containing ~10% acetone-d_6 employed as an internal lock. The average accumulation time was ~20 h.

Preparation of N,N-Dimethylurea Derivatives. Derivatives **6a**, **7a**, and **7b** were prepared as previously described.[1] Derivative **2a** was obtained in 77% yield from addition of gaseous dimethylamine to the product of irradiation of 2.0 g of **1** in THF solvent as described previously.[3] Derivatives **8a** and **9a** were prepared in 65 and 95% yields, respectively, by addition of gaseous dimethylamine to a solution containing 1.0 g of the respective isocyanates in 10 mL of dry THF until GLC analysis using a 2 m × 0.64 cm column of 5% FS-1265 on 60/80 mesh Diatoport S at 100 °C (He 55 mL/min) indicated complete destruction of starting material.

N,N-Dimethyl-N'-(1-ethoxycyclopropyl)urea (2a). An analytical sample obtained by recrystallization from acetonitrile had mp 113–113.5 °C and the following spectral properties: IR (CH$_2$Cl$_2$) 2.90, 3.41, 6.00, 6.65 μ; NMR (CDCl$_3$) δ 0.87–1.20 (m, 4 H), 1.13 (t, J = 7 Hz, 3 H), 2.93 (s, 6 H), 3.70 (q, J = 7 Hz, 2 H), 5.50–5.83 ppm (br, 1 H); mass spectrum (70 eV) m/e (rel intensity) 73 (11), 72 (100), 44 (16).

N,N-Dimethyl-N'-[7-(7 ethoxybicyclo[4.1.0]heptyl)]urea (8a). An analytical sample obtained by recrystallization from acetonitrile had mp 140–140.5 °C and the following spectral properties: IR (CH$_2$Cl$_2$) 2.91, 3.41, 5.98, 6.65 μ; NMR (CDCl$_3$) δ 0.87–2.20 (m, 10 H), 1.12 (t, J = 7 Hz, 3 H), 2.98 (s, 6 H), 3.65 (q, J = 7 Hz, 2 H), 5.15–5.38 ppm (br, 1 H); mass spectrum (70 eV) m/e (rel intensity) 226 (0.76), 197 (76), 144 (13), 109 (37), 88 (12), 80 (15), 72 (100), 46 (11), 44 (15).

N,N-Dimethyl-N'-[7-(7-ethoxybicyclo[4.1.0]hept-3-enyl)]urea (9a). An analytical sample obtained by recrystallization from acetonitrile had mp 141.0–141.5 °C and the following spectral properties: IR (CH$_2$Cl$_2$) 2.88, 3.30, 3.44, 5.98, 6.61 μ; NMR (CDCl$_3$) δ 1.13 (t, J = 7 Hz, 3 H), 1.40–1.65 (m, 2 H), 2.07–2.47 (m, 4 H), 2.90 (s, 6 H), 3.70 (q, J = 7 Hz, 3 H), 4.96–5.23 (br, 1 H), 5.38–5.63 (m, 2 H); mass spectrum (70 eV) m/e (rel intensity) 224 (4), 195 (31), 107 (16), 78 (14), 72 (100).

References and Notes

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# Free-Radical Halogenations. Chlorination of Alkanes by N-Chlorophthalimide

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Abstract: The photoinitiated free-radical chlorination of hydrocarbons with N-chlorophthalimide, NCP, has been investigated. The product distribution obtained at the completion of the reaction was found to be the result of the equilibration of the initially formed alkyl radicals with the product of the abstraction step, hydrogen chloride. The equilibration of the intermediate alkyl radicals, through reversible hydrogen abstraction from hydrogen chloride, was found to complicate the expected Goldfinger-type mechanism for the reaction of this N-chloroimide.

The free-radical chlorination reactions of N-chlorophthalimide (NCP), would be expected to be similar to those reported for N-chlorosuccinimide (NCS), or other N-chloroimides. The mechanism of action of NCS has been reported to involve a free radical chain mechanism with chlorine as the hydrogen atom abstracting species, Scheme I.[1] Based upon a comparison of the relative reactivities for NCP chlorinations of hydrocarbons of different structures with the relative rates of reaction obtained for molecular chlorine, NCP appears to proceed by a mechanism different than that described by Scheme I. These discrepancies have been studied and the

Scheme I
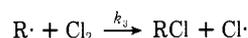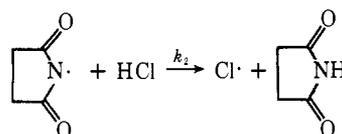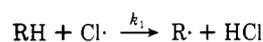
Table I. Relative Reactivities of Several Alkanes toward N-Chlorophthalimide as Compared to Molecular Chlorine

| Substrate	Relative reactivities	
	NCP	Cl$_2$
Cyclohexane[a]	1.00	1.00
Cyclopentane	0.54 ± 0.04	0.82 ± 0.04
Cycloheptane	1.83 ± 0.02	1.19 ± 0.07[b]
2-Chloropropane	1.1 ± 0.03 × 10^{-3}	0.9 ± 0.1 × 10^{-3}
Toluene	0.23 ± 0.02	0.21 ± 0.02[c]

[a] Assigned a relative rates of reaction of 1.00. [b] Literature values, 1.09 ± 0.03.[5] [c] Taken from ref 6.

mechanism of the photolytic free-radical chlorinations of hydrocarbons with NCP is reported here.

Results and Discussion

In the photolytic reactions of NCP with hydrocarbons, the relative rates of reactions obtained were different from those obtained with molecular chlorine with the two substrates, cyclopentane and cycloheptane. This observation would seem to preclude chlorine atoms as the hydrogen abstracting species, Table I. The obtained reactivities of the compounds toward the attacking radical from NCP as compared to the reactivities of these substrates with chlorine suggest that the abstracting radical can distinguish between hydrogen atoms in different chemical environments more precisely than chlorine atoms. The more precise differentiation between chemically different hydrogen atoms is also reflected in the tertiary to primary selectivity. In the photolytic reaction of NCP with 2,3-dimethylbutane a selectivity per hydrogen abstracted was found to be 170/1, a value considerably larger than the selectivity observed for chlorine atoms of 5/1.

Several radicals lend themselves as possible hydrogen-abstracting species when NCP is used as a free-radical chlorinating agent, Scheme II. The abstracting radical could be

Scheme II

$$X = H \text{ or } Cl$$
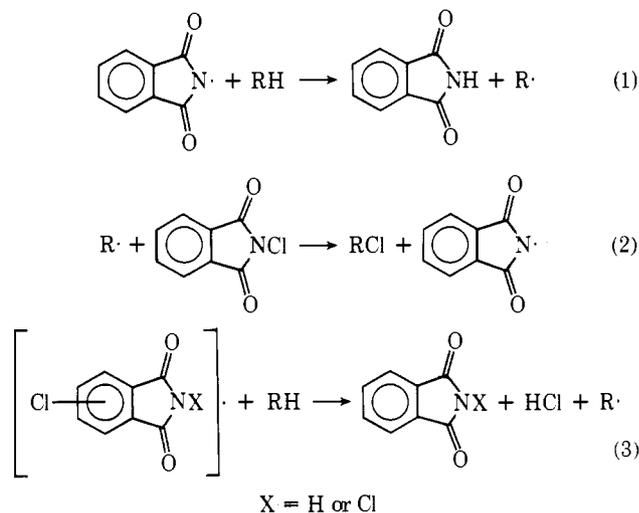
considered to be the phthalimido radical derived from the homolytic cleavage of the N–Cl bond. The phthalimido radical would be expected to be more selective in its hydrogen-abstracting reactions than chlorine atoms. Traynham has reported the reactivity of the succinimide radical derived from N-bromosuccinimide, with several alkanes.[2] The reported mode of attack of the succinimidyl radical involves more C–H bond breaking in the transition state than observed for chlorine atoms, making the succinimido radical more selective than molecular chlorine.

Greene has also demonstrated that amidyl radicals, derived from N-chloroamides, in their hydrogen-abstracting reactions

are more selective than chlorine atoms. A tertiary to primary selectivity for the N-methyl amidyl radical was found to be ~95/1, a selectivity more comparable with the value reported here for NCP. Furthermore, Greene has found that the mode of generation of the radical from the N-chloroamides will change the nature of the hydrogen-abstracting species. Photolytic generation of the radical favors the amidyl radical as the chain-carrying species, while initiation of the reaction with peroxides favors chlorine atoms.[3]

A similar behavior was noted in our NCP chlorinations. Initiation with benzoyl peroxide or azobisisobutyronitrile (AIBN) of mixtures of NCP and 2,3-dimethylbutane gave tertiary to primary selectivities of 23.4 ± 3.3 and 18.3 ± 2.1, respectively. In the thermally initiated reactions, the chain length for the production of the product was quite low, <2 for both initiators. The low value for the chain length would indicate that a large amount of hydrogen atom abstraction is by the initiator.

A second possible radical for the selectivity in the photochemical reactions could be a complexed chlorine atom, or possibly a complexed imido radical, Scheme II reaction 3. The chlorine atom could be complexed to the π system of the phthalimide or N-chlorophthalimide. Russell[4] has shown that complexed chlorine atoms are less reactive, more selective than free chlorine atoms in their tertiary to primary differentiation. A selectivity of 4/1 for chlorine atoms can be changed to 225/1 for chlorine atoms that are complexed in 12 M carbon disulfide. The change in the selectivity of chlorine atoms is less when aromatic solvents are used, but the effect is still present. In reactions of chlorine in 8 M benzene, the selectivity was found to change from 4/1 to 32/1.[4] Owing to the very low amount of phthalimide or N-chlorophthalimide present for complexing with the abstracting radical, the increase in the selectivity observed in this system would not appear to be due to a complexed radical.

A third possibility for the nature of the abstracting radical could be the involvement of a mixed chain of either a complexed chlorine, chlorine atoms, or the phthalimido radical.

The reaction of NCP with hydrocarbons is found to require long irradiation times, considerably longer times than required for the reaction of NCS. The implication is that there is at least one step in the reaction sequence that proceeds with some difficulty. In reactions of this type, with at least one slow step, the major assumption of free-radical reactions, that the observed products are in the same ratios as the intermediately formed radicals, is not always valid. Some of these reactions are not under the expected kinetic control, but instead the reaction is governed by thermodynamic control, the thermodynamic equilibrium arising by the reversible attack of the intermediately formed alkyl radical upon the product of the abstraction step, the hydrogen halide.

Reversible hydrogen abstraction from hydrogen bromide is a well-documented phenomenon.[7] The reversible attack of alkyl radicals upon hydrogen chloride is less well known, but has previously been observed in the radical addition of hydrogen chloride to propene,[8] where the product is the unexpected 2-chloropropane. In addition, hydrogen abstraction from hydrogen chloride by alkyl radicals has been reported in the photocyanation of alkanes by cyanogen chloride[9] and in the free-radical chlorination of alkanes by benzoyl hypochlorite.[10]

Reversible hydrogen abstraction could then modify either Scheme I or II. To demonstrate the possible involvement of reversible hydrogen abstraction, the selectivity was studied as a function of the percent conversion of NCP into chlorinated products, Table II. The selectivity was found to rapidly increase from a minimal value of 6.0/1 at <0.1% conversion to over 150/1 at 10.5% conversion.

The effect of hydrogen chloride on the reaction was also

Table II. Variation of the Tertiary to Primary Selectivity per Hydrogen with the Percentage Reaction for the Free-Radical Chlorination of 2,3-Dimethylbutane with N-Chlorophthalimide

Set I[a]	
Selectivity	% reaction
5.41	0.06
32.0	3.89
63.1	6.14
77.7	7.66
80.4	8.18
120.1	14.4

Set II[b]			
	% reaction		
Selectivity	NCP	RCl	Time[c]
7.3	0.3	0.3	0.5
45.6	21.1	4.2	5
60.6	24.3	9.4	13
63.9	25.0	7.4	
75.8	33.3	15.7	18
84.0	40.9	18.1	20.5
141.0	50.2	23.5	32

Set III[d]		
Selectivity	% reaction	Time[c]
6.1	0.08	0.5
43.5	2.18	3.0
55.2	2.54	4.5
70.6	2.82	5.0
88.5	4.19	7.0
92.1	4.78	9.0
97.8	5.70	10.0
102.8	7.81	16.0
152.9	10.47	21.0

[a] All tubes in set I were 14.6 ± 0.3 cm long. The percent reaction is based upon the percent conversion of NCP into alkyl chlorides. [b] All tubes in set II were 12.0 ± 0.2 cm long. The percent reaction is based upon both the percent conversion of NCP into alkyl chlorides, column RCl, and upon the percent NCP consumed, column NCP. [c] Time in days. [d] All tubes in set III were 11.5 ± 0.3 cm long. The percent reaction is based upon the conversion of NCP into alkyl chlorides.

demonstrated in another manner. In the reaction of NCP with a mixture of cyclohexane and perdeuteriocyclohexane, the unreacted starting materials were found to have increased the amount of deuterium and hydrogen respectively. The percentage of the hydrogen in the perdeuteriocyclohexane could have only increased by the reaction of the perdeuteriocyclohexyl radical with a molecule of hydrogen chloride. Similarily, the increase in the deuterium content of the cyclohexane could have arisen only by the reaction of the secondary cyclohexyl radical with deuterium chloride. The reaction of the perhydrocyclohexyl radical with hydrogen chloride, the energetically favorable pathway, could not be detected. Likewise, any reaction of the perdeuteriocyclohexyl radical with deuterium chloride could not be determined. The amount of reversible hydrogen abstractions from hydrogen chloride by alkyl radicals, as measured by incorporation, must be a minimal value, Table III.

The reaction of perdeuteriocyclohexane and 2,3-dimethylbutane with NCP, Table III, showed increase in the hydrogen and deuterium content of the respective hydrocarbon starting materials after irradiation. It can be seen that reversal of the intermediate alkyl radical is a process of major importance, for the value of E/RCl (ratio of exchange to product formation) approaches unity. Nearly one reversible abstraction of hydrogen from hydrogen chloride occurs for every attack of the alkyl radical upon molecular chlorine. The values reported in Table III are a lower limit of the actual extent of the exchange reaction.

The usually high selectivity found in the reaction of NCP with hydrocarbons is due to hydrogen chloride reversibility, Scheme III. Since chlorine atoms abstract tertiary (or secon-

Scheme III

$$R\cdot + Cl_2 \xrightarrow{k_3} RCl + Cl\cdot \quad (1)$$

$$R^IH + Cl\cdot \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} R^I\cdot + HCl \quad (2)$$

$$R^{III}H + Cl\cdot \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} R^{III}\cdot + HCl \quad (3)$$
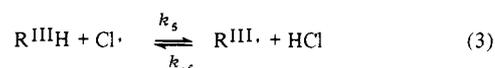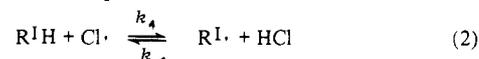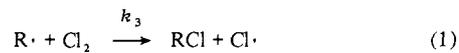
dary) hydrogens more rapidly than primary hydrogens, the values of the rate constants would be $k_5 > k_4$. From known bond dissociation energies[11] and the kinetics of gas phase chlorinations of alkanes,[12] it can be shown that primary alkyl radicals will react faster with hydrogen chloride than tertiary (or secondary); therefore $k_{-5} < k_{-4}$. The results of these two inequalities upon Scheme III is to increase the apparent selectivity of the abstracting radical.

Table III. The Photolytic Reaction of N-Chlorophthalimide with Alkanes at 37 °C

Mol of starting material[a]				% increase of[b]				
C_6H_{12}	C_6D_{12}	NCP	% reaction	H in C_6D_{12}	D in C_6H_{12}	H in $C_6D_{11}Cl$	D in $C_6H_{11}Cl$	E/RCl[c]
4.19	4.31	3.95	67.7	24.6	15.4	5.3	4.0	0.78
				1±1.4	±2.0	±1.2	±1.4	
2.75	2.79	3.18	77.8	22.6	17.6	7.9	5.6	0.60
				±3.0	±1.9	±0.5	±1.3	
2.60	2.68	2.91	87.1	27.6	16.2	8.5	6.8	0.63
				±2.1	±1.1	±1.0	±0.5	

Mol of starting material[a]				% increase of		
C_6H_{14}	C_6D_{12}	NCP	% reaction	H in C_6D_{12}	D in C_6H_{14}	E/RCl[d]
1.93	2.19	1.03	62.9	18.4	11.1	0.94
				±0.4	±1.3	
0.94	1.06	0.99	23.2	6.7	1.6	0.37
				±1.0	±0.2	

[a] C_6H_{12}, cyclohexane; C_6D_{12}, perdeuteriocyclohexane; C_6H_{14}, 2,3-dimethylbutane. [b] Increased amounts of either hydrogen or deuterium are for only monoexchanges, disubstitution not calculated. [c] E/RCl is defined as the number of exchanges (either hydrogen or deuterium) in the starting material plus the chlorinated product, divided by the total amount of chlorinated product. [d] E/RCl is defined as the number of exchanges (either hydrogen or deuterium) in the starting material divided by the total amount of chlorinated product.

Table IV. The Tertiary to Primary Selectivity for[b] the Reaction of N-Chlorophthalimide with 2-Methylpropane in Acetonitrile Solutions, as a Function of Percentage Reaction

Selectivity[a]	% reaction
5.42	1.25
6.10	14.2
5.50	83.8
5.97	94.2
6.19	95.0

[a] The abstraction rate for primary hydrogens assigned a value of 1. [b] Temperature for the reaction 36 °C.

Since chlorinations of alkanes with molecular chlorine or NCS do not exhibit hydrogen chloride reversibility, it is necessary to explain why it is observed in this system. The product-forming reaction (Scheme III, reaction 1) is in competition with the reaction of alkyl radicals with hydrogen chloride. Normally, in chlorinations with either chlorine or NCS, there is an abundant supply of molecular chlorine, and the faster exothermic reaction of the alkyl radical with chlorine will dominate. In this system, the supply of chlorine is limited by a process similar to Scheme I, if $k_3 > k_2$. Chlorine is therefore used up as fast as it is formed. The concentration is therefore always very low. As a result the alkyl radical is able to react with hydrogen chloride to equilibrate the intermediate alkyl radicals before they encounter a chlorine molecule.

The explanation for the low concentration of chlorine is due to the exceedingly low solubility of NCP in alkanes. There is little NCP in solution to react with the hydrogen chloride formed in the abstraction step. The solubility was found to effect the selectivity, when the reaction was run in acetonitrile as a solvent, a solvent where NCP is reasonably soluble, the selectivity was found not to change with percent conversion of the chlorinating agent into product, and the selectivity was found to be 6/1 for tertiary to primary attack per hydrogen, Table IV. In addition the reaction time was decreased markedly. A 99% conversion of the NCP into chlorinated products was obtained with <2 days' irradiation, while in 2,3-dimethylbutane the reaction required up to 1 month. Similar increased reaction times were noted in homogeneous solutions of 2,3-dimethylbutane and NCP in chloroform.

An alternative explanation for the complication observed when NCP is used in hydrocarbon solvents, not noted for NSC or other N-chloroimides, could be the fact that hydrogen chloride reacts faster with NCS than with NCP. Unfortunately attempts to determine a relative rate of reaction of hydrogen chloride with NCP and NCS by NMR spectrometry were

unsuccessful. It was not possible to resolve the imide protons of succinimide and phthalimide on the instrument used.

Experimental Section

N-Chlorophthalimide was prepared by the method of Zimmer.[13] Its purity was determined by iodometric titration to be between 98 and 101% after recrystalization from petroleum ether or chloroform. Cyclohexane-d_{12} was obtained from Columbia Organic Chemical Co. and was shown to be 99.8% deuterated. By GLC analysis the cyclohexane-d_{12} was shown to contain < 0.01% cyclohexene. Hydrocarbons were commercially available, their purity checked by GLC, and if required purified by distillation before use.

General Procedure. Reactions were carried out in sealed Pyrex ampules which had been twice degassed by the freeze-thaw method. The ampules containing the thermal initiators (either benzoyl peroxide or AIBN) were allowed to stand in a constant-temperature bath (98 ± 2 °C) for over 4 half-lives. The photolytic ampules were allowed to stand in a constant-temperature bath (36 ± 0.5 °C) and photolyzed with two 150-W tungsten lamps. The ampules were opened, a weighted amount of an appropriate standard was added to the tubes, and the contents were analyzed by GLC on one of the followish types of columns: (a) 20% SE-30 silicone rubber on 60/80 mesh Chromosorb W, or (2) 15% Carbowax 20M on 100/120 mesh Chromosorb W. After triplicate analyses, the contents of the tubes were reacted with acidified potassim iodide, to determine the amount of remaining N-chloro compound, and the hydrocarbon layer was reanalyzed by GLC. The amounts of chlorinated products determined by these two methods were always within experimental error. Products were identified by comparison of their retention times with those of authentic samples.

Reactions of NCP with Hydrocarbons. Thermally Initiated Heterogeneous Reactions. A large excess of the hydrocarbon (~100-fold molar excess) was added to an accurately weighted sample of the N-chloroimide and the thermal initiator (either benzoyl peroxide or AIBN) in a Pyrex ampule. The amount of NCP was in the region of 10^{-4} mol/tube and the initiator varied from <2 to 30% of the molar amount of the chlorinating agent. The reaction tubes were degassed by the freeze-thaw method, the ampules sealed, and the tubes placed in a boiling water bath for between 2 and 3 h. All of the tubes were protected from light during the time in the bath, and until they were analyzed. The only alkyl chlorides detected from 2,3-dimethylbutane were 1-chloro-2,3-dimethylbutane and 2-chloro-2,3-dimethylbutane. The only alkyl product from cyclohexane was the monochlorocyclohexane. The chain lengths and the product yields are reported in Table V.

Heterogeneous Photochemical Reactions. Relative Rates of Reaction. An equimolar mixture of cyclohexane and the other substrate was prepared. A large excess of the hydrocarbon mixture was added to accurately weighted sample of NCP (~10^{-4} mol) in Pyrex ampules. The ampules were degassed, sealed, and irradiated in a constant-temperature bath. The tubes were removed and opened, and an internal standard was added. The amounts of the chlorinated hydrocarbons were determined by GLC. The relative reactivities were calculate from the molar yields of the products by the equation relative

Table V. Values for the Chain Length in the Thermally Initiated Reactions of Either Cyclohexane or 2,3-Dimethylbutane with N-Chlorophthalimide. The Thermal Initiators Used Were Both AIBN and Benzoyl Peroxide

mol of NCP × 10^{-4}	mol of AIBN × 10^{-4}	Cyclohexane mol of benzoyl peroxide × 10^{-4}	mol of chlorocyclohexane × 10^{-4}	Chain length
7.32		0.98	1.81	1.8
4.61		1.76	1.68	1.9
5.51	0.12		0.63	0.5
5.51	0.18		0.87	0.46

mol of NCP × 10^{-4}	mol of AIBN × 10^{-4}	2,3-Dimethylbutane mol of benzoyl peroxide × 10^{-4}	mol of primary chloride × 10^{-5}	mol of tertiary chloride × 10^{-5}	Selectivity	Chain length
7.45		1.53	5.92	18.42	18.7	1.4
11.44		1.46	7.02	21.41	18.3	1.9
4.31		0.38	1.17	4.04	20.7	1.4
7.91	0.15		0.16	0.47	17.9	0.4
5.55	0.12		0.063	0.20	19.4	0.2

Table VI. Material Balance on *N*-Chlorophthalimide Used in the Chlorination of 2,3-Dimethylbutane in Heterogeneous Reactions

mol of NCP × 10^{-4}	mol of chlorohexanes × 10^{-5}	mol of phthalimide × 10^{-4}	mol[a] of chlorophthalimide × 10^{-5}	% convn of NCP to chlorides	Material balance
7.26	0.24	6.99	0.8	3.8	97.5
4.57	4.32	3.46	6.1	24.2	98.5
4.31	18.38	2.04	4.0	53.0	99.3
4.07	9.6	2.08	7.1	51.1	92.1

[a] Moles of ring chlorinated phthalimide. The amount of chlorinated NCP in the reaction mixture could not be determined since the remaining NCP was destroyed before GLC analysis.

Table VII. The Molal Solubility of *N*-Chlorophthalimide in Various Solvents as a Function of Temperature. All Molalities Reported in the Table are × 10^{-2}

	Temp °C[a]					
	24.5		48.5		58.5	
Solvent	titrn	wt	titrn	wt	titrn	wt
Acetonitrile	22.7	20.3	37.1		47.1	42.6
	±0.1	±0.3	±0.3		±0.5	±1.4
Benzene	11.7				27.1	25.3
	±0.1				±0.1	±0.1
Carbon tetrachloride	0.72	1.00	2.14	2.75	3.22	3.34
	±0.17	±0.08	±0.63	±0.21	±0.30	±0.31
Chloroform	18.6	20.1				
	±0.2	±0.2				
Cyclohexane	0.31	0.40	1.20	1.08	1.48	1.67
	±0.01	±0.07	±0.18	±0.05	±0.05	±0.20
2,3-Dimethylbutane	0.45	0.43	0.81		1.42	1.24
	±0.1	±0.01	±0.08		±0.1	±0.12

[a] The molalities were determined by either one of two methods: titrn, titration of NCP in solution; or wt, weight of NCP after removal of solvent.

rates = moles of chlorinated substrate/moles of chlorocyclohexane. The values for the relative rates of reactions are found in Table I.

Heterogeneous Photochemical Reactions. Chlorination of 2,3-Dimethylbutane. The photolytic reactions of NCP and 2,3-dimethylbutane were carried out similar to the reactions described above, except that the thermal initiator was omitted. The sealed, degassed ampules were irradiated in a constant-temperature bath and the ampules removed at various times and analyzed as above. The selectivity and the percent reaction of the hetrogenous chlorinations are found in Table II. With selected tubes, after analysis for the chlorinated hexanes, the reaction mixture was dissolved in toluene and analyzed by GLC for the amount of phthalimide and ring chlorinated phthalimides. Table VI presents the results of these determinations.

Homogeneous Photochemical Reactions. Chlorination of Isobutane. Solutions of iosbutane (5.8 M) and NCP (0.06 M) in purified acetonitrile were degassed, sealed, and irradiated as above. The selectivity as a function of the percent conversion of NCP into product, either *tert*-butyl chloride or isobutyl chloride, are reported in Table IV. In the homogeneous reactions, the length of time required for the reaction was considerably shorter than for the heterogeneous reactions.

Scrambling Experiments. A. Cyclohexane and Perdeuteriocyclohexane. A nearly equimolar mixture of cyclohexane and perdeuteriocyclohexane was prepared. An accurately weighted sample of this solution was added to an accurately weighted sample of NCP in a Pyrex ampule. The mixtures were degassed, sealed, and irradiated. The tubes were opened, the supernatent solution was removed, and an internal standard was added. The percentage conversion was calculated from the yield of the chlorinated cyclohexanes present. The amount of incorporation of either deuterium into cyclohexane and hydrogen into perdeuteriocyclohexane was determined by mass spectrometry by comparing the peak ratios of the fragments 84/85 and 96/95 for the recovered hydrocarbons with the 84/85 and 96/95 mass fragments in the original mixture of cyclohexanes. The incorporation in the chlorinated products was determined by comparing the mass spectrometry fragmentation peaks of 119/120 and 131/130 in the products to the 84/85 and 96/95 fragment peaks in the original hydrocarbon mixture.

B. 2,3-Dimethylbutane and Perdeuteriocyclohexane. Similarly a nearly equimolar mixture of the two hydrocarbons was prepared and an accurately weighted sample of this mixture added to accurately weighted samples of NCP. The reaction mixtures were treated as described in part A. The incorporation was calculated from the mass spectral peak ratios of 86/87 and 96/95 in the original mixture of hydrocarbons before reaction with the peak ratios in the recovered hydrocarbons after reaction. The amount of incorporation for both parts A and B is found in Table III.

Solubilities. In the dark, excess NCP was added to a hydrocarbon or other solvent in a flask. The mixture was placed in a constant-temperature bath (maintained to within 0.5 °C). The flask was stirred repeatedly for several hours and then allowed to stand. Small aliquots of the solution were removed and weighed, the solvent was removed by evaporation, and the remaining NCP was determined by weight. In alternate tests, the NCP was determined in the weighed solutions by iodometric titration. The solubilities at each temperature were determined at least three times by both methods. The values for the two methods are listed in Table VII.

References and Notes

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