Table I
Relative Reactivities of Aromatics toward Undecyl Radicals at 81°

Registry no.	Compd	Relative reactivity[a]
104-85-8	*p*-Cyanotoluene	2.03 ± 0.02
100-47-0	Benzonitrile	1.78 ± 0.02
620-22-4	*m*-Cyanotoluene	1.66 ± 0.02
108-41-8	*m*-Chlorotoluene	1.24 ± 0.03
104-93-8	*p*-Methoxytolutne	1.24 ± 0.01
352-70-5	*m*-Fluorotoluene	1.16 ± 0.03
100-84-5	*m*-Methoxytoluene	1.12 ± 0.01
106-43-4	*p*-Cholorotoluene	1.09 ± 0.01
352-32-9	*p*-Fluorotoluene	1.04 ± 0.03
108-88-3	Toluene	1.00[b]
108-38-3	*m*-Xylene	0.97 ± 0.01[c]
106-42-3	*p*-Xylene	0.89 ± 0.02[c]
108-90-7	Chlorobenzene	0.72 ± 0.01
100-66-3	Anisole	0.45 ± 0.04

[a] Against toluene; each entry represents the results of at least two runs, each analyzed in triplicate. [b] Assigned. [c] Normalized.

only 14% greater than that of benzonitrile, an indication of preponderance of addition over benzyl hydrogen abstraction for this toluene. *p*-Chlorotoluene is 50% more reactive than chlorobenzene, indicating that addition and benzyl hydrogen abstraction are roughly comparable in this case. *p*-Methoxytoluene is 270% more reactive than anisole, indicating that benzyl hydrogen abstraction is predominant for this toluene.

A study of all the data in Table I supports the inferences that (1) electron-withdrawing groups on the aromatic nucleus increase the rate of addition by undecyl radicals, and (2) electron-donating groups increase the rate of benzyl hydrogen abstraction. The first inference is in agreement with the conclusions of Shelton and Uzelmeir on additions of secondary alkyl radicals to substituted benzenes,[8] and the second with our predictions regarding abstractions by alkyl radicals.[2]

Our analyses indicate that the amount of undecane obtained exceeds the combined amounts of toluenes reacted, in all cases, often by as much as 25%. The stoichiometry of alkane formation following addition is not clear enough to warrant any additional quantitative conclusions. However, it is well known that methane-*d* is one of the products of the reaction of methyl radicals with ring-deuterated toluene.[9]

A serious discrepancy exists between the value of relative reactivity for *p*-methoxytoluene determined by us (1.24 by GLC) and that of Pryor et al.[5] (0.69 by NMR of the benzylic CH_3).

If the data for *p*-methoxytoluene and for the benzenes are disregarded (Table I), a Hammett plot of *total* reactivity for the remaining toluenes gives $\rho = 0.4$, with tolerable scatter. This is near the value of 0.47 reported by Henderson and Ward,[4] and 0.50 by Pryor and Davis;[5] both groups have described their Hammett plots as reflecting benzylic hydrogen abstraction exclusively.[10]

It must be pointed out that our results can support only tentative interpretations at this point. Kinetic studies, such as this and similar ones,[3-6] without fairly complete mass balance, should be interpreted with care.[11]

Experimental Section

Relative reactivities were determined by direct competition against toluene. Each toluene or substituted benzene was made approximately 0.67 *M* in benzene and brought to a gentle reflux; a solution of lauroyl peroxide in benzene was added over a 15-min period to a final concentration of 0.47 *M*. Reflux was continued for 36 hr. A blank (no peroxide) was treated in the same way. Each experiment was performed at least twice. Analyses were performed by GLC in triplicate; *p*-dichlorobenzene was added at the completion of the reaction as an internal standard.

Registry No.—Undecyl radical, 55101-35-4.

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Reaction of Ketene Bis(trimethylsilyl) Acetals with *m*-Chloroperbenzoic Acid. Synthesis of α-Hydroxycarboxylic Acids

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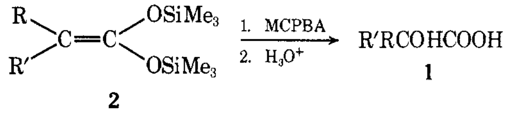
Available methods for the preparation of α-hydroxycarboxylic acids, **1**, include the aeration of lithiated carboxylic acids,[1] the hydrolysis of α-acyloxycarboxylic acids,[2] and the Favorski reaction.[3] Recently, also syntheses of **1** via trihalomethylcarbinols[4] and by use of the Pummerer reaction[5] have been noted.

We should like to report here that the oxidation of ketene bis(trimethylsilyl) acetals, **2**, with *m*-chloroperbenzoic acid (MCPBA), followed by mild acid hydrolysis, affords an extremely general, high-yield method for the preparation of **1** (Scheme I). The data included in Table I indicate the utility of the method.

Scheme I



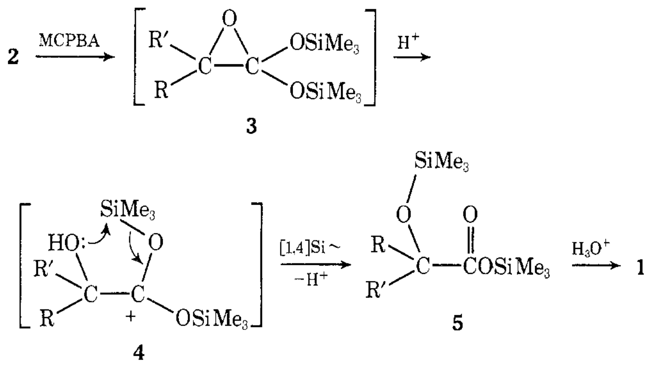
The mode of reaction of **2** with MCPBA may be envisioned as shown in Scheme II. This mechanistic route follows closely the scheme proposed for the reaction of trimethylsilyl enol ethers with MCPBA.[6] The presence of **5b** in the reaction mixture obtained from treating **2b** with MCPBA, prior to hydrolysis, was ascertained by direct distillation of the crude reaction mixture. Despite a great deal of decomposition, a 32% yield of **5b** was obtained. The structure of **5b** was verified by NMR and mass spectral comparison with authentic **5b.** The low yield of **5b** obtained by this procedure makes mechanistic considerations somewhat tenuous, but, based on analogy,[6] a [1,4]silatropic shift accounting for the production of **5b** seems to best fit the data.[6,7] No evidence for the presence of **3** was noted, but, in

Table I
Preparation of α-Hydroxycarboxylic Acids 1

2[a]	1[a]	% yield of 1[b]	Mp (lit. mp), °C
$Ph_2C{=}C(OSiMe_3)_2$ (**2a**)	Ph_2COHCO_2H (**1a**)	81	149–150.5 (148–150[c])
$PhCH{=}C(OSiMe_3)_2$ (**2b**)	$PhCHOHCO_2H$ (**1b**)	82	119–120.5 (118–120[c])
p-OMe—$PhCH{=}C(OSiMe_3)_2$ (**2c**)	*p*-OMe—$PhCHOHCO_2H$ (**1c**)	83	101–103 (98–102[c])
t-$BuCH{=}C(OSiMe_3)_2$ (**2d**)	*t*-$BuCHOHCO_2H$ (**1d**)	50	84–86 (91[d])
$C_5H_{10}C{=}C(OSiMe_3)_2$ (**2e**)	$C_5H_{10}COHCO_2H$ (**1e**)	80	106–107 (106–107[e])

[a] All compounds show ir, NMR, and mass spectral data consistent with the proposed structure. [b] Yields based on isolated, pure **1**; average of at least two runs. [c] Values taken from ref 1. [d] Authentic **1d** prepared by the method of M. Charpentier-Morize, *Bull. Soc. Chim. Fr.*, 920 (1962), gave a melting point of 84–86°, and showed no melting point depression upon admixture with **1d** prepared by the present method. [e] J. Rouzoud, G. Cauquil, and L. Giral, *ibid.*, 2908 (1964).

Scheme II



the case of the oxidation of trimethylsilyl enol ethers, an analogous epoxide has been isolated,[6b] making **3** a likely intermediate in the oxidation of **2**.

Experimental Section

Preparation of Ketene Bis(trimethylsilyl) Acetals, 2. The method of Ainsworth and Kuo[8] afforded the ketene bis(trimethylsilyl) acetals, **2a–e**, in yields of ca. 80%. Physical properties of **2a**, **2b**, **2d**, and **2e** were in accord with the literature values. Compound **2c**: bp 113–114° (0.5 mm); $n^{26.5}D$ 1.5868; ir ($CHCl_3$) 1655 cm^{-1}; NMR (CCl_4-Me_4Si) δ 0.18 (9 H, s), 0.22 (9 H, s), 3.65 (3 H, s), 4.41 (1 H, s), 6.50–7.30 (4 H, m); MS M^+ *m/e* (rel abundance) 310 (31), 295 (3), 148 (95), 147 (40), 120 (17), 75 (20), 73 (100).

Anal. Calcd for $C_{15}H_{26}O_3Si_2$: C, 58.02; H, 8.44. Found: C, 58.30; H, 8.37.

Preparation of α-Hydroxycarboxylic Acids, 1. General Procedure. A precooled (ice–methanol bath), stirred solution of 1.8 mmol of MCPBA in 10 ml of dry hexane under 1 atm of N_2 was treated with a solution containing 1.8 mmol of **2** in 10 ml of dry hexane (ca. 5 min addition time). After the addition was complete, the resulting slurry was stirred at room temperature for 30 min. After filtration of the mixture to remove the bulk of *m*-chlorobenzoic acid formed in the reaction, the crude filtrate was partitioned between 20 ml of ether and 20 ml of 1.5 *N* hydrochloric acid. After brief shaking, the layers were separated and the aqueous layer was extracted with 3 × 20 ml of ether. The combined ethereal portion was dried with anhydrous magnesium sulfate. Filtration, followed by solvent removal in vacuo, afforded crude **1** which was purified by a combination of sublimation and crystallization from chloroform–hexane mixtures.

Preparation of Trimethylsilyl-α-(trimethylsiloxy) Phenylacetate (5a). To a solution containing 20 mmol of dry triethylamine, 40 mmol of chlorotrimethylsilane, and 120 ml of dry THF was added, with stirring, under N_2, a solution containing 10 mmol of *dl*-mandelic acid (**1b**) in 30 ml of dry THF (ca. 5 min addition time). The resulting mixture was then stirred overnight at room temperature. The slurry was then filtered and the solvent removed in vacuo. The residue was then diluted with 60 ml of dry ether and the resulting mixture filtered once again. Removal of solvent in vacuo, followed by distillation at reduced pressure, afforded a 91% yield of pure trimethylsilyl-α-(trimethylsiloxy) phenylacetate (**5b**): bp 78–79° (0.65 mm); $n^{22}D$ 1.5688; ir (CCl_4) 1740 cm^{-1}; NMR (CCl_4-CH_2Cl_2) δ 0.18 (9 H, s), 0.22 (9 H, s), 5.10 (1 H, s), 7.2–7.5 (5 H, m); M^+ *m/e* (rel abundance) 296 (1), 281 (4), 179 (100), 147 (26), 75 (9), 73 (65).

Anal. Calcd for $C_{14}H_{24}O_3Si_2$: C, 56.71; H, 8.16. Found: C, 56.65; H, 7.89.

Acid hydrolysis of **5b** (see above) afforded a quantitative yield of **1b**, mp 118.5–119.5°.

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Registry No.—**1a**, 76-93-7; **1b**, 611-72-3; **1c**, 10502-44-0; **1d**, 4026-20-4; **1e**, 1123-28-0; **2a**, 31469-27-9; **2b**, 31491-21-1; **2c**, 56817-43-7; **2d**, 31469-23-5; **2e**, 40348-04-7; **5a**, 2078-19-5; *m*-chloroperbenzoic acid, 937-14-4.

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Transformation of 1-Azirines to 1*H*-Indoles with Benzyne. Evidence for the Intermediacy of the 3*H*-Indole System

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The synthetic capabilities of *o*-benzyne have been examined and utilized effectively in recent years.[1] It appears to possess a symmetric singlet ground state,[2] behaves as a highly reactive ethylenic component, and participates in cycloadditions with olefins and dienes in a [2 + 2], [2 + 4], or "ene" fashion.[1-10] Although the reaction of benzyne with enamines has been studied,[5,16] little is known about the reactivity of benzyne toward C=N bonds. We wish to report on the reaction of benzyne with the reactive C=N bond of the 1-azirine ring system.

Results and Discussion

2,3-Diphenyl-1-azirine (**1**) reacts with excess *o*-benzyne, generated by the thermal decomposition of benzenediazonium 2-carboxylate,[11] to give two products. The major product, a 1:1 adduct produced in 50% yield, was identified as