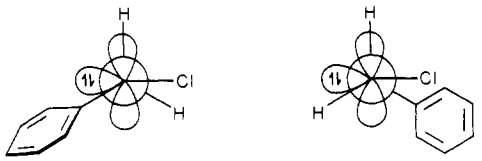
$$\frac{Z2}{E2} = \exp -(\Delta G^{\ddagger}_{Z} - \Delta G^{\ddagger}_{E} + \Delta G)/RT$$

where $\Delta G^{\ddagger}_{Z}$ and $\Delta G^{\ddagger}_{E}$ are standard free energies of activation for the formation of Z2 and E2 from cZ and cE, respectively. ΔG is the standard free-energy difference between the two conformers.

Plots of log Z2/E2 vs $1/T$ are displayed in Figure 1. The difference in standard free energies, $\Delta G^{\ddagger}_{Z} - \Delta G^{\ddagger}_{E} + \Delta G$ is 1.83 ± 0.03 kcal mol^{-1} for isooctane, 1.21 ± 0.06 kcal mol^{-1} for EtOAC, and 1.16 ± 0.04 kcal mol^{-1} for CH_3CN.



In the cE carbene conformer, the plane of the phenyl ring is coplanar with the C_1–C_2–Cl bond axis. This orientation facilitates the resonance interaction between the phenyl ring and the migrating C–H bond.[13] In the case of the cZ conformer, the plane of the phenyl ring is perpendicular to the C_1–C_2–Cl bond. As a result, resonance interaction is not possible in the latter, hence $\Delta G^{\ddagger}_{Z} > \Delta G^{\ddagger}_{E}$. If $\Delta G^{\ddagger}_{Z}$ is taken[2] to be approximately 2 kcal mol^{-1} higher than $\Delta G^{\ddagger}_{E}$ (e.g., $\Delta G^{\ddagger}_{Z}$ = 9.5 kcal mol^{-1} and $\Delta G^{\ddagger}_{E}$ = 7.5 kcal mol^{-1}), it follows that $\Delta G \sim$ zero from the following relationship, $\Delta G^{\ddagger}_{Z} - \Delta G^{\ddagger}_{E} + \Delta G$ = 1.83 kcal mol^{-1} in isooctane solvent. The barriers to conformer interconversion will be low and the equilibration is rapid. The product ratio Z2/E2 is exclusively determined by the difference in Gibbs function of the two transition states and hence conforms to the Curtin–Hammett principle.[14] The energy diagram (Figure 2) summarizes these relationships.

Experimental Section

GLC analyses of absolute yields of products were performed on a Varian Vista 6000 gas chromatograph fitted with a 6 ft × 0.125 in. stainless steel column packed with CSP-20M and by using a flame ionization detector. The GC traces were calibrated by using authentic samples of the reaction products. Peak areas were integrated with a Hewlett-Packard 3390A recorder.

Irradiation was carried out with 3500-W UV lamps in a Rayonet photoreactor until all the diazirine 1 (0.03 M in solution) was destroyed. Temperature control was within ±0.1 °C. The thermal decomposition of 1 in various concentrations of TME was carried out to 10 half-lives and product ratios were determined at different temperatures. 3-Chloro-3-benzyldiazirine was prepared by Graham's method[7] and purified by chromatography on silica gel. Absence of chlorostyrene prior to photolysis or thermolysis was confirmed by ^{1}H NMR spectroscopy.

Product Studies. 3-Chloro-3-benzyldiazirine (2.5 × 10^{-3} mol) and TME (0.116 mol) were dissolved in dry acetonitrile (100 mL) and the solution was photolyzed for 4 h at 15 °C. The unreacted TME and solvent were distilled off under reduced pressure. The chlorostyrene and cyclopropane were analyzed by GC. The residue was chromatographed on a column of silica gel (25 mm × 300 mm) and eluted with hexane and 2% hexane–ethyl acetate. In every instance, the chlorostyrene 2 were eluted in the first 200 mL of the solvent and the fractions contained the cyclopropane 3. The ^{1}H NMR of both styrene and the cyclopropane compared well with the reported data.[1] The yield of cyclopropane was 23.5% on the basis of the amount of diazirine used. Authentic samples of 3 and 2 were used to calibrate GC.

The thermal decompositions of 0.02 M solutions of 1 in acetonitrile, ethyl acetate, and isooctane were carried out to 10 half-lives and the product ratios were determined at different temperatures.

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Note added in proof: Our recent work on LFP of 3-chloro-3-(*p*-nitrophenyl)diazirine indicated that (nitrophenyl)chlorocarbene reacts with pure CH_3CN to form nitrile ylide with $k_{ylide} \simeq 10^5$ M^{-1} s^{-1}. It is possible that BzCCl can also form ylide with CH_3CN in the absence of other substrates. The values for k_i and k_t are at least 2–3 orders of magnitude larger than k_{ylide}; therefore the formation of nitrile ylide in the BzCCl system is not significant as suggested in the text.

Registry No. 1, 88211-05-6; TME, 563-79-1; benzylchlorocarbene, 88211-07-8.

(13) Nickon, A.; Bronfenbrenner, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 2022.

(14) Hammett, L. P. *Physical Organic Chemistry*; McGraw Hill: New York, 1970; p 119.

Synthesis of 8-(Methoxycarbonyl)[6]paracyclophane-3,4-dione

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The chemistry of small-bridged [*n*]paracyclophanes has attracted much attention in recent years[1] as exemplified by the spectroscopic characterization of [5]paracyclophane[2] and even lower [4] congener.[3] The smallest bridged cyclophane that has been isolated thus far is [6]paracyclophane (**1a**) and its derivatives.[4] Although many derivatives of larger bridged [7]–[8]paracyclophanes having functional groups on the bridge have been synthesized,[1,5] little is known of the [6] derivatives. Tochtermann has reported the synthesis and conformation of the 3-hydroxy and 3-keto derivatives.[6] We have succeeded in synthesizing (*Z*)-[6]paracycloph-3-ene (**2**) and its derivatives having a cis double bond in the bridge and found remarkable effect of the double bond on the physical and chemical properties of this system.[7] As an extension of

(1) For a recent review: Rosenfeld, S. M.; Choe, K. A. In *Cyclophanes*; Keehn, P. M.; Roselfeld, S. M., Eds.; Academic: New York, 1983; Vol. I, Chapter 5.

(2) (a) Jenneskens, L. W.; de Kanter, F. J. J.; Kraakman, P. A.; Turkenburg, L. A. M.; Koolhaas, W. E.; de Wolf, W. H.; Bickelhaupt, F.; Tobe, Y.; Kakiuchi, K.; Odaira, Y. *J. Am. Chem. Soc.* **1985**, *107*, 3716. (b) Tobe, Y.; Kaneda, T.; Kakiuchi, K.; Odaira, Y. *Chem. Lett.* **1985**, 1301. (c) Kostermans, G. B. M.; de Wolf, W. H.; Bickelhaupt, F. *Tetrahedron Lett.* **1986**, *27*, 1095. (d) Kostermans, G. B. M.; Bobeldijk, M.; de Wolf, W. H.; Bickelhaupt, F. *Chem. Ber.* Submitted for publication.

(3) (a) Kostermans, G. B. M.; Bobeldijk, M.; de Wolf, W. H.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1987**, *109*, 2471. (b) Tsuji, T.; Nishida, S. *J. Chem. Soc., Chem. Commun.* **1987**, 1189. (c) *J. Am. Chem. Soc.* **1988**, *101*, 2157.

(4) (a) Kane, V. V.; Wolf, A. D.; Jones, M., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 2643. (b) Kammula, S. L.; Iroff, L. D.; Jones, M., Jr.; van Straten, J. W.; de Wolf, W. H.; Bickelhaupt, F. *Ibid.* **1977**, *99*, 5815. (c) Liebe, J.; Wolff, C.; Krieger, C.; Weiss, J.; Tochtermann, W. *Chem. Ber.* **1985**, *118*, 4144. (d) Gunter, H.; Schmitt, P.; Fischer, H.; Tochtermann, W.; Liebe, J.; Wolff, C. *Helv. Chim. Acta* **1985**, *68*, 801. (e) Tobe, Y.; Ueda, K.; Kakiuchi, K.; Odaira, Y.; Kai, Y.; Kasai, N. *Tetrahedron Symposia-in-Print* **1986**, *42*, 1851. (f) Tobe, Y.; Nakayama, A.; Kakiuchi, K.; Odaira, Y.; Kai, Y.; Kasai, N. *J. Org. Chem.* **1987**, *52*, 2639.

(5) (a) Allinger, N. L.; Walter, T. J.; Newton, M. G. *J. Am. Chem. Soc.* **1974**, *96*, 4588. (b) Noble, K.-L.; Hopf, H.; Ernst, L. *Chem. Ber.* **1984**, *117*, 474.

(6) Jessen, J. L.; Wolff, C.; Tochtermann, W. *Chem. Ber.* **1986**, *119*, 297.

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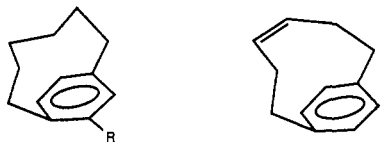
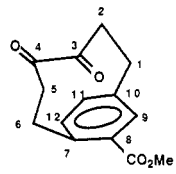
our work in this area, we disclose herein the synthesis of the title compound **3** possessing vicinal dicarbonyl functionality in the center of the bridge.



1a R=H
1b R=CO_2Me

2

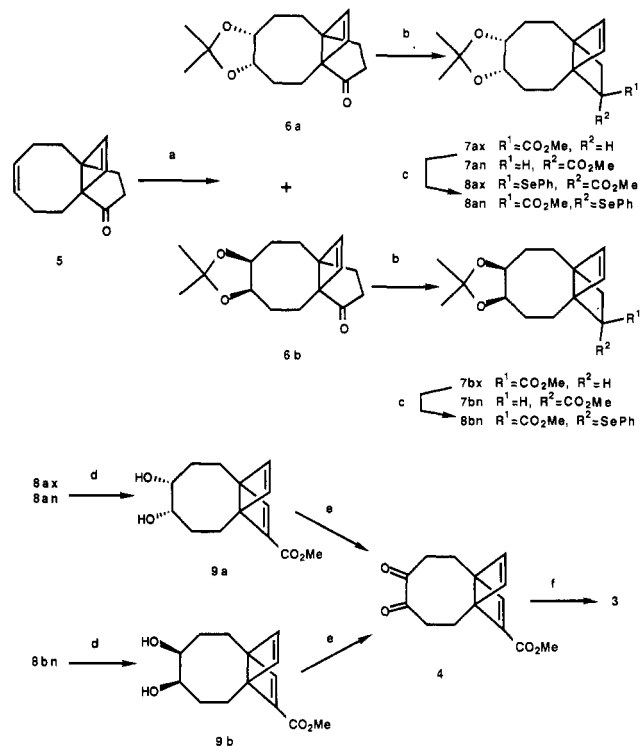


3

The synthesis of **3** was undertaken by utilizing the thermal valence isomerization of the Dewar benzene type valence isomer **4** of the cyclophane **3** as outlined in Scheme I. Hydroxylation of the propelladienone **5**[7a] with a catalytic amount of osmium tetraoxide and *N*-methylmorpholine *N*-oxide[8] followed by protection with 2,2-dimethoxypropane afforded a 1:1 mixture of two isomeric acetonides **6a** and **6b** in 43% yield. The stereochemistry of **6a** and **6b** was deduced on the basis of the ^1H NMR chemical shift difference and the stereoselectivity observed in the following reactions described below. Ring contraction of **6a** using the photo-Wolff rearrangement[3c,4e,f,7a] in methanol gave two esters **7ax** and **7an** in a ratio of ca. 1:1 in 57% yield. Similarly, ring contraction of **6b** yielded **7bx** and **7bn** (ca. 3:1) in 66% yield. The cyclobutene vinyl protons of **6b** (∂ 6.10 and 6.34) as well as **7bx** (∂ 6.05 and 6.31) and **7bn** (∂ 6.28 and 6.30) appear at a lower field than the corresponding protons of **6a** (∂ 6.00 and 6.30), **7ax** (∂ 6.00 and 6.24), and **7an** (∂ 6.26). Moreover, the ester methyl protons of **7an** (∂ 3.84) are observed downfield relative to those of **7bn** (∂ 3.71), as is the methine proton adjacent to the ester group of **7ax** (∂ 3.10) compared with that of **7bx** (∂ 2.78). These observations are ascribed to the anisotropic deshielding effect of the acetonide oxygen atoms on the protons disposed on the same side of that group. Phenylselenenylation[9] of **7ax** and **7an** (1:1) gave a mixture of selenides **8ax** and **8an** (ca. 2:3, 92%) while reaction of a mixture of **7bx** and **7bn** (3:1) afforded endo selenide **8bn** predominantly (79%). Deprotection of the acetonide group followed by oxidative elimination furnished the Dewar benzene **9a** (52% from **8ax** and **8an**) and **9b** (18% from **8bn**), respectively. Swern oxidation[10] of **9a** or **9b** afforded the diketo-Dewar benzene **4** in 14–35% yield. Finally, thermal isomerization of **4** took place smoothly (50 °C, 12 h) to give the cyclophanedione **3** as yellow prisms in 61% isolated yield after chromatography. The activation energy for the isomerization of **4** to **3** (E_a = 22.7 kcal/mol, log A = 9.86) is slightly lower than that of the Dewar benzene isomer of 8-(methoxycarbonyl)[6]-paracyclophane (**1b**).[4d]

In analogy with [6]paracyclophanes,[4] the dione **3** exhibits temperature dependence in the ^1H NMR spectra due to the conformational change of the bridge methylenes. At temperatures higher than 25 °C, the aromatic proton H(9) appears as a sharp doublet (J = 1 Hz) at ∂ 7.76. As the temperature decreases, the signal becomes broad and

Scheme I



[a] (a) (i) OsO_4, *N*-methylmorpholine *N*-oxide, (ii) $Me_2C(OMe)_2$, $(p\text{-}O_2NC_6H_4O)_2PO_2H$, acetone; (b) (i) HCO_2Et, EtONa, (ii) TsN_3, Et_3N, (iii) $h\nu$, MeOH; (c) LDA, Ph_2Se_2; (d) (i) HCl, (ii) H_2O_2, Pyr; (e) $(COCl)_2$, DMSO, Et_3N; (f) heat (50 °C).

reaches a coalescence point at −15 °C. At temperatures below −30 °C, the signal split into two doublets (J = 1 Hz) at ∂ 7.75 and 8.02 with an integration ratio of 4:1. Free energy of the conformational change was estimated from the coalescence temperature (T_c = 258 K, $\Delta\nu$ = 27 Hz) to be 12.9 kcal/mol. In view of the similarities in the ratio of the conformers and the barrier to the conformational change in this system to those of the [6]paracyclophane **1b**,[4e] it is reasonable to ascribe these observations to the conformational inversion between two conformers A and B with preference of the former. Consequently, it is deduced that, in contrast to the [6]paracycloph-3-ene system bearing a cis carbon–carbon double bond in the bridge,[7a] the two vicinal carbonyl groups in the bridge of **3** do not cause much difference in the conformational behavior of [6]paracyclophanes.

A B

As shown in Figure 1, the electronic absorption due to the aromatic ring of **3** exhibits a hypsochromic shift relative to **1b** by about 10 nm. This indicates that the out-of-plane

(7) (a) Tobe, Y.; Ueda, K.; Kaneda, T.; Kakiuchi, K.; Odaira, Y.; Kai, Y.; Kasai, N. *J. Am. Chem. Soc.* **1987**, *109*, 1136. (b) Tobe, Y.; Sorori, T.; Kobiro, K.; Kakiuchi, K.; Odaira, Y. *Tetrahedron Lett.* **1987**, *28*, 2681.
(8) VanRheenen, V.; Kelly, R. C.; Cha, D. Y. *Tetrahedron Lett.* **1976**, 1973.
(9) (a) Sharpless, K. B.; Lauer, R. F.; Teranishi, A. *J. Am. Chem. Soc.* **1973**, *95*, 6137. (b) Reich, H. J.; Renga, J. M.; Reich, I. L. *Ibid.* **1975**, *97*, 5434.
(10) Omura, K.; Swern, D. *Tetrahedron* **1978**, *34*, 1651.

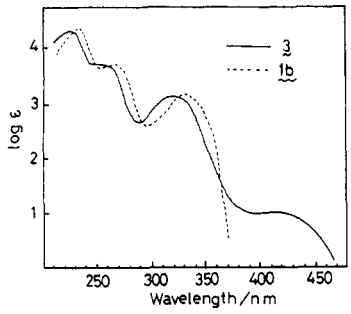


Figure 1. Electronic spectra of **1b** and **3** in ethanol.

bending of the benzene ring of **3** is smaller than that of **1b** in view of the relationship between the deformation angle of the benzene ring and the absorption maximum.[11] Through X-ray crystallographic studies of [6]paracyclophane derivatives, we and Tochtermann have clarified that deformation of the bridge methylene chain due to expansion of the bond angles is greater than that due to elongation of the bond distances.[4c,e,f] It is, therefore, reasonable to assume that the two sp^2 carbons with a larger bond angle than the sp^3 carbon makes the distance between the benzyl carbons of **3** longer than that of **1b** to effectively release the out-of-plane deformation of the benzene ring in **3**. The electronic absorption maximum of the α dione chromophore of **3** is observed in a very long wavelength region (λ_{max} 405 nm). Taking into account the relationship between the dihedral angle and the absorption maximum in the cyclic α-diketones,[12] it is deduced that the dicarbonyl moiety of **3** has a transoid conformation with a considerably wide dihedral angle. The electronic spectrum of **3**, however, does not seem to indicate electronic interaction between the benzene ring and the carbonyl groups in the bridge because the shape of the spectrum in the aromatic region is quite similar to that of **1b**.

Experimental Section

Acetonides of 4,5-Dihydroxy[6.3.2]propell-12-en-9-ones (6a and 6b). To a solution of *N*-methylmorpholine *N*-oxide monohydrate[8] (4.88 g, 36.2 mmol) in *tert*-butyl alcohol (150 mL) and water (15 mL) was added osmium tetraoxide (16 mg, 0.063 mmol), followed by 5.59 g (29.7 mmol) of the propelladienone **5**[7a] in 45 mL of tetrahydrofuran (THF). The mixture was stirred at room temperature overnight and then 30 mL of 0.2 M sodium hydrogen sulfite solution was added. The solvent was evaporated and the residue diluted with 10% sulfuric acid to make the solution acidic (pH 3–4). The solution was extracted 3 times with dichloromethane. The combined extract was dried ($MgSO_4$) and the solvent evaporated to give a brown oil. Chromatography on silica gel with ether/methanol (97:3) as eluent gave 3.42 g (54%) of a mixture of 4,5-dihydroxypropellenones as an oil that partially solidified: IR (neat) 3400, 1720, 980, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.1–4.1 (m, 16 H), 5.94, 5.98 (2 d, 1 H), 6.16 (d, 1 H). A mixture of 3.20 g (14.4 mmol) of the above diols, 11.9 g (114 mmol) of 2,2-dimethoxypropane, and 576 mg (1.69 mmol) of bis(4-nitrophenyl)phosphoric acid[13] in 216 mL of acetone was stirred at room temperature for 1 h. The solvent was evaporated and the residue was diluted with $NaHCO_3$ solution. The mixture was filtered and the filtrate was extracted with ether. The extract was dried ($MgSO_4$) and concentrated. The residue was chromatographed on silica gel with ether/petroleum ether (15:85) eluent and gave 1.52 g (40%) of **6a**, 1.11 g (29%) of **6b**, and 358 mg (9.5%) of a mixture of **6a** and **6b**. Analytical samples of **6a** and **6b** were obtained by recrystallization from petroleum ether. **6a**: mp 71–72 °C; IR (KBr) 1720, 1210, 1040, 870 cm^{-1}; MS, *m/e* (relative intensity) 262 (M^+, 75), 247 (94), 204 (60), 91 (100); ^1H NMR ($CDCl_3$) δ 0.9–2.5 (m, 17 H), 2.98 (ddd, J = 18, 10, 10 Hz, 1 H), 4.1–4.4 (m, 2 H), 6.00 (d, J = 2 Hz, 1 H), 6.30 (d, J = 2 Hz, 1 H). Anal. Calcd for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45. Found: C, 73.26; H, 8.49. **6b**: mp 64–65 °C; IR (KBr) 1720, 1200, 1040, 880 cm^{-1}; MS, *m/e* (relative intensity) 262 (M^+, 22), 247 (91), 204 (84), 91 (100); ^1H NMR ($CDCl_3$) δ 1.1–2.4 (m, 17 H), 2.94 (ddd, J = 19, 12, 10 Hz, 1 H), 4.1–4.4 (m, 2 H), 6.10 (d, J = 2 Hz, 1 H), 6.34 (d, J = 2 Hz, 1 H). Anal. Calcd for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45. Found: C, 73.23; H, 8.48.

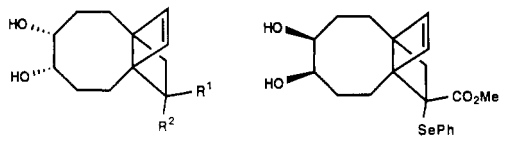
Acetonides of 4,5-Dihydroxy-9-(methoxycarbonyl)-[6.2.2]propell-11-enes (7ax, 7an, 7bx, and 7bn). To a suspension of 412 mg (8.59 mmol) of 50% sodium hydride in mineral oil and 0.1 mL of ethanol in 17 mL of ether was added a mixture of 1.51 g (5.73 mmol) of the propellenone **6a** and 636 mg (8.59 mmol) of ethyl formate in 5 mL of ether. The mixture was stirred at room temperature for 2 h and 50 mL of water was added. The organic layer was separated and extracted with 5% NaOH solution. The combined aqueous phase was washed with ether, acidified with 0.5 N HCl while being cooled with ice, and extracted with ether. The ether extract was washed with brine and dried ($MgSO_4$). Evaporation of the solvent gave a brown oil (IR (neat) 3600–2000, 1590, 1210, 1060 cm^{-1}), which was used without purification. To a solution of the above hydroxymethylene derivative and 1.17 g (11.6 mmol) of triethylamine in 5.7 mL of dichloromethane was added dropwise 1.26 g (6.38 mmol) of *p*-toluenesulfonyl azide[14] while the solution was cooled with an ice–salt bath. The mixture was stirred at 0 °C for 2 h, a solution of 390 mg (6.96 mmol) of KOH in 5.2 mL of water was added, and the mixture was stirred at room temperature for 15 min. The organic layer was separated and the aqueous layer was extracted with dichloromethane. The combined organic phase was washed with 10% KOH solution and water and dried ($MgSO_4$). Evaporation of the solvent gave a brown oil (IR (neat) 2070, 1650 cm^{-1}), which was dissolved in 100 mL of methanol and irradiated with a 500-W high pressure mercury lamp in a Pyrex vessel for 14 h. The solvent was evaporated and the residue was chromatographed on silica gel with ether/petroleum ether (25:75) as eluent to give 447 mg (27%) of **7an** as a colorless oil and 502 mg (30%) of **7ax** as a colorless solid. A similar reaction of 3.91 g (14.9 mmol) of **6b** gave 577 mg (13%) of **7bn** (colorless oil) and 2.03 g (37%) of **7bx** (colorless solid) and 702 mg (16%) of a mixture of **7bn** and **7bx**. **7an**: IR (neat) 1730, 1160, 1040, 760 cm^{-1}; MS, *m/e* (relative intensity) 292 (M^+, 8), 277 (29), 202 (52), 157 (100), 131 (70), 105 (77), 91 (100); ^1H NMR ($CDCl_3$) δ 1.2–2.2 (m, 15 H), 2.45 (dd, J = 12, 6 Hz, 1 H), 2.87 (dd, J = 9, 6 Hz, 1 H), 3.84 (s, 3 H), 4.0–4.2 (m, 2 H), 6.26 (s, 2 H). **7ax**: mp 50–51 °C (from petroleum ether); IR (KBr) 1730, 1220, 1040, 870, 750 cm^{-1}; MS, *m/e* (relative intensity) 292 (M^+, 6), 277 (25), 202 (40), 157 (100), 131 (72), 105 (87), 91 (91); ^1H NMR ($CDCl_3$) δ 1.0–2.3 (m, 16 H), 3.10 (dd, J = 10, 7 Hz, 1 H), 3.64 (s, 3 H), 4.0–4.3 (m, 2 H), 6.00 (d, J = 2 Hz, 1 H), 6.24 (d, J = 2 Hz, 1 H). Anal. Calcd for $C_{17}H_{24}O_4$: C, 69.83; H, 8.27. Found: C, 70.02; H, 8.24. **7bn**: IR (neat) 1730, 1170, 1050, 760 cm^{-1}; MS, *m/e* (relative intensity) 292 (M^+, 5), 277 (47), 202 (56), 157 (100), 131 (77), 105 (60), 91 (89); ^1H NMR ($CDCl_3$) δ 1.1–2.5 (m, 16 H), 2.84 (dd, J = 9, 7 Hz, 1 H), 3.71 (s, 3 H), 4.0–4.3 (m, 2 H), 6.28 (d, J = 2 Hz, 1 H), 6.30 (d, J = 2 Hz, 1 H). **7bx**: mp 72–73 °C (from petroleum ether); IR (KBr) 1730, 1200, 1050, 1030, 860, 760 cm^{-1}; MS, *m/e* (relative intensity) 292 (M^+, 6), 277 (60), 202 (37), 157 (96), 131 (69), 105 (95), 91 (100); ^1H NMR ($CDCl_3$) δ 1.1–2.5 (m, 16 H), 2.78 (dd, J = 10, 9 Hz, 1 H), 3.65 (s, 3 H), 4.0–4.3 (m, 2 H), 6.05 (d, J = 2 Hz, 1 H), 6.31 (d, J = 2 Hz, 1 H). Anal. Calcd for $C_{17}H_{24}O_4$: C, 69.83; H, 8.27. Found: C, 69.66; H, 8.37.

4,5-Dihydroxy-9-(methoxycarbonyl)[6.2.2]propella-9,11-dienes (9a and 9b). To a solution of 13.6 mmol of lithium diisopropylamide in 38 mL of THF was added 2.76 g (9.45 mmol) of **7an** and **7ax** (ca. 1:1 mixture) in 13 mL of THF at −78 °C, and the solution was stirred at that temperature for 1 h. A mixture of 3.83 g (12.3 mmol) of diphenyl diselenide and 2.20 g (12.3 mmol) of hexamethylphosphoramide in 13 mL of THF was added and the solution was stirred there for 30 min before it was warmed

(11) Allinger, N. L.; Sprague, J. T.; Liljefors, T. *J. Am. Chem. Soc.* **1974**, *96*, 5100.
(12) Leonard, N. J.; Mader, P. M. *J. Am. Chem. Soc.* **1950**, *72*, 5388.
(13) Hampton, A. *J. Am. Chem. Soc.* **1961**, *83*, 3640.
(14) Regitz, M.; Hocker, J.; Liedhegener, A. *Organic Syntheses*; Wiley: New York, 1968; Collect. Vol. 5, p 179.

up to room temperature slowly. The solution was diluted with water and ether and the organic layer was separated. The aqueous layer was extracted with ether and the combined organic phase was washed with 1 N HCl and $NaHCO_3$ solution and dried ($MgSO_4$). Evaporation of the solvent followed by chromatography on silica gel with ether/petroleum ether (25:75) as eluent gave 1.87 g (44%) of **8an** and 2.04 g (48%) of a mixture of **8an** and **8ax** as a colorless solid. A sample of **8an** was recrystallized from petroleum ether: mp 118–119 °C; IR (KBr) 1720, 1240, 1040, 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.2–2.4 (m, 14 H), 2.4–2.9 (m, 2 H), 3.56 (s, 3 H), 4.0–4.4 (m, 2 H), 6.04 (d, J = 2 Hz, 1 H), 6.34 (d, J = 2 Hz, 1 H), 7.2–7.7 (m, 5 H). A mixture of **8an** and **8ax** in THF (8 mL) was treated with 3 N HCl at room temperature for 3 h. The mixture was neutralized with $NaHCO_3$ solution and extracted with dichloromethane. The extract was dried ($MgSO_4$) and the solvent was evaporated. Chromatography of the residue on silica gel with ether/methanol (97:3) as eluent gave the diol **10an** (69 mg, 23%), **10ax** (127 mg, 42%), and their mixture (92 mg, 30%) as colorless oil. **10an**: IR (neat) 3400, 1720, 1260 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.6–3.0 (m, 12 H), 3.57 (s, 3 H), 3.8–4.2 (m, 2 H), 6.12 (d, J = 2 Hz, 1 H), 6.40 (d, J = 2 Hz, 1 H), 7.2–7.6 (m, 5 H). **10ax**: IR (neat) 3400, 1720, 1260 cm^{-1}; ^1H NMR ($CDCl_3$) 1.6–3.1 (m, 12 H), 3.58 (s, 3 H), 3.7–4.1 (m, 2 H), 6.42 (s, 2 H), 7.2–7.6 (m, 5 H). To a mixture of 3.83 g (9.41 mmol) of **10an** and **10ax** and 1.35 g (17.1 mmol) of pyridine in 23 mL of dichloromethane was added 3.9 mL of 15% hydrogen peroxide (17.1 mmol) at room temperature. The mixture was stirred vigorously for 1.5 h and diluted with water, and the organic layer was separated. The aqueous layer was extracted with dichloromethane and the combined organic phase was washed with 5% HCl, $NaHCO_3$ solution, and water. After being dried ($MgSO_4$), the solvent was evaporated and the residue chromatographed quickly on silica gel (ether/methanol (97:3) as eluent) to give 1.29 g (55%) of **9a** as a colorless oil: IR (neat) 3400, 1710, 1600, 1270, 780 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.5–2.5 (m, 10 H), 3.69 (s, 3 H), 3.5–4.0 (m, 2 H), 6.46 (d, J = 2 Hz, 1 H), 6.63 (d, J = 2 Hz, 1 H), 7.13 (s, 1 H).

Similarly, phenylselenenylation of 2.00 g (6.86 mmol) of a mixture of **7bn** and **7bx** (1:3) gave **8bn** (2.12 g, 79%) as a colorless oil. The corresponding stereoisomer was not obtained in pure state. **8bn**: IR (neat) 1720, 1250, 1050, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0–2.2 (m, 15 H), 2.56 (d, J = 14 Hz, 1 H), 3.53 (s, 3 H), 3.9–4.4 (m, 2 H), 6.03 (d, J = 2 Hz, 1 H), 6.30 (d, J = 2 Hz, 1 H), 7.3–7.6 (m, 5 H). Hydrolysis of 2.10 g (4.70 mmol) of **8bn** as described above gave 1.91 g (100%) of the diol **10bn** as a colorless oil: IR (neat) 3400, 1720, 1260, 1060, 740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.4–2.7 (m, 11 H), 2.47 (d, J = 14 Hz, 1 H), 3.53 (s, 3 H), 3.8–4.1 (m, 2 H), 5.95 (d, J = 2 Hz, 1 H), 6.27 (d, J = 2 Hz, 1 H), 7.3–7.6 (m, 5 H). Oxidation of 1.91 g (4.70 mmol) of **10bn** afforded 208 mg (18%) of **9b** as a colorless oil: IR (neat) 3400, 1710, 1600, 1280, 790 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.5–2.3 (m, 10 H), 3.71 (s, 3 H), 3.8–4.0 (m, 2 H), 6.39 (d, J = 2 Hz, 1 H), 6.55 (d, J = 2 Hz, 1 H), 7.22 (s, 1 H).



10ax R^1=SePh, R^2=CO_2Me
10an R^1=CO_2Me, R^2=SePh

10bn

8-(Methoxycarbonyl)[6]paracyclophane-3,4-dione (3). To a solution of 1.97 g (15.5 mmol) of oxalyl chloride in 31 mL of dichloromethane was added 1.61 g (20.6 mmol) of dimethyl sulfoxide in 4.1 mL of the same solvent at −78 °C. The mixture was stirred there for 40 min and then a solution of 1.29 g (5.16 mmol) of **9a** in 25 mL of dichloromethane was added. The mixture was stirred for 1 h before 5.20 g (51.6 mmol) of triethylamine was added. The mixture was warmed up slowly to ca. −5 °C, where water was added. The organic layer was separated and the aqueous layer was extracted with dichloromethane. The combined organic phase was washed with 5% HCl, $NaHCO_3$ solution, and water and dried ($MgSO_4$). Evaporation of the solvent followed by quick chromatography on silica gel (ether/petroleum ether (40:60) as eluent) gave 439 mg (35%) of **4** as a yellow oil: IR (neat) 1710, 1700, 1600, 1260, 790 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.8–2.4 (m, 4 H), 2.5–2.7 (m, 4 H), 3.70 (s, 3 H), 6.44 (d, J = 2 Hz, 1 H), 6.60 (d, J = 2 Hz, 1 H), 7.12 (s, 1 H). A similar reaction of **9b** gave **4** in 14% yield. A solution of **4** (439 mg, 1.78 mmol) in hexane (200 mL) was heated under nitrogen at 50 °C for 12 h. The solvent was evaporated and the residue chromatographed on silica gel (ether/petroleum ether (25:75) eluent) to afford 269 mg (61%) of **3** as a yellow solid. Recrystallization from hexane gave an analytical sample: mp 123–125 °C; IR (KBr) 1700, 1580, 1540, 1260, 1060, 690 cm^{-1}; MS, m/e (relative intensity) 246 (M^+) was not observed, 228 (100), 176 (66), 158 (70); ^1H NMR ($CDCl_3$) δ 1.8–2.5 (m, 2 H), 2.4–3.1 (m, 5 H), 3.90 (m + s, 4 H), 7.17 (d, J = 10 Hz, 1 H), 7.35 (dd, J = 10, 1 Hz, 1 H), 7.77 (d, J = 1 Hz, 1 H); UV (EtOH) λ_{max} (log ϵ) 405 (1.01), 322 (2.99), 251 (3.73), 223 (4.31) nm. Anal. Calcd for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.11; H, 5.69. The rates of isomerization of **4** to **3** were measured as described before[4e,f,7a] to give the following data: k(25 °C) = (5.55 ± 0.14) × 10^{-6}, k(33 °C) = (1.58 ± 0.06) × 10^{-5}, k(40 °C) = (3.52 ± 0.12) × 10^{-5} s^{-1}.

Reductive Deoxygenation of Aryl Aldehydes and Ketones by *tert*-Butylamine–Borane and Aluminum Chloride

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Reductive deoxygenation of aryl ketones is an important and valuable procedure in organic synthesis.[1] Recently, we reported a mild and selective method for the reductive deoxygenation of aryl aldehydes and ketones using sodium cyanoborohydride in the presence of zinc iodide.[2] Although the method works well with most substrates, it does not deoxygenate aryl ketones having a *p*-chloro substituent. It was found that even lithium aluminum hydride in combination with aluminum chloride does not readily reduce *p*-chloroacetophenones to *p*-(chloroethyl)benzene. Recently, Ono et al. reported that sodium borohydride and aluminum chloride also hydrogenolyzed *p*-chloroacetophenone to the corresponding hydrocarbon.[3] Meanwhile, in our continuous search for better reducing agents for reductive deoxygenation of aryl ketones, we have found that *tert*-butylamine–borane in the presence of aluminum chloride in dichloromethane can reduce not only *p*-chloroacetophenone but also dichloroaryl ketone to the corresponding hydrocarbon. The reagent is also quite mild and selective. *tert*-Butylamine–borane is a very mild reducing agent and is used in the selective reduction of aldehydes and ketones to the corresponding alcohol.[4-7] The reagent as well as other amine–boranes has been used in the presence of a Lewis acid like boron trifluoride etherate and aluminum chloride to reduce alicyclic and aryl ketones to the corresponding alcohols only.[8,9] The increase in

(1) (a) *Reduction*; Augustine, R. L., Ed.; Marcel Dekker: New York, 1968. (b) House, H. O. *Modern Synthetic Reactions*, 2nd ed.; W. A. Benjamin: Menlo Park, CA, 1972; Chapter 4. For a recent review of various methods of reductive deoxygenation of arylketones, see the references cited in ref 2.

(2) Lau, C. K.; Dufresne, C.; Belanger, P. C.; Piétré, S.; Scheigetz, J. *J. Org. Chem.* **1986**, *51*, 3038–3043.

(3) Ono, A.; Suzuki, N.; Kamimura, J. *Synthesis* **1987**, 736–738.

(4) Paquette, L. A. *J. Org. Chem.* **1981**, *46*, 3768.

(5) Chang, F. C. *Synth. Commun.* **1981**, *11*, 875–879.

(6) Andrews, G. C. *Tetrahedron Lett.* **1980**, *21*, 693–696.

(7) Andrews, G. C.; Crawford, T. C. *Tetrahedron Lett.* **1980**, *21*, 697–700.

(8) Jones, W. M. *J. Am. Chem. Soc.* **1960**, *82*, 2528–2532.

(9) Grundon, M. F.; McCleery, D. G.; Wilson, J. W. *Tetrahedron Lett.* **1976**, 295–296.

0022-3263/89/1954-0491$01.50/0