Nucleophilic Cleavage of Quadricyclene-2,3-dicarboxylate Derivatives by Iodide

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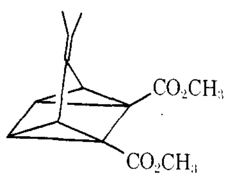
Abstract: Both 7-oxa-1,4-dimethyl-2,3-biscarbomethoxyquadricyclene (**6**) and 7-isopropylidine-2,3-biscarbomethoxyquadricyclene (**2**) undergo C_5–C_3 cleavage upon treatment with sodium iodide in acetonitrile at room temperature. The products are exo C_5 iodides obtained as mixtures of endo and exo C_3 epimers. The structure of the endo HI-1 adduct (**2a**) was determined by X-ray diffraction. Mechanisms are discussed.

Cyclopropane cleavages by nucleophiles have been reported for several compounds in which the intermediate carbanions are stabilized by carbonyl, cyano, and sulfoxide substituents.[1] Studies of cyclopropanes substituted at C_1 with two carbanion stabilizing substituents and at C_2 with a cation stabilizing substituent demonstrate that C_1–C_2 bond cleavage precedes nucleophilic attack in some cases,[2] although complete inversion of stereochemistry at C_2 has been observed for the reaction of 1-cyano-1-carboethoxy-2-phenylcyclopropane with methanol[2a–d] and 2-vinyl-1,1-dicarbomethoxycyclopentane with pyrrolidine.[2f] Increased strain in the cyclopropane ring being cleaved should make cleavage more facile, but even the relatively strained 5-carbomethoxytetracyclo[2.2.1.0^{2,5}]hexane required prolonged heating at 100° for methoxide-catalyzed methanol addition.[3] Koser and Yu[4] have recently reported extremely facile additions to 2-substituted quadricyclane derivatives, which were interpreted as being nucleophilic cleavages of the cyclopropane rings. We report additions to similar systems, and show that cleavage prior to nucleophilic attack, such as that observed by Yankee and Cram,[2a] is not responsible for product formation in at least the reaction of iodide with 7-oxa-2,3-dicarbomethoxyquadricyclene.

Results

In the course of using sodium iodide to remove silver from the complexed products obtained by reaction of dimethyl 7-isopropylidenequadricyclene-2,3-dicarboxylate (**1**) with silver salts,[4] we observed that sodium iodide reacts rapidly with **1** in acetonitrile at room temperature. Two products were obtained in a 60 (mp 114–116°):40 (mp 91–92°) ratio, and each gave the proper analysis for **1** + HI. They had very similar nmr spectra, and were indicated to be epimers at the carbon bearing both carbomethoxy and hydrogen substituents because the 91–92° compound was converted to a 60:40 mixture of the two upon heating in *tert*-butyl alcohol containing *tert*-butoxide. The nmr spectra strongly suggested the higher melting isomer was the endo one, because the endo hydrogen at the carbon bearing iodine (C_5) appeared 0.3 ppm downfield from that hydrogen in the lower melting isomer. This would be expected for the C_3 endo ester, because of the proximity of the ester group to H_5. We therefore assigned the adducts as **2a** (114–116°) and **2b** (91–92°) on the basis of spectral data. The stereochemical assignment was verified by chemical reactions. The major product **2a** gave immediate precipitation of silver iodide upon treatment with silver perchlorate in methylene chloride, and a 71% yield of a strained lactone, assigned structure **4** on the basis of spectral data, was isolated. In contrast **2b** reacted noticeably more slowly with silver perchlorate and produced no **4**. Instead, the major product has been assigned structure **5** because of the general similarity of the nmr spectrum to that of **2a** and **2b**, except for the unusually deshielded H_3 hydrogen, which appears 0.4 ppm below that of any of our C_5 exo ad-



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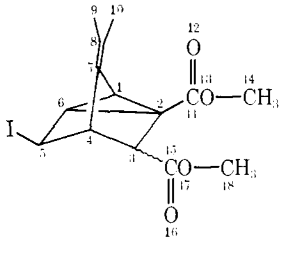
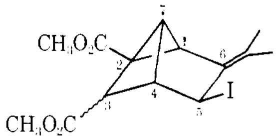
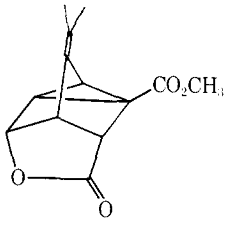


2a, C_3 ester endo
b, C_3 ester exo



3a, C_3 ester endo
b, C_3 ester exo



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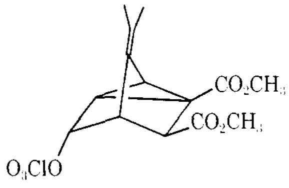

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[1] See S. J. Cristol and B. B. Jarvis, *J. Amer. Chem. Soc.*, **89**, 5885 (1967), and references therein.

[2] (a) E. W. Yankee and D. J. Cram, *ibid.*, **92**, 6328, 6329, 6331 (1972); (b) E. W. Yankee, F. D. Badea, N. E. Howe, and D. J. Cram, *ibid.*, **95**, 4210 (1973); (c) E. W. Yankee, B. Spencer, N. E. Howe, and D. J. Cram, *ibid.*, **95**, 4220 (1973); (d) N. E. Howe, E. W. Yankee, and D. J. Cram, *ibid.*, **95**, 4230 (1973); (e) A. B. Chmurny and D. J. Cram, *ibid.*, **95**, 4237 (1973); (f) S. Danishefsky and G. Rovnyak, *J. Chem. Soc., Chem. Commun.*, 820, 821 (1972).

[3] J. Meinwald and J. K. Crandall, *J. Amer. Chem. Soc.*, **88**, 1292 (1966).

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

ducts.[5] We did not attempt further characterization of this cyclopropylcarbinyl perchlorate, which is potentially a dangerous explosive.

A referee pointed out that structure **3** would have similar spectral properties to those of **2**, and that cleavage of vinylcyclopropanes at the carbon bearing vinyl has ample precedent.[2b] Although we believe **3** can be ruled out adequately on the basis of the nmr spectra of **2a**, **2b**, and **4**, the expected differences are rather small.[6] Since structure **2a** is of central importance not only to this work but also that of the accompanying paper,[4b] its structure was determined by X-ray diffraction.

The X-ray results unambiguously substantiate (*vide infra*) the structure to be that depicted in **2a** in accord with the spectroscopic and chemical observations. The crystal structure of **2a** consists of discrete molecules of **2a** separated by normal van der Waals distances in accord with the premise that the molecular parameters are primarily a consequence of intramolecular interactions. All bond distances and angles in the molecule (*cf.* Tables I and II) appear within the expected tolerances. The parameters for the nortricyclene moiety show no significant deviations from those obtained in recent microwave[7] and electron diffraction[8] studies of 4-chloronortricyclene. That the substituents on the nortricyclene do not markedly alter its approximate threefold geometry is evidenced by the small variations from 120° of the three torsional angles defined by the following three-atom planes: a, C_4–C_7–C_1; b, C_4–C_3–C_2; and c, C_4–C_5–C_6; with $\angle ab = 118.1\ (7)°$, $\angle ac = 123.9\ (8)°$, $\angle bc = 119.0\ (7)°$.

Table I. Intramolecular Bond Lengths (Å) for **2a**

C_1–C_2	1.540 (9)	C_8–C_9	1.533 (11)
C_2–C_3	1.525 (10)	C_8–C_{10}	1.510 (10)
C_3–C_4	1.568 (10)	C_2–C_{11}	1.453 (10)
C_4–C_5	1.535 (10)	C_{11}–O_{12}	1.219 (8)
C_1–C_6	1.515 (9)	C_{11}–O_{13}	1.329 (9)
C_2–C_6	1.501 (10)	O_{13}–C_{14}	1.456 (10)
C_5–C_6	1.496 (10)	C_3–C_{15}	1.487 (10)
C_1–C_7	1.488 (10)	C_{15}–O_{16}	1.205 (8)
C_4–C_7	1.507 (9)	C_{15}–O_{17}	1.322 (8)
C_7–C_8	1.313 (10)	O_{17}–C_{18}	1.462 (10)
		C_5–I	2.172 (8)

Table II. Bond Angles (deg) for **2a**

C_2–C_1–C_6	58.8 (5)	C_1–C_6–C_2	61.4 (4)
C_2–C_1–C_7	104.6 (5)	C_1–C_6–C_5	106.3 (6)
C_6–C_1–C_7	106.6 (6)	C_2–C_6–C_5	105.7 (6)
C_1–C_2–C_3	106.6 (5)	C_1–C_7–C_4	100.5 (6)
C_1–C_2–C_6	59.7 (5)	C_1–C_7–C_8	129.3 (6)
C_1–C_2–C_{11}	116.0 (6)	C_4–C_7–C_8	130.2 (6)
C_3–C_2–C_6	107.5 (6)	C_7–C_8–C_9	124.0 (7)
C_3–C_2–C_{11}	125.7 (7)	C_7–C_8–C_{10}	123.8 (7)
C_6–C_2–C_{11}	122.3 (6)	C_9–C_8–C_{10}	112.2 (7)
C_2–C_3–C_4	96.7 (5)	C_2–C_{11}–O_{12}	123.9 (7)
C_2–C_3–C_{15}	117.8 (6)	C_2–C_{11}–O_{13}	112.7 (7)
C_4–C_3–C_{15}	112.8 (5)	O_{12}–C_{11}–O_{13}	123.4 (7)
C_3–C_4–C_5	99.2 (5)	C_{11}–O_{13}–C_{14}	117.9 (6)
C_3–C_4–C_7	99.8 (5)	C_3–C_{15}–O_{16}	123.1 (7)
C_5–C_4–C_7	101.6 (5)	C_3–C_{15}–O_{17}	114.7 (6)
C_4–C_5–C_6	99.2 (5)	O_{16}–C_{15}–O_{17}	122.1 (7)
C_4–C_5–I	111.0 (5)	C_{15}–O_{17}–C_{18}	117.6 (6)
C_6–C_5–I	111.9 (5)		

The six atoms comprising the ethylene linkage are essentially planar with no atom lying more than 0.01 Å out of the mean plane. The distortion of the C_9–C_8–C_{10} angle to 112.2 (7)°, a value significantly less than 120°, is also found[9] in other exocyclic dimethylethylenes. The five atoms of both carbomethoxy groups are also planar, as expected, and are rotated with respect to the nortricyclene cage to give 176.9 (7)° between the two planes defined by C_2–C_3–C_{15} and C_3–C_{15}–O_{16} and 168.6 (6)° between the two planes specified by C_3–C_2–C_{11} and C_2–C_{11}–O_{12}.

Returning to the formation of **2a** and **2b** from **1**, we suspected that they were the result of nucleophilic attack of iodide, followed by proton abstraction. Although reaction of **1** with hydroiodic acid proceeded more slowly than with sodium iodide, the same products were formed.

Methanolic solutions of HI required refluxing for addition to occur, and gave **2a** and **2b** in about 80:20 ratio. For the sodium iodide reaction, addition was still rapid at room temperature with an equivalent of triethylamine (43:57 **2a**:**2b**) or sodium methoxide (55:45 ratio). Use of acetonitrile-d_3 as solvent gave **2a**-*3-d* and **2b**-*3-d*, showing the expected changes in the nmr spectrum. There is clearly a good chance that C_3–C_5 bond cleavage of protonated **1** occurs prior to attack of the nucleophile in the reaction of **1** with HI. Since the same products were formed in the reaction of **1** with sodium iodide, reasonable doubt exists as to whether C_3–C_5 bond cleavage prior to iodide attack occurs under these conditions as well.

We therefore turned to studies on the 7-oxaquadracyclene derivative **6**. Cleavage of the 1,2 bond of **6** is known to occur upon treatment with electrophiles, since both cuprous chloride[10] and sulfuric acid in methylene chloride[11] gave **7** as the rearrangement product. This product was interpreted as being formed by rearrangement of carbonium ion **8**. We found that treatment of **6** with sulfuric acid in methanol gave a 74% yield of a mixture of two compounds with very similar chemical shifts. Although partial separation was apparently achieved by tlc on silica gel, recrystallization of both zones gave the same compound, which proved to be *trans,trans,trans*-1,2-diacetyl-3,4-dicarbomethoxycyclobutane (**9**), previously prepared by Griffin and Hager,[12] using a different route. We suspect that the compound which was converted to **9** during work-up has *cis*-acetyl groups, since the cis isomer should be initially formed upon opening of the hemiketal formed by reaction of **8** with adventitious water (see **10**). Although products in which the C_3–C_5 bond of **6** remained intact were only isolated from the sul-

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[5] (a) S. F. Nelsen, P. J. Hintz, and J. P. Gillespie, *Tetrahedron Lett.*, 2361 (1971); (b) S. F. Nelsen, P. J. Hintz, J. P. Gillespie, and E. D. Seppanen, *J. Amer. Chem. Soc.*, **95**, 8380 (1973).

[6] Arguments include the difference in the *C*-methyl splitting for **2b** (large) compared to **2a** (small) being unexplainable on the basis of structure **3**, and the fact that the long-range coupling pattern observed for **4** is not very consistent with that required for the lactone from **3a** ($J_{6,7}$ would have to be 1.0 Hz, and $J_{4,7}$ = 0.8 Hz, neither of which is particularly reasonable).

[7] *Cf.* V. W. Laurie and W. M. Stigliani, *J. Amer. Chem. Soc.*, **95**, 4163 (1973), and references cited therein.

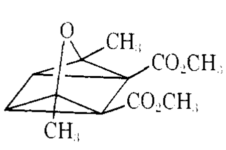
[8] J. F. Chiang, C. F. Wilcox, Jr., and S. H. Bauer, *Tetrahedron*, **25**, 369 (1969).

[9] *Cf.* H. Dietrich, *Acta Crystallogr., Sect. B*, **26**, 44 (1970).

[10] H. Prinzbach and P. Vogel, *Helv. Chim. Acta*, **52**, 397 (1969).

[11] A. W. McCulloch, B. Stanovnik, D. G. Smith, and A. G. Innes, *Can. J. Chem.*, **49**, 241 (1967).

[12] G. W. Griffin and R. B. Hager, *Rev. Chim., Acad. Repub. Pop. Roum.*, **7**, 901 (1962). We thank Professor Griffin for a reprint.



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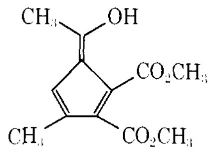

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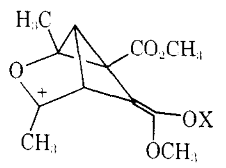

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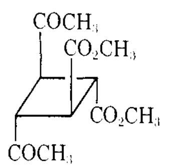

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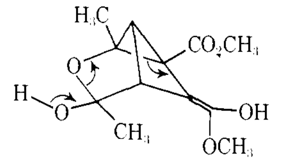

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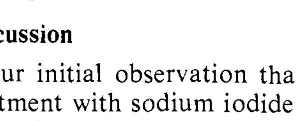
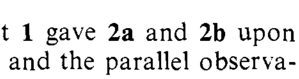
furic acid–methanol experiment, we believe it is clear that in the absence of strong nucleophiles, electrophiles cause C_3–C_4 (C_1–C_2) cleavage of **6**, and that the products are derived from reactions of carbonium ion **8**. Since **8** as compared to the carbonium ion derived by C_3–C_5 cleavage is favored by stabilization by both an α methyl and an α oxygen, this is certainly not surprising. Furthermore, the C_3–C_4 (C_1–C_2) bond is that broken in thermal decomposition of **6**,[10] in contrast to **1** where the C_2–C_6, C_3–C_5 bonds break upon heating.

Sodium iodide in acetonitrile rapidly cleaves **6**, giving a 59% yield of the C_3–C_5 cleaved products **11a** and **11b**, in about a 4:1 ratio. The major isomer was assigned as **11a** on the basis of the chemical shift of **5**, and by analogy with **2a** and **2b**. Since attack at the C_1–C_2 bond is sterically hindered by the C_1 methyl group, a nucleophile would be expected to attack at C_5 if prior cleavage had not occurred.



11a



11b

Discussion

Our initial observation that **1** gave **2a** and **2b** upon treatment with sodium iodide and the parallel observations of Koser and Yu[4] on 2-substituted quadricyclenes seemed to imply nucleophile cleavage of the cyclopropane ring by iodide ion, but the fact that the same bond is cleaved both thermally and by electrophiles suggests another likely possibility. Yankee and Cram[2a] showed elegantly that in cyclopropane derivatives with both ester and cyano at C_1 and phenyl at C_2 prior reversible C_1–C_2 cleavage to zwitterions (or extremely polarized singlet diradicals—the distinction is not entirely clear) can occur preceding "nucleophilic attack." The increased strain of the quadricyclane system[13] might well allow formation of such zwitterions for **1**, as the ester could stabilize the C_3 carbanion, and the C_5 cation would be cyclopropylcarbinyl stabilized.

By turning to **6**, we have a system in which both electrophiles and thermolysis cause C_3–C_4 cleavage, and so if cleavage were occurring prior to nucleophilic attack, products derived from addition of the nucleophile to C_4 should result. Instead, we observed formation of the C_3, C_5 HI adducts, as would only be expected by nucleophilic attack on **6** before cyclopropane bond cleavage. Prior complexation of **6** with the iodide counterion (sodium in our case) presumably occurs, but this does not give cyclopropane cleavage before interaction with the iodide.

The objection has been raised that initial C_3–C_4 bond cleavage to give **8** (X = ⊖) could be occurring, but that C_5 to C_4 shift of the C_3–C_5 bond occurs prior to capture by iodide, giving **2a** and **2b** as the final products. Such rearrangement did not occur with water as nucleophile, and does not appear likely to us because of the far greater expected stability of the carbonium ion at C_5 over that at C_4. It would also be difficult to explain why nucleophilic solvents such as water do not react with **8** (X = ⊖) if it is being formed at room temperature, as is required by this mechanism.

Experimental Section

Spectral instruments: nmr, Varian A60, HA100, XL100, or Jeolco MH100; ir, Beckman IR.8; mass spectra, AEI MS 902. Analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich.

5-*exo*-Iodo-2,3-*endo*-biscarbomethoxy-7-isopropylidenenortricyclene (2a) and Its 3-*exo* Epimer 2b. A mixture of 250 mg of **1**[14] (1 mmol) and 250 mg of sodium iodide (1.67 mmol) was stirred in 3 ml of acetonitrile for 30 min, and the solvent was removed *in vacuo*. The residue was dissolved in ether, washed with water, dried with sodium sulfate, and concentrated, giving a 60:40 mixture of **2a**:**2b** (by nmr integration of the H_5 peaks, which are separated from each other and all other absorptions). The isomers were separated by tlc on Brinkmann silica gel Pf-254 (chloroform as eluent), giving pure **2a** (mp 114–116°) and **2b** (mp 91–92°) after crystallization from hexane. Spectral data for **2a**: ir 5.79 μ (br); nmr ($CDCl_3$) δ 2.63 (dd, 5, 2, H_1), 2.83 (d, 2, H_3),[15] 3.02 (pent, 2, H_4), 4.38 (t, 2, H_5), 2.84 (dt, 5, 2, H_6), 1.76 and 1.80 (CMe, 2 s), 3.75 and 3.79 (OMe, 2 s). *Anal.* Calcd for $C_{14}H_{17}IO_4$: C, 44.70; H, 4.56; I, 33.74. Found: C, 44.79; H, 4.53; I, 33.86. For **2b**: ir 5.79 μ (br); nmr ($CDCl_3$) δ 2.84 (dd, 5, 2, H_1), 2.98 (d, 2, H_3),[15] 3.09 (pent, 2, H_4), 4.38 (t, 2, H_5), 2.59 (dt, 5, 2, H_6), 1.68 and 1.82 (CMe, 2 s), 3.69 and 3.75 (OMe, 2 s). *Anal.* Found: C, 44.63; H, 4.50; I, 33.73. The nmr multiplicities quoted require that J_{14} = J_{34} = J_{45} = J_{46} = J_{56} = 2 Hz, and they all fall in the range *ca.* 1.5–2.2 Hz, giving the multiplicities indicated.

5-*endo*-Hydroxy-2-carbomethoxy-7-isopropylidenenortricyclene-3-*endo*-carboxylic Acid Lactone (4). Addition of 200 mg of silver perchlorate to a mixture of 350 mg of **2a**, 5 ml of methylene chloride, and 100 mg of sodium carbonate resulted in immediate precipitation of a yellow solid (AgI). After 30 min the mixture was filtered, concentrated, and separated by tlc, giving 60 mg of recovered **2a** (17%) and 120 mg of **4** (58%, 71% conversion), which was recrystallized from hexane, mp 107–108°. Spectral data: ir 5.56 (strained lactone) and 5.78 μ (ester); nmr ($CDCl_3$) δ 4.71 (ddd, center lines overlap, J_{45} = 2.6 Hz, J_{56} = 1.9 Hz, J_{35} = 0.8 Hz, H_5), 3.71 (s, OCH_3), (3.12 m, H_4), 3.02 (dd, J_{34} = 2.4 Hz, J_{35} = 0.8 Hz), 2.94 (dd, J_{16} = 5.2 Hz, J_{14} = 1.6 Hz, H_1), 2.62 (ddd, J_{16} = 5.2 Hz, J_{56} = 1.9 Hz, J_{46} = 0.8 Hz, H_6), assignment consistent which changes seen upon decoupling H_5 and H_6 individually, 1.76 and 1.69 (2 s, CCH_3); mass spectrum (70 eV) *m/e* (% of base) 234 (100). *Anal.* Calcd for $C_{13}H_{14}O_4$: C, 66.65; H, 6.02. Found: C, 66.43; H, 6.10.

Reaction of 2b with Silver Perchlorate. Addition of 150 mg of silver perchlorate to a mixture of 220 mg of **2b**, 5 ml of methylene

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

(14) H. Prinzbach, *Pure Appl. Chem.*, **16**, 17 (1968). It has not been pointed out that **6** is a powerful skin irritant, and should be handled only with rubber gloves and considerable care.

(15) By running the reaction in acetonitrile-d_3 **2a** and **2b** were isolated which lacked the peaks assigned to H_3, and also showed the H_1 signal as an approximate quartet.

chloride, and 100 mg of sodium carbonate gave gradual precipitation of a yellow solid (AgI). After the mixture was stirred for 4 hr, filtered, and concentrated, the residue was separated by tlc. The fastest moving zone gave only 20 mg of material, but comparison with the nmr of the crude material indicated that this was the major product. Since the nmr indicated the perchlorate **5** had been formed, hydrolysis as the plate was expected: nmr ($CDCl_3$) δ 4.99 (t, 2, H_5), 3.23 (pent, 2, H_4), 3.39 (d, 2, H_3), 2.95 (dd, 5, 2, H_1), 2.43 (dt, 5, 2, H_6), 3.69 and 3.78 (2 s, OMe), 1.67 and 1.80 (2 s, CMe). No **4** was observed in the nmr of the crude product.

***trans,trans,trans*-1,2-Diacetyl-3,4-biscarbomethoxycyclobutane (9).** A solution of 720 mg of **6**[10] in 34 ml of methanol was treated with 8 drops of concentrated sulfuric acid, stirred at room temperature for 18 hr, concentrated, and separated by tlc, giving 520 g (74%) of crude **9**, which was recrystallized several times from benzene–hexane. Above the zone containing **9** was a zone containing 50 mg of material which initially showed nmr peaks at δ 3.73, 3.33 (br s), and 2.15, but upon recrystallization gave indistinguishable melting point and ir from that of **9**: mp 84–85.5° (lit. mp 81–82°); ir (cm^{-1}) 1736, 1715, 1704 cm^{-1} (lit. 1730, 1720, 1710 cm^{-1}); nmr ($CDCl_3$) δ 3.76 (s, 6 H, OMe), 3.47 (A_2B_2 pattern, 4.3 Hz sepn. of major doublet at 100 MHz, 4 H), 3.22 (s, 6 H, CMe).

5-*exo*-Iodo-2,3-*endo*-dicarbomethoxy-7-oxanortricyclene (11a) and Its 3-*exo* Epimer 11b. A solution of 720 mg of **6** in 20 ml of acetonitrile was treated with 1.5 g of sodium iodide and stirred at room temperature for 1.5 hr. After the solution was concentrated and the residue was extracted with ether, washed with water, dried with sodium sulfate, and concentrated, 680 mg of crude product which was seen to be an 80:20 mixture of **11a**:**11b** by nmr integration was obtained (59%). Separation by tlc gave 510 mg of **11a** (44%) and 150 mg of **11b** (13%); 72:23 ratio by isolated weight. After crystallization from pentane, **11a** had mp 90–91°, **11b** had mp 66–68°. Spectral data for **11a**: nmr ($CDCl_3$) δ 4.33 (br s, H_5), 2.59 and 2.81 (2 br s, H_3 and H_6), 1.37 and 1.64 (2 s, CMe), 3.73 and 3.70 (2 s, OMe). *Anal.* Calcd for $C_{12}H_{15}IO_5$: C, 39.36; H, 4.13; I, 34.66. Found: C, 39.40; H, 4.14; I, 34.73. For **11b**: nmr ($CDCl_3$) δ 4.02 (br s, H_5), 2.47 and 2.81 (2 br s, H_3 and H_6), 1.32 and 1.76 (2 s, CMe), 3.71 (s, 2 OMe). *Anal.* Found: C, 39.30; H, 4.16; I, 34.80.

X-Ray Diffraction Structure Determination for 2a. A needle-shaped crystal of **2a** with dimensions 0.3 × 0.15 × 0.35 mm was obtained from the slow evaporation of a pentane solution of the compound. The sample was glued to a glass fiber approximately parallel to the needle axis of the crystal and carefully centered on a Syntex $P\bar{1}$ auto diffractomer equipped with graphite monochromated Mo Kα radiation. The preliminary Syntex routines indicated the compound was orthorhombic (Laue point group D_{2h}-*mmm*) with lattice parameters a = 14.459 (3) Å, b = 12.361 (2) Å, c = 16.925 (8) Å; V = 3025 (2) Å^3. The experimental density of 1.63 g cm^{-3} agrees with the calculated value of 1.65 g cm^{-3} for 8 molecules per unit cell. Data were collected in the usual θ-2θ scan mode from $3 \leq 2\theta \leq 40°$ with the take-off angle of the tube set at 4.0°. Two standard reflections monitored every 50 reflections indicated no significant drift in intensity. The data were reduced in the usual manner[16] with $\sigma(F)$ including a term of $0.003(I)^2$ to avoid overweighting the strong reflections in least squares. Of the 1636 total independent measurements, the 1087 with $I > 2\sigma(I)$ were used in the structural analysis.[17] No corrections for absorption effects were made due to the relatively small value of μ (*viz.*, 21.5 cm^{-1} for Mo Kα radiation) for which the maximum variation in $|F_o|$'s based upon the crystal dimensions and its orientation was minimal.

The structure was solved by the heavy atom method. The choice of the centrosymmetric space group *Pbca* ($D_{2h}{}^{15}$, No. 61),[18] first indicated by an examination of the weak and zero-intensity reflections, was confirmed by the successful interpretation of the seven most intense Patterson peaks as iodine Harker vectors. A Fourier map phased on the initial iodine coordinates (for which R_1 = 28.4%)[19] clearly revealed the positions of the remaining nonhydrogen atoms. After several cycles of isotropic least-squares refinement R_1 and R_2[19] were reduced to 10.9 and 13.6%, respectively.[20] At this stage a difference Fourier map yielded coordinates for all hydrogen atoms except for two on the methyl C_{14} atom. This map also indicated strong thermal anisotropy about the iodine, the ester oxygen, and several of the carbon atoms. Hence, several additional cycles which included coordinates for all hydrogen atoms (with idealized values for the C_{14} methyl hydrogens) as fixed atom contributions with B_{iso} = 6.0 Å^2, with anisotropic thermal parameters for all nonhydrogen atoms, and with corrections for the anomalous dispersion of iodine ($\Delta f' = -0.5$; $\Delta f'' = 2.4$) reduced R_1 and R_2 at convergence to 3.4 and 4.2%, respectively. Final atomic coordinates and temperature factors as well as a listing of the observed and calculated structure factor amplitudes are available.[21]

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number JACS-73-8385.

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(16) *Cf.* V. A. Uchtman and L. F. Dahl, *J. Amer. Chem. Soc.*, **91**, 3756 (1969).

(17) Computer programs used in the analysis included the following: FOBS, SORTMERGE for data reduction, and MAP for all Fourier calculations, written by the author (J. C. C.); ORFLS and ORFFE, the Busing-Martin-Levy least-squares and error analyses programs.

(18) "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1952, p 150.

(19) $R_1 = [\Sigma||F_o| - |F_c||/\Sigma|F_o|] \times 100$ and $R_2 = [\Sigma w_i||F_o| - |F_c||^2/\Sigma w_i|F_o|^2]^{1/2} \times 100$. All least-squares refinements were based on the minimization of $\Sigma w_i||F_o| - |F_c||^2$ with the individual weights $w_i = 1/\sigma(F_o)^2$.

(20) Atomic scattering factors used for all non-hydrogen atoms are from H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964); those for the hydrogen atoms are from R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(21) See paragraph at end of paper regarding supplementary material.