cussions. Sincere appreciation is expressed to Mrs. J. Capitaine for her excellent cooperation and to Mrs. D. Thibault and Mrs. G. Pelletier for technical assistance. We acknowledge with gratitude the financial and material support from the National Research Council of Canada, The Natural Sciences and Engineering Research Council of Canada, the Ministère de l'Education du Québec, and Ayerst Laboratories, Montreal.

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Thermal Isomerization of Isodicyclopentadiene and Its Cycloaddition Reactions

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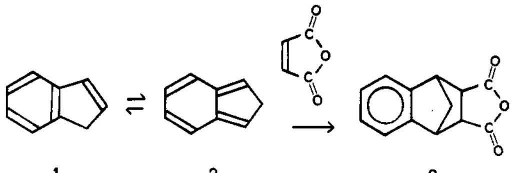
Isodicyclopentadiene (**4**) undergoes a [1,5] sigmatropic hydrogen shift at elevated temperatures (170–180 °C) to form an isomeric, highly reactive diene intermediate **5** which readily undergoes [4 + 2] cycloaddition reactions with dienophiles like dichlorovinylene carbonate (DCVC, **8**), vinylene carbonate (VC, **7**), and maleic anhydride (**9**). In all cases addition to **5** occurs exclusively from the exo face. While **7** and **8** under these high-temperature conditions give one major addition product each (**12** and **13**, respectively), in accord with Alder's rule, **9** at high temperature yields the two isomeric products **15** and **16** initially in the ratio 1:3 of which the isomer **16** (Alder's rule product) on prolonged heating is converted into the stable isomer **15** (anti Alder's rule product). The cycloaddition reactions of 4-cyclopentene-1,3-dione (**10**), 2,2-dimethyl-4-cyclopentene-1,3-dione (**11**), and dimethyl acetylenedicarboxylate (**28**) with **4** and **5** are also discussed. In situ formation of **5** at 0 °C by photolytic cleavage of diketone **14** is proved by trapping **5** with maleic anhydride. X-ray crystallographic data are provided for the adducts **12**, **13**, **15**, **16**, and **21**.

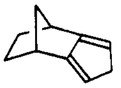
Cyclopentadiene is such an active diene that its presence as a unit in an organic structure generally determines the course of a Diels–Alder reaction in such a compound. However, cases are known in which, depending on the dienophile, the Diels–Alder reaction occurs only after an isomerization of the diene system.

Indene provides a special example of this behavior. It was observed years ago[2] that maleic anhydride at 250 °C adds to indene (**1**) to yield the symmetrical adduct **3**. The intermediacy of the isoindene **2** has been established by deuterium tracer studies.[3] Although the rearrangement of **1** into **2** might be accelerated by bases, the isomerization during a Diels–Alder reaction is not base catalyzed and has been shown[5] to belong to the class of concerted [1,5] sigmatropic rearrangements,[4] since bases preferentially redistribute hydrogen between positions 1 and 3 in indene, while the concerted rearrangement equilibrates these with position 2.


1 **2** **3**

Although isoindene **2** is highly reactive, there are dienophiles which will attack the original indene structure at the expense of the aromatic ring system; dimethyl acetylenedicarboxylate is one of these and yields successive reaction products which depend upon temperature and substitution in the indene.[6]

Another hydrocarbon of great interest in connection with [1,5] sigmatropic shifts is isodicyclopentadiene **4**. Unlike **2**, which has an interrupted aromatic π system, **4** is favored at equilibrium over its isomers **5** and **6**, which have not been isolated. Isomer **4** reacts at moderate temperatures with acrylic and propiolic esters[7] and with phenylvinyl sulfone[8] to yield derivatives of *syn*-sesquinorbornene, while with maleic anhydride it yields mixtures of *syn*-sesquinorbornene *exo*-anhydride **29** and *anti*-sesquinorbornene *endo*-anhydride **30**.[9]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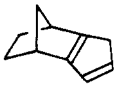
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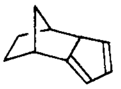
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Because there is an obvious balance of forces determining the products of these reactions, we have investi-

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[1] Inquiries about the X-ray crystallographic studies should be addressed to these authors.

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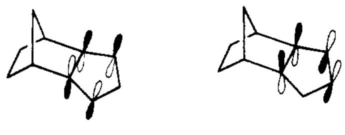


4 5

Figure 1. HOMOs of the π systems in 4 and 5.

Scheme I

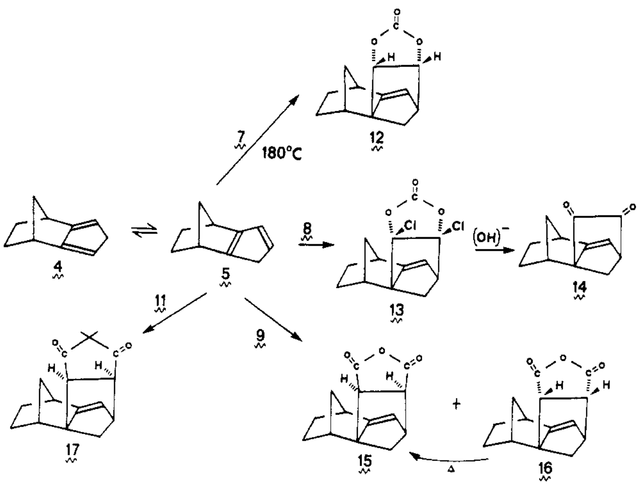


Chart I

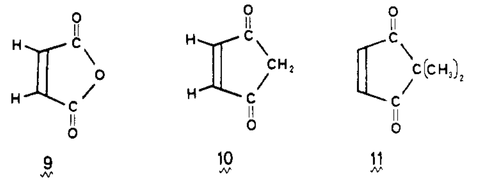
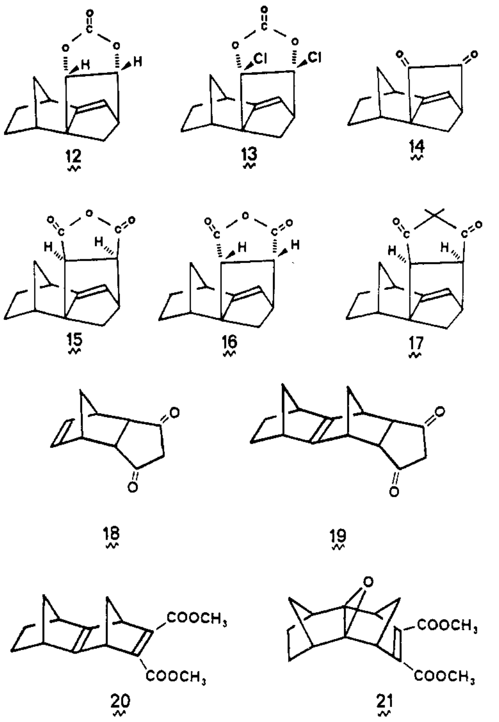
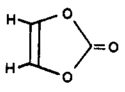


Chart II



gated the behavior of isodicyclopentadiene (4) toward several dienophiles, covering a range of reactivity in the Diels–Alder reaction. Dichlorovinylene carbonate (DCVC, 8) is a versatile but relatively unreactive dienophile and enophile,[10] which adds to cyclopentadiene only above 140 °C[11,12] and is of interest for the α-diketones that its cycloaddition products readily yield on alkaline hydrolysis.[13] Vinylene carbonate (VC, 7)[10,14–17] is a still less reactive dienophile, used in the preparation of glycolic cycloadducts. Consistently, these weak dienophiles show reactivity toward isodicyclopentadiene at 170–180 °C, but the products are those derived from 5 rather than from 4.



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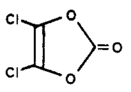

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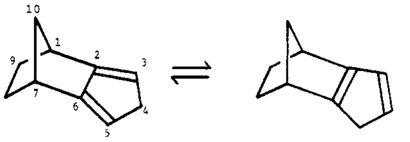
Results and Discussion

Dichlorovinylene Carbonate (DCVC, 8) plus Isodicyclopentadiene (IDCP, 4). Diels–Alder reaction between 4 and 8 did not proceed thermally at temperatures below 140 °C and was very slow between 140 and 160 °C. Acetophenone-sensitized photochemical addition[18] was also not successful. When a mixture of 4 and 8 was heated to 170 °C, 13 was obtained as the major product. Treatment of 8 with anhydrous Na_2CO_3 before the addition of 4 removed any acid impurity present in 8 and thereby prevented polymerization of 4 during the reaction. Dimerization of 4 was inevitable in all reactions carried out above 100 °C, and the amount of the four dimers (analyzed by GC/MS) was dependent on concentration and time of the reaction.

The adduct 13 was easily hydrolyzed by sodium hydroxide at room temperature to bright orange diketone 14.

It is evident that 4 undergoes a [1,5] sigmatropic hydrogen shift at high temperature to produce an isomer (5) which readily cycloadds to DCVC (Scheme I). Unlike IDCP (4), the isomer 5 undergoes addition from the *exo face*, obeying Alder's rule. In terms of σ–π orbital interactions,[19] the HOMO of the π system in 5 lacks the node between C2 and C6 which is present in 4 (Figure 1) which possibly can account for the preferred mode of addition through marginal effects on the dihedral angle between rings at that point.[20]



4 5

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Table I. ^{13}C NMR Chemical Shifts for Adducts 12–17^{a}

12		13		14		15		16		17	
δ	C	δ	C	δ	C	δ	C	δ	C	δ	C
163.5	C-13	198.3	C-2	163.0	C-13	172.3	C-13	172.6	C-13	217.7	C-13
		193.8	C-3	155.6	C-6	171.6	C-14	171.5	C-14		C-14
149.4	C-6	167.7	C-6	113.6	C-5	164.9	C-6	164.5	C-6	165.9	C-6
115.6	C-5	119.4	C-5	80.2	C-2	118.6	C-5	116.8	C-5	119.5	C-5
107.9	C-2	69.7	C-1	78.8	C-3	66.7	C-1	68.2	C-1	68.2	C-1
107.7	C-3	54.4	C-4	64.3	C-1	50.3	C-2	55.6	C-4	59.5	C-15
72.0	C-1	44.7	C-12	48.9	C-4	49.6	C-3	49.6	C-2	54.2	C-4
59.5	C-4	41.5	C-11	43.7	C-12	47.2	C-4	48.0	C-3	50.9	C-2
45.6	C-12	39.2	C-7	42.2	C-11	43.9	C-12	47.6	C-12	50.6	C-3
41.9	C-11	35.3	C-10	38.6	C-7	42.0	C-11	42.2	C-11	45.6	C-12
38.5	C-7	31.6	C-8		C-10	39.2	C-7	39.8	C-7	41.8	C-11
38.2	C-10	22.6	C-9	31.7	C-8	36.7	C-10	38.2	C-10	39.3	C-7
31.5	C-8			25.1	C-9	31.4	C-8	32.4	C-8	37.0	C-10
24.6	C-9					24.4	C-9	26.1	C-9	31.7	C-8
										24.3	C-9
										24.3	C-10
										16.9	C-17

^{a} All spectra were run in $CDCl_3$ with Me_4Si as an internal standard [$\delta(Me_4Si) = 0$].

In addition to the classical thermal sigmatropic shifts of indene,[2–6] photochemical isomerization of dienes at low temperature and trapping with reactive dienophiles have been reported for 1-alkylstyrenes,[21] *o*-methylbenzophenones,[22] indenes,[23] and pentachloroazacyclopentadiene.[24]

Vinylene Carbonate (VC). From its first discovery by Newman and Addor in 1953,[14] vinylene carbonate (VC, 7) has been widely used in thermal as well as in photochemical cycloadditions.[10,15] VC, like DCVC, reacted with diene 4 only in the neighborhood of 180 °C, the diene isomerizing prior to cycloaddition. Since VC is an even less active dienophile compared to DCVC,[17] the addition took about twice as long. The reaction course is shown in Scheme I.[38]

Maleic Anhydride. Isodicyclopentadiene (4) has recently been shown to react with maleic anhydride[9] (9, Chart I) at room temperature to form *syn*-sesquinorbornene *exo*-anhydride 29 and *anti*-sesquinorbornene *endo*-anhydride 30, the structures being established by X-ray crystallography. Addition of 9 to preheated isodicyclopentadiene at 170 °C occurred to yield exclusively 15 and 16 (Chart II) by addition on the exo face of 5. If the products, without isolation from the solution, were further refluxed, isomer 16, initially formed as the major product, was converted into 15. It is evident that 16, an Alder's rule product, undergoes retro-Diels–Alder reaction on prolonged heating and then recombines to form 15, the anti-Alder's-rule product and also thermodynamically the more stable. It is interesting to note that even in the presence of 4, maleic anhydride (9) preferentially adds to 5.

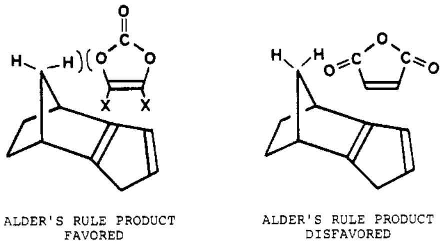
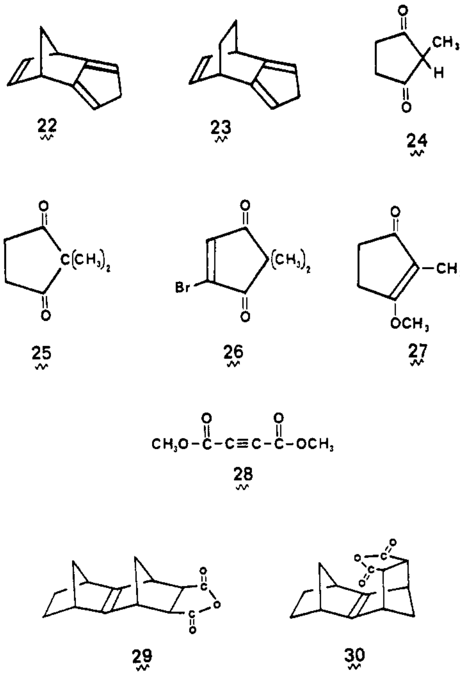


Figure 2.

Chart III



2,2-Dimethyl-4-cyclopentene-1,3-dione (11). In the next step, it was of interest to study a dienophile which incorporates into it the steric crowding of both maleic anhydride (C=O groups α to the double bond) and vinylene carbonates (C=O group at the apex carbon) and which is also not very reactive. 2,2-Dimethyl-4-cyclopentene-1,3-dione (11), a favorable candidate, was prepared by following the procedure of Agosta and Smith,[25] starting from 2-methylcyclopentane-1,3-dione[26] (24, Chart III). Methylation of 24 with sodium ethoxide/methyl iodide gave, in addition to 25, O-alkylated product 27. Interestingly, the ^{13}C NMR spectrum of 27 indicates that shielding of CCH_3 is pronounced [$\delta(CCH_3)$ 6.0] due to

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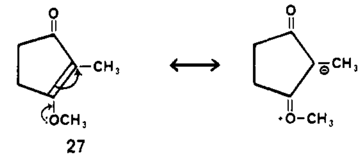
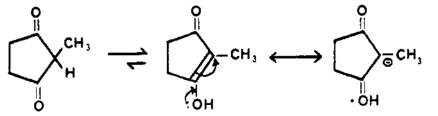


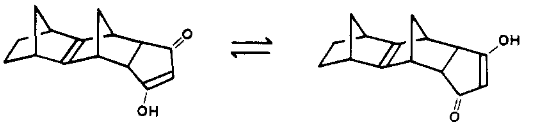
27

delocalization of oxygen lone-pair electrons (normally $=CCH_3$ appears at 18–20 ppm). A similar shielding effect is also observed for the CCH_3 group of **24** [δ (CCH_3) 5–7], indicative of the predominance of the enolic form in solution. The conversion of **25** to **11**, in the present study, always yielded a mixture of **11** and the bromo enedione **26**. 2,2-Dimethylcyclopent-4-ene-1,3-dione (**11**) is known to be a poor dienophile and its addition to cyclopentadiene proceeds very slowly[27] compared with the addition of the unmethylated **10** to cyclopentadiene. A mixture of IDCP (**4**) and **11** failed to react at 100 °C but on being heated to 169 °C (refluxing *tert*-butylbenzene) yielded **17** as the only product. From the cycloaddition reactions of **7–9** and **11** to **4** it appears likely that steric interaction in the transition state between the protons on the bridge methylene group of the diene and the nearest atoms on the dienophile determines whether product formation obeys Alder's rule (Figure 2). A comparison of ^1H NMR and ^{13}C NMR spectral data of **12**, **13**, and **15–17** (Table I) and the stability of **15** and **16** suggests that **17** is also an anti-Alder product like **15** even though unequivocal proof is not available since a suitable crystal of **17** for X-ray studies was not obtained.



24

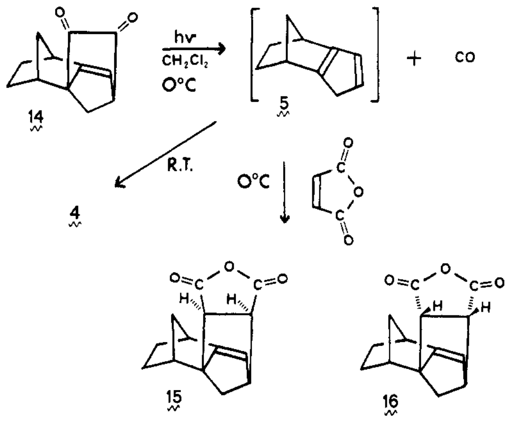
4-Cyclopentene-1,3-dione (10). Although **10** is less reactive than **9**[9] in cycloaddition reactions, it reacts readily with cyclopentadiene[11] at room temperature and with anthracene[28] without a Lewis acid catalyst. The addition of **10** to **4** also proceeded smoothly at 50 °C in benzene to give **19**. Attempts to add **10** to **4** at high temperatures (170–180 °C) were not successful because **10** decomposed at high temperatures.[29] The adduct **19** is very acidic (soluble in sodium hydroxide) and essentially exists in enolic form as evidenced by NMR studies. While the ^1H NMR spectrum of **19** in Me_2SO-d_6 showed the presence of enolic hydrogen at 11.0 ppm, rapid equilibration between **19A** and **19B** on the NMR time scale was indicated by the simple eight-line ^{13}C spectrum corresponding to an effective plane of symmetry in the molecule, and, in fact, one more coincidence than would be expected.



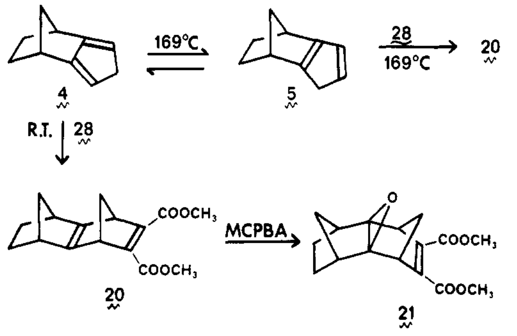
19A **19B**

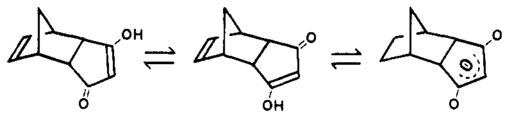
The syn stereochemistry of **19** was deduced from the fact that, like other syn compounds reported, **19** has shielded protons in its ^1H NMR spectrum (0.6–1.0 ppm (2 H)). In earlier studies, DePuy[11] has indicated that the adduct **18** from cyclopentadiene and **10** exists completely in the enolic form. For comparison, **18** was prepared, and ^1H NMR and ^{13}C NMR spectra were run (see Experimental Section). As expected, since ionization of both **18A** and **18B** is fast on the NMR time scale and the enolate ion **18C** has a plane of symmetry, only six ^{13}C NMR peaks were observed.

Scheme II



Scheme III





18A **18B** **18C**

Irradiation of 14 and in Situ Generation of 5. The α-diketone **14** can formally be considered as a Diels–Alder adduct from **5** and "ethenedial", C_2O_2, whose preparation was unsuccessfully attempted by Staudinger.[30]

Photolysis of **14** at 0 °C generated the unstable **5** in solution. On warming to room temperature **5** immediately isomerized to **4**. The transient existence of **5** was corroborated by irradiating **14** in the presence of maleic anhydride (**9**) which combined readily with **5** to give **15** and **16** in the ratio of 1:3. Incidentally, the same ratio of **15** and **16** appears to result from this reaction at 0 °C as from thermally equilibrated **4** and **5** at 170 °C (Scheme II).

The much weaker dienophiles, DCVC[8] and VC,[7] added to the solution containing **14** prior to irradiation, failed to cycloadd to **5** on irradiation at 0 °C. The corresponding formation of CO from norbornenedione was observed by Scharf.[31]

Addition of Dimethyl Acetylenedicarboxylate (28) to 4 and 5. Exothermic addition between **28** and **4** at room temperature as well as the addition of **28** to an equilibrium mixture of **4** and **5** at 169 °C yielded the same product **20**. The *syn*-sesquinorbornadiene skeleton is very reactive toward oxygen, and the assignment of structure **20** for the adduct is based on X-ray studies done on the epoxide **21**

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obtained by peracid oxidation of **20**.[32]

Inability of **28** to add to **5** in equilibrium with the parent diene at high temperature (Scheme III) can only be attributed to steric crowding. The transition state in any addition of the linear dimethyl acetylenedicarboxylate (**28**) to **5** would have a severe spatial conflict between an ester group and the bridge of **5**. This feature overcomes the greater inherent diene reactivity of **5** when linear **28** is the reacting partner: when equimolar mixtures of **9** and **28** were added to thermally equilibrating **4** and **5** at 170 °C, the product consisted of two parts of **20** to one part of mixed **15** and **16**. This, of course, affords no measure of either the **4** $\rightleftharpoons$ **5** equilibrium constant or the relative rate constants of the competing diene additions. Attempts are being made to quantify the results by using high-temperature ^{1}H NMR investigations in finding the individual concentrations of **4** and **5**.

Geometry of the Adducts. Compounds **12** and **13** are similar in structure, with slight differences in interplanar angles imposed by the replacement of the C(2) and C(3) hydrogen atoms by chlorine atoms. The two oxygen atoms of the vinylene carbonate ring lie almost equidistant above the C(5)–C(6) double bond with O(2)···C(6) and O(3)···C(5) separations of 2.822 (5) and 2.865 (6) Å in **12** and of 2.789 (5) and 2.794 (5) Å in **13**. The closer approach in **13** presumably is associated with a repulsive interaction between the vinylene carbonate ring and the chlorine atoms. The C···O distances are closer than the sum of the normal van der Waals radii. Although the exact distribution of nonbonding and π electrons associated with the two atoms cannot be ascertained, a significant electrostatic interaction is present and leads to shifts in the ^{13}C NMR resonances for C(5) and C(6). A weak interaction also exists between H(11en) and O(2) with distances of 2.47 (5) and 2.29 (5) Å for **12** and **13**. The variation in the distance probably indicates the difficulty in locating the hydrogen atom positions accurately, rather than implying any structural changes.

In compound **16** the anhydride ring lies over the C(5)–C(6) double bond with C(13)···C(6) and C(14)···C(5) distances of 3.018 (3) and 2.843 (8) Å. The distances are not equivalent due to the O(13)···H(11en) interaction of 2.30 Å which prevents the ring from approaching the double bond more closely. This interaction leads to an expansion of the interplanar angle between the anhydride ring and C(1)–C(2)–C(3)–C(4) as compared with the equivalent angle in **12** and **13**. Although the distances between the π systems of the carbonyl carbon atoms and the double bond are less than the sum of the normal van der Waals radii, the ^{13}C NMR resonances of the carbonyl carbon atoms in **16** are identical with those in **15** where the anhydride ring is oriented away from the double bond.

The norbornane ring systems in compounds **12**, **13**, **15**, and **16** are essentially identical as indicated by torsion angles, bond distances, valence angles, and intramolecular contacts. The shortest intramolecular contact arising from the fusion of the ring systems is the H(9en)···H(12en) distance which varies from 2.14 to 2.34 Å in the four compounds. The molecules exhibit no unusual bond distances or valence angles, and the structures represent an accommodation between optimum bonding geometries and minimal repulsive interactions.

In compound **21** short intramolecular contacts of 2.27 (3) and 2.24 (3) Å are observed between O(1)···H(9en) and O(1)···H(10en). Previous studies suggest that most norbornene double bonds are nonplanar and exhibit an asymmetric electron distribution with the greatest density lying on the methylene bridge side of the double bond.[9] In the present structure, intermolecular packing interactions involving the ester side chains lead to a twist of C(11)–C(2)–C(3)–C(13) from coplanarity as indicated by the 4.9° (5) torsion angle. The expected double bond deformation is masked by this deviation from coplanarity.

Experimental Section

Isodicyclopentadiene[37] and DCVC (**8**)[21] were prepared as described in the literature. Maleic anhydride, 99% pure, was purchased from Aldrich Chemical Co. and further purified by sublimiation (52 °C, 1 torr). Vinylene carbonate was commercially available from Aldrich Chemical Co. IR spectra were obtained with Perkin-Elmer 197 and Beckman IR 4250 spectrophotometers. ^{1}H NMR spectra and ^{13}C NMR spectra were obtained on Varian EM390 (90 MHz) and JEOL FX 60 spectrometers, respectively. Vapor chromatography was performed on a Perkin-Elmer Sigma-3 machine by using a 6-ft nickel column packed with 5% SE-30 on Chromosorb W-AW (60–80 mesh). Mass spectral analysis was performed on a Finnigan OWA 1020 GC-MS-DS equipped with a 6-ft column of 5% Carbowax 20M on Chromosorb W-AW (60–80 mesh). Melting points are uncorrected and were taken on a Thomas-Hoover capillary melting point apparatus (for mp <200 °C).

2,3-Dichlorotetracyclo[4.4.0.1^{1,4}.1^{7,10}]dodec-5-ene-2,3-diyl Carbonate (13). Anhydrous sodium carbonate (2 g) was added to 10 mL of *o*-dichlorobenzene (freshly distilled and dried over molecular sieves) containing 0.30 g (0.0019 mol) of DCVC (**8**) and the mixture heated to 180 °C under an N$_2$ atmosphere. IDCP (**4**; 0.18 g, 0.0013 mol) dissolved in 5 mL of *o*-dichlorobenzene was added and the resulting solution maintained at 180 °C for 2 h (reaction was followed by VPC analysis). At the end of the reaction the solvent was removed by vacuum distillation, and the adduct **13** distilled over at 180 °C (0.1 torr): yield 0.25 g (65% based on the weight of IDCP); mp 100–101 °C; ^{1}H NMR (CDCl$_3$) δ 5.5 (d, 1 H), 3.5 (m, 1 H), 2.85 (m, 8 H), 2.45 (m, 2 H); ^{13}C NMR (CDCl$_3$) δ 163.5, 149.4, 115.6, 108.0, 107.8, 72.0, 59.5, 45.6, 41.9, 38.5, 38.2, 31.5, 24.6; IR (KBr) 1800 cm^{-1}. In the absence of Na$_2$CO$_3$ the yield of the adduct was poor (35%) due to loss of the diene by polymerization catalyzed by acid (HCl) impurity present in **8**. This effect occurs only in the case of DCVC as the dienophile.

Tetracyclo[4.4.0.1^{1,4}.1^{7,10}]dodec-5-ene-2,3-dione (14). To a stirred solution of **13** (0.85 g, 2.97 mmol) dissolved in 5 mL of dioxane was added 2 mL of 30% NaOH in drops, and the resulting solution was stirred for 12 h. The solution turned red, indicating formation of the diketone. Sodium chloride, which precipitated from the reaction mixture, was filtered and washed with small portions of dioxane. From the combined filtrate dioxane–water was removed by vacuum distillation. The residue was dissolved in chloroform (25 mL), extracted with water, and dried over MgSO$_4$, and the solvent was removed. The crude diketone weighed 0.5 g (92%). The product was further purified by vacuum distillation (142–44 °C, 0.1 torr). A sample crystallized from hexane melts at 83–84 °C: IR 1740, 1750 cm^{-1}; ^{1}H NMR δ 5.73 (d, 1 H), 3.23 (m, 1 H), 2.86 (m, 2 H), 2.63 (m, 1 H), 1.4–2.26 (m, 7 H); ^{13}C NMR (CDCl$_3$) δ 198.3, 193.8, 167.7, 119.4, 69.7, 54.4, 44.7, 41.5, 39.2, 35.3, 31.6, 22.6.

Tetracyclo[4.4.0.1^{1,4}.1^{7,10}]dodec-5-ene-2,3-diyl Carbonate (12). VC (**7**; 1.0 g, 0.011 mol), dissolved in 10 mL of *o*-dichlorobenzene, was added to a stirred solution of IDCP (**4**; 1.5 g, 0.011 mol) in 20 mL of *o*-dichlorobenzene, and the resulting mixture was refluxed at 180 °C for 4 h (the course of the reaction was followed by VPC analysis). The solvent was removed by vacuum distillation, and on further distillation the adduct **12** distilled over at 150 °C and 0.02 torr (1.6 g, yield 75%). The adduct, initially a viscous colorless liquid, solidified on standing in a desiccator: mp 114–115.5 °C (crystallized from hexane); ^{1}H NMR (CDCl$_3$) δ 5.40 (d, 1 H), 4.88 (dd, 1 H), 4.72 (d, 1 H), 3.17 (m, 1 H), 2.83 (m, 1 H), 2.36 (m, 2 H), 1–2 (m, 7 H); ^{13}C NMR (CDCl$_3$) δ 162.9, 155.5, 113.6, 80.2, 78.8, 64.3, 48.9, 43.7, 42.2, 38.6, 31.7, 25.1 (12 of the expected 13 peaks); MS *m/e* 218, 190, 132, 117; IR 2950, 1175, 1140, 1040 cm^{-1}.

Tetracyclo[4.4.0.1^{1,4}.1^{7,10}]dodec-5-ene-2,3-*exo*-dicarboxylic Anhydride (15). Isodicyclopentadiene (**4**; 500 mg, 3.78 mmol)

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[32] Roof, A. A. M., unpublished results.

was added as a neat liquid to 25 mL of *tert*-butylbenzene, and the resulting solution was refluxed for 30 min under an N_2 atmosphere. Maleic anhydride (**9**; 200 mg, 2.04 mmol) was added as a solid (compressed to form a pellet) to the diene and the resulting solution refluxed for 7 h. Initially two isomeric products, **15** and **16**, are formed as seen by VPC analysis. On continued heating of the mixture, all of the **16** is converted into **15**. The crude product obtained after removal of the solvent (350 mg, 75%) was stirred with 25 mL of pentane, and the adduct separated as a pale brown solid while the dimers of **4** remained in solution. When 100 mg of the adduct was chromatographed through 4 g neutral silica with pentane/ether (85:15) as the eluent, 80 mg of **15** was obtained. Final crystallization of **15** was done in hexane/ether (20:1): mp 124–125 °C; ^{1}H NMR ($CDCl_3$) δ 5.53 (d, 1 H), 3.36 (t, 1 H), 3.16 (m, 1 H), 2.87–2.97 (m, 3 H), 1.3–2.13 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 172.3, 171.6, 164.9, 118.6, 66.7, 50.3, 49.6, 47.2, 43.9, 42.0, 39.2, 36.7, 31.4, 24.4.

Tetracyclo[4.4.0.1^{1,4}.1^{7,10}]dodec-5-ene-2,3-*endo*-dicarboxylic Anhydride (16). Isodicyclopentadiene (**4**; 1 g, 3.78 mmol) was added to 50 mL of *tert*-butylbenzene at its boiling point. After the solution was refluxed for 30 min under an N_2 atmosphere, maleic anhydride (**9**; 400 mg, 4.08 mmol) was added (as solid pellet) to the diene and the solution refluxed for 15 min. Further conversion of **16** → **15** was avoided at this point by rapidly cooling the flask in an ice bath. After removal of the solvent and stirring of the residue with pentane, the crude product obtained weighed 650 mg (69%, based on **3**). Pure adduct **16** was obtained by chromatographing the product mixture on a preparative TLC plate (silica, 100 mg/plate; 15% ether (in pentane) as the eluent). Crystalline **16** was obtained from ether/hexane (1:2): ^{13}C NMR ($CDCl_3$) δ 172.6, 171.5, 164.5, 116.8, 68.2, 55.6, 49.6, 48.0, 47.6, 42.2, 39.8, 38.2, 32.4, 26.1.

2-Methylcyclopentane-1,3-dione[26] (24). To 40 g of anhydrous $AlCl_3$ placed in a 500-mL three-necked flask provided with a condenser, a dropping funnel equipped with a drying tube, and a mechanical stirrer with an N_2 gas inlet–outlet was added 40 mL of water-free nitromethane in drops under an N_2 atmosphere. The mixture was vigorously stirred, and after the dissolution of $AlCl_3$ in nitromethane the solution was cooled to room temperature. Under a positive pressure of N_2 inside the flask, finely divided and predesiccated succinic acid (11.8 g, 0.1 mol) was added in portions, allowing the CO_2 liberated to escape between successive additions. When the gas evolution stopped, freshly distilled propionyl chloride (28.7 g, 0.3 mol) was added and the mixture heated to 80 °C. After 3 h the mixture was cooled to room temperature and carefully poured over 80 g of crushed ice with constant stirring. The solution was cooled to -10 °C and kept at that temperature for 12 h. The solid that separated was filtered, washed with 10% sodium chloride solution and ether, and finally air-dried. The crude product **24** (8.3 g, 79%) was crystallized from hot water by using animal charcoal; mp 214–216 °C (lit.[26] mp 214–216 °C). Attempted synthesis of **25** by substituting isobutyryl chloride for propionyl chloride in the above synthesis was not successful. For **24**: ^{13}C NMR (Me_2SO-d_6) δ 194.5, 111.7, 30.2, 5.7; ^{1}H NMR (Me_2SO-d_6) δ 2.33 (s, 4 H), 1.46 (s, 3 H), 11.26 (br s, 1 H).

2,2-Dimethylcyclopentane-1,3-dione (25).[25] A solution of 5 g of pure enone **24**, 2.5 g of KOH, and 6.7 g of CH_3I was heated to reflux in 50 mL of a dioxane–water (3:1) mixture. After 5 h and again after 8.5 h, 1 g of KOH and 2.7 g of CH_3I in 8 mL of dioxane and 3 mL of water was added to the refluxing mixture. After a total of 12 h the mixture was cooled and extracted with ether several times. After removal of ether, the residue was heated with 50 mL of 10% HCl to the boiling point, cooled, and treated with excess 10% $NaHCO_3$. This solution was extracted with chloroform, dried, and evaporated. The pale yellow residue was further purified by sublimation (50–52 °C, 1 torr): 2.5 g (44%); mp 45–47 °C (lit.[25] mp 45–47 °C).

2,2-Dimethyl-4-cyclopentene-1,3-dione (11). A solution of **25** (2.14 g, 16.98 mmol) in 25 mL of CCl_4 was heated in an oil bath to 60 °C, 3.03 g of *n*-bromosuccinimide (16.98 mmol) was added, and the mixture was irradiated with a projector lamp (500 W) for 2 h. VPC analysis showed the presence of **11** and **26** in the product mixture. The solution was cooled to room temperature, filtered to remove succinimide, washed with sodium bicarbonate solution and water, and then dried. After removal of the solvent the crude product (1.5 g) was chromatographed on 100 g of neutral silica gel with hexane as the eluent until all of the **26** was removed (0.5 g). Elution with a hexane/ether (90/10) mixture gave **11**: bp 100 °C (40 torr); 1.0 g (yield 50%); ^{1}H NMR ($CDCl_3$) δ 7.2 (s, 2 H), 1.2 (s, 6 H); IR (neat) 1748 (m), 1710 (s), 1470 (m) cm^{-1}.

2-Methyl-3-methoxycyclopent-2-en-1-one (27). Finely cut and dried sodium (0.46 g, 0.02 mol) was added to 25 mL of absolute ethanol with constant stirring. After gas evolution (H_2) stopped, 7.3 g of (**24**) was added at room temperature. All of the **24** dissolved within 15 min to give a clear solution. If necessary, a few more milliliters of absolute ethanol was added to get a clear solution followed by 27.9 g of CH_3I (0.06 mol) dissolved in 19 mL of ethanol. The clear solution was refluxed for 3 h and then cooled to room temperature. When treated with excess anhydrous ether, sodium iodide precipitated from the solution. This solution was filtered, and the filtrate was evaporated to dryness. The residue was dissolved in ether and extracted with water. The organic layer was then dried and evaporated, and a mixture of **25** and **27** was obtained. On vacuum distillation pure **25** was obtained first [2.4 g (30%); 55 °C (1 torr)] followed by **27** [90 °C (1 torr)]: 0.6 g (7%); mp of **27** 58–60 °C; ^{1}H NMR ($CDCl_3$) δ 3.9 (s, 3 H), 2.5 (m, 4 H), 1.6 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 205.3, 184.4, 116.2, 56.4, 33.4, 24.8, 6.0.

2,3-Dicarbomethoxy-*syn*-sesquinorborna-2,4a-diene (20). In *tert*-Butylbenzene. Isodicyclopentadiene (1.32 g, 0.01 mol) was dissolved in 60 mL of *tert*-butylbenzene and the solution heated to boiling (169 °C). Compound **28** (0.55 g, 0.003 mol) dissolved in 5 mL of the solvent was added and the solution refluxed for 10 min. The reaction mixture was cooled to room temperature. The solvent was removed by vacuum distillation. On saturation of the residual concentrate with pentane, 90 mg (86%) of **20** separated: ^{1}H NMR ($CDCl_3$) δ 3.6 (s, 6 H), 3.0 (br, 2 H), 2.3 (m, 2 H), 1.5–1.0 (m, 5 H), 0.6–0.4 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 165.9, 158.7, 150.3, 70.2, 52.0, 48.5, 42.9, 22.2 (eight of the nine expected peaks).

In Benzene. In 3 mL of $CDCl_3$ were mixed together 0.246 g of **4** (0.002 mol) and 0.284 g of **28** (0.002 mol) at room temperature. The reaction was exothermic and went to completion in 10–15 minutes to give **20**.

Addition of Cyclopentadiene to 10. This cycloaddition was carried out as reported by DePuy and Zarveski.[11] ^{1}H NMR, ^{13}C NMR, and IR spectral data are reported here for the adduct **18**: IR (KBr) 3400 (w), 2500–2000 (m, br), 1900 (w), 1600–1400 cm^{-1} (s, br); ^{1}H NMR (Me_2SO-d_6) δ 7.1 (s, 1 H), 5.9 (t, 2 H), 4.9 (s, 1 H), 3.0 (m, 4 H), 1.6 (AB q, 2 H); ^{13}C NMR (Me_2SO-d_6) δ 197.3, 132.7, 107.6, 51.7, 48.2, 43.0.

Addition of 4-Cyclopentene-1,3-dione (10) to 4. To a stirred solution of **4** (1.05 g, 7.9 mmol) in 15 mL of anhydrous benzene was added 0.765 g of **10** (7.9 mmol) dissolved in 15 mL of benzene, and the resultant solution was maintained at 50 °C for 12 h under an N_2 atmosphere. The precipitated product (**19**) was collected by filtration and air-dried: 1.4 g (77%); mp 250 °C; IR (KBr) 3400 (w), 2700–2200 (m, br), 1900 (w), 1600–1400 cm^{-1} (s, br); ^{1}H NMR (Me_2SO-d_6) δ 12.0 (br, 1 H), 5.0 (s, 1 H), 2.90 (m, 4 H), 2.3 (s, 2 H), 0.6–1.0 (m, 2 H), 1.0–1.8 (m, 6 H); ^{13}C NMR (Me_2SO-d_6) δ 196.6, 153.5, 107.9, 50.6, 49.7, 42.7, 25.9, 25.0.

Addition of Isodicyclopentadiene to 11. To a refluxing solution of 0.45 g of **4** (3.4 mmol) in 50 mL of *tert*-butylbenzene was rapidly added a solution of 0.24 g of **11** (1.9 mmol) in 5 mL of *tert*-butylbenzene under an N_2 atmosphere. The mixture was allowed to react at reflux for an additional 3 h. After removal of the solvent in vacuo the viscous residue was further distilled under vacuum (145 °C, 9.1 torr), and **17** was obtained: mp 98–99 °C (crystallized from hot hexane–Norite); 0.45 g (yield 90%); ^{1}H NMR ($CDCl_3$) δ 5.56 (d, 1 H), 3.3 (br s, 1 H), 3.0–2.6 (m, 4 H), 2.1 (br d, 1 H), 1.7–1.27 (m, 6 H), 1.16 (s, 3 H), 1.13 (s, 3 H), 1.0–0.6 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 217.7, 165.9, 119.5, 68.2, 59.5, 54.2, 50.9, 50.6, 45.6, 41.8, 39.3, 36.9, 31.7, 24.3, 16.9.

Trapping of Unstable 5 at 0 °C with 9. Compound **9** (44 mg, 30.5 mmol) was dissolved in a dilute solution of the diketone **14** (94 mg, 0.5 mmol) in 50 mL of dry methylene chloride. Nitrogen was bubbled through the system for 30 min. The solution, contained in a Pyrex test tube fitted with a ground-joint stopper, was irradiated at 0 °C with a Honovia medium-pressure lamp that was water cooled in a Pyrex well. When the red color due to **14** disappeared, irradiation was stopped and the product (s) isolated by evaporating the solvent (yield 90%). From the integration values of the peaks in the VPC analysis the ratio of **15** and **16** in the product mixture was found to be 1:3.

Competitive Addition of 9 and 28 to the Dienes 4 and 5. To a refluxing solution of 200 mg of **4** (1.51 mmol) in 50 mL of *tert*-butylbenzene was added quickly a premixed solution of **9** (148.5 mg, 1.51 mmol) in 2.5 mL of chloroform and **28** (213 mg, 1.51 mmol) in 2.5 mL of *tert*-butylbenzene. Reaction was allowed to continue at reflux (160 °C) for an additional 10 min. The product solution was cooled to 0 °C, and the composition was determined by VPC. The ratio of the products (**15** + **16** and **20**) was 1:2.

X-ray Analysis. All data were collected on a Syntex $P2_1$ diffractometer system by the θ–2θ scanning technique by using a variable scan speed and graphite-monochromated Cu Kα radiation (λ = 1.54178 Å, compounds **12**, **13**, **15**, **21**) or Mo Kα radiation (λ = 0.71069 Å, compound **16**). Room-temperature lattice parameters were refined by a least-squares procedure using 15 reflections whose angles were measured by a centering routine associated with the diffractometer. Space groups were determined by systematic absences and statistics. Periodically monitored reference reflections showed no significant changes in intensity. Lorentz and polarization corrections were applied, but no absorption corrections were made. The direct methods program MULTAN78[33] was used to calculate phases for the larger $|E|$ values. Full-matrix least-squares refinements were terminated when the average shift/error ratio was on the order of 0.1. R is defined as $\sum||F_o| - |F_c||/\sum|F_o|$ and R_w as $(\sum\omega(|F_o| - |F_c|)^2/\sum\omega|F_o|^2)^{1/2}$. The function minimized in the refinement was $\sum\omega(|F_o| - |F_c|)^2$ where $\omega = 1/[\sigma^2(F_o) + (0.01F_o)^2]$.

Final differerence maps were checked for residual electron density. Atomic scattering factors were calculated by the XRAY76 program.[34] Bond distances and valence angles are presented in the supplementary material for compounds **12**, **13**, **15**, **16**, and **21**. Tables of atomic positional parameters, anisotropic thermal parameters, short intramolecular contacts, torsion angles, and interplanar angles are also included in the supplementary material.

Compound 12. A crystal of dimensions 0.3 × 0.25 × 0.16 mm was used to collect all data. The unit cell is orthorhombic, and systematic absences are consistent with space group *Pbca*.

Crystal data: $C_{13}H_{14}O_3$, M_r = 218.25, a = 11.609 (1) Å, b = 15.621 (2) Å, c = 11.406 (1) Å, V = 2068.4 (5) Å^3, Z = 8, d_c = 1.40 g cm^{-3}, μ = 8.20 cm^{-1} (Cu Kα).

Of the 1887 independent reflections measured 837 had intensities greater than $3\sigma(I)$. Phases were calculated for the 172 $|E|$ values greater than 1.20, and the phase set with the highest combined figure of merit yielded an E map which revealed the positions of all nonhydrogen atoms. All hydrogen atoms were located in a difference Fourier map, and full-matrix least-squares refinement with anisotropic thermal parameters for nonhydrogen atoms led to a final R of 0.038 and a weighted R of 0.042.

Compound 13. A crystal of dimensions 0.30 × 0.30 × 0.25 mm was used to collect all data. The unit cell is monoclinic, and systematic absences are consistent with space group $P2_1/c$.

Crystal data: $C_{13}H_{12}O_3Cl_2$, M_r = 287.14, a = 7.638 (1) Å, b = 19.714 (4) Å, c = 8.872 (2) Å, β = 111.91 (1)°, V = 1239.4 (4) Å^3, Z = 4, d_c = 1.54 g cm^{-3}, μ = 47.10 cm^{-1} (Cu Kα).

Of the 2022 independent reflections measured, 1214 had intensities greater than $3\sigma(I)$. Phases were calculated for the 250 $|E|$ values greater than 1.52, and the phase set with the highest combined figure of merit yielded an E map which revealed the positions of all nonhydrogen atoms. All hydrogen atoms were located in a difference Fourier map, and full-matrix least-squares refinement with anisotropic thermal parameters for nonhydrogen atoms led to a final R of 0.061 and a weighted R of 0.069.

Compound 15. A crystal of dimensions 0.40 × 0.33 × 0.23 mm was used to collect all data. The unit cell is monoclinic, and systematic absences are consistent with space groups *Cc* and $C2/c$. Structure solution proved the correct space group to be $C2/c$.

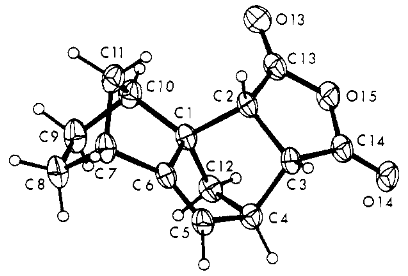

Figure 3. ORTEP drawing of compound **15**.

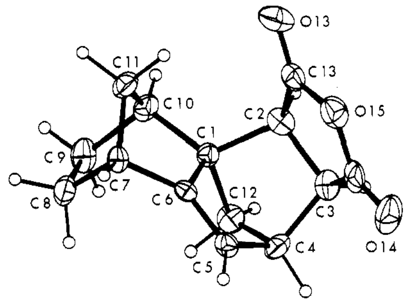

Figure 4. ORTEP drawing of compound **16**.

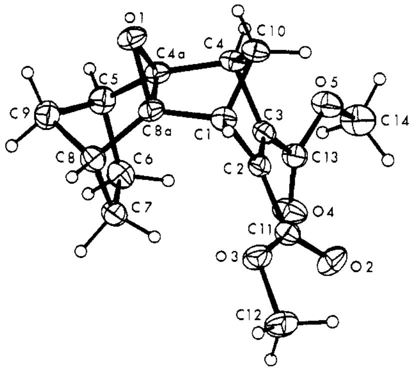

Figure 5. ORTEP drawing of compound **21**.

Crystal data: $C_{14}H_{14}O_3$, M_r = 230.27, a = 24.641 (9) Å, b = 6.309 (2), c = 15.417 (5) Å, β = 112.05 (3)°, V = 2221 (1) Å^3, Z = 8, d_c = 1.38 g cm^{-3}, μ = 7.96 cm^{-1} (Cu Kα).

Of the 1825 independent reflections measured, 1539 had intensities greater than $3\sigma(I)$. Phases were calculated for the 200 $|E|$ values greater than 1.50, and the phase set with the highest combined figure of merit revealed the positions of all nonhydrogen atoms. All hydrogen atoms were located in a difference Fourier map, and full-matrix least-squares refinement with anisotropic thermal parameters for nonhydrogen atoms led to a final R of 0.063 and a weighted R of 0.067. H(5) did not refine smoothly, and the positional parameters of the H atoms were fixed during the refinement. Figure 3 is an ORTEP drawing[35] of compound **15**.

Compound 16. A crystal of dimensions 0.5 × 0.23 × 0.15 mm was used to collect all data. The unit cell is monoclinic and systematic absences are consistent with space group $P2_1/c$.

Crystal data: $C_{14}H_{14}O_3$, M_r = 230.27, a = 14.016 (1) Å, b = 6.5765 (8) Å, c = 12.076 (2) Å, β = 98.374 (9)°, V = 1101.3 (2) Å^3, Z = 4, d_c = 1.39 g cm^{-3}, μ = 0.91 cm^{-1} (Mo Kα).

Of the 1715 independent reflections measured, 976 had intensities greater than $3\sigma(I)$. Phases were calculated for the 200 $|E|$ values greater than 1.42, and the phase set with the highest combined figure of merit revealed the positions of all nonhydrogen atoms. All hydrogen atoms were located in a difference Fourier map, and full-matrix least-squares refinement with anisotropic thermal parameters led to a final R of 0.062 and weighted R of 0.056. H(5) did not refine smoothly, and the positional parameters of hydrogen atoms were fixed during the refinement. Figure 4

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[33] Main, P.; Lessinger, L.; Woolfson, M. M.; Germain, G.; Declercq, J. P. "MULTAN 78, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray diffraction Data"; Universities of York, England, and Louvain, Belgium, 1978.

[34] Stewart, J. M.; Machin, P. A.; Dickinson, C. W.; Ammon, H. L.; Flack, H.; Heck, H. Technical Report No. TR-446; Computer Science Center, University of Maryland: College Park, Md, 1976.

[35] Johnson, C. K. Report ORNL-3794 (revised); Oak Ridge National Laboratory: Oak Ridge, TN, 1971.

is an ORTEP drawing[35] of compound **16**.

Compound 21. A crystal of dimensions 0.42 × 0.17 × 0.17 mm was used to collect all data. The unit cell is orthorhombic, and the systematic absences are consistent with space group *Pbca*.

Crystal data: $C_{16}H_{18}O_5$, $M_r = 290.32$, $a = 26.059$ (3) Å, $b = 11.132$ (1) Å, $c = 9.542$ (1) Å, $V = 2768.0$ (6) Å^3, $Z = 8$, $d_c = 1.39$ g cm^{-3}, $\mu = 8.69$ cm^{-1} (Cu Kα).

Of the 2015 independent reflections measured, 1160 had intensities greater than $3\sigma(I)$. Phases were calculated for the 200 $|E|$ values greater than 1.28, and the phase set with the highest combined figure of merit yielded all nonhydrogen atoms. All hydrogen atoms were located in a difference Fourier map, and full-matrix least-squares refinement with anisotropic thermal parameters for nonhydrogen atoms led to a final R of 0.029 and a weighted R of 0.032. The data were corrected for extinction through use of the equation[36] $|F_c^*| = k|F_c|(1 + 2r^*|F_c|^2\delta)^{-1/4}$, where δ is a dimensionless constant. During the final cycle of refinement r^* was refined to a value of 6.79 (8) × 10^{-3}. Figure 5 is an ORTEP drawing[35] of compound **21**.

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Registry No. **4**, 6675-72-5; **5**, 75725-33-6; **7**, 872-36-6; **8**, 17994-23-9; **9**, 108-31-6; **10**, 930-60-9; **11**, 26154-22-3; **12**, 82918-59-0; **13**, 82918-60-3; **14**, 82918-61-4; **15**, 82918-62-5; **16**, 82950-40-1; **17**, 82918-63-6; **18**, 82918-64-7; **19**, 82918-65-8; **20**, 82918-66-9; **21**, 82918-67-0; **24**, 765-69-5; **25**, 3883-58-7; **26**, 26154-26-7; **27**, 3883-56-5; **28**, 762-42-5; succinic acid, 110-15-6; propionyl chloride, 79-03-8; cyclopentadiene, 542-92-7.

Supplementary Material Available: Tables 1–5, atomic positional parameters for compounds **12**, **13**, **15**, **16**, and **21**; Tables 6–10, anisotropic thermal parameters for compounds **12**, **13**, **15**, **16**, and **21**. Table 11, interatomic distances (in angstroms) for **12**, **13**, **15**, and **16**. Table 12, valence angles (degrees) for **12**, **13**, **15**, and **16**. Table 13, interatomic distances (in angstroms) for **21**. Table 14, valence angles (degrees) for **21**. Table 15, short intramolecular contacts. Table 16, interplanar angles. Table 17, selected torsion angles. Figure 18, ORTEP drawing of compound **12**. Figure 19, ORTEP drawing of compound **13** (19 pages). Ordering information is given on any current masthead page.

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Inert Carbon Free Radicals. 3. Monofunctionalized Radicals from Perchlorotriphenylcarbenium Hexachloroantimonate

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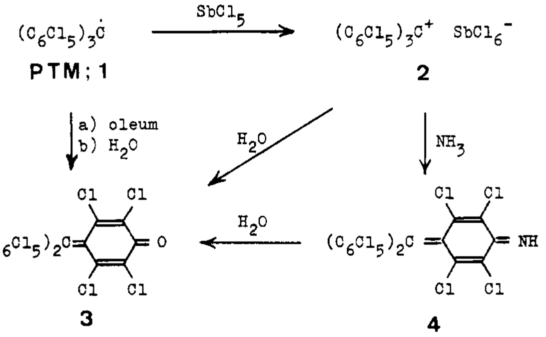
Perchlorotriphenylcarbenium hexachloroantimonate (**2**) is prepared from perchlorotriphenylmethyl radical (PTM; **1**) and $SbCl_5$. Salt **2** by hydrolysis or ammonolysis yields perchlorofuchsone (**3**) or *NH*-tetradecachlorofuchsonimine (**4**), respectively, two quinonoid compounds which are shown to be direct and indirect precursors for the synthesis of some new inert carbon free radicals, monofunctionalized at the 4-position with hydroxy (**13**), sodium oxido (**12**), methoxy (**14**), acetoxy (**15**), bromoacetoxy (**16**), (ethoxyformyl)oxy (**17**), amino (**19**), sodium amido (**20**), chloroacetamido (**21**), and bromoacetamido (**22**) groups. Most of them are isolated in pure (magnetic susceptibility), crystalline form, being insensitive to O_2 and displaying the characteristic chemical inertness of the radicals of the PTM series, caused by steric shielding. Spectral (IR, UV–vis, and ESR) data, including hyperfine couplings with ^{14}N, ^{1}H, and ^{13}C and some remarkable effects of solvents are reported and discussed. Other reactions either giving some of these radicals or starting from them are described, particularly one-electron transfers caused by $SbCl_5$, cycloheptatriene, 9,10-diphenylanthracene, KBr, KI, HI/I_2, ascorbic acid, and NaOH/Me_2SO. Supporting evidence for two-step hydride-shift mechanisms to carbenium ions is given. Evidence for steric shielding of cation **2** in some reactions leading to the formation of abnormal, novel products is described here.

The so-called "inert carbon free radicals", such as those of the perchlorotriphenylmethyl (PTM) radical series,[1,2] are passive in bond-formation processes on account of steric shielding of their central carbon atom by their six ortho chlorines and three benzene rings.[3] They do not dimerize, are quite insensitive to oxygen, even near 300 °C, and do not react with typical radical reagents or with aggressive chemical species such as concentrated mineral acids, halogens, etc.[1,2] However, they are active in electron-transfer processes, where shielding is ineffectual.[1,2,4,5] In fact, this paper concerns the synthesis and some prop-

Scheme I



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[3] See ref 1a, Figure 2.

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