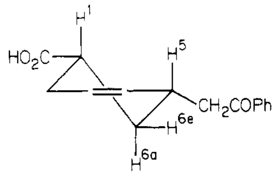
in 78% yield: IR (neat) 1710 (s), 1450 (m), 1130 (m), 830 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.0–2.6 (m with peaks at 1.60, 1.67, and 2.00 ppm, 24 H), 4.9–5.25 (m, 2 H).

Palladium-Catalyzed Allylation of Lithium Enolates in the Presence of Triethylborane (Table II, Entries 12 and 13). These reactions were carried out in a manner similar to those described above, the use of 2–3 equiv of triethylborane being the only difference. The yields of **7** obtained by the reaction of lithium cyclohexenolate with geranyl acetate catalyzed by 5 mol % of $Pd(PPh_3)_4$ and run in the presence of 1, 2, and 3 equiv of BEt_3 were 55%, 78%, and 78%, respectively.

The yield of **3** obtained by this procedure was 62%, and the regioselectivity determined by ^{13}C NMR was 91%.

Palladium-Catalyzed Allylation of Potassium Enoxyborates. The Pd-catalyzed allylation of potassium enoxyborates was carried out as described previously.[2a] Although BEt_3 is, in principle, recoverable by distillation, it was destroyed by oxidation with 3 M NaOH and 30% H_2O_2. This oxidation makes the subsequent workup free from any complication due to the presence of BEt_3.

(*Z*)-5-(2-Oxo-2-phenylethyl)-3-cyclohexenecarboxylic Acid. The potassium enoxytriethylborate of acetophenone was prepared from 2.40 g (20 mmol) of acetophenone, KH (0.8 g, 20 mmol), 20 mL of THF, and 22 mL of 1 M solution of BEt_3 in THF, as described above. Its reaction with 7-oxabicyclo[3.2.1]oct-2-en-6-one (2.48 g, 20 mmol) in the presence of $Pd(PPh_3)_4$ (1.16 g, 1 mmol) was carried out overnight at room temperature according to the procedure reported previously.[2a] After oxidation with 3 M NaOH and 30% H_2O_2, the mixture was acidified to pH 3 by adding HCl and was extracted with ether. The organic extract was washed with saturated aqueous $NaHCO_3$, dried over $MgSO_4$, and evaporated to give an oil, which solidified later. The solid product was recrystallized from methanol–water to give the title compound: 4.05 g (83% yield); mp 103–105 °C; IR (Nujol) 1705, 1685 cm^{-1}; ^{1}H NMR (470 MHz, $CDCl_3$, Me_4Si) δ 1.15–1.25 (m, H-6a, 1 H), 2.0–2.25 (m, H-2a, H-2e, and H-6e, 3 H), 2.5–2.6 (m, H-1, 1 H), 2.75–2.95 (m, H-5, H-α, 3 H), 5.5–5.9 (H-3 and H-4, 2 H), 7.3–8.1 (m, 5 H), 10.4 (br s, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 27.52, 31.86, 32.94, 39.49, 44.50, 125.60, 128.06, 128.62, 130.66, 133.66 137.12, 181.75 198.90. The ^{13}C NMR spectrum indicates that the compound is stereochemically ≥95% pure. Selectively ^{1}H-decoupled ^{1}H NMR spectra (470 MHz) with $CDCl_3$ or benzene-d_6 as a solvent not only permit the peak assignments shown above but also provide the following coupling information indicating the cis stereochemistry for the compound.



$$J_{H^1-H^{6a}} \simeq J_{H^5-H^{6a}} = 10.5 \text{ Hz}$$

The corresponding reaction of the zinc enolate **2f** gave a product which yielded ^{1}H and ^{13}C NMR spectra that are virtually the same as those described above. Thus this product must also be the cis isomer.

Asymmetric Reaction of the Zinc Enolate of 3-Pentanone with 2,3-Dichloropropene in the Presence of Chiral Palladium–Phosphine Complexes. The zinc enolate of 3-pentanone was generated, and it was reacted with 2,3-dichloropropane in the presence of a catalyst generated in situ by treating Cl_2Pd-[(+)-DIOP] (2 mol %) with DIBAH (4 mol %), following the representative procedures described above. 6-Chloro-4-methyl-6-hepten-3-one (**8**) was obtained in 56% yield (62% by GLC): IR (neat, 1715 (s), 1630 (s), 1455 (s), 1375 (s), 1150 (s), 970 (m), 880 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.9–1.2 [m consisting of a triplet at 1.04 (J = 7 Hz) and a doublet at 1.08 (J = 7 Hz, 6 H)], 2.1–3.1 (m, 5 H), 5.1–5.2 (m, 2 H).

The product obtained above was further examined by ^{1}H NMR by using tris[3-[(heptafluoropropyl)hydroxymethylene]-*d*-camphorato]europium [$Eu(hfc)_3$] as a chiral shift reagent. To a 0.2 M solution of the ketone product in benzene were added 10 mol % portions of solid $Eu(hfc)_3$. Integrations of the diastereomeric 1-Me and 4-Me proton signals, shifted down to the 3–4-ppm range in the presence of ca. 50 mol % of $Eu(hfc)_3$, indicate that the product is 34% ee.

(4*E*)-2,2,5,9-Tetramethyl-4,8-decadien-1-al (10). The preparation of the potassium triethylenoxyborate of 2-methylpropanal (**9**) and its reaction with neryl acetate in the presence of 5 mol % of $Pd(PPh_3)_4$ were carried out according to the representative procedures described above. The yield of **10** by isolation was 60%: IR (neat) 2700 (m), 1720 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.00 (s, 6 H), 1.60 (s, 3 H), 1.67 (s, 6 H), 1.9–2.3 (m, 6 H), 4.9–5.2 (m, 2 H), 9.45 (s, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 17.12, 20.75, 23.07, 25.21, 26.06, 31.54, 34.85, 45.72, 60.54, 118.96, 123.72, 131.04, 137.76, 205.19. The ^{13}C NMR spectrum indicates that the product is ca. 95% pure and that the byproduct probably is the stereoisomer. The ^{1}H NMR indicates the *Z* stereochemistry of **10**.

Acknowledgment. We thank the National Science Foundation and the National Institutes of Health for support of this work. Dr. J. C. Fiaud has kindly informed us of some unpublished results related to those reported here. The high-field NMR study was supported by the Purdue University Biochemical Magnetic Resonance Laboratory (Grant NIH RR 01077). We also thank Professor H. C. Brown for allowing us to use their ^{11}B NMR facilities. Dr. R. G. Naik, Dr. E. John, and S. Chatterjee kindly provided technical assistance in obtaining spectra.

Registry No. **2c**, 82167-45-1; **2b**, 86901-70-4; **2e**, 43131-80-2; **2f**, 86901-71-5; **2g**, 86901-72-6; **2h**, 86901-65-7; **2i**, 86901-66-8; **2j**, 19980-33-7; **2k**, 41294-51-3; **2l**, 86901-67-9; **3**, 86941-23-3; **4**, 17392-07-3; **5**, 72009-04-2; **6**, 78461-63-9; **7**, 74016-20-9; **8**, 86901-75-9; **9**, 86901-69-1; **10**, 58558-37-5; acetophenone potassium enoxytriethylborate, 86901-68-0; lithium cyclohexenolate, 56528-89-3; 7-oxabicyclo[3.2.1]oct-2-en-6-one, 4720-83-6; (*Z*)-5-(2-oxo-2-phenylethyl)-3-cyclohexenecarboxylic acid, 86901-73-7; 3-pentanone zinc enolate, 86901-74-8; BEt_3, 97-94-9; $Pd(PPh_3)_4$, 14221-01-3; neryl acetate, 141-12-8; 2,3-dichloropropene, 78-88-6; isoprenyl chloride, 503-60-6; geranyl acetate, 105-87-3; acetophenone, 98-86-2.

Photoadducts of 1-Cyclohexene-1,2-dicarboxylic Anhydride

T. S. Nimry and E. K. Fields*

Research and Development Department, Amoco Chemicals Corporation, Naperville, Illinois 60566

Seymour Meyerson

Research Department, Standard Oil Company (Indiana), Naperville, Illinois 60566

M. E. Wright and H. K. Hall, Jr.

Department of Chemistry, University of Arizona, Tucson, Arizona 85721

Received February 14, 1983

1-Cyclohexene-1,2-dicarboxylic anhydride (I) reacts with butadiene, isoprene, and dimethylbutadiene only under vigorous conditions (12 hours at 175 °C) to give 50–60% yields of thermal [2 + 4] adducts.[1,2] It does not react even at 175 °C with furan, chloroprene, or cyclopentadiene.[2]

We have found that, in contrast to its reluctance to undergo thermal cycloaddition, I reacts readily with a variety of olefins under irradiation with weak ultraviolet light at 25–80 °C to give [2 + 2] cycloadducts.[3] The lower

---

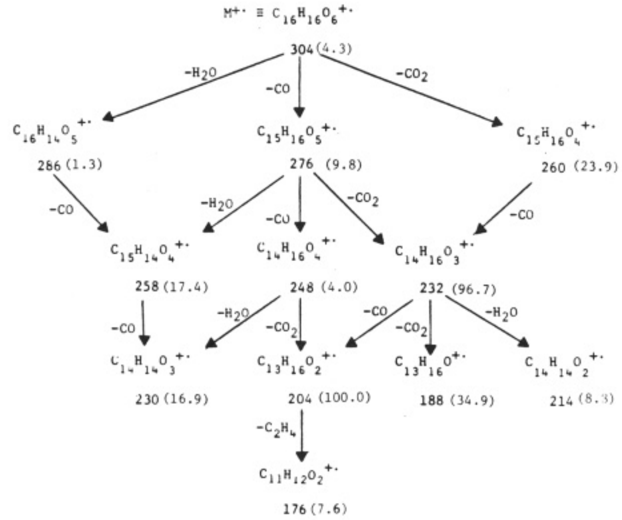
[1] Alder, K.; Backendorf, K. H. *Ber.* **1938**, *71B*, 2199. Brigl, P.; Herrmann, R. *Ibid.* **1938**, *71B*, 2280.

[2] Buckles, R. E.; Deets, M. L. *J. Org. Chem.* **1958**, *23*, 485.

Table I. Mass Spectral Data for V

mass scanned	precursor mass found	mass scanned	precursor mass found
258	276	214	232
	286	204	232
	304		248
248	276		276
	304	188	232
232	260		260
	276	176	204
	304		
230	248		
	258		
	276		
	304		

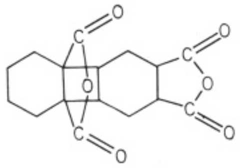
Scheme I[a]



[a] Relative intensities in the 70-eV spectrum are given in parentheses.

olefins employed, 1-hexene and 1-octene, gave adducts that were oils at room temperature. The adduct from 1-octadecene was a solid.

4-Cyclohexene-1,2-dicarboxylic anhydride (IV), the Diels–Alder adduct from butadiene and maleic anhydride, is isomerized to I by 2% P_2O_5 at 200 °C.[4] The adduct of IV and I, formed in 60% yield, is a white crystalline solid, tricyclo[6.4.0.0^{2,7}]dodecane-1,8,4,5-tetracarboxylic dianhydride (V), whose structure was investigated by its



V

high-resolution mass spectrum. V gave the molecular ion at mass 304, with especially intense peaks at mass 260 and 232. Metastable scanning of selected peaks gave the results in Table I.

A partial decomposition scheme is shown in Scheme I and is based on observed metastable peaks, with elemental compositions derived from precise masses measured at high resolution (relative intensities in the 70-eV spectrum in parentheses). Only the three primary steps shown, leading from mass 304 to 286, 276, and 260, are not backed up by metastable peaks, which would seem superfluous.

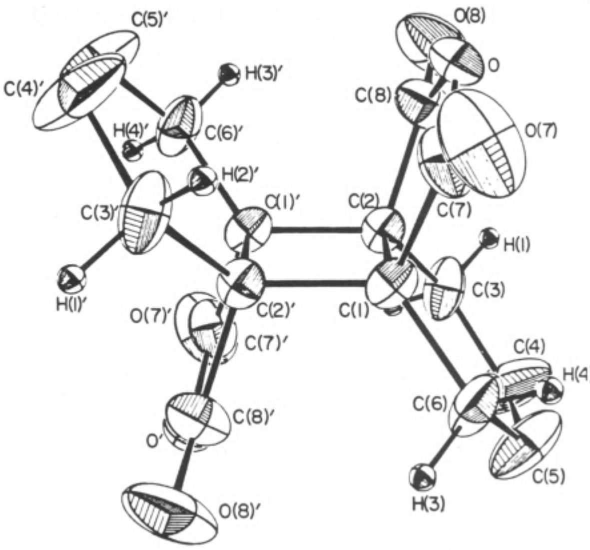
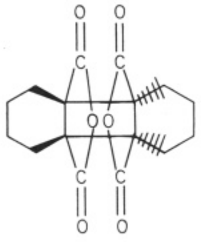


Figure 1. ORTEP[8] drawing of VI with nonhydrogen atoms represented by thermal vibration ellipsoids drawn to encompass 30% of the electron density. Hydrogen atoms are represented by arbitrarily small spheres for clarity. Primed atoms are related to nonprimed atoms by the crystallographic inversion center at $x = {}^1/_2$, $y = 0$, and $z = {}^1/_2$.

In the preparation and purification of I photoadducts, usually in benzene or toluene solution, we found no evidence of complications that might be caused by dimerization of I. However, this apparent lack of dimerization proved to be solvent-related. In acetone or chloroform, I gave the photodimer, mp 276–278 °C. By analogy with the structures determined for dimers of methyl-[5] and dimethylmaleic[6,7] anhydrides, we surmised that the configuration of VI is probably trans.



VI

To determine unambiguously the geometry of the anhydride groups on the cyclobutane ring we undertook an X-ray diffraction study of VI.[8] An ORTEP[9] perspective drawing of VI and the labeling scheme utilized are presented in Figure 1. Compound VI crystallizes with half a molecule in the asymmetric unit, thus imposing a crystallographic inversion center in the molecule. The C(4) and C(5) carbon atoms are found to be disordered in the structure, accounting for the noticeably short C(4)–C(5) bond (1.364 Å). This type of disordering between two conformations with the apparent result of a short C–C bond distance has been observed previously.[10] Further-

---

(3) Askani, R. *Chem. Ber.* **1965**, *98*, 2322. This author formed an adduct of 2-butyne with I using a high-pressure Hg lamp. Owsley, C. D.; Bloomfield, J. J. *J. Org. Chem.* **1971**, *36*, 3768. These authors added ethylene to I at −78 °C using a medium-pressure Hg lamp.

(4) Bailey, M. E.; Amstutz, E. D. *J. Am. Chem. Soc.* **1956**, *78*, 3828.

(5) Ziffer, H.; Williams, J. R. *J. Org. Chem.* **1968**, *33*, 920.

(6) Schenck, G. E.; Hertmann, W.; Mannsfeld, S. P.; Metzner, W.; Krauch, C. H. *Ber.* **1962**, *95*, 1642.

(7) Bryce-Smith, D.; Bullen, G. C.; Clark, N. H.; Connett, B. E.; Gilbert, A. *J. Chem. Soc. C* **1968**, 167.

(8) Complete details of the crystallographic study can be found in the supplementary material.

(9) Johnson, C. K. "ORTEP"; Oak Ridge National Laboratory: Oak Ridge, TN.

J. Org. Chem. **1983**, *48*, 4104-4106

more, both spectroscopic and analytical data prove that the C(4)–C(5) bond is single. The results of the X-ray study do not allow a rigorous comparison to related studies; however, the structure of VI clearly is shown to be the trans isomer with respect to the anhydride functionalities.

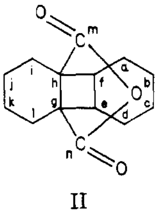
The thermal and chemical behavior of these new photoadducts is under investigation.

Experimental Section

General Methods. The mass spectrum of V was measured on a CEC Model No. 21-110B instrument at a resolution of 10000 by using 70-eV electrons and direct probe injection. Probe and source temperatures for the scan giving the intensity data shown in Scheme I were 264 and 250 °C. Metastable scans were made by focusing on a selected fragment ion, decoupling the electric-sector voltage from the ion-accelerating voltage, and scanning the latter to increasing values.[11,12]

X-ray quality crystals of VI are obtained by recrystallization from hot acetone. Single crystals of VI are monoclinic: space group $P2_1/a$ [an alternate setting of $P2_1/c$ (No. 14)]; $a = 11.958$ (4), $b = 8.128$ (3), $c = 7.656$ (3) Å; $\beta = 110.07$ (3)°; $Z = 2$. Three-dimentional X-ray diffraction data are collected for the 1849 independent reflections having $4° < 2\theta < 55°$ on a computer-controlled four-circle Syntex $P2_1$ autodiffractometer using graphite monochromated Mo K$\bar{\alpha}$ radiation and θ–2θ scanning technique. The entire structure of nonhydrogen atoms is solved by using the direct methods program MULTAN.[13] The hydrogen atoms are placed in their calculated positions by using idealized sp^3 geometry and a bond length of 0.95 Å for C–H. The resulting structural parameters for the nonhydrogen atoms in VI are refined to convergence [$R_1 = 0.120$ and $R_2 = 0.133$ for 889 reflections having $I > 3.0\sigma(I)$] by using counter-weighted full-matrix least-squares techniques with anisotropic thermal parameters for all nonhydrogen atoms and isotropic thermal parameters for the hydrogen atoms. The lattice constants with estimated standard deviations are as follows: $\alpha = 11.958$ (4) Å, $b = 8.128$ (3) Å, $c = 7.656$ (3) Å, $\sigma = 89.97$ (3)°, $\beta = 110.07$ (3)°, $\gamma = 90.01$ (3)°, $V = 698.9$ (4) Å^3, $Z = 2$, $\lambda = 0.71073$ Å. A complete listing of final atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and hydrogen atomic coordinates can be found in the supplementary material.

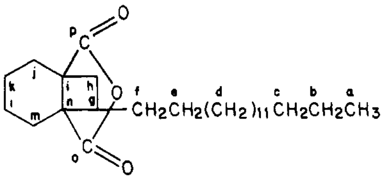
Formation of Adducts. A solution of 4.56 g (30 mmol) of I and 0.2 g of benzophenone in 20.3 mL (0.2 mol) of cyclohexene was irradiated in a Pyrex Erlenmeyer flask under reflux by a General Electric 275-W sunlamp for 40 h. Distillation of the excess cyclohexene left an oil that solidified rapidly to give II: mp 131.5–133 °C (after crystallization from heptane); yield 6.65 g (94%); ^{13}C NMR (Me_4Si) δ (a) 26.7, (b) 25.7, (c) 25.6, (d) 27.4, (e) 50.3, (f) 42.7, (g) 52.5, (h) 51.5, (i) 21.8, (j) 20.3, (k) 20.3, (l) 27.7, (m) 173.8, (n) 174.8. Anal. Calcd. for $C_{14}H_{18}O_3$ (II): C, 71.8; H, 7.7. Found: C, 71.8; H, 7.7.



II

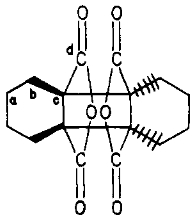
The 1-octadecene adduct, 100% after 20 h of irradiation, was III (mp 55–55.5 °C) as shown by its ^{13}C NMR: δ (a) 14.1, (b) 22.7, (c) 32.0, (d) 29.7, (e) 26.7, (f) 32.1, (g) 41.2, (h) 29.7, (i) 44.1, (j) 44.1, (k) 20.5, (l) 20.5, (m) 27.9, (n) 49.4, (o) 175.2, (p) 177.1.

Irradiation of equimolar amounts of IV and I in toluene containing 3 mol % of benzophenone with a GE sunlamp for 5 days gave 60% of adduct V, mp 272–274 °C. Anal. Calcd for $C_{16}H_{16}O_6$: C, 63.2; H, 5.3. Found: C, 63.3; H, 5.4.



III

Irradiation for 120 h by a sunlamp of a 0.35 M solution of I in acetone or chloroform containing 0.03 mol of benzophenone gave an 88% yield of the photodimer tricyclo[6.4.0.0^{2,7}]dodecane-1,8,2,7-tetracarboxylic dianhydride (VI): ^{13}C NMR (Me_4Si) δ (a) 20.1, (b) 25.5, (c) 51.1, (d) 172.3. Anal. Calcd for $C_{16}H_{16}O_6$: C, 63.2; H, 5.3; mol wt 304. Found: C, 63.1; H, 5.3; mol wt (VPO) 310.



VI

Acknowledgment. We are happy to acknowledge the contributions in this work of Steven J. Behrend of Amoco Chemicals Corp. and of R. William Dunlap and Eugene S. Kuhn, Research Department, Standard Oil Co. (Indiana), Naperville, IL.

Registry No. I, 2426-02-0; II, 85672-83-9; III, 86863-36-7; IV, 85-43-8; V, 84115-53-7; VI, 738-90-9; cyclohexene, 110-83-8; butadiene, 106-99-0; maleic anhydride, 108-31-6; 1-octadecene, 112-88-9.

Supplementary Material Available: Crystallographic summary consisting of tables of final atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and hydrogen final atomic coordinates (5 pages). Ordering information is given on any current masthead page.

---

[10] Sato, M.; Miller, K. F.; Enemark, J. H.; Strouse, C. E.; Callahan, K. P. *Inorg. Chem.* **1981**, *20*, 3571.

[11] (a) Futrell, J. H.; Ryan, K. R.; Sieck, L. W. *J. Chem. Phys.* **1965**, *43*, 1832. (b) Jennings, K. R. *Ibid.* **1965**, *43*, 4176.

[12] For leading references to early work utilizing metastable peaks to help delineate reaction paths, see: Meyerson, S.; Vander Haar, R. W.; Fields, E. K. *J. Org. Chem.* **1972**, *37*, 4114.

[13] Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *27*, 368.

Reaction of Bis(trifluoromethyl)aminoxyl with Cyclopropane[1]

M. Anpo,[2] C. Chatgilialoglu,[3] and K. U. Ingold*

Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6

Received February 23, 1983

Bimolecular homolytic substitutions at sp^3-hybridized carbons are uncommon.[4,5] Although cyclopropane (which does not have sp^3-hybridized carbons[6]) and ring-substituted cyclopropanes undergo ring-opening when attacked

---

[1] Issued as NRCC No. 22650.

[2] NRCC Research Associate 1981–82.

[3] NRCC Research Associate 1979–82.

[4] Ingold, K. U.; Roberts, B. P. "Free Radical Substitution Reactions"; Wiley: New York, 1971; pp 72–90.

[5] Jackson, R. A.; Townson, M. *Tetrahedron Lett.* **1973**, 193–196; *J. Chem. Soc., Perkin Trans. 2* **1980**, 1452–1456. Iyer, R. S.; Rowland, F. S. *Chem. Phys. Lett.* **1973**, *21*, 346–348. Espenson, J. H.; Shveima. J. S. *J. Am. Chem. Soc.* **1973**, *95*, 4468–4469. Espenson, J. H.; Sellers, T. D. *Ibid.* **1974**, *96*, 94–97. Chrzastowski, J. Z.; Cooksey, C. J.; Johnson, M. D.; Lockman, B. L.; Steggles, P. N. *Ibid.* **1975**, *97*, 932–934. Crease, A. E.; Johnson, M. D. *Ibid.* **1978**, *100*, 8013–8014. Bougeard, P.; Bury, A.; Cooksey, C. J.; Johnson, M. D.; Hungerford, J. M.; Lampman, G. M. *Ibid.* **1982**, *104*, 5230–5232. Bougeard, P.; Gupta, B. D.; Johnson, M. D. *J. Organomet. Chem.* **1981**, *206*, 211–219.

[6] Weigert, F. J.; Roberts, J. D. *J. Am. Chem. Soc.* **1967**, *89*, 5962–5963.