then added dropwise during 30 min, and the mixture was poured into an 0.1 M HCl solution (20 mL) and washed with 0.1 M aqueous K_2CO_3 solution and the organic phase was separated, dried ($MgSO_4$), and evaporated. Crystallization of the yellow solid from ethanol gave 0.7 g (41%) of **2-2**, mp 150 °C: UV λ_{max}(hexane) 220 nm (ϵ = 6000), 261 (600); IR ν_{max} (Nujol) 1600 (m, Ar) cm^{-1}; ^1H NMR δ ($CDCl_3$, room temperature) 1.23 (12 H, s, 4 Me), 1.31 (36 H, s, 4 *t*-Bu), 1.42 (4 H, s, 2 CH_2), 7.12 (4 H, d, Ar H), 7.21 (2 H, t, Ar H); ^{13}C NMR δ ($CDCl_3$, room temperature) 28.98 (Me), 31.60 (Me_3C), 34.93 (CMe_3), 37.65 (CH_2), 39.05 (C_2), 119.10 (C_p), 119.96 (C_o), 148.74 (C_{ipso}), 149.74 (C_m); mass spectrum (*m/z*, 70 eV, relative abundance, assignment) 490 (9, M), 246 (6, *t*-$Bu_3C_6H_3$), 231 (100, *t*-$Bu_2C_6H_3CMe_2$). Anal. Calcd for $C_{36}H_{58}$: C, 88.08; H, 11.79. Found: C, 88.06, H, 11.81.

(b) From 1-Li and Diethyl Oxalate. To a stirred solution of **1-Br** (3.75 g, 11.5 mM) in dry ether (100 mL) at 0 °C was added a solution of BuLi in hexane (1.05 equiv), and the mixture was stirred for 1.5 h at 0 °C in an argon atmosphere. Diethyl oxalate (0.75 mL, 5.5 mM) was added and the temperature was raised gradually overnight to 20 °C. Water (100 mL), followed by 10% AcOH (20 mL), was added. The organic phase was separated, washed with 5% $NaHCO_3$ solution (70 mL) and water, and dried ($MgSO_4$). The ether was evaporated, the residue dissolved in petroleum ether (30 mL), and the remaining solid was filtered, recrystallized (EtOH), and characterized as **2-2** (170 mg, 6%) by mp, IR, and ^1H NMR. **1-H** was also isolated.

1-(2,4,6-Tri-*tert*-butylphenyl)-2-(3,5-di-*tert*-butylphenyl)-2-methylpropane (1-2). From 1-Li and Oxalyl Chloride. To a stirred solution of **1-Br** (3.5 g, 1.08 mM) in freshly distilled THF (100 mL) at −78 °C under argon was added a solution of BuLi in hexane (1.1 equiv, 11.2 mM). After 2.5 h oxalyl chloride (0.5 mL, 5.8 mM) was added, stirring at −78 °C was continued for 18 h, and the solution was allowed to reach 0 °C. Water (120 mL) was added, the solvent was evaporated, and the residue was dissolved in EtOAc (150 mL), washed successively with water (100 mL), 5% aqueous $KHCO_3$ solution and water, dried ($MgSO_4$), and evaporated, leaving a greenish oil. Chromatography on silica using petroleum ether (60–80 °C) as eluent gave several fractions from which bis(2,4,6-tri-*tert*-butylphenyl) diketone (80 mg, 2.7%), mp 202–204 °C (lit.[9] mp 203–205 °C), **1-H** and 1,3,5-tri-*tert*-butylbenzoic acid, mp 277–9 °C (lit.[6b] mp 297 °C) (70 mg, 8.4%), and **1-2** (R_f 0.4) were obtained. Recrystallization (EtOH) yielded 250 mg (9.5%) of pure **1-2**, mp 82 °C: UV λ_{max} (hexane) 212 nm (42 700), 238 sh (9300); IR ν_{max} (Nujol) 1590 cm^{-1} (s, Ar); ^1H NMR δ ($CDCl_3$) 1.00 (6 H, s, 2 Me), 1.25 (18 H, s, 2-*o*-*t*-Bu tetrasubstituted ring), 1.29 (18 H, s, 2-*o*-*t*-Bu, trisubstituted ring), 1.31 (9 H, s, *p*-*t*-Bu, tetrasubstituted ring), 3.50 (2 H, s, CH_2), 6.99 (2 H, d, J = 1.8 Hz, *m*-Ar H, trisubstituted ring), 7.19 (2 H, s, *m*-Ar H, tetrasubstituted ring), 7.20 (1 H, t, J = 1.8 Hz, *p*-Ar H, trisubstituted ring); ^{13}C NMR δ ($CDCl_3$, room temperature, tentative assignment) 28.70 (Me), 31.52 (Me_3C), 31.56 (Me_3C), 34.38 (Me_3C), 34.90 (Me_3C), 38.44 (Me_3C), 41.00 (CH_2), 42.86 (C_2), 119.26, 120.80, 121.68 (C_o, C_p), 134.28 (C_m), 144.86 (C_m), 149.49 (C_{ipso}), 149.80 (C_{ipso}), 149.96 (C_{ipso}); mass spectrum (*m/z*, 70 eV, relative abundance, assignment) 259 (32, *t*-$Bu_3C_6H_2CH_2$), 231 (100, *t*-$Bu_2C_6H_3CMe_2$); (chemical ionization, CH_5^+; *m/z*, relative abundance, assignment) 489 (7, M − 1), 475 (19, M − Me), 379 (33, MH − $2C_4H_8$), 259 (78, *t*-$Bu_3C_6H_2CH_2$), 245 (100, *t*-$Bu_3C_6H_3$), 231 (70, *t*-$Bu_2C_6H_3CMe_2$), 219 (13, 245 − C_2H_2), 189 (42, *t*-$Bu_2C_6H_3$). Anal. Calcd for $C_{36}H_{58}$: C, 88.06; H, 11.81. Found: C, 88.34; H, 11.79.

Reaction of 1-Li with Methyl Chloroglyoxylate. A solution of **1-Br** in dry THF (7.4 g, 22.8 mM) at −10 °C under argon, to which a solution of BuLi (1.05 equiv) was added, was stirred for 1 h. Methyl chloroglyoxylate (0.7 mL, 7.6 mM) was added and the temperature increased gradually to room temperature. A mixture of several compounds (by NMR) was precipitated. After being washed with water (20 mL), the solvent was evaporated. When the residue was dissolved in MeOH, a second precipitate was formed. Recrystallization ($CHCl_3$) yielded 170 mg (1.5%) of **2-2**. Evaporation of the filtrate to dryness and redissolution in MeOH gave **1-2** as a white precipitate (110 mg, 1%), which was characterized by NMR, IR, mp, and X-ray crystal diffraction. Methyl (2,4,6-tri-*tert*-butylphenyl)glyoxylate and **1-H** were also isolated.

X-ray crystal structure analysis of 1-2: space group $P1$, a = 16.030 (6) Å, b = 19.743 (7) Å, c = 10.659 (3) Å, α = 95.51 (3)°, β = 94.85 (3)°, γ = 90.79 (4)°, V = 3345 (1) Å^3, Z = 4, ρ_{calcd} = 0.98 g cm^{-3}, μ(Mo K_α) = 0.26 cm^{-1}, number of unique reflections 8756, number of reflections with $I > 3\sigma_I$ 4799, R = 0.090.

Collection of data and analysis was as reported previously.[13]

Acknowledgment. We are indebted to Dr. Shmuel Cohen for X-ray diffraction. This work was supported by the Commission for Basic Research, the Israel Academy for Sciences and Humanities, to whom we are grateful.

Supplementary Material Available: Tables giving bond lengths (Table S1), bond angles (Table S2), and positional (Table S4) and thermal parameters (Table S5) and Figures S1–S3 giving the unit cell and the stereoscopic views of **1-2** (14 pages); observed and calculated structure factors for **1-2** (Table S3) (29 pages). Ordering information is given on any current masthead page.

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Facile and Selective Epoxidation with the H_2O_2/Vilsmeier Reagent System

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Direct epoxidation of an alkene is typically accomplished by using the combination of an organic peroxide and a metal catalyst[1] or by an organic peracid.[2] *m*-Chloroperbenzoic acid (MCPBA)[3] is one of the most commonly used oxidants in this field. Utilization of hydrogen peroxide as primary oxidant[4] has received much attention, but because of its low electrophilicity it requires, for nonconjugated carbon–carbon double bonds, activation either by coordination to a metal[5] or by addition to a polarized multiple bond. Peroxycarboximidic acid formed in situ by addition of H_2O_2 to a nitrile[6] is one of the most useful applications of this O–O bond activation.

More recently it has been shown that a trichloromethyl substituent enhances the reactivity of the nitrile.[7] Peroxycarboximidic acids exhibit almost the same reactivity, but are less chemoselective reagents, than MCPBA or magnesium monoperphthalate (MMPP)[8] toward polyolefins.[9] *N*-Arylperoxycarbonic acids,[10] peroxy-

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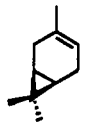
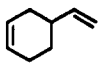
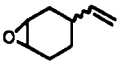
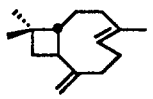
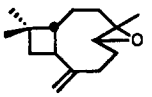
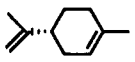
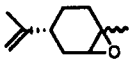
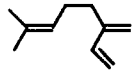
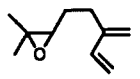
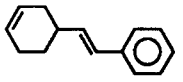
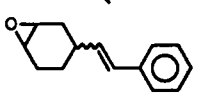
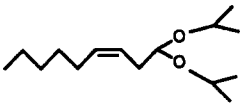
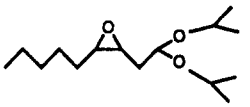
Table I

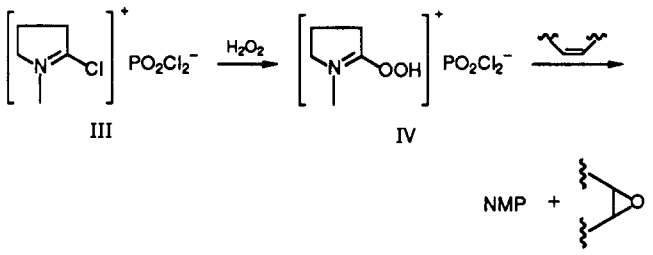
entries	substrates	salt III (equiv)	epoxides (yields, %)[a]		dichloro compounds[c] (%)[a]	recovery (%)
1		1.5		(27)[24]		70
2		2.5		(81)[24]	*d*	10
3		3.0		(63)[b,9]	10	*e*
4		3.4		(77)[25]		4[f]
5		3.0		(66)[b,9]	3	22
6		2.5		(52)[26]	12	27
7		2.5		(33)[b,27]	17	50
8	2,3-dimethyl-2-butene	2.5	2,3-dimethyl-2-butene oxide	(95)	<5	
9	1-methylcyclohexene	2.5	1-methylcyclohexene oxide	(90)		5
10	cyclohexene	1.3	cyclohexene oxide	(46)	4	50
11	cycloheptene	1.2	cycloheptene oxide	(48)	16	36
12	cycloheptene	3.0	cycloheptene oxide	(60)	30	5
13	*cis*-cyclooctene	2.5	*cis*-cyclooctene oxide	(78)	7	15
14	*cis*-bicyclo[3.3.0]oct-2-ene	1.2	*cis*-bicyclo[3.3.0]oct-2-ene oxide	(50)[28]	<5	45
15	*cis*-bicyclo[3.3.0]oct-2-ene	3.0	*cis*-bicyclo[3.3.0]oct-2-ene oxide	(59)[28]	28	13
16		3.0		(38)[29]		40[g]
17	styrene	3.6	styrene oxide	(<5)		95

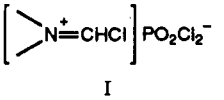
[a] Isolated yields. [b] Mixture (ca: 1:1) of cis and trans isomers. [c] The same double bond reacts either with chlorine to afford dichloro compounds or with salt IV to give rise to epoxides. [d] 5% of nonidentified byproducts. [e] Not determined. [f] 19% of chlorohydrin formed during the workup. [g] 20% of nonidentified byproducts; no products arising from acetal hydrolysis were detected.

carbamates,[11] peroxycarbonic acids[12] and related α-substituted hydroperoxides[13] form oxiranes under mild conditions. Activations of H_2O_2 by reaction with alkoxysulfuranes,[14] benzeneselenic acid,[15] hexafluoroacetone,[16] and organosilane derivatives[17] have also been reported.

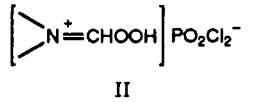
The ability of Vilsmeier reagent[18] I to give rise to substitution products with substrates bearing a labile hydrogen atom[19] led us to study the reaction of substitution between Vilsmeier reagent I and 30% hydrogen peroxide. We found that (hydroperoxymethylene)dimethylammonium salt II could be generated in situ and could either act as an oxidant of HCl or as a powerful epoxidizing reagent, depending on the reaction conditions.[20] The strongly electrophilic character of II, together with the substantial driving force resulting from the formation of the stable DMF molecule, can account for the reactivity of this new hydrogen peroxide activating system. Attempts to isolate the highly reactive salt II were unsuccessful.[21] Further, the epoxidation reaction was quite limited by the

Scheme I





I



II

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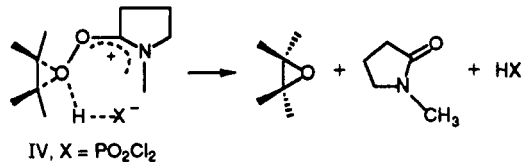
Scheme II



IV, X = PO_2Cl_2

subsequent formation of HCl.[22]

Our objective in the present study was to develop a new oxygen-transfer reagent based upon 30% H_2O_2/Vilsmeier reagent system that could compete advantageously with other ones. Since the formation of HCl during the progression of the reaction could not be avoided, we chose to pursue an approach where the generated HCl would not be available to cause undesired side reactions. Thus, we ran the reaction in a biphasic system, which removes the HCl to the aqueous phase and effects the epoxidation in the nonpolar organic phase where such reactions have been shown to be accelerated.[7] Another important factor could be the influence of the amide structure toward the reactivity of the intermediate hydroperoxyammonium salt. As anticipated, the Vilsmeier reagent III, prepared by reaction of *N*-methylpyrrolidone with $POCl_3$,[23] affords a nicely efficient oxygen-transfer reagent by reaction with 30% H_2O_2 using a phase-transfer catalysis procedure (Scheme I). Reaction times are very short and the epoxides are obtained in fair to very good yields only accompanied by dichloro byproducts. All reactions are unoptimized but give reproducible results. Results obtained are summarized in Table I, and spectral data are listed in refs 24–29. This new procedure is extremely clean and offers a distinct advantage in chemoselectivity with polyfunctional substrates over more commonly used oxidants such as MCPBA or peroxycarboximidic acids.[9] The attempted Baeyer–Villiger oxidation of cyclohexanone with 3 equiv of salt III and H_2O_2 resulted in a complete recovery of the starting material. ϵ-Caprolactone could not be detected in the crude reaction mixture. A competitive experiment between 1-methylcyclohexene and 2-butanone with 3.5 equiv of salt III and H_2O_2 resulted in a quantitative epoxidation of the olefin.

On the other hand, the oxygen transfer is extensively chemoselective, none of the other possible epoxides being observed in the reaction of polyfunctional olefins. A disubtituted double bond is epoxidized selectively in the presence of a monosubstituted one (entry 3). (−)-*trans*-Caryophyllene and (*R*)-(+)-limonene (entries 4 and 5) are selectively oxidized on the trisubstituted double bond. Finally a nonconjugated carbon–carbon double bond preferentially reacts with the salt IV to give the corresponding epoxide (entries 6 and 7). Acid-sensitive olefin (entry 16) gives no detectable amount of compounds arising from the hydrolysis of the acetal function. The rate of epoxidation for a weakly nucleophilic terminal double bond is generally lower than that for a more highly substituted one. Consequently in the case of styrene (entry 17), epoxide is formed in very low yield and decomposition of the oxidizing agent with the anion of H_2O_2 becomes the major reaction.[6a]

Although the structure of hydroperoxyammonium salt IV is not established, its formation seems fairly straightforward by the observation of facile oxirane formation (Scheme II).

On the other hand, the fact that (+)-α-3,4-epoxycarane is obtained as the unique diastereoisomer from the reaction of IV with (+)-Δ^3-carene (entries 1 and 2) implies that the epoxide results from a direct stereoselective oxygen atom transfer and is not formed by ring closure of an α-chloro, β-hydroxy intermediate, which would have given rise to the β-3,4-epoxycarane.[30]

Experimental Section

In a typical experiment, anhydrous Na_2CO_3 (12 g, 113.2 mmol) was suspended in 30% H_2O_2 (40 mL) and CH_2Cl_2 (40 mL). 18-Crown-6 (0.10 g, 0.378 mmol) and 1-methylcyclohexene (0.92 g, 9.6 mmol) were added to this heterogeneous biphasic system. Then the Vilsmeier reagent III[23] (24 mmol) in CH_2Cl_2 (30 mL) was added dropwise over 1 h under a nitrogen atmosphere to the well stirred reaction mixture at −20 °C. The mixture was further stirred until the temperature reached 20 °C; then it was filtered through Celite and the phases were separated. The aqueous layer was extracted with CH_2Cl_2 (20 mL) and the combined organic fractions were washed with water (30 mL), 3% $NaHSO_3$ (30 mL), and brine (30 mL) and dried over $MgSO_4$. Distillation of the solvent under atmospheric pressure gave a colorless residue constituted of 1-methylcyclohexene oxide, traces of starting material, and *N*-methylpyrrolidone. Purfication by flash chromatography on silica gel using a mixture of pentane–ether (98–2) as eluent gave pure 1-methylcyclohexene oxide (0.97 g; 90%).

Alternatively, pentane (100 mL) was added to the crude residue and the mixture washed with H_2O (3 × 60 mL) and dried over $MgSO_4$. Distillation of the solvent at atmospheric pressure gave almost pure 1-methylcyclohexene oxide by ^1H NMR.

Supplementary Material Available: Spectral data for compounds prepared including IR, ^1H NMR, ^{13}C NMR, and elemental analyses (2 pages). Ordering information is given on any current masthead page.

(22) Rodriguez, J.; Thesis, Faculté des Sciences et Techniques de St Jérôme, Marseille, France, 1984.

(23) For preparation of the Vilsmeier reagent III, see: Bredereck, H.; Bredereck, K. *Chem. Ber.* **1961**, *94*, 2278. III: ^{13}C NMR ($CDCl_3$) 178,64, 62,10 41,27, 39,05, 18,31; ^{31}P NMR (H_3PO_4) −7,31.

(24) ^1H NMR ($CDCl_3$, 200 MHz) δ 2.84 (1 H, s), 2.30 (1 H, ddd, *J* = 16.2, 8.6, 1.4 Hz), 2.14 (1 H, dd, *J* = 16.2, 8.6 Hz), 1.53 (1 H, dt, *J* = 16.4, 2.1 Hz), 1.45 (1 H, dd, *J* = 16.4, 2.2 Hz), 1.26 (3 H, s), 1.01 (3 H, s), 0.73 (3 H, s), 0.5 (2 H, m).

(25) ^1H NMR ($CDCl_3$, 200 MHz) δ 4.90 (1 H, s), 4.79 (1 H, s), 2.81 (1 H, dd, *J* = 10.5, 3.9 Hz), 2.52 (1 H, m), 2.23 (2 H, m), 2.04 (2 H, m), 1.74–1.49 (5 H, m), 1.45–1.21 (2 H, m), 1.13 (3 H, s), 0.94 (3 H, s), 0.92 (3 H, s).

(26) ^1H NMR ($CDCl_3$, 200 MHz) δ 6.29 (1 H, dd, *J* = 17.6, 10.5 Hz) 5.15 (1 H, d, *J* = 17.6 Hz), 4.98 (1 H, d, *J* = 10.5 Hz), 4.96 (1 H, s), 2.66 (1 H, t, *J* = 6.3 Hz), 2.29 (2 H, m), 1.64 (2 H, q, = 7.7 Hz), 1.22 (3 H, s), 1.17 (3 H, s).

(27) ^1H NMR ($CDCl_3$, 200 MHz) δ 7.36–7.16 (5 H, m), 6.40–6.29 (1 H, m), 6.15–5.99 (1 H, m), 3.24–3.14 (2 H, m), 2.31–1.15 (7 H, m).

(28) ^1H NMR ($CDCl_3$, 200 MHz) δ 3.48 (1 H, m), 3.32 (1 H, d, *J* = 2.5 Hz), 2.70–2.59 (1 H, m), 2.42–2.18 (2 H, m), 1.77–1.48 (5 H, m), 1.45–1.24 (2 H, m).

(29) ^1H NMR ($CDCl_3$, 200 MHz) δ 4.77 (1 H, dd, *J* = 7.2, 4 Hz), 3.89 (2 H, m), 3.06 (1 H, m), 2.86 (1 H, m), 1.88 (1 H, m), 1.71 (1 H, m), 1.49 (4 H, m), 1.33 (4 H, m), 1.19 (15 H, m).

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Approaches to the Preparation of Silyl Cations

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Introduction

Silicon has a lower electronegativity than carbon, and it might be expected that silylenium ions (R_3Si^+) would

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