Gas-Phase Atomic Halogenation Reactions Using Iodine Monochloride

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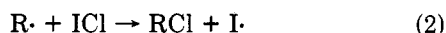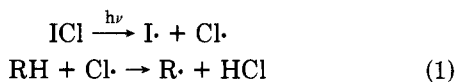
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The mechanism of the photoinitiated gas-phase halogenation reactions of alkanes using iodine monochloride has been reported previously as proceeding via a radical chain process to form the corresponding alkyl chlorides. This is in marked contrast to analogous reactions with bromine–chlorine mixtures, thought to form bromine chloride, which produce alkyl bromides via a radical process. An attempt has been made to rationalize this anomaly. In this paper evidence is offered to demonstrate that under photolytic conditions, alkanes and iodine monochloride react via a radical chain process to produce initially the corresponding alkyl iodide. The reaction is shown to proceed by a chain process where the chain-carrying species is the chlorine atom. However, the reaction is complicated by further ionic reactions of the alkyl iodides, with iodine monochloride, which produce alkyl chlorides and other polyhalogenated materials.
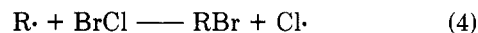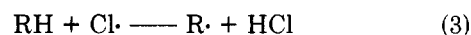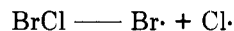
In the course of a study to investigate its potential use as a halogenating agent, the reagent formed by mixing *tert*-butyl hypochlorite and iodine[3] (a reagent which had previously been considered to be "*tert*-butyl hypoiodite"[4-6]) was used to halogenate cyclohexane as an example of a representative substrate. Similarly, comparative reactions were carried out by using iodine chloride and iodine trichloride[7,8] since these reagents were thought to be involved in the above reaction mixture. These reactions were demonstrated to be initiated by light. In all cases, four products were produced: iodocyclohexane, chlorocyclohexane, *trans*-1,2-dichlorocyclohexane, *trans*-1-iodo-2-chlorocyclohexane. These studies indicated that the reaction proceeded initially by a radical process to produce iodocyclohexane followed by ionic reactions to yield the remaining products.

The results observed when iodine trichloride was used were very similar to previously published results of Huyser[9] who proposed that a mixed chain radical mechanism was operative and led to the production of the mono-halogenated products. To explain the dihalogenated products Huyser proposed an ionic, acid-catalyzed dehydrogenation followed by addition across the olefin bond.

A search of the literature revealed that the photoinitiated reaction of iodine monochloride with aliphatic substrates in the gas phase had been observed to produce only chlorinated products.[10,11] The reaction was tentatively proposed to follow a mechanism where a chlorine atom abstracts a hydrogen from the substrate (reaction 1), followed by capture of the alkyl radical by iodine chloride to form the alkyl chloride (reaction 2). However, the stoichiometry of the reaction and the fate of the iodine was not elaborated upon.

$$\text{ICl} \xrightarrow{h\nu} \text{I·} + \text{Cl·}$$

$$\text{RH} + \text{Cl·} \rightarrow \text{R·} + \text{HCl} \tag{1}$$

$$\text{R·} + \text{ICl} \rightarrow \text{RCl} + \text{I·} \tag{2}$$

This is in marked contrast to similar reactions using an equimolar mixture of bromine and chlorine, which is thought to form bromine chloride, where brominated compounds are the sole products. This method has been used to introduce bromine into trimethylchlorosilane[12] and methylene fluoride.[13] These substrates are difficult to brominate by a free radical chain process but are readily chlorinated. The method takes advantage of the lower activation energy for abstraction of a hydrogen by a chlorine atom. Although no detailed mechanistic studies have been carried out, the reaction is thought to proceed via a hydrogen-abstraction step by a chlorine atom (reaction 3), followed by transfer of a bromine atom to the alkyl radical by bromine chloride to form alkyl bromide (reaction 4).

$$\text{BrCl} \longrightarrow \text{Br·} + \text{Cl·}$$

$$\text{RH} + \text{Cl·} \longrightarrow \text{R·} + \text{HCl} \tag{3}$$

$$\text{R·} + \text{BrCl} \longrightarrow \text{RBr} + \text{Cl·} \tag{4}$$

It is interesting that the resulting alkyl radicals transfer with bromine rather than the chlorine end of Br–Cl, since the C–Br bond is weaker and consequently its formation is less exothermic than that of the corresponding C–Cl bond. These results have been rationalized by Walling on both steric and polar grounds.[14] It has been proposed that because the larger size of the Br end occupies most of the surface of the molecule, collision with this part of the molecule is more probable. Also it is thought that the high electron density of the carbon radical reacts preferentially with the positive end of the Cl←+Br dipole.

Logically a similar effect would be anticipated for the corresponding halogenation reactions with ICl. The anomaly between the atomic halogenation reactions of Br–Cl and I–Cl has been commented upon by Poutsma[15] but has not previously been experimentally investigated. In order to rationalize this observation, and our own solution phase results, a study of the gas-phase reactions of iodine monochloride with three aliphatic substrates, cyclohexane, neopentane, and propane was undertaken and is the subject of this paper.

Results and Discussion

The Reaction with Cyclohexane. A tenfold excess of cyclohexane was allowed to react with iodine chloride, under photolytic conditions, in a glass reaction vessel which had been equilibrated at 36 °C. The reactants were irra-

(1) Taken in part from: Rowe, J. E., Ph.D. Thesis, University of Alberta, 1974.

(2) Postdoctoral Fellow, University of Alberta, 1982–1985.

(3) Tanner, D. D.; Gidley, G.C.; Das, N.; Potter, A. *J. Am. Chem. Soc.* **1984,** *106,* 5261.

(4) Akhtar, M.; Barton, D. H. R. *J. Am. Chem. Soc.* **1964,** *86,* 1528.

(5) Barton, D. H. R.; Beckwith, A. L. J.; Goosen, A. *J. Chem. Soc.* **1965,** 181.

(6) Britten-Kelly, M. R.; Goosen, A.; Scheffen, A. *J. S. Afr. Chem. Inst.* **1975,** *28,* 224.

(7) Unpublished results from this laboratory.

(8) Rowe, J. E. Ph.D. Thesis, University of Alberta, 1974.

(9) Hess, W. W.; Huyser, E. S.; Kleinberg, J. *J. Org. Chem.* **1964,** *29,* 1106.

(10) Kelly, C. C.; Wijnen, M. H. J. *J. Phys. Chem.* **1969,** *73,* 2447.

(11) Kelly, C. C.; Yu, W. H. S.; Wijnen, M. H. J. *Can. J. Chem.* **1970,** *48,* 603.

(12) Speier, J. L. *J. Am. Chem. Soc.* **1951,** *73,* 826.

(13) Rue, R. P.; Davis, R. A. U.S. Patent 2 658 086, 1953.

(14) Walling, C. "Free Radicals in Solution"; Wiley: New York, 1957; p 379.

(15) Poutsma, M. L. "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 2, p 204.

Table I. The Photoinitiated Reaction of Iodine Monochloride with Cyclohexane

reacn	10^{-3}[ICl]	10^{-3}[ICl + C$_6$H$_{12}$]	relative yield, %[a]				material balance[b]
1	0.015[c]	0.185	82.3	3.2	14.5		105.6
2	0.033[c]	0.360	49.0	16.5	34.5		107.0
3	0.080[c]	0.900	10.2	23.8	66.0	f	95.8
4	0.120[c]	1.535	5.3	23.7	69.1	1.9	
5	13.3[d]		8.8	22.2	35.7	33.5	79.9
6	13.6	e		28.7	67.2	4.1	

[a] The *relative* yields of iodocyclohexane, chlorocyclohexane, *trans*-1-iodo-2-chlorocyclohexane, and *trans*-1,5-dichlorocyclohexane. [b] Balance based upon the amount of ICl consumed. [c] Gas phase, *T* = 36 °C. [d] Liquid phase, *T* = 10 °C. [e] Liquid-phase reaction of iodocyclohexane with ICl, *T* = 10 °C. [f] Trace.

Table II. The Gas-Phase Photoinitiated Reaction of Iodine Monochloride with Neopentane at 36 °C

10^{-3}[ICl]	10^{-3}[ICl + C$_5$H$_{12}$]	relative yield, %[a]			material balance[b]
0.145	1.600	100			94.4
0.20	2.125	100	d		88.1
0.715	7.865	55.8	39.4	4.5	74.8
1.800[c]	19.800	26.5	40.1	33.4	54.7

[a] The *relative* yields of neopentyl iodide, 2-chloro-2-methylbutane, and 2,3-dichloro-2-methylbutane. [b] Balance based upon the amount of ICl consumed; small amounts of polyhalogenated materials could always be detected. [c] Reactants partially condensed on wall of reaction vessel. [d] Trace.

diated for 10 min; the contents of the flask were observed to change from a brown to a purple color quite rapidly. The molar ratio of cyclohexane to iodine monochloride was kept constant (10:1), and the reaction was repeated at different absolute concentrations of iodine chloride and cyclohexane. The yields of products were determined by gas chromatographic analysis (see Table I, reactions 1–4).

Four major products were identified from the gas-phase reaction of iodine monochloride with cyclohexane: iodocyclohexane, chlorocyclohexane, *trans*-1,2-dichlorocyclohexane, and *trans*-1-iodo-2-chlorocyclohexane. Material balances were calculated on the assumption that a monoiodide consumed 1 mol of iodine monochloride, 2 mol for a monochloride or an iodochloride, and 3 mol for a dichloride; in all cases the material balance reasonably accounted for most of the iodine chloride consumed.

At low concentration of reactants the major product was iodocyclohexane with lower relative yields of chlorocyclohexane and *trans*-1-iodo-2-chlorocyclohexane. As the absolute concentration of reactants in the vessel was increased the yield of iodocyclohexane diminished, and the yield of the chlorinated products correspondingly increased.

The liquid phase reaction of iodine monochloride with cyclohexane produced the same products, albeit, in different yields (reaction 5, Table I). If the reaction was repeated in the absence of light no reaction products were observed. When iodocyclohexane and iodine monochloride were allowed to react, in the dark, under the same conditions as the photoinitiated liquid-phase reaction, the three chlorinated products were produced (reaction 6, Table I). These liquid-phase results indicate that there is an initial radical process to form the alkyl iodide, followed by ionic reactions to produce the chlorine containing products.

It can be proposed that a similar process occurs in the gas-phase reaction. At low concentrations, when the reaction must be primarily in the gas phase, the major product, and in all probability the sole product at increasing dilution, was iodocyclohexane. When the reaction

is repeated under more concentrated conditions, i.e., the chance of solution-phase reactions occurring on the wall of the vessel increases, the relative yield of iodocyclohexane diminishes, and the yields of the chlorinated products increase. It was apparent that the iodocyclohexane which was produced initially by a radical chain process reacted further with iodine monochloride via an ionic mechanism to yield the chlorinated products.

The ionic reaction between alkyl iodides and iodine monochloride is well documented. Keefer and Andrews[16,17] observed that alkyl iodides react with iodine monochloride via an ionic halogen-exchange reaction to yield the corresponding alkyl chloride (reaction 5) and by an ionic substitution reaction to yield the corresponding 1-iodo-2-chloroalkane (reaction 6).

$$RI + ICl \rightarrow RCl + I \qquad (5)$$

$$RCH_2CH_2I + 2ICl \rightarrow RCH(Cl)CH_2I + I_2 + HCl \qquad (6)$$
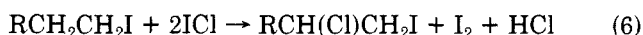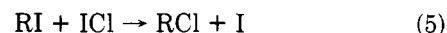
However, the evidence that the subsequent reactions of the iodocyclohexane was an ionic process was not completely conclusive. Consequently, the reaction was repeated with neopentane, which is a much better diagnostic probe for a subsequent ionic reaction.

The Reaction with Neopentane. The reaction with neopentane was carried out under the same conditions as the cyclohexane reactions: reaction temperature, 36 °C; irradiation time, 10 min. Three major products were identified: neopentyl iodide, 2-chloro-2-methylbutane, and 2,3-dichloro-2-methylbutane, as well as minor amounts of oter polychloro- and iodochloro-isomers of pentane.

At low absolute concentrations of iodine chloride, the major product was neopentyl iodide (see Table II). As the concentration of iodine chloride was increased, the yield of neopentyl iodide decreased while the yields of chlorinated products correspondingly increased. The major chlorinated products were 2-chloro-2-methylbutane

(16) Keefer, R. M.; Andrews, L. J. *J. Am. Chem. Soc.* 1953, 75, 543.
(17) Keefer, R. M.; Andrews, J. J. *J. Am. Chem. Soc.* 1954, 76, 253.

Scheme I

dihalogenated material
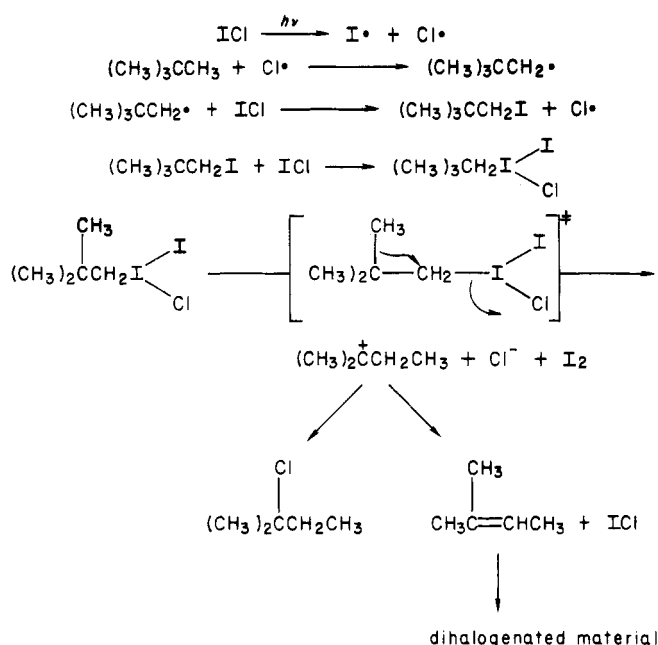
and 2,3-dichloro-2-methylbutane. As the yields of the two chlorinated compounds increased there was also a noticeably increased amount of polyhalogenated material produced. Although the amount of this material was not estimated, it is evident that this polyhalogenated material accounts for the poor material balance observed in the reactions carried out under concentrated conditions. The production of small amounts of polyhalogenated material consumes a considerable portion of the ICl.

When neat neopentyl iodide and iodine monochloride were allowed to react in the dark there was a vigorous reaction. Analysis of the mixture revealed that 2-chloro-2-methylbutane and 2,3-dichloro-2-methylbutane were the major products, along with noticeable amounts of polyhalogenated material.

It is apparent that a similar reaction to that observed in the cyclohexane system is occurring. The initial reaction proceeds via a radical reaction to form neopentyl iodide. At low concentrations all the iodine chloride has been used up and there is little chance of a further ionic reaction on the walls of the reaction vessel. As the concentration of iodine chloride is increased, the neopentyl iodide formed by the initial reaction reacts, via an ionic mechanism, to form chlorinated products. Since the neopentyl system is resistant to both S_N2 and simple S_N1 substitution a subsequent ionic process leads only to rearranged chloride. As predicted the ionic reaction proceeds to form 2-chloro-2-methylbutane, presumably via a halogen-exchange reaction through a hypervalent halogen intermediate which concomitantly rearranges to the more stable tertiary carbonium ion. This reacts to form either a tertiary chloride or eliminates to form olefin which subsequently dihalogenates via an ionic process, see Scheme I.

The Reaction with Propane. Propane and iodine chloride were allowed to react in the gas phase under the same conditions as described above: i.e., temperature, 36 °C; irradiation time, 10 min. The concentrations of the reactants were kept low ([ICl] = 0.017 mmol/L; [C_3H_6] = 0.170 mmol/L) to ensure that the reaction occurred totally in the gas phase and that any chance of subsequent solution phase reactions on the wall of the reaction vessel was kept to a minium. Only two products were produced, 2-iodopropane (54.5%) and 1-iodopropane (46.5%). There was no evidence of the presence of the corresponding

chlorinated materials in contrast to the results from the experiments reported by Wijnen,[10,11] which were carried out under much more concentrated conditions.

The relative selectivity (per hydrogen atom) for secondary to primary hydrogen abstraction for this reaction at 36 °C can be calculated from the product ratio, $RS_p{}^s$ = 3.5. This value is in good agreement with the published value of 4.0[18,19] for the selectivity of the corresponding gas-phase chlorination of propane.

These results provide further evidence that the photoinitiated reaction of iodine monochloride and alkanes occurs initially via a radical process. The chlorine atom generated from the photolysis of the iodine chloride abstracts hydrogen. Subsequently, the alkyl radical transfers with the iodine end of iodine chloride to produce the alkyl iodide. As would be expected the process demonstrates the selectivity of the corresponding chlorination reaction.

Experimental Section

Iodine monochloride (British Drug Houses Ltd.), neopentane, propane, and cyclohexane (Phillips Research Grade), 1-chloropropane, 2-chloropropane, 1-iodopropane, 2-iodopropane, and undecane (Aldrich Chemical Co.) were used as supplied.

Freon 113, 1,1,2-trifluoro-1,2,2-trichloroethane (Matheson Chemical Co.), was distilled prior to use.

trans-1,2-Dichlorocyclohexane and chlorocyclohexane (Aldrich Chemical Co.) and iodocyclohexane and 2-chloro-2-methylbutane (Eastman Organic Chemicals) were distilled prior to use.

trans-1-Chloro-2-iodocyclohexane was prepared by the procedure of Birchkenbach and Goubeau[20] by the reaction of a slight excess of cuprous chloride with a large excess of cyclohexene in anhydrous ether. The product was obtained as a slightly pink liquid in 80% yield, bp 58 °C (0.8 mm) [lit.[20] 117 °C (14 mm)]. The NMR spectral data were identical with the data for *trans*-1-chloro-2-iodocyclohexane published by Premuzic and Reeves.[21]

Neopentyl iodide was prepared by the reaction of neopentyl alcohol with triphenyl phosphite and methyl iodide according to the procedure of Rydon.[22] The product was a clear liquid obtained in 45% yield: bp 21 °C (1.5 mm) [lit. 55 °C (55 mm)]: NMR (CCl₃D) δ 1.1 (9 H, s), 3.2 (2 H, s).

Identification of Products. Reaction mixtures were analyzed by capillary GC/mass spectrometry to identify reaction products, and their assignment was confirmed by comparison of their GC retention times with those of the authentic materials (50-m methyl-silicone capillary column, 35–180 °C).

The analysis of the mixture from the reaction of cyclohexane with iodine chloride revealed as the major products iodocyclohexane (P^+ = 210), chlorocyclohexane (P^+ = 118, 120; 3:1), and iodochlorocyclohexane (P^+ = 244, 246; 3:1). These compounds were confirmed to be iodocyclohexane, chlorocyclohexane, and *trans*-1-iodo-2-chlorocyclohexane by comparison of retention times with those of authentic compounds. This technique also revealed the presence of *trans*-1,2-dichlorocyclohexane. Trace amounts of compounds which correspond to $C_6H_9ICl_2$ (P^+ = 278, 280, 282) were also detected.

GC/mass spectral analysis of the mixture from the reaction of neopentane and iodine monochloride showed the major products to be an iodopentane (P^+ = 198), a chloropentane ((P − ethyl)$^+$ = 77, 79; 3:1), and a dichloropentane ((P − 1)$^+$ = 139, 141, 143; 9:6:1). The products were identified to be neopentyl iodide, 2-chloro-2-methylbutane, and 2,3-dichloro-2-methylbutane by comparison of their GC retention times with those of authentic compounds. The GC/mass spectral analysis also revealed the presence of compounds corresponding to the formulae $C_5H_{10}Cl_2$, $C_5H_9Cl_3$, and $C_5H_{10}ICl_2$.

GC/mass spectral analysis of the product of the reaction between propane and ICl indicated the presence of the two isomeric iodopropanes (P^+ = 170); their structures were confirmed by the

(18) Knox, J. H.; Nelson, R. L. *Trans. Faraday Soc.* **1959**, *55*, 937.
(19) Anson, P. C.; Tedder, J. M. *J. Chem. Soc.* **1957**, 4390.
(20) Birckenbach, L.; Goubeau, J. *Ber.* **1934**, *67*, 1420.
(21) Premuzic, E.; Reeves, L. W. *Can. J. Chem.* **1962**, *40*, 1870.
(22) Rydon, H. N. *Org. Synth.* **1971**, *51*, 44.

comparison of their retention times with those of the authentic primary and secondary iodides.

Procedure for Gas-Phase Reaction. Reactions were carried out in 100-, 500-, and 1000-mL reaction vessles. Iodine monochloride was weighed into a small glass tube and placed in a reaction vessel which had been wrapped with aluminum foil. Similarly, the appropriate amount of cyclohexane was weighed into the vessel. The reaction vessel was then attached to a vacuum line and degassed by using the freeze–thaw method. in the case of the reactions with neopentane or propane a known amount of alkane was distilled into the reaction vessel. The vessel was then sealed under vacuum and placed in a thermostatically controlled water bath set at 36 °C. After adequate time to reach thermal equilibrium (15 min) was allowed, the vessel was irradiated for 10 min with a 300-W incandescent light.

The reactants were frozen (–198 °C), the vessel opened, a known amount of an external standard (undecane) added, and the contents extracted with Freon 113. The resulting solution was analyzed with an HP5840 gas chromatograph fitted with a 50-m methylsilicone capillary column. Yields of compounds were calculated by using calibration factors determined with known mixtures of standard and the authentic compounds. Results are summarized in Tables I and II.

The Liquid-Phase Reaction with Cyclohexane. A 2-mL

aliquot of a 0.25 M iodine chloride solution in carbon tetrachloride was added to 2 mL of cyclohexane in a Pyrex ampule. After being degassed, sealed, under vacuum, and equilibrated in a water bath at 10 °C, the ampule was irradiated with a 140-W Hanovia UV lamp for 5 h. Other ampules were wrapped in aluminum foil and placed in the water bath at the same temperature for the same time. Solutions were analyzed by gas chromatography; results are summarized in Table I.

The Liquid-Phase Reaction with Iodocyclohexane. Solutions of iodine monochloride (0.00341 mmol) and iodocyclohexane (0.0065 mmol) in carbon tetrachloride (5 mL) were prepared. Aliquots of each (2 mL) were added to Pyrex ampules at –78 °C. The ampules were wrapped in foil, evacuated, sealed under vacuum, and then placed in a water bath at 10 °C for 5 h. The products were determined by GC analysis; results are given in Table I.

Modification of Chemical Reactivity via Inclusion Complex Formation: Photochemistry of Dibenzyl Ketones and Benzyl Phenylacetates

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In the context of employing "inclusion complexes" as a medium for organic photochemical reactions, we have investigated the photochemical behavior of dibenzyl ketones and benzyl phenylacetates using deoxycholic acid (DCA), Dianin's compound, and cyclodextrin (CD) as hosts in the solid state. Results on cage effect suggest that the translational motion of the benzyl radical pairs is restricted in all three media and totally in Dianin's compound. Products resulting from rearrangement of dibenzyl ketones were formed upon photolysis in Dianin's compound and cyclodextrin and were absent in deoxycholic acid. The absence of rearrangement in DCA and its presence to varied extents in Dianin's compound and cyclodextrin is suggested to be an indication of the restriction imposed by the host on the reorientational process of geminate radical pairs.

In the context of the study of reactivities of guest molecules and the way in which this reactivity is governed by the environment, the field of "inclusion complex" holds considerable promise. An essential characteristic of the host in the inclusion complex is its ability to form a solid structure with hollow spaces of large enough dimension to house prospective guests. Crystalline inclusion compounds may be subclassified as true clathrate-type, in which the guest molecules are imprisoned in discrete closed cavities or cages (Dianin's compound, cyclodextrin), the channel-type, in which the guest species are accommodated in continuous canals running through the crystal (deoxycholic acid, urea), and the layer-type where the guest component is situated between bands of the host structure (graphite). Zeolites belong to an intermediate class possessing cavities interconnected by channels. Significant changes in reaction product ratios have been effected by carrying out photochemical reactions in DCA and related matrices.[1] Thus the way was opened for employing in-

clusion complexes as a medium for organic photochemical studies.[2] Results described below on photochemical studies of dibenzyl ketones and benzyl phenylacetates using deoxycholic acid (DCA), Dianin's compound, and cyclodextrin (CD) as the host in the solid state represent our further interest in exploring the "host–guest" chemistry

(1) Friedman, N.; Lahav, M.; Leiserowitz, L.; Popovitz-Biro, R.; Tang, C. P.; Zaretzkii, Z. *J. Chem. Soc., Chem. Commun.* **1975,** 864. Farina, M.; Audisio, G.; Natta, G. *J. Am. Chem. Soc.* **1967,** *89,* 5071. Brown, J. F.; White, D. M. *J. Am. Chem. Soc.* **1960,** *82,* 5671.

(2) Turro, N. J.; Wan, P. *Tetrahedron Lett.* **1984,** *25,* 3655. Turro, N. J.; Wan, P. *J. Am. Chem. Soc.* **1985,** *107,* 678. Turro, N. J.; Cheng, C. C.; Lei, X. G.; Flanigen, E. M. *J. Am. Chem. Soc.* **1985,** *107,* 3739. Goswami, P. C.; de Mayo, P.; Ramnath, N.; Bernard, G.; Omkaram, N.; Scheffer, J. R.; Wong, Y. F. *Can. J. Chem.,* in Press. Padmanabhan, K.; Venkatesan, K.; Ramamurthy, V. *Can. J. Chem.* **1984,** *62,* 2025. Casal, H. L.; de Mayo, P.; Miranda, J. F.; Scaiano, J. C. *J. Am. Chem. Soc.* **1983,** *105,* 5155. Aoyama, H.; Miyazaki, K.; Sakamoto, M.; Omote, Y. *J. Chem. Soc., Chem. Commun.* **1983,** 333. Tanaka, H.; Toda, F. *J. Chem. Soc., Chem. Commun.* **1983,** 593. Popovitz-Biro, R.; Tang, C. P.; Chang, H. C.; Lahav, M.; Leiserowitz, L. *J. Am. Chem. Soc.* **1985,** *107,* 4043. Tang, C. P.; Chang, H. C.; Popvitz Biro, R.; Frolow, F.; Lahav, M.; Leiserowitz, L.; McMullan, R. K. *J. Am. Chem. Soc.* **1985,** *107,* 4058. Arad-Yellin, R.; Brunie, S.; Green, B.; Knossow, M.; Tsoucaris, G. *J. Am. Chem. Soc.* **1979,** *101,* 7529.

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