Absolute rate constants for abstraction of chlorine from three chlorinating agents by alkyl radicals

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Using the cyclopropylcarbinyl ⟶ homoallyl free radical clock, absolute rate constants for the abstraction of chlorine from molecular chlorine (Cl_2), *tert*-butyl hypochlorite (Bu^tOCl) and *N*-chloro-3,3-dimethylglutarimide (NCG) have been determined (k_{Cl_2}) = 3.0×10^{10}, k_{Bu^tOCl} = 2.6×10^9 and k_{NCG} = 3.6×10^7, all in l mol^{-1} s^{-1}).

Free radical chlorination is an important process on both a laboratory and preparative scale for the preparation of alkyl chlorides from hydrocarbons. There is renewed interest in this chemistry as a number of interesting mechanistic features of this reaction have recently been uncovered.[1] The propagation steps of the reaction are outlined in Scheme 1, where Z–Cl refers to an appropriate chlorinating agent (Cl_2, Bu^tOCl, *etc.*).

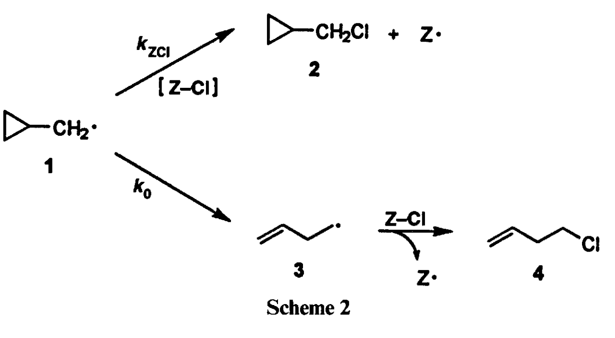
$$Z\cdot + R\text{–}H \longrightarrow Z\text{–}H + R\cdot$$
$$R\cdot + Z\text{–}Cl \longrightarrow R\text{–}Cl + Z\cdot$$

Scheme 1

There is a great deal of information available regarding the hydrogen abstraction step of this process. In terms of overall reactivity, it is generally found that 3° R–H > 2° R–H > 1° R–H.[2] However, the selectivities actually observed depend strongly on the identity of the hydrogen abstractor (Z•) and reaction conditions (temperature in general, and solvent when Z = Cl).[3–6] In many cases, absolute rate constants for these hydrogen abstractions have been measured (*e.g.* Cl•,[4d] RO•).[7] In contrast, there have been far fewer reports regarding the absolute rate constant for the halogen atom abstraction step, although this process is generally assumed to be quite rapid.

Using the cyclopropylcarbinyl radical 'clock',[8] we have measured absolute rate constants for chlorine atom abstraction from several common chlorinating agents (Cl_2, Bu^tOCl and *N*-chloroimides). This paper summarizes the results of our investigation.

The general design of these experiments is as outlined in Scheme 2. Abstraction of hydrogen from the methyl group of methylcyclopropane (MCP) generates the cyclopropylcarbinyl radical **1**, which partitions between two pathways: (*a*) chlorine atom abstraction from Z–Cl (k_{ZCl}) yielding cyclopropylcarbinyl chloride **2** and (*b*) ring opening (k_o) inevitably resulting in the formation of 4-chlorobut-1-ene **4**. The ratio of these two products yields the rate constant ratio k_{ZCl}/k_o in accordance with eqn. (1), under the condition that the reaction is run to low percentage conversion. Because k_o is known, k_{ZCl} is readily obtained. (This method has been utilized previously to determine absolute rate constants for bromine atom abstraction from Br_2 and *N*-bromoimides.)[9]



Scheme 2

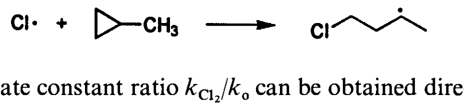
$$\frac{\text{Yield } \mathbf{2}}{\text{Yield } \mathbf{4}} = \frac{k_{ZCl}}{k_o}[ZCl] \qquad (1)$$

Results

Reaction of methylcyclopropane with Cl_2

Walling reported the liquid phase chlorination of methylcyclopropane in 1962.[10] The major product of the reaction was cyclopropylcarbinyl chloride (56%), but small amounts of 2-chlorobutane (9.8%), 1,3-dichlorobutane (8%), 1,3-dichloro-2-methylpropane (3.5%), 1,2,4-trichlorobutane (trace) and several unidentified compounds (23%) were noted. (Walling hypothesized that the unidentified products might arise from further reaction of 4-chloro-1-butene.)[11]

Because these competition experiments require a thorough and accurate analysis of products, a re-examination of this reaction was in order. The products arising from the photochlorination of methylcyclopropane are summarized in Table 1. As observed by Walling, the major product was cyclopropylcarbinyl chloride. Ring-opened products were also observed, 4-chlorobut-1-ene and 1,2,4-trichlorobutane (arising from electrophilic addition of Cl_2 to the former), in addition to a small amount of products arising from ring chlorination. 1,3-Dichlorobutane arises from the S_H2 reaction between Cl• and methylcyclopropane [eqn. (2)].



(2)

The rate constant ratio k_{Cl_2}/k_o can be obtained directly from the ratio of ring-closed (cyclopropylcarbinyl chloride) to ring-opened products (4-chlorobut-1-ene and 1,2,4-trichlorobutane) when the reaction is carried out to low percentage conversion. In order to avoid possible distortion of the results because of the chlorine atom cage effect,[12] we opted to carry out the kinetic runs in benzene, which has been previously shown to suppress this phenomenon.[12]

In a series of reactions, the product ratio cyclopropylcarbinyl chloride : ring-opened products was found to vary linearly with $[Cl_2]_i$ (Fig. 1). All reactions were carried out with at least

Table 1 Photoinitiated reaction of Cl_2 with methylcyclopropane[a]

Product	Yield (%)
$CH_2{=}CHCH_2CH_2Cl$	10.3
1,2,4-Trichlorobutane	19.1
$c\text{-}C_3H_5CH_2Cl$	34.4
1,3-Dichlorobutane	6.2
3 C_4H_7Cl isomers	2.1

[a] 0.014 mol l^{-1} Cl_2 and 0.17 mol l^{-1} methylcyclopropane in Freon 113 solvent, irradiated with a 75 W tungsten lamp through two Pyrex layers at 20 °C for 20–30 min

a 10-fold excess of MCP and run to $\leqslant 10\%$ Cl_2-conversion. Linear least-squares analysis of the results in accordance with eqn. (1) yielded $k_{Cl_2}/k_o = 379 \pm 16$ l mol^{-1} (at 20 °C). At this temperature, $k_o = 7.9 \times 10^7$ s^{-1},[13] therefore $k_{Cl_2} = 3.0\ (\pm 0.1) \times 10^{10}$ l mol^{-1} s^{-1}.

Reaction of methylcyclopropane with *tert*-butyl hypochlorite

Products of the reaction between MCP and Bu^tOCl were reported by Walling to include cyclopropylcarbinyl chloride (28%) and 4-chloro-but-1-ene (20%). In addition, a compound suspected (but not confirmed) to be cyclobutyl chloride was reported to be formed in 10% yield, in addition to several unidentified materials (45%).[10]

Products and yields of the photo-initiated reaction of Bu^tOCl and MCP in Freon 113 solvent are summarized in Table 2. As noted by Walling, cyclopropylcarbinyl chloride and 4-chlorobut-1-ene are the major chlorinated products of this reaction. Formation of a small amount of 1,3-dichlorobutane and 1,2,4-trichlorobutane suggests the possible intervention of a competing Cl_2-based chain process. Products derived from the *tert*-butoxyl radical include *tert*-butyl alcohol and acetone, the latter arising from β-cleavage of $Bu^tO\cdot$.[14]

One of the experimental difficulties traditionally associated with studying the kinetics of reactions of Bu^tOCl involves the intervention of a Cl• based chain process (Scheme 3). Generally,

$$\begin{aligned} Cl\cdot + R{-}H &\longrightarrow H{-}Cl + R\cdot \\ R\cdot + Cl_2 &\longrightarrow R{-}Cl + Cl\cdot \\ Bu^tOCl + HCl &\longrightarrow Bu^tOH + Cl_2 \end{aligned}$$

Scheme 3

this chemistry is suppressed by the addition of an appropriate Cl• scavenger (*e.g.* trichloroethylene).[15] In this system, methylcyclopropane itself serves as an excellent Cl• scavenger *via* the S_H2 process since this reaction does not yield HCl.[9] [For the purposes of these experiments, the identity of the hydrogen abstractor is *unimportant* because the kinetic determinations are based upon the partitioning of the resulting cyclopropylcarbinyl radical (Scheme 2). However, the presence of a small amount of Cl_2 in solution could prove troublesome since the rate constant for its reaction with an alkyl radical is so rapid (*vide supra*).]

In a series of experiments, the product ratio cyclopropylcarbinyl chloride : 4-chlorobut-1-ene was found to vary linearly with $[Bu^tOCl]$ (Fig. 2). In all of these runs, MCP was present in 10-fold excess relative to Bu^tOCl and the reactions were run to < 10% Bu^tOCl-conversion. The amount of 1,3-dichlorobutane produced in these experiments never exceeded 1% of the total chlorinated products and no 1,2,4-trichlorobutane was detected. Consequently, we are confident that for these experiments (*a*) Cl• chains were effectively suppressed and (*b*) the $[Cl_2]$ in solution was extremely low. (As a final test to ensure that Cl• chains were not operative, some of the runs were repeated in the presence of 4.5 mol l^{-1} $CHCl{=}CCl_2$. Within experimental error, identical results were obtained.) Linear least-squares analysis of the data in Fig. 2, in accordance with eqn. (1), yields $k_{Bu^tOCl}/k_o = 33 \pm 1$ l mol^{-1} (20 °C) leading to $k_{Bu^tOCl} = 2.6\ (\pm 0.1) \times 10^9$ l mol^{-1} s^{-1}.

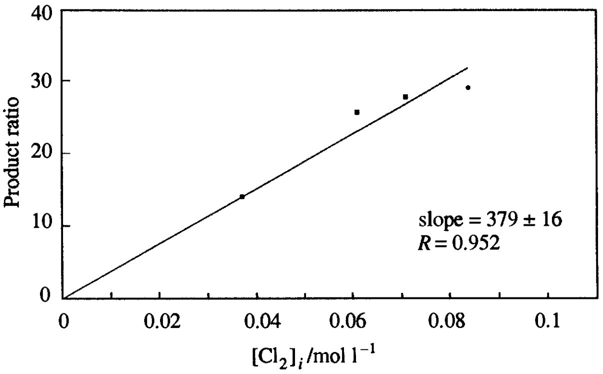


Fig. 1 Reaction of Cl_2 with methylcyclopropane. Product ratio cyclopropyl chloride : ring-opened products (see text) as a function of initial Cl_2 concentration.

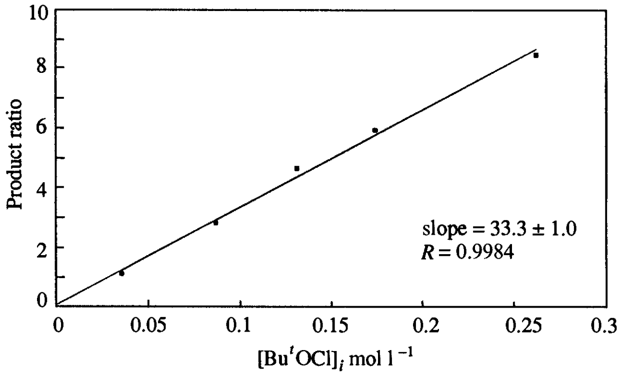


Fig. 2 Reaction of Bu^tOCl with methylcyclopropane. Product ratio cyclopropylcarbinyl chloride : ring-opened products (see text) as a function of initial Bu^tOCl concentration.

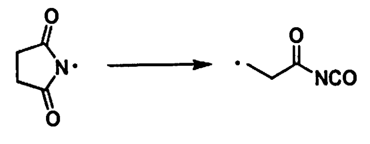
Table 2 Photoinitiated reaction of *tert*-butyl hypochlorite with methylcyclopropane[a]

Product	Yield (%)
$CH_2{=}CHCH_2CH_2Cl$	17.0
1,2,4-Trichlorobutane	6.5
$c\text{-}C_3H_5CH_2Cl$	24.2
1,3-Dichlorobutane	3.2
3 C_4H_7Cl isomers	7.7
Bu^tOH	76.5
Acetone[b]	14.5

[a] 0.035 mol l^{-1} Bu^tOCl and 0.88 mol l^{-1} methylcyclopropane in Freon 113 solvent, irradiated with a 75 W tungsten lamp through two Pyrex layers at 20 °C for 2.5 h. [b] Resulting from β-scission: $Bu^tO\cdot \longrightarrow CH_3\cdot + CH_3COCH_3$.

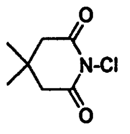
Reaction of 3,3-dimethyl-*N*-chloroglutarimide (NCG) with methylcyclopropane

Imidyl radicals, typically generated in a free radical chain process from the corresponding *N*-haloimides, undergo a variety of reactions including addition to alkenes, hydrogen abstraction, and β-cleavage [the latter process is illustrated in eqn. (3) for succinimidyl radical].[16] In order to characterize the



5 **6** (3)

rate constant for chlorine atom abstraction from an *N*-chloroimide, we selected 3,3-dimethyl-*N*-chloroglutarimide (NCG, **7**) as substrate because of its increased solubility in organic solvents (compared to the more common *N*-chlorosuc-



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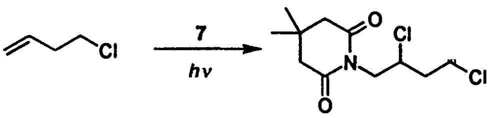
cinimide) and because the resulting imidyl radical is known not to undergo rearrangment.[17]

The products derived from the photo-initiated reaction of NCG with MCP in CH_2Cl_2 are summarized in Table 3. Both cyclopropylcarbinyl chloride and 4-chlorobut-1-ene are produced in small amounts, in addition to ring-chlorinated products and chloroform (produced *via* hydrogen abstraction from solvent). The presence of 1,3-dichlorobutane and 1,2,4-trichlorobutane is attributable to reaction of chlorine atom. The major product derived from reaction of MCP and NCG is addition product **8**, which results from subsequent reaction of primary reaction product 4-chlorobut-1-ene under these conditions [eqn. (4)]. (In a separate experiment, it was shown that 4-chlorobut-1-ene reacts with NCG under the reaction conditions to generate **8** in 85% yield.)



(4)

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In a series of runs, MCP (0.4 mol l^{-1} in CH_2Cl_2) was reacted with varying concentrations of NCG. Most of the reactions were carried out to $\leqslant 10\%$ NCG conversion. {For [NCG] $\leqslant$ 0.1 mol l^{-1}, it was necessary to carry out the reactions to slightly higher conversion (*ca.* 15%) in order to accurately quantitate all the reaction products.} As is the case with reactions involving Bu^{t}OCl, MCP itself effectively suppressed competing Cl• chains. In all these runs, a small amount of 1,3-dichlorobutane was produced with only a trace of 1,2,4-trichlorobutane indicating [Cl_2] was extremely low. The product ratio cyclopropylcarbinyl chloride : ring-opened products (4-chlorobut-1-ene, 1,2,4-trichlorobutane and addition product **8**) varied linearly as a function of [NCG] (Fig. 3). Analysis of the data according to eqn. (1) yields $k_{NCG}/k_o = 0.49 \pm 0.01$ (18 °C); $k_{NCG} = 3.6\,(\pm 0.04) \times 10^7\ l\ mol^{-1}\ s^{-1}$.

Discussion

Absolute rate constants for halogen atom abstractions from Y–X ($R\cdot + Y\text{–}X \longrightarrow R\text{–}Y + X\cdot$, Y = Cl, Br) by the cyclopropylcarbinyl radical obtained in this and earlier work and pertinent thermodynamic information are summarized in Table 4. With the exception of the rate constant for Bu^{t}OCl, the results reported herein are consistent with earlier observations. Ingold has estimated that the rate constant for the reaction of alkyl radicals with Cl_2 is at least 10^7 l mol^{-1} s^{-1}.[4d] In the gas phase, rate constants for $R\cdot + Cl_2 \longrightarrow R\text{–}Cl + Cl\cdot$ (R = CH_3, CH_3CH_2, *etc.*) have been measured. Activation energies for these processes are less than 1 kJ mol^{-1}.[21] Hence, it is reasonable to expect this reaction to be diffusion-controlled in solution. [Based upon $k_{diff} = 8RT/3000\eta$ and the known viscositites of these solvents (η), the calculated diffusion-controlled rate constant is 1.0×10^{10} l mol^{-1} s^{-1} for benzene.]

The fact that the observed rate constant is slightly higher than the calculated diffusion-controlled rate constant in benzene is not unusual based upon the limitations of the model. Diffusion-controlled rate constants calculated from viscosities are reasonably accurate when the solvent and solute are of comparable size. However, high diffusion-controlled rate constants ($\approx 10^{11}$ l mol^{-1} s^{-1}) have been reported for a number of small atoms or molecules in solution (*e.g.* F, O).[22]

Table 3 Photoinitiated reaction of 3,3-dimethyl-*N*-chloroglutarimide (NCG) with methylcyclopropane[a]

Product	Yield (%)
$CH_2{=}CHCH_2CH_2Cl$	3.0
1,2,4-Trichlorobutane	3.0
$GCH_2CHClCH_2CH_2Cl$ **8**[b]	20.0
c-$C_3H_5CH_2Cl$	0.5
1,3-Dichlorobutane	12.8
3 C_4H_7Cl isomers	4.5
$CHCl_3$	29.2
G–H[b]	90.0

[a] 0.12 mol l^{-1} NCG and 0.33 mol l^{-1} methylcyclopropane in CH_2Cl_2 solvent, irradiated with a 400 W medium pressure mercury arc lamp through two Pyrex layers at 22 °C for 48 h. [b] G = 3,3-dimethylglutarimidyl.

Table 4 Kinetic and thermodynamic data for halogen atom abstractions by primary alkyl radicals ($R\cdot + Y\text{–}X \longrightarrow R\text{–}Y + X\cdot$)

Y–X	k/mol l^{-1} s^{-1}	BDE(Y–X)/kJ mol^{-1}	$\Delta H°$/kJ mol^{-1} [a]
Y = Br			
X = Br	2.2×10^{10} [b]	192	−92
X = G[c]	1.3×10^{10} [b]	272[d]	−13
Y = Cl			
X = Cl	3.0×10^{10} [e]	247	−96
X = Bu^{t}O	2.6×10^{9} [e]	142[f]	−201
X = G[c]	3.6×10^{7} [e]	305[d]	−38

[a] $\Delta H° = BDE(R\text{–}Y) - BDE(Y\text{–}X)$; 1° R–Cl and R–Br BDEs are 341 and 285 kJ mol^{-1}, respectively (ref. 18). [b] Ref. 9. [c] G = 3,3-dimethylglutarimidyl. [d] Values for S–Cl and S–Br, where S = succinimidyl (ref. 19). [e] This work. [f] Ref. 20.

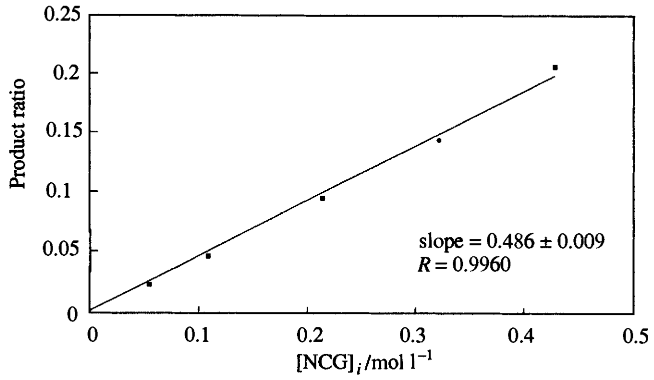

Fig. 3 Reaction of *N*-chloro-3,3-dimethylglutarimide (NCG) with methylcyclopropane. Product ratio cyclopropylcarbinyl chloride : ring-opened products (see text) as a function of initial NCG concentration.

Skell has estimated that 1° radical **6**, derived from ring opening of the succinimidyl radical [eqn. (3)] is at least 50 times more reactive towards NBS than NCS.[17] Based upon the reported rate constant for reaction of 1° radicals with *N*-bromoimides,[9] this would mean that the rate constant for the analogous reaction of *N*-chloroimides would be $\leqslant 2.6 \times 10^8$ l mol^{-1} s^{-1}, again consistent with these results.

The measured rate constant for reaction of alkyl radicals with Bu^{t}OCl is somewhat larger than previously suspected. By examining the overall kinetics of the chlorination of cyclohexane using Bu^{t}OCl, Zavitsas has estimated the rate constant for $c\text{-}C_6H_{11}\cdot + Bu^tOCl \longrightarrow C_6H_{11}Cl + Bu^tO\cdot$ to be *ca.* 3.8×10^5 l mol^{-1} s^{-1}.[23] (Cl-abstraction, rather than the H-abstraction by Bu^{t}O•, was reported to be the rate-limiting propagation step.) The cyclopropyl group is a good electron donating substituent, and as a consequence, the cyclopropylcarbinyl radical is comparable to a secondary alkyl radical in stability.[24] Thus the difference between our value for the cyclopropylcarbinyl radical and the reported value for c-C_6H_{11} is significant, and likely to be attributable to artifacts rather than any significant difference in the reactivities of these two radicals.

Kinetic studies of chlorinations by *tert*-butylhypochlorite have yielded conflicting and contradictory results. In contrast to the Zavitsas report, Carlsson and Ingold reported that for chlorinations by Bu^{t}OCl, hydrogen abstraction by Bu^{t}O• is the rate-limiting step.[25] (Relative reactivities of several hydrocarbons obtained from the overall kinetics based upon this assumption agree well with values obtained from direct competitions.)

The strength of the competition approach employed in our work is that no assumptions regarding the rate-limiting step, mechanism of termination, *etc.* are needed. Partitioning of the intermediate cyclopropylcarbinyl radical is solely a function of the rate of ring opening (k_o) and the rate of halogen atom abstraction ($k_{Z\text{-}Cl}$ [Z–Cl], Scheme 2). Hence, we are confident that the rate constant we report for c-$C_3H_5CH_2$• + Bu^{t}OCl is accurate.

Overall, these results do not reveal any apparent activation-driving force relationship for these halogen atom abstractions. Despite the fact that these reactions are all substantially exothermic, the rate constants vary from as low as 10^7 l mol^{-1} s^{-1} in the case of *N*-chloroimides to the diffusion controlled limit in the case of the molecular halogens and *N*-bromoimides.

Experimental

General

NMR spectra (^{1}H, ^{13}C) were obtained on a 270 MHz Bruker FT NMR spectrometer. Chemical shifts are reported in δ units relative to hexamethydisiloxane (δ 0.07) in $CDCl_3$ unless otherwise noted. Infrared spectra were recorded on a Perkin-Elmer model 283 B spectrophotometer. Low and high resolution mass spectral data were obtained on a VG Analytical model 7070 E-HF double focusing, magnetic sector mass spectrometer. Electron impact ionization (70 eV) was used for all mass spectra. Low resolution GC–MS was performed on a Hewlett-Packard model 5890 gas chromatograph with an HP methylsilicone capillary column (12 m × 0.2 mm) interfaced to an HP 5097B EI mass spectrometer and an HP series computer. All reactions were conducted in 30 ml pressure tubes, equipped with O-ringed Teflon needle valves, vacuum line adapter, and magnetic stirrer bar. All gas chromatographic analyses were performed in triplicate on a Hewlett-Packard model 5890 instrument equipped with both FID and TCD detectors and an HP 3393A reporting integrator. Analyses were accomplished on either an Alltech SE-54 capillary column (15 m × 0.25 mm) or a Supelco SE-54 capillary column (30 m × 0.25 mm). Reaction products were quantified using predetermined response factors (and chlorobenzene as internal standard). Flash column chromatography was performed on silica gel (230–400 mesh) using hexane–ethyl acetate solvent mixtures. Thin layer chromatography (TLC) was performed on precoated silica gel 60 F-254 plates (purchased from EM Science).

Materials

The following materials were purchased from Aldrich and used as received (unless otherwise noted): 1,1,2-trichlorotrifluoroethane (Freon 113, HPLC grade), dichloromethane (HPLC grade), chlorobenzene (HPLC grade), carbon tetrachloride (ACS grade), deuteriated chloroform (HPLC grade), silica gel (230–400 mesh), sodium thiosulfate pentahydrate, 3,3-dimethylglutarimide, 1,3-dichlorobutane and cyclopropylcarbinyl chloride. Benzene (Fisher, ACS grade) was washed repeatedly with sulfuric acid to remove thiophene and olefinic impurities and then fractionally distilled over calcium chloride. Methylcyclopropane (Columbia Organics) was treated with excess Br_2 to remove olefinic impurities. Unreacted Br_2 was quenched with corn oil (Mazola), and the methylcyclopropane was distilled through two −78 °C traps and collected at −196 °C. Chlorine (Matheson) was transferred to a glass pressure tube, degassed, and stored at 0 °C. *N*-Chloro-3,3-dimethylglutarimide,[26] 4-chlorobut-1-ene[27] and *tert*-butyl hypochlorite[15] were prepared according to literature procedures.

Reactions involving molecular chlorine

Light reaction of chlorine with methylcyclopropane. Freon 113 (5 ml) was added to a 30 ml pressure tube and cooled to −196 °C. Methylcyclopropane (0.857 mmol) was condensed into the pressure tube under high vacuum. The mixture was degassed three times by the freeze-pump-thaw method (cooling to −196 °C, evacuating and warming to room temperature). Chlorine (0.679 mmol) was transferred *via* a gas pipette to a trap on the vacuum line, cooled to −196 °C under high vacuum and freeze-pump-thaw degassed. The chlorine was subsequently transferred (in the dark) to the pressure tube cooled to −196 °C under high vacuum. The tube was transferred to a constant temperature water bath (in the dark in order to prevent premature initiation of the reaction by ambient room light). After the temperature was allowed to equilibrate (*ca.* 5 min), the reaction mixture was irradiated with a 75 W tungsten lamp until the Cl_2 was completely consumed. Products were analysed by GLC and the results are summarized in Table 1.

Dark reaction of chlorine with methylcyclopropane. To determine the extent of reaction which occurs in the dark (or which is initiated by adventitious room light), the above procedure was repeated using 0.960 mmol methylcyclopropane and 0.119 mmol chlorine with the exception that the reaction mixture was left to stand in the the dark for 10 min. Corn oil was added to quench the chlorine, and the mixture was analysed by GLC. No products were formed within the limits of detection.

Competition experiments. Benzene (5 ml) was added to a 30 ml pressure tube and cooled to −196 °C. A 10-fold excess of methylcyclopropane (relative to the amount of Cl_2 to be used) was condensed into the pressure tube under high vacuum. The mixture was freeze-pump-thaw degassed three times. The appropriate quantity of chlorine was transferred *via* gas pipette to a trap on the vacuum line cooled to −196 °C under high vacuum. The chlorine was freeze-pump-thaw degassed and distilled into the pressure tube (cooled to −196 °C) under high vacuum in the dark. The pressure tube was allowed to warm to the desired temperature in a constant water bath (in the dark) and irradiated with a 75 W tungsten lamp (distance 9–15 feet) for 3–15 s. Unreacted chlorine was quenched immediately with styrene, and the products were analysed by GLC. The results are summarized in Fig. 1.

Reactions involving *tert*-butyl hypochlorite

Reaction of *tert*-butyl hypochlorite with methylcyclopropane. Freon 113 (5 ml) was added to a 30 ml pressure tube and cooled to −196 °C. Methylcyclopropane (4.38 mmol) was condensed into the tube under high vacuum. The resulting mixture was freeze-pump-thaw degassed three times. *tert*-Butyl hypochlorite (0.0191 g, 0.176 mmol) was degassed on the vacuum line and distilled into the reaction mixture at −196 °C. The tube was placed in a constant temperature water bath and irradiated with a 75 W tungsten lamp (at a distance of 4 inches) for 2.5 h. The products were analysed by GLC and the results are summarized in Table 2.

Competition experiments. Freon 113 (5 ml) was added to a 30 ml pressure tube and cooled to −196 °C. Approximately 7.0 mmol methylcyclopropane was condensed into the tube under high vacuum and the resulting mixture was freeze-pump-thaw degassed three times. The appropriate quantity of *tert*-butyl hypochlorite was distilled into a trap on the vacuum line (cooled to −196 °C), degassed once and distilled into the reaction mixture (at −196 °C) under high vacuum. The pressure tube was placed in a constant temperature water bath, irradiated with a 75 W tungsten lamp (at a distance of 1 foot) for 3–5 min, and the products were analysed by GLC.

Reactions involving *N*-chloro-3,3-dimethylglutarimide (NCG)

Preparation of *N*-(2,4-dichlorobutyl)-3,3-dimethylglutarimide 8. *N*-Chloro-3,3-dimethylglutarimide (0.22 g, 1.25 mmol), 4-chlorobut-1-ene (0.17 g, 1.89 mmol) and 5 ml CH_2Cl_2 were added to a 30 ml pressure tube. The contents were freeze-pump-thaw degassed three times. The tube was placed in a constant temperature water bath and irradiated with a 400 W medium pressure mercury arc lamp (distance 7–8 inches) for 24 h. The solvent and unreacted 4-chlorobut-1-ene were removed by rotary evaporation. The remaining residue was dissolved in 40 ml diethyl ether and washed successively with saturated aq. sodium thiosulfate and 5% NaOH, then dried over $MgSO_4$ and evaporated. The crude product was purified by flash column chromatography using an ethyl acetate–hexane solvent mixture (25:75); δ_H[270 MHz, $CDCl_3$, $(Me_3Si)_2O$] 1.07 (6 H, s, CH_3), 2.10 (2 H, m, CH_2), 2.50 (4 H, s, $CH_2C{=}O$), 3.68 (2 H, m, CH_2Cl), 3.86 (1 H, m, CHCl), 4.35 (2 H, m, CH_2); δ_C(67 MHz, $CDCl_3$, Me_4Si) 28 (CH_3), 29, 30, 39, 41, 45, 47, 172 (C=O); ν_{max}/cm^{-1} 2955 (CH), 2920 (CH), 1732, 1679 (C=O), 1572, 1430 (CH_3), 1397 (CN), 1362 (CH_3), 1349, 1311, 1298, 1273, 1139, 1093, 1021, 960, 937, 895, 818; *m*/*z* (EI) 269 (1.4%, M + 4), 267 (5.5, M + 2), 265 (8.8, M^+), 230 (8.8), 216 (6.2), 194 (10), 154 (40), 142 (55), 126 (25), 98 (10), 83 (100), 69 (20), 55 (60); *m*/*z* (EI) 265.064 32 (M^+, calculated 265.063 63, error +2.6 ppm).

Reaction of *N*-chloro-3,3-dimethylglutarimide (NCG) with methylcyclopropane. NCG (0.1025 g, 0.584 mmol) and 5 ml CH_2Cl_2 were added to a 30 ml pressure tube and cooled to −196 °C. Methylcyclopropane (1.66 mmol) was condensed into the mixture under high vacuum. The reaction mixture was freeze-pump-thaw degassed three times and the pressure tube was placed in a constant temperature water bath and irradiated with a 400 W medium pressure mercury arc lamp at a distance of 7–8 inches for 48 h. The volatile products (mono-, di- and tri-chlorides of methylcyclopropane) were removed under high vacuum *via* a room temperature trap-to-trap distillation and analysed by GLC. The non-volatile materials (unreacted NCG, 3,3-dimethylglutarimide and adduct **8**) were analysed by ^1H NMR (*vs.* hexamethyldisiloxane internal standard). The results are summarized in Table 3.

Competition experiments. The appropriate amount of NCG and 5 ml CH_2Cl_2 were added to a 30 ml pressure tube and cooled to −196 °C. Approximately 2.0 mmol methylcyclopropane was condensed into the pressure tube under high vacuum, and the mixture was degassed three or four times (freeze-pump-thaw). The tube was placed in a constant temperature water bath and irradiated with two 400 W medium pressure mercury arc lamps at a distance of 7–8 inches for 4 h. The reaction mixture was analysed by GLC. The amount of unreacted NCG was further verified by ^1H NMR analysis. The results are summarized in Fig. 3.

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