

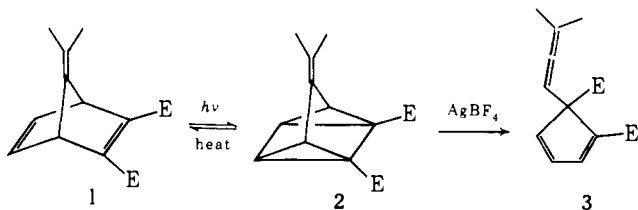
Formation and Decomposition Reactions of
5-(3',3'-Dimethylallenyl)-
1,5-bis(carbomethoxy)cyclopentadiene

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Abstract: The title compound (**3**) is formed when 7-isopropylidene-2,3-bis(carbomethoxy)quadricyclane is treated with silver fluoroborate. Heating **3** at 80° causes isomerism to 5-isopropylethynyl-2,5-bis(carbomethoxy)cyclopentadiene as the major product, and the 1,5,5- to 2,5,5-substituent rearrangement is suggested as proceeding by a series of 1,5 ester and hydrogen shifts, since the product of a single ester migration, 1-(3',3'-dimethylallenyl)-2,5-bis(carbomethoxy)cyclopentadiene, was trapped as the Diels-Alder adduct with dimethyl acetylenedicarboxylate. Photolysis of the title compound results in formation of 3-isopropylidene-4,7-dicarbomethoxytricyclo-[2.2.1.0^{2,7}]heptene.

Prinzbach and coworkers have shown¹ that the dimethylfulvene-dimethyl acetylenedicarboxylate Diels-Alder adduct **1** closes to the quadricyclene **2** upon photolysis, and that, disappointingly, the thermal decomposition of **2** gives exclusively **1**. In a preliminary re-



E = CO₂CH₃, throughout

port,² we described the unprecedented isomerization of **2** to the allenylcyclopentadiene derivative **3** using silver fluoroborate. We now report this work, and some transformations of **3** in greater detail.

Results

Formation of 3. When **2** is stirred with 1-1.2 equiv of silver fluoroborate in methylene chloride for 2 days, nmr spectra indicated formation of **3** and **1** in about a 3:1 ratio. We were most successful in purifying **3** by stirring the reaction mixture with sodium iodide to remove silver salts, concentration, and fractional crystallization from pentane, isolating **3** in 10-25% yield. Since **2** is readily available in three steps from acetone, cyclopentadiene, and dimethyl acetylenedicarboxylate,¹ **3** is relatively easy to prepare.

The proton nmr spectrum of **3** consists of two carbomethoxyl absorptions, three coupled vinyl hydrogens, and a fourth vinyl hydrogen equally coupled to two nonequivalent methyl groups. The coupling pattern for the three vinyl hydrogens was shown by decoupling studies to consist of H₂ (δ 7.27, *m*, $J_{23} \sim J_{24} \sim 2$ Hz), H₃ and H₄ (ABX centered at δ 6.51, $J_{34} \sim 5$). The chemical shifts compare closely with those of 1-carbomethoxycyclopentadiene, H₂ (7.28, *ca. t*, $J = 2$ Hz), H₃ and H₄ (6.58, *m*), and the couplings resemble those of cyclopentadiene,³ $J_{23} = 1.94$, $J_{24} = 1.09$, $J_{34} = 5.06$

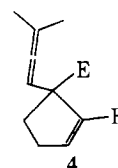
(1) For a review, see H. Prinzbach, *Pure Appl. Chem.*, **16**, 17 (1968).

(2) S. F. Nelsen, J. P. Gillespie, and P. J. Hintz, *Tetrahedron Lett.*, 2361 (1971).

(3) J. B. Lambert, L. J. Durham, P. Lepoutere, and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 3896 (1965).

Hz. The fourth vinyl hydrogen, H₆ (5.59, heptet, $J = 2.9$ Hz), is equally coupled to two methyl groups (appearing as a double doublet at 1.62), which is consistent with the presence of a dimethylallenyl group; for 1,1-dimethylallene, $J_{\text{HMe}} = 3.03$.⁴ Although the trisubstituted allene is, as expected,⁵ too symmetric to show a characteristic ir band, the ¹³C nmr spectrum of **3** clearly requires the presence of an allenic carbon⁶ to account for the peak at 201.5 ppm from TMS, and the rest of the spectrum is also entirely consistent with structure **3**.

Although we were unsuccessful in several tries at catalytic hydrogenation of **3** without extensive degradation, diimide reduction gave a dihydro compound, to which we assign structure **4**. Its nmr spectrum showed



the characteristic dimethylallenyl absorption, but only one ring vinyl hydrogen at δ 7.02, appearing as a triplet, $J = 2$ Hz. Since J_{15} for cyclopentadiene⁴ is 2.1 Hz, this result confirms the 1,5,5-substitution pattern of the cyclopentadiene ring of **3**.

Other Electrophilic Reactions of 2. The reaction which forms **3** from **2** is quite sensitive to the presence of nucleophiles, and overall addition of "HX" to the C₃,C₅ cyclopropyl bond of **2** was observed when a nucleophile "X" was present in the reaction mixture. Either silver salts or sulfuric acid in methanol convert **2** into the methanol adduct **5a**, and similarly, hydroiodic acid in methanol gives an 82:18 mixture of **6a**:**6b**.⁷ Analogous electrophilic additions have been reported for both the diacid⁸ and diester⁹ of 2,3-dicarbomethoxy-

(4) S. Sternhell, *Quart. Rev., Chem. Soc.*, **23**, 236 (1969).

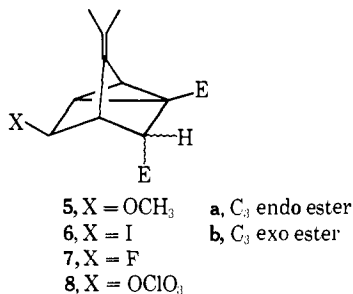
(5) J. H. Wotiz and D. E. Mancuso, *J. Org. Chem.*, **22**, 207 (1957).

(6) (a) R. Steur, J. P. van Dongen, M. J. deBie, W. Drenth, J. W. de Haan, and L. J. Van de Ven, *Tetrahedron Lett.*, 3307 (1971); (b) J. K. Crandall and S. A. Sojka, *J. Amer. Chem. Soc.*, **94**, 5084 (1972).

(7) S. F. Nelsen and J. Calabrese, *J. Amer. Chem. Soc.*, **95**, 8385 (1973).

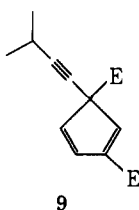
(8) S. J. Cristol, W. Y. Lim, and A. R. Dahl, *ibid.*, **92**, 4013 (1970).

(9) G. F. Koser and P. S. Pappas, Abstracts, 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972, No. ORGN-139.



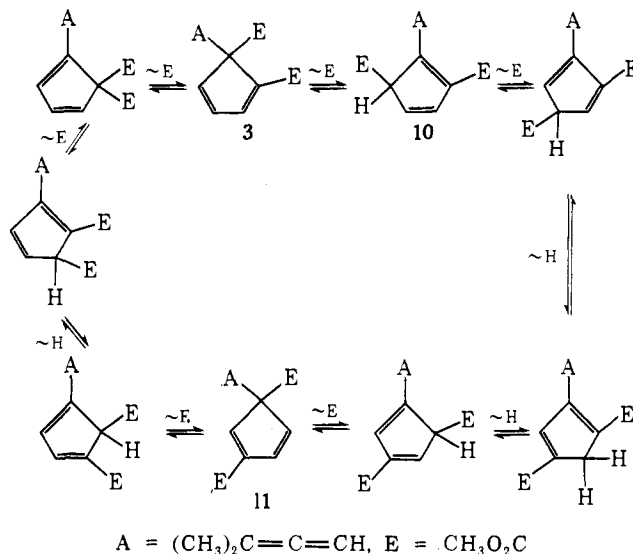
quadricyclane. For the case of the diacid, the product isolated had the endo acid configuration at C₃ for both addition of bromine and water;⁸ mixtures of C₃ epimers were observed from the diester.⁹ This electrophilic addition of HX is a problem in the synthesis of **3**, since some samples of commercial silver fluoroborate give appreciable amounts of the HF adduct **7a**. We found that vacuum desiccation of the silver fluoroborate over phosphorus pentoxide eliminates the formation of **7a**. Even perchlorate was shown to be too reactive as a nucleophile to be present when **2** is reacted with silver ion, if efficient formation of **3** is desired. In an experiment in which silver perchlorate was used, comparable amounts of **3** and a product which we assign as **8a** were formed. The nmr spectrum of this compound indicates that it is a 2,3-dicarbomethoxy-7-isopropylidenenortricyclene derivative bearing a C₃ substituent containing no hydrogens which deshields the C₃ hydrogen considerably, and the mass spectrum showed a parent peak containing one chlorine at 348,350 (2 + HClO₄). We discarded this cyclopropylcarbonyl perchlorate derivative immediately, since alkylperchlorates are notoriously explosive.

Rearrangement of 3. Although the allenic cyclopentadiene **3** is easily isolable, it is not very stable to heating, and either neat or in solution (benzene, hexane, or carbon tetrachloride) it turns dark and obviously decomposes. The major decomposition product, isolated in about 50% yield by tlc, was shown to be isomeric with **3** by analysis and mass spectra. Its nmr spectrum shows that there has been an allene-acetylene interconversion, since the characteristic vinyl heptet-methyl double doublet of the dimethylallenyl group of **3** is replaced by the absorptions of an isopropyl group. Furthermore, the chemical shifts of the three vinyl ring hydrogens show that the decomposition product is a 2,5,5-substituted cyclopentadiene, **9**.



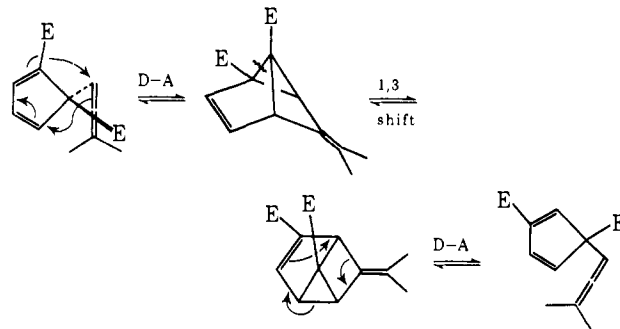
Thinking it likely that the ring-substituent isomerization and the acetylene-allene conversion take place separately, we followed the decomposition by nmr, but did not observe intermediates building up. Two basically different possibilities were considered for the 1,5,5 → 2,5,5 trisubstituted cyclopentadiene conversion. One possibility is a series of 1,5 shifts, as outlined in Scheme I, assuming ester migration is more facile than allenyl migration. Another mechanism seemed at-

Scheme I. 1,5 Shift Mechanism for Conversion of **3** to the 2,5,5 Derivative **11**



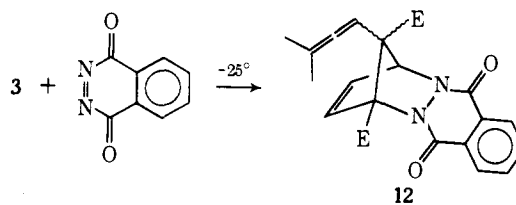
tractively more direct: intramolecular Diels-Alder addition of the C₆-C₇ olefinic bond to the cyclopentadiene ring followed by allylic shift and reverse Diels-Alder reaction also causes the 1,5,5 → 2,5,5 conversion (Scheme II). The 1,3 shift would presumably proceed

Scheme II. Diels-Alder Mechanism to Convert **3** to **11**



through a diradical intermediate, since it is symmetry forbidden.

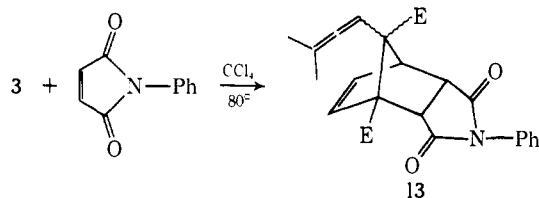
Diels-Alder Reaction of 3. Since a host of different dienes would be formed if 1,5 shifts as shown in Scheme I were actually taking place, and one might be able to trap these intermediates, we have investigated the reactions of **3** with dienophiles. We found that 2,3-diazanaphthoquinone¹⁰ is reactive enough to trap **3** below room temperature, giving a mixture of the Diels-Alder adducts **12**, having spectral data consistent with



the structure proposed. It is not surprising that **3** does not react at room temperature with less potent dienophiles, since it not only has bulky C₃ substituents, but also has the diene system deactivated by the 1-carbomethoxy substituent. Although no reaction took place at room temperature, *N*-phenylmaleimide formed

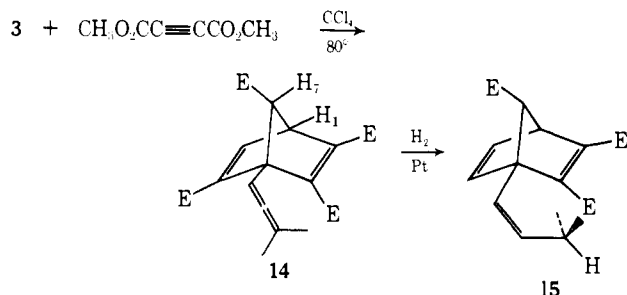
(10) T. J. Kealy, *J. Amer. Chem. Soc.*, **84**, 966 (1962).

a 1:1 adduct with **3** in refluxing carbon tetrachloride, and the nmr spectrum shows clearly that both the allenyl group and the 1,5,5-substitution pattern of the diene attacked were still present; the simple Diels–Alder adduct of **3**, **13**, was formed. Diethylazodicarboxylate

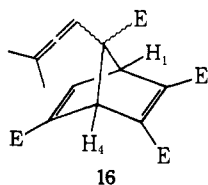


appeared to give ene reaction of the dimethylallenyl portion of the molecule (NH absorption in the ir, only one C–Me by nmr), so reaction with this reagent was not investigated further.

Using dimethyl acetylenedicarboxylate as dienophile, only rearrangement to **9** was observed in dilute solution, but at higher concentration in refluxing carbon tetrachloride, a 33% yield of 1:1 adduct which clearly was not a simple Diels–Alder adduct of **3** was isolated. The characteristic dimethylallene nmr absorptions were present in this adduct (**14**), as was verified by catalytic



hydrogenation of the C₉–C₁₀ double bond to give the dihydro adduct **15**, which had spectral properties in keeping with this transformation. Other single proton absorptions were observed for **14** at δ 7.66 (dd, J = 3.5 Hz, 0.8), 4.28 (dd, J = 3.5 Hz, 1.6), and 3.53 (m). Since **14** and **15** have only one norbornadiene vinyl proton a substituent must have been present at C₂ of the diene precursor of these compounds, and from the chemical shift of the remaining vinyl proton (H₆ in the adducts, at δ 7.55 for **14**), this substituent must have been an ester group. We write the adducts as **14** and **15** from the observed chemical shifts of the two tertiary protons. In particular, adduct **16**, which would result

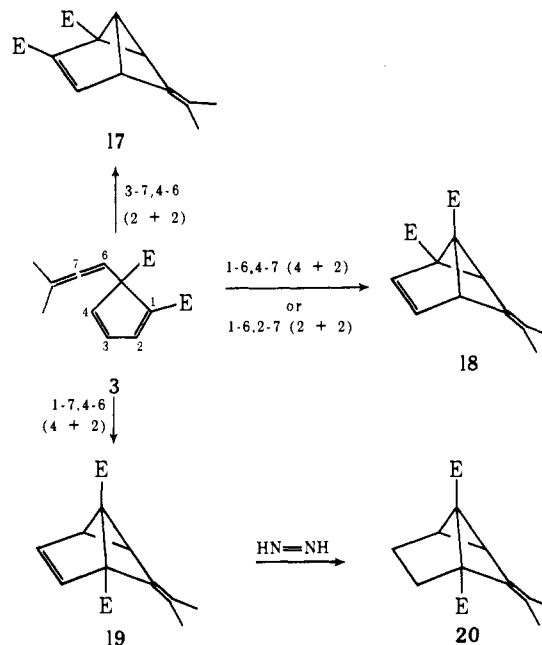


from trapping **11**, can be ruled out, since H₁ would have to be assigned to the δ 3.53 peak, making it appear δ 0.75 above H₄, which is completely unreasonable considering the distribution of ester substituents. Since a diene which is neither **3** nor **11** was trapped, ester migration clearly occurs in refluxing carbon tetrachloride.

Photolysis of 3. Additional information concerning the tricyclic ring system shown in Scheme II which results from internal Diels–Alder reaction of **3** was gained by investigating the photolysis of **3**. Photolysis

of an ether solution using a Pyrex filter results in a quite clean conversion of **3** to a photoisomer with only two vinyl hydrogens, implying that the C₆, C₇ double bond has been added to the diene system. The photo adduct was observed to revert to **3** upon storage. Reformation of **3** suggests that a simple cycloaddition has occurred, and not an extensive skeletal rearrangement. In principle, cycloaddition of the C₆, C₇ double bond to the diene system could result in three isomers of dicarbomethoxy-3-isopropylidene-tricyclo[2.2.1.0^{2,7}]heptene, **17–19**, as shown in Scheme III. Structure **17**

Scheme III. Intramolecular Cycloaddition Products from **3**



may be ruled out for the photo adduct, since it does not have the two vinyl hydrogens observed. The nmr spectrum of the photo adduct shows two vinyl hydrogens with a 5.5 Hz coupling (δ 7.17 and 5.85 (dd)), and two aliphatic hydrogens with a 5 Hz coupling (δ 3.31 (d), 3.01 (dd)). One aliphatic hydrogen is coupled to both vinyl hydrogens, while the other is coupled to neither. If the observed nmr is attributed to **18**, J_{24} would have to be 5 Hz, and the bisallylic H₄ absorption must be assigned to the δ 3.01 peak, which appears δ 0.3 above the monoallylic, cyclopropyl H₂ absorption. Neither of these problems exists if **19** is assigned as the structure, and both couplings and splittings are reasonable; we therefore identify the photoproduct of **3** as **19**. Diimide reduction gave the 5,6-dihydro compound **20**, as expected. The relatively large difference in C-methyl chemical shifts for this compound (δ 0.23) is also more reasonable for dihydro **19** than for dihydro **18**.

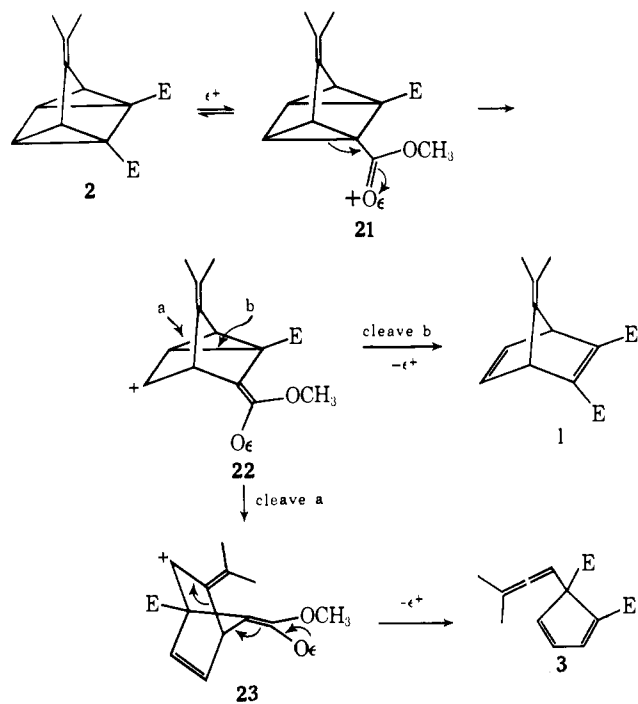
Discussion

Reaction of **2** with acids leads to addition of the conjugate base to C₅, and protonation at C₃. The facile cyclopropane cleavage observed is not surprising, considering the great strain present in **2** (quadricyclane itself has a strain energy of 78.7 kcal/mol¹¹).

The formation of **3** as well as **1** upon treatment of **2** with silver fluoroborate was a surprising result to us, but is easily rationalized in terms of a carbonium ion

(11) H. K. Hall, Jr., C. D. Smith, and J. H. Baldt, *J. Amer. Chem. Soc.*, **95**, 3197 (1973).

Scheme IV. Electrophilic Rearrangement of 2



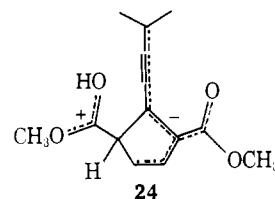
rearrangement, as shown in Scheme IV. In the presence of nucleophiles, **22** (or **21**, which might be only a resonance form) can be trapped by exo addition to C₃. If only BF₄⁻ is available, however, a stable product cannot be formed, and the ion can cleave cyclopropylcarbinyl bond a or b. Although both are equivalently disposed for overlap with the cationic center of **22**, delocalization of bond b leads to a partial positive charge at C₂ (next to ester), while delocalization of bond a puts a partial positive charge on C₇ (next to a vinyl group). The difference in substitution presumably contributes to the observed 3:1 preference for cleavage of bond a. We do not know that Ag⁺ is the active electrophile in the rearrangement of **2** to **3**, but have been unable to detect **3** as a product using other reagents.

Our trapping experiment establishes that ester shift occurs in **3** at 80°; the product of the first ester shift, **10** (see Scheme I), was captured as the dimethyl acetylenedicarboxylate adduct **14**. It has recently been established that thermal 1,5 shifts of ester groups occur in cyclohexadiene derivatives near 300°,¹² and in pentacarbomethoxyalkylcyclopentadienes at 100–130°,¹³ so the fact that ester shift occurs at 80° in **3** is no longer particularly surprising. Although the thermal decomposition of **3** is by no means clean, **9** is certainly the major product, and we could not observe buildup of other ring substitution patterns by nmr. Simply because hydrogen shift is much faster than ester, and the 1,5,5-substituted starting material rather sterically hindered, conversion to predominantly 2,5,5-substituted material is quite reasonable. The allene to acetylene conversion proceeds under surprisingly mild conditions, as strong base is usually required for such reactions. We can only offer sheer speculation as to why this par-

(12) (a) J. A. Berson and R. G. Salomon, *J. Amer. Chem. Soc.*, **93**, 4620 (1971); (b) P. Schiesl, Abstracts, 164th National Meeting of the American Chemical Society, New York, N. Y., No. ORGN-120.

(13) P. Schmidt, R. W. Hoffmann, and J. Backes, *Angew. Chem., Int. Ed. Engl.*, **11**, 513 (1972).

ticular one proceeds in refluxing benzene. We suggest as a possibility an intramolecular proton transfer from the H₆ carbon of **10** to the saturated ester, which could proceed through a six-membered transition state and would give a highly delocalized zwitterion, depicted as **24**. Protonation of the anion at C₈ (presumably



not intramolecular) would give **9**.

Isolation of photoisomer **19** is further evidence that Scheme I, not Scheme II, is involved in the 1,5,5-trisubstituted cyclopentadiene to 2,5,5 isomerization, since it suggests that the 3-isopropylidencyclo[2.2.1.0^{2,7}]heptene ring system is stable enough so buildup of **18** would be expected in the pyrolysis mixture, if Scheme II were actually the mechanism. We believe that **19** is the first example of the ring system reported.

Experimental Section

Mass spectra were determined on an AEI MS 9, ir spectra on a Beckman IR 8 in carbon tetrachloride unless otherwise noted, uv spectra on a Cary 15, and nmr spectra on Varian A60, XL100, or JELCO MH 100 equipment and shifts are reported in δ units, couplings in hertz in CDCl₃ unless otherwise noted. The ¹³C spectrum was determined on the XL100 in CDCl₃. Analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich., or Microtech Analytical Laboratory, Skokie, Ill. Thin-layer chromatography (tlc) refers to use of Brinkman silica gel PF-254 plates, 1.5-mm thick, eluted with chloroform. Compounds **6a** and **6b** have been described separately.⁷ Silver fluoroborate was purchased from Ozark-Mahoning.

5-(3,3'-Dimethylallenyl)-1,5-biscarbomethoxycyclopentadiene (3). Typically, to 3.12 g (16 mmol) of silver fluoroborate (desiccated over P₂O₅ *in vacuo*) in 260 ml of methylene chloride was added 4 g (16 mmol) of **2**,¹ and the mixture was stirred under nitrogen for 48 hr (wrapped in foil to exclude light). After addition of 8 g of sodium iodide and stirring for 30 min, the solution was filtered through a pad of silica gel and the solid washed with 100 ml of CH₂Cl₂. After removal of solvent, the residue was dissolved in pentane, sealed, and crystallized several times at -15°, giving 0.5–1.0 g of colorless **3**: mp 44–46° (12–24%); ir (μ . CCl₄) 5.74, 5.81 (unsat. and sat. ester); nmr (δ , CDCl₃) 7.27 (H₂, t, $J_{23} \approx J_{24} \approx 2$ Hz), 6.51 (H₃, H₄, ABX centered at 6.51, $J_{34} \approx 5$), 5.59 (H₅, hept., $J_{6-Me} = 2.9$ Hz), 3.64, 3.77 (2 OCH₃, s), 1.62 (2 CCH₃, d); ¹³C nmr (ppm from TMS, CDCl₃) 201.5 (C₇), 170.7 and 163.7 (CO's), 145.5 and 131.6 (C₃ and C₄), 143.2 (C₂), 142.4 (C₁), 98.0 (C₈), 81.6 (C₆), 66.3 (C₅), 52.9 and 51.6 (OCH₃), 20.2 (both CCH₃) (assignments were made using off-resonance decoupling and NOE experiments); uv (95% EtOH) λ_{max} (log ϵ) 283 (3.6), 253 (3.6);¹⁴ ms (70 eV) m/e (% of base peak) 248 (P, 17), 189 (100). *Anal.* Calcd for C₁₄H₁₆O₄: C, 67.73; H, 6.50. Found: C, 67.84; H, 6.57.

5-(3,3'-Dimethylallenyl)-1,5-biscarbomethoxycyclopentene (4). To a mixture of 800 mg of **3** (3.2 mmol), 6.32 g of dipotassium azodicarboxylate (32 mmol), and 25 ml of pyridine, 4.92 g of acetic acid (82 mmol) in 20 ml of pyridine was added dropwise over a 4-hr period. After stirring for 18 hr, the solution was filtered, pyridine was removed by distillation, and the residue was triturated with 100 ml of ether. After extraction with 3 \times 5-ml portions of water, the organic layer was dried and concentrated. Tlc of the residue (chloroform) gave 490 mg of an oil, which was mostly **4**: nmr (CDCl₃) δ 7.02 (H₂, t, $J \approx 2$ Hz), 5.68 (H₆, hept., $J \approx 3$ Hz), 3.79 (2 OCH₃, s), 1.68 (CCH₃, dd), 2.42 (4 H, m); mass spectrum exact mass, 250.1210 (calcd for C₁₄H₁₆O₄, 250.1205).

5-*exo*-Methoxy-2,3-*endo*-biscarbomethoxy-7-isopropylidenenortri-

(14) The data quoted for this peak in ref 2 are incorrect.

cyclene (**5a**). A mixture of 1.0 g of **2**, 0.9 g of silver perchlorate, and 35 ml of methanol was stirred for 12 hr and concentrated, the residue was extracted with ether, and the organic layer washed with water and dried with sodium sulfate. Removal of solvent gave 1.2 g of crude **5a**: mp 95–97°; ir 5.76 and 6.95 μ ; nmr 3.87 (H₅, br), 3.71, 3.67, 3.28 (OCH₃, 3, s), *ca.* 2.79 (H₃, H₄, m), *ca.* 2.52 (H₁, H₆, m), 1.88 and 1.92 (CH₃, 2s). *Anal.* Calcd for C₁₅H₂₀O₆: C, 64.72; H, 7.19. Found: C, 64.32; H, 7.16.

5-*exo*-Fluoro-2,3-*endo*-biscarbomethoxy-7-isopropylidenetricyclene (7a). This compound was isolated from attempted preparations of **3** using untreated commercial fluoroborate, and was purified by tlc, mp 75–76.5° (heptane), about 10% yield. When the silver fluoroborate was stored in a desiccator over P₂O₅ at 0.1 mm pressure for several days, the amount of **7a** produced was greatly decreased. Spectral data: ir 5.80 μ (br); nmr 4.78 (H₅, J_{5F} = 59 Hz, J₄₅ ≈ J₅₆ ≈ 2 Hz), 3.79 and 3.70 (OCH₃, 2 s), 3.44 (H₄, m), 2.96 (H₃, m), 2.78 (H₁, dt, J₁₆ ≈ 5, J₁₄ ≈ J_{1F} ≈ 2 Hz), 2.27 (H₆, dq, J₄₆ ≈ J_{4F} ≈ 2 Hz), 1.78 and 1.64 (CH₃, 2, s). *Anal.* Calcd for C₁₄H₁₇FO₄: C, 62.67; H, 6.39. Found: C, 62.64; H, 6.59.

5-*exo*-Perchloryl-2,3-*endo*-biscarbomethoxy-7-isopropylideneortricyclene (8a). A mixture of 2.48 g (10 mmol) of **2**, 2.17 g (10.5 mmol) of AgClO₄, and 1.72 g (10.6 mmol) of (CH₃)₄NBF₄ in 70 ml of methylene chloride was stirred under nitrogen for 71 hr, 8 g of sodium iodide was added, and the mixture was filtered and concentrated to 3.18 g of residue. Separation by tlc on silica gel (CHCl₃) gave small amounts of **8a** as an oil; nmr of the crude mixture indicated comparable amounts of **3** and **8a** before tlc. Spectral data: nmr 5.05 (H₅, t, J₄₆ ≈ J₅₆ ≈ 2 Hz), 3.73 and 3.60 (OCH₃, 2 s), 3.24 (H₄, pentet, J₃₄ ≈ J₄₅ ≈ J₁₄ ≈ 2 Hz), 2.95 (H₃, d), 2.79 (H₁, dd, J₁₆ ≈ 5 Hz), 2.44 (H₆, dt), 1.84 and 1.64 (Me, 2 s); mass spectrum (70 eV), 348,350 (3:1 ratio), 317,319 (P – OCH₃), 248 largest high *m/e* peaks.

5-Isopropylethynyl-2,5-biscarbomethoxycyclopentadiene (9). A mixture of 200 mg of **3** and 5 ml of carbon tetrachloride was refluxed under nitrogen for 20 hr, at which time nmr showed no remaining **3**, and **9** as the major product. After concentration, the residue was extracted with hexane, concentrated, and cooled, giving impure **9**, which was recrystallized from hexane: mp 75–76° (76 mg, 38%); ir 5.90 and 6.11 μ ; nmr (CDCl₃) δ 7.50 (H₁, br d), 7.29 (H₃, d, J₃₄ = 4.7 Hz), 6.57 (H₄, d), 4.21, 3.85 (2 OCH₃, 2 s), 3.20 (H₅, m, 6.7), 1.34 (2 CCH₃, d); uv (95% EtOH), λ 346 nm (log ϵ 3.7), 322 (3.8), 276 (4.5), 271, 244, 238, 218. *Anal.* Calcd for C₁₄H₁₆O₄: C, 67.73; H, 6.50. Found: C, 67.49; H, 6.60.

Diels-Alder Adduct of 3 and 2,3-Diazanaphthoquinone⁹ (12). A mixture of 1.23 g of the sodium salt of phthalhydrazide in 75 ml of acetone was stirred at –50 to –55°, and 0.72 g of *tert*-butyl hypochlorite in 10 ml of acetone was added dropwise. After stirring for 3 hr, 0.83 g of **3** was added to the green solution, and the flask was warmed to –25° (CCl₄ slush) for 4 hr, during which the green color slowly faded. After warming to room temperature overnight, the mixture was filtered, concentrated, and separated by tlc, giving 0.14 g (10%) of a mixture of adducts (presumably C₇ epimers). Spectral data: nmr (partial, for major isomer) 7.14 (H₆, dd, 5, 1.6), 7.00 (H₅, dd, 5, 2.5), 5.52 (H₄, dd, 2.5, 1.4), 5.58 (H₃, hept., 3), 1.75 (2 Me, dd); exact mass, 408.137 (calcd for C₂₂H₂₆N₂O₆, 408.132).

Diels-Alder Adduct of 3 and *N*-Phenylmaleimide (13). A mixture of 132 mg (0.53 mmol) of **3** and 111 mg (0.64 mmol) of *N*-phenylmaleimide in 2 ml of carbon tetrachloride was refluxed for 23 hr, and

the residue was separated by tlc, giving 156 mg (70%) of **13**: mp 162–163° (carbon tetrachloride-pentane); nmr 7–7.5 (arom, m), 6.51 (H₆, dd, J₄₅ = 5.5, J₄₆ = 1 Hz), 6.33 (H₅, dd, J₅₆ = 2 Hz), 5.54 (H_{1'}, hept., J_{3Me} = 2.8 Hz), 3.9 (H₄, m), 3.7 (H₂ and H₃, m), 3.88 and 3.62 (OMe, 2 s), 1.82 and 1.73 (Me, 2 d); ms base peak *m/e* 421; exact mass 521.1526 (calcd for C₂₄H₂₂O₆, 421.1525).

2,3,6,7-*anti*-Tetracarbomethoxy-1-(3',3'-dimethylallenyl)norbornadiene (14). A mixture of 132 mg (0.53 mmol) of **3**, 2 ml of carbon tetrachloride, and 152 mg of dimethyl acetylenedicarboxylate (1.06 mmol) was refluxed under nitrogen 12 hr, and the mixture was separated by tlc, giving 68 mg (33%) of **14**, as an oil: nmr 7.66 (H₅, dd, J₄₅ = 3.5, J₃₇ = 0.8 Hz), 6.08 (H_{1'}, hept., J_{1'Me} = 3 Hz), 4.28 (H₁, dd, J₄₇ = 1.6 Hz), 3.85, 3.78, 3.76, 3.66 (OCH₃, 4 s), 3.53 (H₇, m), 1.68 (2CH₃, dd); mass spectrum 390 (P, 81), 59 (100); exact mass, 390.128 (calcd for C₂₀H₂₂O₈, 390.131).

2,3,6,7-*anti*-Tetracarbomethoxy-1-(3'-methyl-1'-*cis*-buten-1'-yl)-norbornadiene (15). Atmospheric pressure catalytic hydrogenation of 68 mg of **14** over catalyst prepared from 68 mg of PtO₂ in 10 ml of methanol gave, after tlc, 34 mg (50%) of the dihydro compound as an oil. Spectral data: nmr, 7.72 (H₅, d(br), J₄₅ = 3 Hz), 6.42 (H_{1'}, d(br), J_{1'2'} ≈ 11 Hz), 5.38 (H₂, t, J_{2',3'} ≈ 11 Hz), 4.24 (H₄, m), 3.86 (H₇, d), *ca.* 2.6 (H_{3'}, very broad m), 3.77 (3 OCH₃, s), 3.62 (OCH₃, s), 0.92, 0.87 (CH₃, 2 d, J ≈ 6 Hz); ms parent at *m/e* 392.

3-Isopropylidene-4,7-dicarbomethoxytricyclo[2.2.1.0^{2,7}]heptene (19). Photolysis of 0.5 g (2 mmol) of **3** in 350 ml of ether (5.7 *M* solution) through a Pyrex immersion well with a 450-W Hanovia lamp resulted in complete destruction of starting material and formation of **19** within 10 hr. Concentration, solution of the residue in chloroform, and filtration through a silica gel plug gave 400 mg of **19** as an oil. This photo product is thermally unstable, and reverts to **3** over a period of weeks at 0°. Spectral data: ir 5.81 μ (br); nmr 6.17 (H₅, dd, J₃₆ = 5.5, J₁₅ = 1.5 Hz), 5.85 (H₆, dd, J₁₆ = 2.2 Hz), 3.31 (H₂, d, J₁₂ = 5 Hz), 3.01 (H₁, ddd), 3.78 and 3.64 (OCH₃, 2 s), 1.63 and 1.47 (CH₃, 2 s); uv (95% ethanol) 290 (sh, 3.3), 223 (4.2).¹⁵

3-Isopropylidene-4,7-biscarbomethoxytricyclo[2.1.1.0^{2,7}]heptane (20). Dimide reduction of **19** was performed under the same conditions as the conversion of **3** to **4**, and **20** was isolated by tlc as an oil. Spectral data: ir 5.81 μ (br); nmr (CCl₄) 3.65 and 3.59 (OCH₃, 2 s), 2.96 (H₂, d, J₁₂ = 6 Hz), 1.5–2.1 (complex multiplets, 5 H), 1.59, 1.36 (CH₃, 2 s). Decoupling showed that the H₁ signal is centered about 2.38. Mass spectrum *m/e* (% of largest peak) 250 (17), 191 (33), 190 (100).

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(15) A referee correctly suggested that this uv seems anomalous, and that the compound may not be stable in alcohol.¹⁶ We also point out that **19** was never obtained in crystalline form, and the uv sample may have had impurities.

(16) G. F. Koser and S.-M. Yu, *J. Org. Chem.*, **38**, 1755 (1973).