); IR (KBr) ν_{max} 1767 cm^{-1}; UV λ_{max} 267 nm (ϵ 17 200), 460 (11 027); MS m/e 494 (M^+). Anal. Calcd for $C_{34}H_{22}O_4$: C, 82.59; H, 4.45. Found: C, 82.44; H, 4.67.

Formation of 31a. Compound **5a** (0.5 g, 1.02 mmol) was refluxed with ethanolic sodium hydroxide (20.0 mL, 0.05 N solution; 95% ethanol) for 0.5 h. Solvent was removed under diminished pressure, and the residue was dissolved in water and filtered. The precipitate obtained on acidification of the filtrate with HCl (10%) was separated and redissolved in $NaHCO_3$ solution (10%). Insoluble material was removed by filtration, and the filtrate was acidified with HCl (10%) and extracted with ether (100.0 mL). The organic phase was dried over $MgSO_4$, filtered, concentrated to 20.0 mL, and diluted with CCl_4 (15.0 mL). In a few minutes light yellow crystals of **31a** were obtained: mp 180 °C dec; 0.10 g (19% yield); IR ($CHCl_3$) ν_{max} 1786, 1773 cm^{-1}. Anal. Calcd for $C_{34}H_{26}O_6$: C, 76.98; H, 4.98. Found: C, 77.46; H, 4.97.

Formation of 33b. Compound **5a** (0.50 g, 1.02 mmol) was added to a solution of KOH (30.0 mL, 0.3 N in 70% ethanol) and refluxed for 6 h. Alcohol was removed under vacuum, and the residue was treated with water (50 mL) and filtered. The product obtained on acidification of the filtrate with HCl (10%) was separated and dissolved in $NaHCO_3$ solution (10%). The product obtained on acidification of the filtrate with HCl (10%) was extracted in ether and dried over $MgSO_4$. Filtration, evaporation of solvent, and crystallization of the residue from ether and carbon tetrachloride gave **33a**: mp 304–306 °C; 0.20 g (42% yield). **33a** was esterified in methanol with ethereal diazomethane at 0 °C. Solvent was stripped off and the residue purified by thick-layer chromatography (silica gel; ethyl acetate–cyclohexane, 2:3). Diester **33b** was isolated as white needles: mp 210–212 °C (CH_3OH–CH_2Cl_2); 0.180 g (85% yield); NMR δ 3.20 (s, 3 H), 3.38 (s, 5 H), 6.82 (s, 5 H), 7.0–7.8 (m, 15 H); IR ($CHCl_3$) ν_{max} 1733, 1669 cm^{-1}. Anal. Calcd for $C_{36}H_{28}O_5$: C, 80.00; H, 5.18. Found: C, 79.98; H, 5.45.

Catalytic Hydrogenation of 5a to 34. A suspension of **5a** (0.50 g, 1.02 mmol) and palladium over charcoal (0.50 g, 10%) in dry benzene (150.0 mL) was hydrogenated at 45 psi of H_2 for 3 h at room temperature. Solvent was removed under reduced pressure and the residue chromatographed over neutral alumina (Woelm activity II, 15 g) in a coloumn which was eluted with Et_2O. Removal of solvent gave yellow crystals of **34**: 0.090 g (18% yield); mp 240–242 °C (ethyl acetate–cyclohexane); NMR δ 2.28 (m, 2 H), 4.16 (t, 1 H), 4.76 (m, 1 H), 7.0–8.0 (m, 20 H); IR (KBr) ν_{max} 1792, 1776 cm^{-1}; MS m/e 496 (M^+).

Chemical Reduction of 5a to 35. Solution of **5a** (1.0 g, 2.04 mmol) in pyridine (40.0 mL) and glacial acetic acid (10.0 mL) was heated at 80 °C in a constant-temperature bath. Zinc dust (6.0 g) was added in small portions over a period of 1.5 h, and heating was continued until the yellow color of the reaction mixture faded away (1.5 h). Removal of the solvent under diminished pressure and trituration of the residue with HCl (10%) gave solid material which was filtered, washed with water, dried, and chromatographed over neutral alumina (30.0 g, Woelm activity II). The coloumn was eluted successively with ether (200.0 mL), benzene (300.0 mL), and ethyl acetate (1000.0 mL). The solid obtained on evaporation of the ethyl acetate fraction was purified by thick-layer chromatography (silica gel; ethyl acetate–*n*-hexane, 2:3). Dilactone **35** was obtained as colorless needles: mp 233–235 °C (Et_2O–CH_2Cl_2); 0.150 g (15% yield); NMR δ 1.4–2.6 (m, 2 H), 2.91–3.60 (m, 1 H), 3.9–4.6 (m, 2 H), 6.1 (s, 1 H), 6.82–7.85 (m, 20 H); IR (KBr) ν_{max} 1795, 1767 cm^{-1}. Anal. Calcd for $C_{34}H_{26}O_4$: C, 81.91; H, 5.26. Found: C, 81.51; H, 5.13.

Hydrogenolysis of 5a to 36a. To **5a** (0.50 g, 1.02 mmol) in anhydrous ethyl acetate (100.0 mL) was added palladium/charcoal (0.50 g, 10%), and the mixture was subjected to reduction with hydrogen at 50 psi of H_2 at room temperature. After 96 h the catalyst was filtered and washed with ethyl acetate, and the solvent was stripped off under reduced pressure. The residue was treated with $NaHCO_3$ solution (10%) and filtered, and the filtrate was acidified with HCl (10%). The product **36a** was filtered, washed with water, and dried: mp 288–289 °C (Et_2O–CH_2Cl_2); 0.10 g (20% yield).

Preparation of 36b. Compound **36a** (0.1 g, 0.199 mmol) in methanol (10.0 mL) was esterified with ethereal diazomethane at 0 °C. Removal of the solvent under diminished pressure and purification of the residue by thick-layer chromatography (silica gel; ethyl acetate–cyclohexane, 2:3) furnished the dimethyl ester **36b**: 0.77 g (72% yield); mp 188–189 °C (CH_3OH–CH_2Cl_2); NMR δ 3.0 (s, 3 H), 3.43 (s, 3 H), 2.20–4.60 (m, 8 H), 6.72–7.52 (m, 20 H); IR (KBr) ν_{max} 1730 cm^{-1}; MS m/e 530 (M^+). Anal. Calcd for $C_{33}H_{34}O_4$: C, 81.51; H, 6.41. Found: C, 81.37; H, 6.47.

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Registry No. **1a**, 80716-63-8; **1b**, 81555-48-8; **1c**, 81555-49-9; **3a**, 80716-64-9; **3a**-d_2, 81555-50-2; **3b**, 81555-51-3; **4a**, 80716-65-0; **4a** (isomer), 81555-52-4; **4b**, 81555-53-5; **5a**, 80716-67-2; **5b**, 81555-54-6; **5c**, 81572-00-1; **8a**, 80716-70-7; **8b**, 80716-71-8; **9a**, 80716-68-3; **9b**, 80716-69-4; **9b**-d_2, 81555-55-7; **10a**, 80737-08-2; **10b**, 80737-09-3; **10b**-d_1, 81555-56-8; **10b**-d_2, 81600-88-6; **10b**-d_3, 81555-57-9; **12**, 80716-73-0; **12**-d_2, 81555-58-0; **13**, 81555-59-1; **14**, 80716-72-9; **17b**, 81555-60-4; **17b**-d_2 (isomer 1), 81555-61-5; **17b**-d_2 (isomer 2), 81555-62-6; **18**, 81555-63-7; **31a**, 81555-64-8; **31b**, 81555-65-9; **33a**, 81555-66-0; **33b**, 81572-01-2; **33c**, 81555-67-1; **34**, 81555-68-2; **35**, 81555-69-3; **36a**, 81555-70-6; **36b**, 81555-71-7.