2-(2-Methoxybenzoyl)-3-methoxybenzoic Acid (9a). Compound **9a** was obtained by hydrolysis of the crude reaction mixture containing **5** and the desired product oxazoline, followed by a single recrystallization from chloroform–methanol, as white prisms: 56% yield; mp 171.5–173.5 °C; ^{1}H NMR ($(CD_3)_2SO$) δ 3.48 (s, 3, OCH_3), 3.68 (s, 3, *m*-HOOCArOCH_3), 6.95–7.88 (m, 8, Ar H and COOH); ^{13}C NMR ($(CD_3)_2SO$) δ 55.7, 56.0, 113.0, 115.4, 120.3, 121.9, 127.1, 129.1, 129.8, 131.0, 134.2, 156.1, 159.6, 167.3, 193.2. One further recrystallization (chloroform–methanol) gave analytically pure **9a** as large, clear prisms, mp 172–173.5 °C.

Anal. Calcd for $C_{16}H_{14}O_5$: C, 67.13; H, 4.93. Found: C, 67.36; H, 4.81.

2-(4-Methoxybenzoyl)-3-methoxybenzoic Acid (9b). Hydrolysis of the crude reaction mixture containing **5** and the desired oxazoline, followed by one recrystallization from chloroform, afforded **9b** as white prisms: 57% yield; mp 169.5–171.5 °C; ^{1}H NMR ($CDCl_3$/$(CD_3)_2SO$) δ 3.68 (s, 3, OCH_3), 3.79 (s, 3, OCH_3), 6.70–7.80 (m, 7. Ar H), 9.00 (br s, 1, COOH); ^{13}C NMR ($(CD_3)_2SO$) δ 55.4, 56.0, 113.8, 115.8, 122.0, 130.1, 130.2, 130.5, 130.7, 156.3, 162.9, 166.5, 193.4. A small sample was recrystallized once more from chloroform–cyclohexane to provide an analytical sample of **9b** as white prisms, mp 171.5–173 °C.

Anal. Calcd for $C_{16}H_{14}O_5$: C, 67.13; H, 4.93. Found: C, 66.89; H, 4.88.

2-[2,5-Bis(benzyloxy)-4-methylbenzoyl]-3-methoxybenzoic Acid (12). (*m*-Methoxyphenyl)oxazoline **5** (1.68 g, 8.18 mmol) was metalated at −45 °C with butyllithium for 5 h in accordance with the general procedure. Acid chloride **10**[15,16] (3.00 g, 8.18 mmol) was added to the aryllithium reagent at −100 °C as in the general procedure, and then the solution was stirred for 0.5 h at −100 °C. The solution was then warmed to 25 °C over 2 h and stirred overnight at ambient temperature. The orange solution was poured into 50 mL of saturated aqueous NaCl, the resulting mixture was stirred vigorously for 60 min, the layers were separated, and the aqueous layer was extracted with chloroform (3 × 75 mL). The organics were combined, washed with saturated aqueous $NaHCO_3$ (2 × 70 mL) and saturated aqueous NaCl (2 × 70 mL), dried, filtered, and concentrated to afford 5.16 g of heavy orange oil which was methylated by adding methyl iodide (20 mL) and stirring overnight. The reaction mixture was concentrated, THF (30 mL) and 1 N NaOH (20 mL) were added to the residue, and hydrolysis[17] was completed by vigorous stirring for 7 days at ambient temperature. Ether (40 mL) was added to the reaction mixture, the layers were separated, and the aqueous layer was extracted with ether (2 × 50 mL) and chloroform (2 × 50 mL). The combined organic extracts were washed with saturated aqueous $NaHCO_3$ (2 × 50 mL) to remove *m*-methoxybenzoic acid from the bicarbonate-insoluble **12**, with water (10 mL), and with saturated aqueous NaCl (50 mL). The organic extract was dried, filtered, and concentrated to 4.17 g of heavy orange oil. Recrystallization from benzene afforded 1.62 g of **12** (3.36 mmol, 41%) as a white powder: mp 178–181.5 °C; ^{1}H NMR ($CDCl_3$) δ 2.28 (s, 3, $ArCH_3$), 3.63 (s, 3, OCH_3), 4.77 (s, 2, benzylic CH_2 meta to ketone), 5.01 (s, 2, benzylic CH_2 ortho to ketone), 6.50 (br s, 1, COOH), 6.80–7.55 (m, 13, Ar H); ^{13}C NMR ($CDCl_3$) δ 17.0, 56.0, 70.5, 71.2, 112.7, 115.8, 116.2, 121.7, 124.8, 127.4, 127.7, 128.3, 128.4, 129.1, 134.1, 135.9, 136.1, 137.4, 151.1, 153.0, 155.7, 170.5. One further recrystallization from benzene afforded an analytical sample of **12** as a white powder, mp 183.5–185 °C.

Anal. Calcd for $C_{30}H_{26}O_6$: C, 74.67; H, 5.43. Found: C, 74.65; H, 5.42.

2-(2,5-Dihydroxy-4-methylbenzoyl)-3-methoxybenzoic Acid (13). Dibenzyl ether **12** (100 mg, 0.207 mmol) was dissolved in 50 mL of ethyl acetate and placed in a round-bottomed flask with 300 mg of 10% Pd/C and a magnetic stirring bar. The stirred mixture was hydrogenated under 1 atm of H_2 at 20 °C for 5 h, filtered, and concentrated; the residue was recrystallized from methanol–water to give **13** as yellow needles: 50 mg (0.165 mmol, 80%); mp 232–234 °C dec (lit.[18] mp 228–231 °C decomp); ^{1}H NMR ($C(CD_3)_2CO$) δ 2.21 (s, 3, $ArCH_3$), 3.73 (s, 3, OCH_3), 4.70 (br s, 3, OH), 6.48 (s, 1, *o*-CH_3Ar**H**), 6.68 (s, 1, *m*-CH_3Ar**H**), 7.08–7.75 (m, 3, Ar H); ^{13}C NMR ($CDCl_3$/$(CD_3)_2SO$) δ 15.1, 54.5, 114.1, 117.5, 120.9, 128.3, 128.7, 134.1, 145.7, 154.2, 155.2, 164.4.

Registry No. **1a**, 19312-06-2; **3a**, 80764-39-2; **3b**, 80764-40-5; **3c**, 80764-41-6; **3d**, 80764-42-7; **3e**, 80764-43-8; **3f**, 80764-44-9; **4a**, 85-52-9; **4b**, 85-55-2; **4c**, 85-56-3; **4d**, 1151-15-1; **4e**, 2159-36-6; **4f**, 1151-04-8; **5**, 73453-77-7; **9a**, 80764-46-1; **9b**, 80764-47-2; **10**, 40931-17-7; **12**, 80764-48-3; **13**, 80764-49-4; *m*-anisic acid, 586-38-9; benzoyl chloride, 98-88-4; *p*-methylbenzoyl chloride, 874-60-2; *p*-chlorobenzyl chloride, 122-01-0; *p*-methybenzoyl chloride, 100-07-2; *m*-methoxybenzoyl chloride, 1711-05-3; *o*-methoxybenzoyl chloride, 21615-34-9.

Biphasic Sonochemistry. Convenient Generation of Dichlorocarbene[1]

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We herein report an unusually simple procedure for the generation of dichlorocarbene. Our method is based on the action of ultrasound derived from a common laboratory cleaner on stirred $NaOH/CHCl_3$ two-phase systems.[2] Dichlorocarbene formed in this manner adds readily to alkenes, affording excellent yields of corresponding dichlorocyclopropanes.

Effective reaction between sodium hydroxide and chloroform to produce dichlorocarbene normally requires the use of a phase-transfer catalyst.[3-5] We have now discovered that such catalysts are unnecessary in solid/liquid systems, provided that efficient stirring and ultrasonic irradiation are employed. Immersion of a mixture of powdered sodium hydroxide and chloroform solution of styrene (2 mmol) into a bath cleaner, followed by ultrasonic irradiation and mechanical stirring, afforded at 95% isolated yield of 1,1-dichloro-2-phenylcyclopropane after 1.5 h. Similar isolated yields of dichlorocyclopropanes have been obtained for a variety of substituted alkenes and are presented in Table I. In general, reaction times and yields compare favorably with analogous phase-transfer procedures reported in the literature.[3-5] While small-scale preparations gave excellent and reproducible results, larger reactions (>5 mmol of alkene) gave poor conversions; we assume that this is due to the limited power of the bath cleaner used. Competition experiments carried out with cyclohexene as a reference standard further reveal that the selectivity of this carbene is very similar to that produced from $KOC(CH_3)_3/CHCl_3$ systems (Table II).[6]

The major advantage of this new dichlorocarbene generation procedure lies in its simplicity and the avoidance of phase-transfer catalysts. It should find broad use, especially for small-scale preparations of dichlorocyclopropanes.

Experimental Section

General Methods. Unless stated otherwise, all reagents and chemicals were obtained commercially and were used without further purification. Reagent grade chloroform (Aldrich) used in all experiments contained 0.75% ethanol. All ^{1}H NMR and IR spectra were recorded with Varian A-60 and Beckman Acculab

(1) Supported by the National Science Foundation (Grant No. CHE 8103083).

(2) For recent applications of ultrasound in heterogeneous organic reactions, see Raucher, S.; Klein, P. *J. Org. Chem.* **1981** *46*, 3558 and references cited therein.

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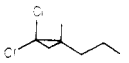
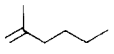
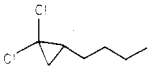
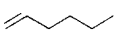
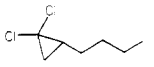
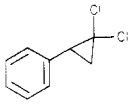
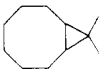
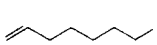
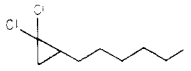
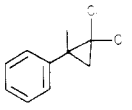
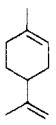
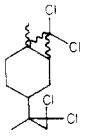
Table I. Dichlorocarbene Addition to Alkenes

reactant	product	time, %	isolated yield, %
		0.7	74
		1.8	80
		1.0	96
		3.0	93
		3.0	62
		1.0 16.0 20.0	96 31 [a] 38 [b]
		5.0	99
		6.5	81
		1.5	97
		3.0	95

[a] Mechanical stirring only. [b] Ultrasonic irradiation only.

Table II. Relative Reactivities toward Dichlorocarbene Addition

alkene	NaOH/$CHCl_3$ [a] (sonication and stirring), 30-40 °C	$KOC(CH_3)_3$/$CHCl_3$, [b] -15 °C
2,3-dimethyl-2-butene	57.2	53.7
2-methyl-1-pentene	4.2	
cyclohexene	1.0	1.0
1-hexene	0.2	0.2

[a] Reaction of 5 mmol of alkene plus 5.0 mmol of cyclohexene (reference standard) with 0.5 mmol of NaOH in 20 mL of $CHCl_3$. [b] See ref 6.

7 spectrometers, respectively. Product mixtures were analyzed by GLC on a Hewlett Packard Model 5830 A flame-ionization instrument (2 ft × 0.125 in. UCW-982 on Chromosorb W column). Ultrasound was produced with a L&R T-9 (Sargent Welch) bath-type sonicator (45 kHz, 35 W).

General Procedure for Preparation of Dichlorocyclopropanes. Procedures similar to that used for the conversion of styrene to 1,1-dichloro-2-phenylcyclopropane were followed for all of the reactions described in Table I. A mixture of powdered NaOH (0.8 g, 20 mmol) and styrene (0.21 g, 2.0 mmol) dissolved in 20 mL of chloroform was placed in a 100-mL, three-necked, round-bottomed flask equipped with a mechanical stirrer (standard 4-cm curved Teflon blade). The flask was immersed in a sonic cleaner and was positioned approximately 0.5 in. above the floor of the cleaning bath. The mixture was then simultaneously stirred and irradiated with ultrasound for 1.5 h (the temperature of the bath never exceeded 40 °C). Analysis of the liquid phase (GLC) indicated the complete disappearance of styrene. The contents was then centrifuged and the organic layer separated. After chloroform was removed under reduced pressure, the residue was dissolved in ether, washed with water, dried ($MgSO_4$), and distilled (Kugelrohr) to give 0.36 g (95%) of 1,1-dichloro-2-phenylcyclopropane having an IR and NMR spectrum which was identical with that of an authentic sample.

Registry No. 2,3-Dimethyl-2-butene, 563-79-1; 2-methyl-1-pentene, 763-29-1; 2-methyl-1-hexene, 6094-02-6; cyclohexene, 110-83-8; 1-hexene, 592-41-6; styrene, 100-42-5; cyclooctene, 931-88-4; 1-octene, 111-66-0; α-methyl styrene, 98-83-9; 1-methyl-4-(1-methylethenyl)-cyclohexene, 138-86-3; 1,1-dichloro-2,2,3,3-tetramethylcyclopropane, 3141-45-5; 1-(1-methyl-2,2-dichlorocyclopropyl)propane, 52259-98-0; 1-(1-methyl-2,2-dichlorocyclopropyl)butane, 80822-57-7; 7,7-dichlorobicyclo[4.1.0]heptane, 823-69-8; 1-(2,2-dichlorocyclopropyl)-butane, 3722-08-5; 1,1-dichloro-2-phenylcyclopropane, 2415-80-7; 9,9-dichlorobicyclo[6.1.0]nonane, 6498-44-8; 1-(2,2-dichlorocyclopropyl)hexane, 5685-42-7; 1,1-dichloro-2-methyl-2-phenylcyclopropane, 3591-42-2; 4-(1-methyl-2,2-dichlorocyclopropyl)-7,7-dichloro-1-methylbicyclo[4.1.0]heptane, 37608-28-9; dichlorocarbene, 1605-72-7.

N-Bromosaccharin: Benzylic and α-Carbonylic Bromination

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N-Bromosaccharin (NBSac) has been used as a brominating agent with cyclohexene[1] and diphenylmethane;[2] the former only gave the addition derivative, while the latter was brominated in the benzylic position; no yield was reported. We previously reported a new method of NBSac preparation[3] where it had been obtained with excellent yield. Now that a suitable NBSac synthesis is available, we herein report its ability as a brominating agent at the benzylic and α-carbonylic positions.

Benzylic Substitution (Table I). The toluene (1) bromination yields obtained corresponded to a 1:1 reactant molar ratio. When this ratio was increased 10% in NBSac, benzal bromide was afforded and a similar result was obtained when those reactants were irradiated with a sunlamp. Reflux or irradiation with a sunlamp dramatically reduced the reaction time. When radical initiators were added, the yields were increased perceptibly. Similar findings were observed in the bromination of diphenylmethane (2). When the bromination reaction was carried out with 2-methylnaphthalene (3), 2-(bromomethyl)-naphthalene (A) and 1-bromo-2-methylnaphthalene (B) were obtained. These results are in agreement with the literature[4] where *N*-bromosuccinimide (NBS) was used as the brominating agent under Ziegler conditions; 63% of A and 35% of B were obtained.

α-Carbonyl Substitution (Table II). Cyclohexanone (4) by bromination should afford 2-bromocyclohexanone,

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