Similar irradiation experiments of **1d** (2 mmol, 666 mg) in benzene (100 mL) or benzene (100 mL) containing zinc powder (131 mg) gave **2d**, **3d**, and **8d** but did not give the allene **9d**.

Photolysis of Vinyl Bromide 1e. A solution of **1e** (500 mg) in benzene (200 mL) was directly irradiated by using a 100-W high-pressure mercury lamp at 10 °C for 4 h. After evaporation of the solvent the crude photoproducts were chromatographed over alumina and separated into three fractions. The first fraction (elution with 20% benzene–hexane) gave an oil which contained **2e** and **3e**. Complete separation by repeated chromatography on alumina with hexane as the eluant failed. The early fraction contained mainly **2e**, and the latter fraction contained mainly **3e**. The structure of **3e** [NMR (CCl_4) δ 3.98 (OMe); UV (cyclohexane) λ_{max} 312, 326 nm] was confirmed as 2-(*o*-methoxyphenyl)benzofuran by comparison of its spectra of an authentic sample.[10] The structure of **2e** which was a constitutional isomer of **3e** [NMR (CCl_4) δ 3.84 (OMe); UV (cyclohexane) λ_{max} 254, 260, 283 nm], having shorter wavelength wavelength absorption in UV spectrum, and was assigned as 3-(*o*-methoxyphenyl)benzofuran but could not be purified for analysis. The second fraction (elution with 30% benzene–hexane) gave a crystalline compound which was confirmed as the starting material **1e** by the mixture melting point (114–115 °C). The third fraction (elution with 50% benzene–hexane) gave bis(*o*-methoxyphenyl)acetylene (**14e**):[13] mp 127–128 °C; NMR(CCl_4) δ 3.88 (s, 6 H), 6.67–7.53 (m, 8 H). The product distribution was determined by the NMR spectrum of each of the fractions.

Acknowledgment. We thank Professor Z. Rappoport for many helpful discussions and suggestions.

Registry No. 1a, 62378-29-4; **1b**, 62378-32-9; **1c**, 79517-71-8; **1d**, 79517-72-9; **1e**, 5293-93-6; **2a**, 62378-40-9; **2b**, 62378-28-3; **2c**, 25433-77-6; **2d**, 79517-73-0; **2e**, 28226-83-7; **3d**, 79517-74-1; **3e**, 42926-53-4; **4a**, 79534-26-2; **4b**, 79534-27-3; **8d**, 79517-75-2; **9d**, 79517-76-3; **14e**, 5293-78-7; *o*-methoxyphenyl bromide, 578-57-4; 1,1-bis(*o*-methoxyphenyl)propanol, 79517-77-4; 1,1-bis(*p*-methoxyphenyl)propene, 4663-13-2; 1,1-bis(*p*-methoxyphenyl)propadiene, 39179-88-9; 10-methyl-3,6,9-trimethoxyphenanthrene, 79534-14-8.

(13) Coleman, G. H.; Holst, W. H.; Maxwell, R. D. *J. Am. Chem. Soc.* **1936**, *58*, 2310.

Synthesis and Bridgehead Reactivities of 1-Substituted Tricyclo[3.2.1.$0^{3,6}$]octanes

Tien-Yau Luh* and Keng Lon Lei

Department of Chemistry, The Chinese University of Hong Kong, Shatin, N.T., Hong Kong

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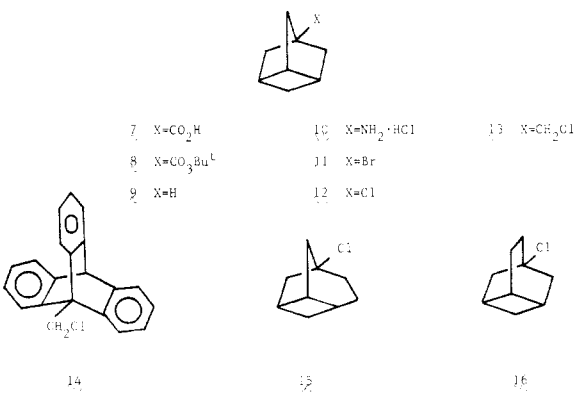
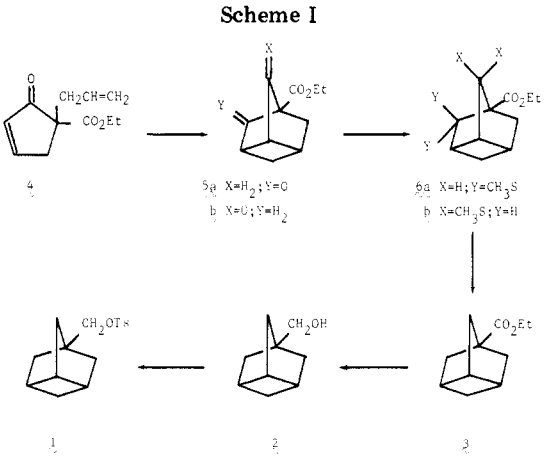
Ten bridgehead 1-substituted tricyclo[3.2.1.$0^{3,6}$]octanes were conveniently synthesized by our newly developed route. Thus, 5-allyl-5-(carboethoxy)cyclopentenone was irradiated to give a mixture of the tricyclic keto esters **5a** and **5b**, which were converted to 1-(carboethoxy)tricyclo[3.2.1.$0^{3,6}$]octane by the reduction of the corresponding thioketals. The ester function was then transformed to various substituents. The pK_a of the bridgehead carboxylic acid was determined. The bridgehead radical reactivity was also examined. The results were compared with those of the related systems.

In our previous communication,[1] we reported a facile synthesis of 1-tricyclo[3.2.1.$0^{3,6}$]octylmethyl *p*-toluenesulfonate (**1**; Scheme I). The solvolytic behavior of **1** is of particular interest. Significant solvent participation in the acetolysis of **1** was noted, which appears to be unusual in the bridgehead neopentyl system. Since the bridgehead ester **3** can be readily synthesized by our route as outlined in Scheme I, we have prepared various bridgehead substituted tricyclo[3.2.1.$0^{3,6}$]octanes **7–13** and undertaken a complementary investigation of the bridgehead reactivities of these highly strained tricyclooctane derivatives.



(1) Luh, T.-Y.; Lei, K. L. *J. Chem. Soc., Chem. Commun.* **1981**, 214.

Scheme I



Results and Discussion

Synthesis. The synthetic details of **3** from **4** are described in the Experimental Section. The carboxylic acid **7** was obtained from the base hydrolysis of **3**. Thermal decomposition of **8**, readily synthesized by the usual manner,[2] afforded the hydrocarbon **9**, which exhibits identical properties with those described in the literature.[3]

(2) Luh, T.-Y.; Stock, L. M. *J. Org. Chem.* **1978**, *43*, 3271.
(3) Sauers, R. R.; Parent, R. A.; Damle, S. B. *J. Am. Chem. Soc.* **1966**, *88*, 2257.

0022-3263/81/1946-5328$01.25/0 © 1981 American Chemical Society

Table I. pK_a Values

carboxylic acid	pK_a 50% MeOH-H_2O (v/v)	50% EtOH-H_2O (w/w)	50% EtOH-H_2O (v/v)
benzoic	5.28[b]	5.76[b]	5.35[e]
bicyclo[2.2.1]-heptane-1	6.04[a]	--	6.37[d]
bicyclo[2.2.2]-octane-1	6.26[a]	6.87[c]	--
tricyclo[3.2.1.0^{3,6}]-octane-1	5.89[b]	6.52[b]	--
nortricyclene-4	--	--	5.89[e]

[a] Reference 8. [b] This study. [c] Reference 9. [d] Reference 10. [e] Reference 11.

Curtius rearrangement of **7** yielded the amine hydrochloride **10**. Attempts to isolate the free amine by careful neutralization were unsuccessful. Skeletal rearrangement leading to an unknown structure was observed.[4]

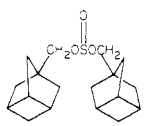
Cristol–Firth modified Hunsdiecker reaction of **7** in dibromomethane afforded the bromide **11** in 69% yield. If carbon tetrachloride was employed as solvent, a mixture of the bromide **11** and the chloride **12** was obtained which could readily be separated by preparative VPC. This reaction was also used to examine the reactivity of this bridgehead radical, which will be discussed later.

On treatment with thionyl chloride at room temperature, **2** was smoothly transformed to **13** in 62% yield. The structure for **13** was assigned on the basis of the ^{13}C NMR spectrum, which shows absorptions at δ 34.9, 35.9, 40.5, 42.6, 43.1, 48.8, and 65.4. The signal at δ 65.4 is attributed to the bridgehead chloromethyl group. The proton NMR spectrum for **13** is interesting. The low-field absorptions at δ 4.08 and 4.20 appear as an AB splitting system with coupling constant J = 10.2 Hz and are assigned to two protons of the bridgehead chloromethyl group. Such a pattern is striking and suggests that these two hydrogen atoms are magnetically nonequivalent. The signals coalesce to a sharp singlet at elevated temperatures (ca. 135 °C).[5]

It is noteworthy that strained bridgehead carbinols generally undergo typical Wagner–Meerwein rearrangement upon treatment with thionyl chloride.[6] In this study, we have not isolated any rearranged product such as **15** or **16**. These results are compatible with our earlier work on the solvolysis of **1**. In other words, there might be little or no release of strain energy if skeletal reorganization from the tricyclooctyl system to those of **15** or **16** would occur.[7]

(4) Similar observation has been found in other strained bridgehead amines; Monti, S. A.; Harless, J. M. *J. Am. Chem. Soc.* **1977**, *99*, 2690. Luh, T.-Y.; Stock, L. M., unpublished results.

(5) (a) The only known example of hindered rotation of the bridgehead chloromethyl group is 1-(chloromethyl)triptycene **14** presumably due to steric interaction between bridgehead substituent and the peripheral hydrogens on the aromatic rings: Sergeyev, M. M.; Abdulla, K. F.; Skvarchenko, V. R. *J. Chem. Soc., Chem. Commun.* **1972**, 368. (b) One referee suggested an alternative structure **17** for **13**. However, our compound does not exhibit absorptions at ca. 1200 cm^{-1} in the infrared region due to S=O stretching. Further studies are required to clarify this point.



17

(6) Klunder, A. J. H.; Zwanenburg, B. *Tetrahedron* **1973**, *29*, 161. Luh, T.-Y. Ph.D. Dissertation, University of Chicago, 1974.

Table II. Bridgehead Radical Selectivity in Halogen Abstraction Reactions

radical	Hunsdiecker reaction (80 °C) [RBr]/[RCl]	r (80 °C)
1-adamantyl	0.14[a,b]	30[a,c]
1-bicyclo[2.2.2]octyl	0.48[b]	59[d]
1-bicyclo[2.2.1]heptyl	0.50[b]	47[d]
1-tricyclo[3.2.1.0^{3,6}]octyl	0.69[a]	65[a]
cubyl	1.05[c]	80[c]

[a] This study. [b] Reference 14. [c] Reference 2. [d] Reference 16.

pK_a Measurement. The pK_a of **7** was determined to be 5.89 and 6.52 respectively in 50% (v/v) methanol–water and 50% (w/w) ethanol–water. Benzoic acid was employed to check the methods. Our results are compared with those of related compounds as outlined in Table I. The tricyclooctanecarboxylic acid **7** is a stronger acid than the bicycloheptane- and bicyclooctanecarboxylic acids but a weaker acid than nortricyclene-4-carboxylic acid. This is consistent with increasing the total strain of the tricyclooctyl molecule by introducing the cyclobutane moiety, and thus the s character in the tricyclooctane C-1 exocyclic orbital is enhanced.[12,13]

Bridgehead Radicals. As described in the previous paragraph, the bridgehead halides **11** and **12** are readily obtained from the Hunsdiecker reaction. This reaction is known to proceed via a free-radical mechanism.[2,14] The relative reactivity of the 1-tricyclo[3.2.1.0^{3,6}]octyl radical was examined by studying the competitive halogen abstraction reaction. Two different approaches were employed.[2,14] One is the Cristol–Firth-modified Hunsdiecker reaction in carbon tetrachloride; the other is the measurement of the competition constant, r[15] for the reaction of the radical with bromotrichloromethane and carbon tetrachloride. The experimental observations for several bridgehead radicals are presented in Table II. As anticipated, the tricyclooctyl radical is more selective than 1-bicycloheptyl but less selective than cubyl radicals. The trend further supports the early argument that polar effects may play an important role in these reactions.[2]

In summary, we have synthesized ten 1-substituted tricyclo[3.2.1.0^{3,6}]octanes as a new class of compounds and have supplemented the study of the bridgehead reactivities of this highly strained system.

(7) The calculated strain energies by molecular mechanics for the skeletons of **13**, **15**, and **16** are comparable: Engler, E. M.; Andose, J. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 8005. Smith, M. R.; Harris, J. M. *J. Org. Chem.* **1978**, *43*, 3588.

(8) Wilcox, C. F.; Leung, C. *J. Am. Chem. Soc.* **1968**, *90*, 336.

(9) Holtz, H. D.; Stock. L. M. *J. Am. Chem. Soc.* **1964**, *86*, 5188.

(10) Wilt, J. W.; Dabek, H. F., Jr.; Berliner, J. P.; Schneider, C. A. *J. Org. Chem.* **1970**, 35, 2402.

(11) Chenier, P. J.; McClure, J. R.; Golembeski, D. J. *J. Org. Chem.* **1978**, *43*, 4306.

(12) Semiempirical calculation by localized molecular orbital theory indicates that the s character in the exocyclic orbital (C-1) of **9** is 28%. We thank Dr. S. P. So for a helpful discussion.

(13) Stock, L. M. *J. Chem. Educ.* **1972**, *49*, 400.

(14) Herwig, K.; Rüchardt, C. *Chem. Ber.* **1972**, *105*, 363.

(15) The competitive constant is defined as $r = k_{Br}/k_{Cl}$ = [RBr] [CCl_4]/[RCl] [$BrCCl_3$], where k_{Br} and k_{Cl} are the rate constants for the bromine and the chlorine atom transfer reactions, respectively. The radicals are generated in situ from the decomposition of the corresponding peresters.

$$RBr \xleftarrow[BrCCl_3]{k_{Br}} R\cdot \xrightarrow[ClCCl_3]{k_{Cl}} RCl$$

(16) Herwig, K.; Lorenz, P.; Rüchardt, C. *Chem. Ber.* **1975**, *108*, 1421.

Experimental Section[17]

5-Allyl-5-(carboethoxy)-2-cyclopentenone (4). To a tetrahydrofuran solution (500 mL) of diisopropylamine (38.8 mL, 0.27 mol) and *n*-butyllithium (0.27 mol) was added a mixture of 2-allyl-2-(carboethoxy)cyclopentanone (49 g, 0.25 mol) and hexamethylphosphoric triamide (88 g, 0.5 mol) at −78 °C. The mixture was stirred for 1 h at −78 °C. A solution of benzeneselenenyl bromide in ether (125 mL) freshly prepared from diphenyl diselenide (43.7 g, 0.14 mol) and bromine (22.4 g, 0.14 mol) was added in one portion and the mixture was stirred for an additional 15 min. Hydrochloric acid (1 N, 500 mL) was then added and the mixture was extracted with ether (3 × 500 mL). The combined organic layers were washed with hydrochloric acid (1 N, 500 mL), sodium bicarbonate solution (5%, 500 mL), water (4 × 500 mL), and brine solution (500 mL), dried over anhydrous magnesium sulfate, and filtered. The solvent was evaporated to give an oily brown residue (96.3 g) which was used for the next reaction without further purification.

The brown residue (96.3 g) was dissolved in tetrahydrofuran (600 mL) to which hydrogen peroxide (32%, 252 g, 2.37 mol) in tetrahydrofuran (240 mL) was added slowly at 0 °C over a period of 2 h. The mixture was stirred at room temperature for 8 h. Water (1 L) was added and the mixture was extracted with ether (3 × 500 mL). The ethereal solution was washed with water and brine solution (400 mL), dried over anhydrous magnesium sulfate, filtered, and evaporated in vacuo to give a brown residue (56 g), which was passed through a short silica gel column and eluted with benzene. Further purification by spinning band distillation gave **4** (17.4 g, 36%): bp 90–92 °C (6 mm); IR (neat) ν 1748 (CO, ester), 1717, 1646, 1597 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.20 (3 H, t, J = 7.2 Hz), 2.27–3.41 (4 H, m), 4.08 (2 H, q, J = 7.2 Hz), 4.82–5.99 (3 H, m), 6.10 (1 H, d, t, J_1 = 6, J_2 = 1.8 Hz), 7.71 (1 H, d, t, J_1 = 6, J_2 = 3 Hz); ^{13}C NMR ($CDCl_3$) δ 14.0 (CH_3), 38.5, 38.7 (C-4 and C-6), 57.3 (C-5), 61.6 (CH_2O), 119.1, 132.1, 132.7, 163.9 (C-3), 170.3 (CO, ester), 205.2 (C-1); mass spectrum, m/e 194.

Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.26. Found: C, 68.49; H, 7.22.

1-(Carboethoxy)tricyclo[3.2.1.0^{3,6}]octan-2-one (5a) and 1-(Carboethoxy)tricyclo[3.2.1.0^{3,6}]octan-7-one (5b). A solution of 5-allyl-5-(carboethoxy)-2-cyclopentenone (**4**; 1.5 g, 7.7 mmol) in tetrahydrofuran (550 mL) was irradiated (400-W, medium-pressure mercury arc lamp, Applied Photophysics 400LQ) under nitrogen at 0 °C for 2–3 h in a Pyrex photochemical reactor. The percentage of conversion was analyzed by gas chromatography. The solvent was evaporated in vacuo and the residue was distilled to afford a mixture of isomers **5a** and **5b** in a ratio of 10:1 (1.07 g, 71%): bp 83–85 °C (0.06 mm); IR (neat) ν 1960, 1732 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.28 (3 H, t, J = 7.2 Hz) 1.53–2.80 (8 H, m), 3.23 (1 H, m), 4.22 (2 H, q, J = 7.2 Hz); ^{13}C NMR for **5a**, δ 14.2 (CH_3), 34.6 (C-5), 36.0 (C-4), 38.8, 40.4 (C-7, C-8), 40.9 (C-6), 45.2 (C-3), 60.9 (CH_2O), 63.8 (C-1), 169.9 (CO, ester), 210.9 (C-2); ^{13}C NMR for **5b**, δ 14.2 (CH_3), 30.1 (C-3 and C-5), 36.0 (C-2 and C-8), 36.4 (C-4), 42.4 (C-6), 61.2 (CH_2O), 62.9 (C-1), 170.0 (CO ester), 212.2 (C-7); mass spectrum, m/e 194. Without further separation of the isomers, the mixture was used for the next reaction.

Thioketals 6a and 6b. To boron trifluoride etherate (10 mL) was added the isomeric mixture of 1-(carboethoxy)tricyclo-[3.2.1.0^{3,6}]octan-2-one (**5a**) and 1-(carboethoxy)tricyclo-[3.2.1.0^{3,6}]octan-7-one (**5b**; 7.5 g, 39 mmol) in ether (80 mL) at 0 °C. Methyl mercaptan (6 mL, 108 mmol, condensed at −78 °C) was added and the mixture was stirred for 2 h at room temperature and then poured into sodium hydroxide solution (10%, 100 mL). The ether layer was separated and washed with sodium hydroxide solution (10%, 2 × 100 mL) and water (2 × 100 mL), dried over anhydrous magnesium sulfate, filtered, and evaporated in vacuo. The residue was distilled to give a mixture of **6a** and **6b** (9.02 g, 85%): bp 105–110 °C (0.05 mm); IR (neat) ν 1732 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.26 (3 H, t, J = 7.0 Hz), 1.48–2.96 (15 H, m, embodied two singlets at 1.88 and 1.99), 4.08 (2 H, q, J = 7.0 Hz); mass spectrum, m/e 272. Without separation of the isomers, the mixture was used for the next reaction.

1-(Carboethoxy)tricyclo[3.2.1.0^{3,6}]octane (3). The isomeric mixture of the thioketals **6a** and **6b** (2.0 g, 7.35 mmol) in absolute ethanol was heated under reflux with an excess of W-2 Raney nickel (50 g) for 4 h. The excess Raney nickel was filtered and washed thoroughly with ethanol (200 mL) and then with benzene (500 mL). The solvent was removed in vacuo to afford a residue which was distilled to give **3** (1.2 g, 91%): bp 120–124 °C (20 mm); IR (neat) ν 1735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.24 (4 H, t, CH_3 embodied a multiplet 1 H), 1.62 (2 H, br s), 1.71–2.56 (7 H, m, embodied a singlet at 1.81), 2.85 (1 H, m), 4.08 (2 H, q); ^{13}C NMR ($CDCl_3$) δ 14.2 (CH_3), 34.6 (C-3 and C-5), 35.9 (C-4), 41.0 (C-2 and C-8), 43.2 (C-6), 44.0 (C-7), 53.1 (C-1), 59.9 (CH_2O), 175.3 (CO); mass spectrum, m/e 180.1167.

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.28; H, 8.95. Found: C, 72.97; H, 8.91.

Tricyclo[3.2.1.0^{3,6}]octane-1-carboxylic Acid (7). A solution of 1-(carboethoxy)tricyclo[3.2.1.0^{3,6}]octane (**3**; 1.3 g, 7.22 mmol) in aqueous sodium hydroxide solution (20%, 75 mL) was heated under reflux for 14 h, cooled to room temperature, and washed with ether (200 mL). The aqueous layer was neutralized with concentrated hydrochloric acid. The mixture was then extracted with ether (3 × 250 mL). The organic layer was washed with water (200 mL), dried over anhydrous magnesium sulfate, filtered, and evaporated to give a colorless solid which was sublimed to yield **7** (1.0 g, 91%): mp 106–107 °C; IR (KBr) ν 2955, 1696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.10–1.35 (1 H, m), 1.71 (2 H, s), 1.82–2.71 (7 H, m, embodied a singlet at 1.91), 2.92 (1 H, m), 11.92 (1 H, s); ^{13}C NMR ($CDCl_3$) δ 34.7 (C-3 and C-5), 35.8 (C-4), 40.9 (C-2 and C-8), 43.4 (C-6), 44.2 (C-7), 52.9 (C-1), 182.5 (CO); mass spectrum, m/e 152.0823.

Anal. Calcd. for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 71.47; H, 8.00.

***tert*-Butyl Tricyclo[3.2.1.0^{3,6}]octane-1-percarboxylate (8).** The carboxylic acid **7** (0.76 g, 5 mmol) in thionyl chloride (10 mL) was refluxed for 2 h. Removal of the excess thionyl chloride in vacuo gave the crude acid chloride, which was taken up in ether (15 mL). The reaction flask was cooled to 0 °C. Pyridine (0.5 mL) and *tert*-butyl hydroperoxide (0.5 g, 5.6 mmol) were added in that order. The mixture was stirred at room temperature for 3 h and poured onto ice–water. After separation of two layers, the organic portion was washed with ice-cold hydrochloric acid (5%, 3 × 10 mL), sodium bicarbonate solution (5%, 3 × 10 mL), and ice-cold water. The organic phase was dried over anhydrous magnesium sulfate and then evaporated in vacuo. The oily residue was chromatographed on a short silica gel column eluted with light petroleum ether to give pure **8** as a colorless thick liquid (0.91 g, 81%): IR (neat) ν 1758, 1345 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.12–1.70 (12 H, m, embodied two singlets at 1.31 and 1.63), 1.80–2.70 (7 H, m, embodied a singlet at 1.85), 2.85 (1 H, m); mass spectrum, m/e 224.1556 (calcd for $C_{13}H_{20}O_3$, 224.1562).

Tricyclo[3.2.1.0^{3,6}]octane (9). The perester **8** (100 mg, 0.45 mmol) in triisopropylbenzene (5 mL) was refluxed for 1 h. The mixture was cooled to room temperature. Careful distillation at ca. 1 mm while keeping the bath temperature below 80 °C afforded the hydrocarbon **9**, which was further purified by sublimation (19.4 mg, 40%): mp 110–112 °C (sealed tube, lit.[3] mp 111 −112 °C).

1-Tricyclo[3.2.1.0^{3,6}]octylamine Hydrochloride (10). Triethylamine (174.9 mg, 1.73 mmol) in acetone (2.8 mL) was added dropwise to a solution of tricyclo[3.2.1.0^{3,6}]octane-1-carboxylic acid (**7**; 200 mg, 1.32 mmol) in acetone (2.8 mL) and water (0.3 mL) at 0 °C. Ethyl chloroformate (176.2 mg, 1.74 mmol) in acetone (1 mL) was added dropwise and the mixture was stirred for 30 min. A solution of sodium azide (135 mg, 2.08 mmol) in water (0.6 mL) was subsequently added and stirred for 2 h at 0 °C. The mixture was poured onto ice–water and extracted with chloroform (4 × 20 mL). The organic solution was dried over anhydrous sodium sulfate, filtered, and evaporated to give crude azide (240 mg) as a yellow oil: IR (neat) ν 2140 cm^{-1}. The crude azide in benzene (35 mL) was refluxed for 1 h, and benzene was removed by distillation at normal pressure to give a yellow oil (200 mg) as the crude isocyanate: IR (neat) ν 2280 cm^{-1}. The crude isocyanate in tetrahydrofuran (10 mL) and concentrated hydrochloric acid (5 mL) was refluxed for 1 h, cooled to room temperature, diluted with water (50 mL), and then washed with ether (2 × 30

(17) Melting points and boiling points are uncorrected. IR spectra were recorded on a Perkin-Elmer 283 spectrophotometer, ^{1}H NMR on a JEOL 60 HL spectrometer, ^{13}C NMR spectra on a JEOL FX 90Q spectrometer (tetramethylsilane as the internal standard), and mass spectra on a VG 7070F mass spectrometer. Microanalyses were performed by the Australian Microanalytical Service, Melbourne.

mL). The aqueous layer was separated and evaporated in vacuo to give a colorless solid which was recrystallized from acetone/methanol to yield **10** (150 mg, 71%): mp 223 °C dec; ^{1}H NMR (Me_2SO-d_6) δ 1.17–1.27 (1 H, m), 1.43–2.38 (9 H, m, embodied two singlets at 1.63 and 1.80), 2.78 (1 H, m), 8.73 (3 H, br s); ^{13}C NMR (Me_2SO-d_6) δ 33.6 (C-3 and C-5), 34.4 (C-4), 40.0 (C-2 and C-8), 40.3 (C-6), 41.8 (C-7), 60.0 (C-1); mass spectrum, *m/e* 123.1044 (M − HCl, calcd for $C_8H_{13}N$ 123.1048).

1-Bromotricyclo[3.2.1.0^{3,6}]octane (11). Tricyclo[3.2.1.0^{3,6}]-octane-1-carboxylic acid (**7**; 200 mg, 1.32 mmol) and red mercuric oxide (286 mg, 1.32 mmol) in dibromomethane (50 mL) was heated to 80 °C and bromine (300 mg, 1.88 mmol) was added dropwise and the mixture was refluxed for 2 h. Dibromomethane was removed by distillation; *n*-pentane (200 mL) was added, and the pentane solution was washed with 10% of sodium hydroxide solution (50 mL), dried over anhydrous magnesium sulfate, filtered, evaporated, and purified by molecular distillation to give a colorless oil, which was further purified by preparative gas chromatography (60 °C, 6, ft, 1% SIL. GUM. GE. XE-60 on 60-70W AW. DMCS) to give the pure bromide **11** (170 mg, 69%): ^{1}H NMR ($CDCl_3$) δ 1.29–1.39 (1 H, m), 1.55 (2 H, s), 1.87 (2 H, s), 2.08–2.45 (5 H, m), 2.71 (1 H, m); ^{13}C NMR ($CDCl_3$) δ 35.3 (C-3 and C-5), 36.1 (C-4), 40.8 (C-2 and C-8), 48.3 (C-6), 49.4 (C-7), 60.1 (C-1); mass spectrum, *m/e* 186.0065, 188.0033 (calcd for $C_8H_{11}{}^{79}Br$, 186.0044; calcd for $C_8H_{11}{}^{81}Br$, 188.0024).

1-(Hydroxymethyl)tricyclo[3.2.1.0^{3,6}]octane (2). A solution of 1-(carboethoxy)tricyclo[3.2.1.0^{3,6}]octane (**3**; 1.07 g, 5.94 mmol) in tetrahydrofuran (10 mL) was added to a slurry of lithium aluminum hydride (2 g, 52.7 mmol) in tetrahydrofuran (30 mL) under nitrogen at 0 °C. It was stirred at 0 °C for an additional 4 h and then at room temperature for 48 h. Sodium sulfate solution (10%, 30 mL) was then added, and the solid was filtered. The solid was washed thoroughly with diethyl ether. The aqueous layer was extracted with ether (3 × 20 mL). The combined ethereal extracts were washed with water (50 mL), dried over anhydrous magnesium sulfate, filtered, and evaporated, and the residue was distilled to give **2** (0.73 g, 89%): bp 112–114 °C (20 mm); IR (neat) ν 3368 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.14–1.17 (8 H, m, embodied two singlets at 1.29 and 1.54), 1.94–2.48 (3 H, m), 2.79 (1 H, m), 3.76 (2 H, s); ^{13}C NMR ($CDCl_3$) δ 34.8 (C-3 and C-5), 35.9 C-4), 40.0 (C-2 and C-8), 42.0 (C-7), 43.0 (C-6), 50.9 (C-1), 66.3 (CH_2O); mass spectrum, *m/e* 138.1110.

Anal. Calcd for $C_9H_{14}O$: C, 78.20; H, 10.22. Found: C, 77.94; H, 10.06.

1-Chlorotricyclo[3.2.1.0^{3,6}]octane (12). Tricyclo[3.2.1.0^{3,6}]-octane-1-carboxylic acid (**7**; 100 mg, 0.66 mmol) and red mercuric oxide (150 mg, 0.69 mmol) in carbon tetrachloride (20 mL) was heated to 80 °C to which bromine (160 mg, 1 mmol) in carbon tetrachloride (5 mL) was added dropwise. The mixture was refluxed for 2 h and then cooled, filtered, and evaporated to give a colorless oil which was a mixture of the bromide **11** and the chloride **12** in a ratio of 14:86 as exhibited on the gas chromatogram. Pure **12** was obtained by preparative gas chromatography (60 °C, 6, 1% SIL. GUM. GE XE-60, ON 60-70W. AW. DMCS) as a colorless liquid (60 mg, 61%): ^{1}H NMR ($CDCl_3$) δ 1.30 (1 H, m), 1.54 (2 H, s), 1.78 (2 H, s), 1.99–2.41 (5 H, m), 2.78 (1 H, m); mass spectrum, *m/e* 142.0520, 144.0521 (calcd for $C_8H_{11}{}^{35}Cl$, 142.0549; calcd for $C_8H_{11}{}^{37}CL$, 144.0519).

Anal. Calcd for $C_8H_{11}Cl$: C, 67.35; H, 7.78. Found: C, 67.11; H, 7.70.

1-(Chloromethyl)tricyclo[3.2.1.0^{3,6}]octane (13). 1-(Hydroxymethyl)tricyclo[3.2.1.0^{3,6}]octane (**2**; 138 mg, 1 mmol) was stirred with excess thionyl chloride (2.5 mL) at room temperature for 22 h. The mixture was poured onto ice and then extracted with ether (3 × 25 mL). The combined ethereal solution was washed with saturated sodium bicarbonate solution (2 × 50 mL) and water (50 mL), dried over anhydrous magnesium sulfate, filtered, and evaporated. The residue was purified by column chromatography on alumina eluted with petroleum ether (50–75 °C) to give **13** (96 mg, 62%) as an oil, which was purified by molecular distillation: ^{1}H NMR ($CDCl_3$) δ 1.12–1.42 (4 H, m), 1.46–1.80 (3 H, m, embodied a singlet at 1.53), 2.04–2.44 (3 H, m), 2.76 (1 H, m), 4.08 and 4.20 (2 H, an AB system, J = 10.2 Hz); ^{13}C NMR ($CDCl_3$) δ 34.9 (C-3 and C-5), 35.9 (C-4), 40.5 (C-2 and C-8), 42.6 (C-7), 43.1 (C-6), 48.8 (C-1), 65.4 (CH_2Cl); mass spectrum, *m/e* 121 (M − Cl).

Anal. Calcd for $C_9H_{13}Cl$: C, 68.98; H, 8.37. Found: C, 68.78; H, 8.26.

pK_a Measurement. (a) 50% (v/v) Methanol-Water.[18] The Chemtrix type 60 A pH meter with BJC pH electrode was employed for pH measurements. Sodium hydroxide solution was prepared by dilution of 0.1 N aqueous sodium hydroxide solution with an equal volume of methanol and was standardized against potassium phthalate. The method was checked by the determination of the pK_a value of benzoic acid. The carboxylic acid was dissolved in 50% (v/v) methanol–water and titrated with the standardized sodium hydroxide solution. After each increment of base was added, the solution was stirred for 45 s followed by a waiting period of 1 min. The pH was then measured. The pK_a value of the carboxylic acid was determined from the pH at the half-neutralization point.

(b) 50% (w/w) Ethanol–Water.[9] The procedure was followed as described above except that 50% (v/v) methanol–water was replaced by 50% (w/w) ethanol–water.

Selectivity Study: Hunsdiecker Reactions. Equal molar quantities of mecuric oxide and the carboxylic acid were mixed with a 100-fold molar quantity of purified carbon tetrachloride. The suspension was heated to reflux (78 °C). An equivalent amount of bromine was added dropwise to the mixture and the mixture was refluxed for 1 h. The cooled solution was filtered to remove any solid residues. The filtrate was analyzed by gas chromatography. The products were identified by spectroscopic methods following their isolation by preparative VPC and comparison with authentic materials. A typical experiment for the carboxylic acid **7** is summarized.

The carboxylic acid **7** (50.6 mg, 0.33 mmol) and mercuric oxide (red, 71.3 mg, 0.33 mmol) in carbon tetrachloride (5.06 g, 33 mmol) were heated to 80 °C. Bromine (17 μL, 0.33 mmol) was added with a microsyringe. The mixture was refluxed for 1 h, cooled, and filtered. The filtrate was analyzed by gas chromatography (60 °C, 6, ft, 1% SIL. GUM. GE XE-60 ON 60-70W. AW. DMCS), which indicated that the ratio of the bromide **11** and the chloride **12** was 42:58.

Selectivity Study: Thermal Decomposition of *tert*-Butyl Peresters in Carbon Tetrachloride and Bromotrichloromethane. A solution of the *tert*-butyl perester and triphenylmethane in bromotrichloromethane and carbon tetrachloride was immersed in a constant temperature bath at 80 °C for several hours. The cooled solution was analyzed by VPC as described for the Hunsdiecker reaction. A typical experiment for the decomposition of the perester **8** is described.

The perester **8** (112 mg, 0.5 mmol), bromotrichloromethane (510 mg, 2.5 mmol), and triphenylmethane (610 mg, 2.5 mmol) were dissolved in carbon tetrachloride (7.7 g, 0.05 mol). The reaction mixture was immersed in a thermostat at 80 °C for 72 h. Analysis of the cooled solution indicated that the chloride **12** and the bromide **11** were produced in a ratio of 1:3.2, respectively.

Registry No. **2**, 78303-65-8; **3**, 78303-64-7; **4**, 78303-58-9; **5a**, 78303-60-3; **5b**, 78303-61-4; **6a**, 78303-62-5; **6b**, 78303-63-6; **7**, 79647-58-8; **7** azide, 79647-63-5; **7** isocyanate, 79647-64-6; **8**, 79647-59-9; **9**, 250-22-6; **10**, 79647-60-2; **11**, 79663-51-7; **12**, 79647-61-3; **13**, 79647-62-4; 2-allyl-2-(carboethoxy)cyclopentanone, 41975-67-1; 1-tricyclo[3.2.1.0^{3,6}]octyl radical, 79647-65-7.

(18) Kuhn, R.; Wassermann, A. *Helv. Chim Acta* **1928**, *11*, 1.