lysis (eq 1), which is likely to proceed via oxirene as an

$$\overset{*}{C}H_2{=}C{=}O \xrightarrow{h\nu} CH_2(\text{singlet}) + \overset{*}{C}O \qquad (1)$$

intermediate, occurs through formylmethylene (**4**) (i.e., **1** ⇄ **4** ⇄ **3**, Figure 4) rather than via a previously suggested[20,23] pathway involving oxiranylidene (**6**) (i.e., **1** ⇄ **6** ⇄ **3** ⇄ **4** ⇄ **1**).

Conclusions

In this paper we have presented the results of a comprehensive study of the C_2H_2O potential energy surface. The following points emerge (cf. Figure 2). (i) The most stable C_2H_2O isomer is ketene (**1**). (ii) Hydroxyacetylene (**2**), lying 152 kJ mol^{-1} higher in energy than ketene but separated from ketene by a barrier of 305 kJ mol^{-1} (via successive 1,2 H shifts), is a potentially observable isomer. (iii) Oxiranylidene (**6**), lying 244 kJ mol^{-1} above ketene (**1**), is also likely to be observable as a stable C_2H_2O isomer, the lowest pathway found for its unimolecular decomposition being dissociation to CH_2 and CO (requiring 105 kJ mol^{-1}). (iv) Two of the possible C_2H_2O isomers, formylmethylene (**4**) and hydroxyvinylidene (**5**), are unstable with respect to intramolecular rearrangement [to ketene (**1**) and hydroxyacetylene (**2**), respectively]. (v) In agreement with previous studies,[6,12–14] we find that oxirene (**3**; 331 kJ mol^{-1} above ketene) lies in a shallow potential well; rearrangement to ketene requires only ~32 kJ mol^{-1} of activation energy and is likely to occur readily under experimental conditions. Consistent with experimental observations, the intermediacy of oxirene in the Wolff rearrangement (as evidenced by scrambling of appropriate labels) is predicted to require energy in excess of the threshold for the reaction.

Acknowledgment. We are indebted to Dr. L. Farnell for the vibrational frequency program. The award of ANU Vacation Scholarship (to C.E.W.) is gratefully acknowledged.

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Free-Radical Halogenations. 5. Reaction of Chlorosulfonyl Isocyanate with Alkanes[1,2]

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The free-radical chain reactions of chlorosulfonyl isocyanate with alkanes can be initiated with either light or thermal initiators. The major products in these reactions are chlorides, with low yields of isocyanates and sulfonyl chlorides. On the basis of a tertiary to primary hydrogen selectivity of about 120:1 and the relative reactivities of various substrates toward the abstracting radical from chlorosulfonyl isocyanate, the hydrogen-abstracting radical is suggested to be the NCO radical.

Chlorosulfonyl isocyanate (CSI) has been found to be a very reactive isocyanate and to be useful for the preparation of many new and novel compounds through its ionic reactions.[3,4] While considerable attention has been given to the ionic reactions of CSI, the ability of this material to give products arising from free-radical intermediates has not been studied.

Four different hydrogen atom abstracting radicals could be envisioned as arising from CSI. Their hydrogen-abstracting steps are illustrated in Scheme I. The initially

Scheme I

$$RH + Cl\cdot \rightarrow R\cdot + HCl \qquad (1)$$

$$RH + [NCO]\cdot \rightarrow R\cdot + HNCO \qquad (2)$$

$$RH + [SO_2Cl]\cdot \rightarrow R\cdot + SO_2 + HCl \qquad (3)$$

$$RH + [SO_2NCO]\cdot \rightarrow R\cdot + SO_2 + HNCO \qquad (4)$$

formed alkyl radical could then proceed to products by chain transfer with CSI as illustrated in Scheme II. The

Scheme II

$$\begin{aligned} R\cdot + ClSO_2NCO &\rightarrow RSO_2Cl + NCO\cdot && (5)\\ &\rightarrow RCl + SO_2NCO\cdot && (6)\\ &\rightarrow RCl + SO_2 + NCO\cdot && (7)\\ &\rightarrow RNCO + SO_2Cl\cdot && (8)\\ &\rightarrow RNCO + Cl\cdot + SO_2 && (9)\\ &\rightarrow RSO_2NCO + Cl\cdot && (10) \end{aligned}$$

expected products could then be either isocyanates (via. eq 8 and/or 9), sulfonyl isocyanates (via. eq 10), sulfonyl chlorides (via. eq 5), or chlorides (via. eq 6 and/or 7).

The actual course of the reaction of the free-radical intermediates from CSI with alkanes could be envisioned as leading to products through synthetically useful and/or mechanistically interesting reactions and has prompted our study.

Discussion of Results

The reaction of cyclohexane with CSI in the presence of benzoyl peroxide afforded 3-substituted cyclohexanes, chlorocyclohexane (93%), cyclohexyl isocyanate (~7%), and cyclohexanesulfonyl chloride (~1%). The chain length for the formation of chlorocyclohexane was found

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[1] A preliminary account of this work was given at the 35th Northwest–5th Biennial Rocky Mountain Joint Regional Meeting Of The American Chemical Society, Salt Lake City, UT, June, 1980; Abstract No. ORGN 22.

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to be 18. In the presence of azobis(isobutyrylnitrile) (AIBN), chlorocyclohexane was formed in 90% yield, with both the isocyanate and the sulfonyl chloride also being formed. The chain length for the formation of chlorocyclohexane involving AIBN was found to be 19. In the reaction with both thermal initiators, an insoluble solid was also formed during the course of the reaction. This material was found to be cyanuric acid, $(HNCO)_3$, in yields of from 95% to 103% (based upon the starting CSI).

Chlorocyclohexane could also be formed in the absence of a thermal initiator by irradiation of the mixture of cyclohexane and CSI with tungsten lamps. In addition to the chloride (92%), the isocyanate (7%) and cyclohexanesulfonyl chloride (~1%) were formed in these reactions. During the course of the irradiation cyanuric acid was also formed as a white film on the inside of the reaction tubes. The ratio of cyanuric acid to chlorocyclohexane was found to be 1.02 ± 0.16. The photochemical reactions were all slow, requiring long irradiation times due to the photolysis being on an end absorption of CSI and to the filming of the tubes due to cyanuric acid.

The ability of both benzoyl peroxide and AIBN to initiate the reaction between CSI and the alkane would preclude a mechanistic pathway similar to those reported for the chlorination of alkanes by thionyl chloride in the presence of benzoyl peroxide[5] and the chlorination of alkanes by inorganic chloride in the presence of benzoyl peroxide.[6] In the former example, thionyl chloride was shown to react with the peroxide to form benzoyl peroxide and (benzoyloxy)sulfinyl chloride. These two materials only formed with an acyl peroxide and not when other thermal initiators were used. These two reactive intermediates were found to be responsible for the observed products.[5] Bunce and Tanner[6] demonstrated that benzoyl hypochlorite was again the source for alkyl chlorides in the reaction of alkanes with inorganic chlorides in the presence of benzoyl peroxide. The hypochlorite was formed by the initial reaction of the inorganic chloride with benzoyl peroxide. The reaction of CSI with alkanes does not seem to involve this mechanistic complication.

The chlorination of 2,3-dimethylbutane with CSI in the presence of benzoyl peroxide gave both 1-chloro-2,3-dimethylbutane (4.6%) and 2-chloro-2,3-dimethylbutane (92.3%) as the only detectable organic products. The tertiary to primary selectivity at 49.2 °C was found to be 117 ± 8. A similar value of 115 ± 11 was observed for the photochemical reaction at the same temperature. The similar tertiary to primary selectivities would suggest that the hydrogen-abstracting species in both of these processes is the same and, furthermore, that the photochemical and thermally initiated reactions proceed by a similar pathway. The tertiary to primary selectivity observed for the hydrogen atom abstracting species is considerably different from that reported for chlorine atoms of 3.9:1 (40 °C)[7] or that for the chlorosulfonyl radical which has a reported tertiary to primary selectivity of 10:1 at 50 °C.[8]

The reaction of CSI with alkanes is characterized by long irradiation times, short chain lengths, and apparent high selectivity. The implication is that there is at least one step in the reaction sequence that proceeds with some difficulty. In other reactions of this type, a major assumption of radical reactions, that the initially formed radicals are reflected in the observed products in exactly the same ratios as initially formed, is not correct. Some of these reactions are not under the expected kintic control but are instead governed by thermodynamic control. The initially formed radicals undergo reversible attack to equilibrate the intermediate radicals.[2,9,10]

Table I. Selectivity as a Function of Percent Conversion of CSI into Alkyl Chloride in the Photochemical Reaction

% conv	selectivities	% conv	selectivities
0.42	154 ± 18	17.4	154 ± 9
8.7	156 ± 8	32.4	137 ± 11
15.7	137 ± 10	39.3	162 ± 17

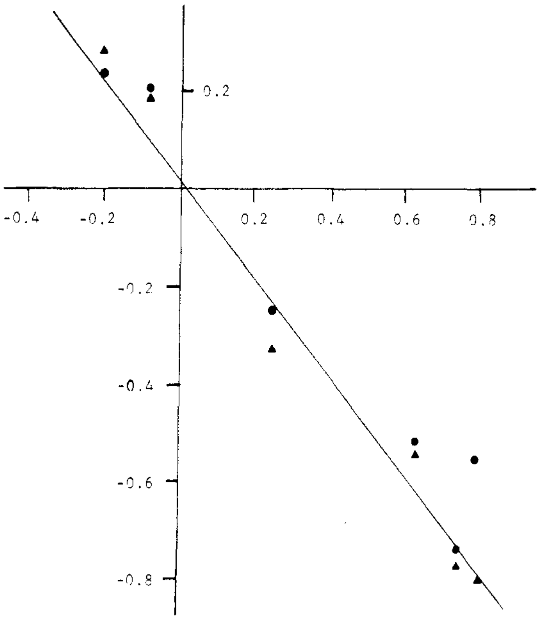

Figure 1. Plot of log (relative reactivities) for substituted aromatics vs. Hammett σ values for the reaction of CSI with various toluenes. The triangles represent the values obtained with benzoyl peroxide as an initiator and the circles represent the photochemical values.

The possible involvement of radical equilibration was investigated by studying the tertiary to primary selectivity as a function of the percent conversion of CSI into products. With the photochemically initiated reactions the selectivity was found to remain constant irrespective of the percent conversion (Table I). The selectivity observed is then the true selectivity of the hydrogen-abstracting radical from CSI.

The nature of the hydrogen-abstracting radical from CSI was also studied as to its relative reactivity toward selected alkanes and aromatics, and the values obtained are reported in Tables II and III. In both cases the values obtained are considerably different from those reported for either chlorine or the chlorosulfonyl radical.

Using the data in Table II, for the relative reactivities of hexamethylethane, cyclohexane, and 2,3-dimethylbutane, one can calculate a tertiary to secondary to primary hydrogen selectivity for the hydrogen-abstracting species. The value for the thermal reactions with benzoyl peroxide was found to be 101/4.8/1, and that for the photochemical reaction was found to be 94/4.3/1. The data in Table II also lead to a comparison of the deuterium isotope effect for the abstracting radical. The k_H/k_D for the thermal reaction was found to be 1.72 while the k_H/k_D for the photochemical reaction was found to be 1.94. Both of these values are considerably different from those reported for

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Table II. Relative Reactivities of Various Substrates toward the Abstracting Radical from Chlorosulfonyl Isocyanate and the Reported Relative Reactivities for Chlorine Atoms and the Chlorosulfonyl Radical

compd	CSI photo[a]	CSI thermal[b]	Cl	SO_2Cl
cyclohexane[c]	1.00	1.00	1.00	1.00
toluene	1.34 ± 0.10	1.38 ± 0.21	0.27[5]	0.21[18]
cycloheptane	1.37 ± 0.21	1.27 ± 0.21		
cyclooctane	2.60 ± 0.30	2.40 ± 0.10	1.16[18]	1.34[18]
cyclopentane		4.77 ± 0.50	0.82[5]	2.19[18]
2,3-dimethylbutane	2.06 ± 0.11	1.95 ± 0.03	0.75[5]	0.99[18]
2,2,3,3-tetramethylbutane	0.35 ± 0.04	0.31 ± 0.04	0.33[5]	
perdeuteriocyclohexane	0.51 ± 0.03	0.58 ± 0.04	0.78[5]	0.70[12]
1-chlorobutane	0.43 ± 0.10	0.49 ± 0.05	0.25[5]	0.26[18]

[a] At 42.9 °C with irradiation by two 150-W lamps. [b] At 98 °C for 4 half-lives of benzoyl peroxide. [c] Taken to be 1.00.

Table III. Relative Reactivities of Selected Toluenes toward the Abstracting Radical from Chlorosulfonyl Isocyanate and, for Comparison, the Relative Reactivities for Both Chlorine Atoms and the Chlorosulfonyl Radical

compd	CSI photo[a]	CSI thermal[b]	Cl	SO_2Cl
toluene[c]	1.00	1.00	1.00	1.00
p-xylene[d]	1.77	1.92	1.62[19]	1.26[12]
m-xylene[d]	1.57	1.54	1.33[19]	1.00[12]
p-chlorotoluene	0.58	0.46	0.72[19]	
m-cyanotoluene	0.29	0.28	0.36[19]	0.79[12]
m-nitrotoluene	0.18	0.17		0.41[20]
p-nitrotoluene	0.28	0.15	0.32[21]	0.43[20]

[a] Reactions ran at 42 °C with irradiation by two 150-W lamps. [b] Reactions ran at 97.5 °C for 4 half-lives of benzoyl peroxide. [c] Taken as the standard. [d] Statistically corrected.

either chlorine (k_H/k_D = 1.28[5,11]) or for the chlorosulfonyl radical (k_H/k_D = 1.42[12]). The higher value for the reactions involving CSI would imply an abstraction transition state with more C–H bond breaking than with the reactions involving either chlorine or the chlorosulfonyl radical.

The increased polarity of the transition state for the abstraction step is further shown by a Hammet plot of the data from Table III (Figure 1). The ρ value using both the thermal and the photochemical relative rates of reaction is −1.10, a value considerably higher than that obtained for chlorine (ρ = −0.79[5]). The ρ value again is indicative of a process involving more charge separation during the hydrogen abstraction than encountered for chlorine atoms.

The comparisons from above between the hydrogen-abstracting radical from CSI and either the chlorine atom or the chlorosulfonyl radical would seem to preclude both of these radicals as candidates for the hydrogen-abstracting species. The possible exception would be low yields of cyclohexyl isocyanate. This material most likely arises due to hydrogen abstraction by chlorine atoms, but attempts to completely suppress this mixed chain process by use of trichloroethene all failed. The CSI reacted rapidly with the olefin, and no products arising from radical attack upon cyclohexane could be detected.

The other two possible radicals to carry out the hydrogen abstraction would be either the NCO radical (Scheme I, eq 3) or the SO_2NCO radical (Scheme I, eq. 4), both of which are previously uncharacterized and unreported.

The high yields of HNCO, isolated as its trimer, would further suggest the involvement of either of these two radicals as the hydrogen-abstracting species. It would be expected that if the SO_2NCO radicals were the abstracting species, the resulting HSO_2NCO would rapidly decompose to sulfur dioxide and HNCO. A further complication of the involvement of a possible SO_2NCO radical would be the equilibrium of this species (eq 11) into SO_2 and the

$$\cdot SO_2NCO \rightleftharpoons SO_2 + NCO\cdot \qquad (11)$$

NCO radical. This type of equilibrium is similar to the process suggested for the SO_2Cl radical by Russell in the free-radical chlorinations involving sulfuryl chloride.[8] A similar equilibrium has been suggested for the (trichloromethyl)sulfonyl radical into SO_2 and a trichloromethyl radical by Huyser.[13]

While no experimental evidence was found to preclude either the SO_2NCO radical or the NCO radical as the hydrogen-abstracting species or to preclude a mixed chain process involving both of these radicals, several facts would seem to make the SO_2NCO radical a very unlikely choice for the abstracting species. the SO_2NCO radical appears to have some other similarities with the reported SO_2Cl radical. For both radicals, the radical site would be expected to be on the same atom, either oxygen or sulfur. Both radicals would also be expected to have similar electronic properties since the NCO group and the Cl group have approximately the same electronegatives, 3.1 and 3.0, respectively.[14]

A further similarity between the two radicals would be in their steric requirements. Both the Cl and the NCO group would be directed linearly away from either of the two possible radical sites and should not interfere with approach to alkyl hydrogens, even at tertiary carbons.

The same behavior patterns have been observed for the attacking radicals in a few reported cases where the radical site is on a common atom and in which the molecules have similar electronic and steric properties. The rate constants for attack of either methyl or ethyl radicals upon aldehydic hydrogens were found to be within experimental error.[15] Both the methyl and ethyl radical would be expected to have similar steric and electronic properties. The hydrogen-abstraction selectivies for the methoxy and the *tert*-butyl radicals are again well within experimental error at 1/14/46 and 1/12/44, respectively.[16] A third example is the hydrogen-abstracting behavior of the protonated amino

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Table IV. Yields of the Products from the Reaction of CSI with Cyclohexane

	% yield		
product	AIBN	benzoyl peroxide	photochemical
chlorocyclohexane	90.4 ± 3.4	93.4 ± 1.6	91.8 ± 3.7
cyclohexyl isocyanate	8.0 ± 1.4	6.2 ± 1.5	6.9 ± 3.0
cyclohexanesulfonyl chloride	0.60 ± 0.07	0.49 ± 0.16	1.1 ± 0.2
cyanuric acid	96.7 ± 11.3	92.4 ± 7.8	90.5 ± 4.9
sulfate	79.0 ± 15.1	92.1 ± 4.3	85.3 ± 9.1

radical from dimethylamine and from piperidine. Both radicals have similar polar effects in their abstraction reaction from 1-chlorobutane.[17]

From the information above, it would seem, therefore, that the SO_2NCO radical would have hydrogen-abstracting properties which, while not necessarily the same as those of the SO_2Cl radical, were more closely alined than those observed for the attacking radical from CSI. This would then seem to exclude this radical as the sole hydrogen atom abstracting species and would tend to support an abstraction process by the NCO radical.

Experimental Section

Materials. Cyclohexyl isocyanate and chlorosulfonyl isocyanate were obtained from Aldrich Chemical Co. and used without purification. All hydrocarbons and aromatics are commercially available. The purity of the hydrocarbons and aromatics was checked by gas chromatography, and, if required, they were purified by distillation before use. Cyclohexane and 2,3-dimethylbutane were both dried over sodium and distilled before use.

General Procedure. Reactions were carried out in sealed Pyrex ampules which had been degassed by the freeze–thaw method. The ampules containing the thermal initiator (either benzoyl peroxide or AIBN) were allowed to stand in a constant-temperature bath for at least 4 half-lives of the initiator. The photolytic ampules were allowed to stand in a constant-temperature bath for from 3 weeks to 2 months, depending upon the bath temperature, and photolyzed by two 150-W tungsten lamps. The ampules were opened, and the contents were analyzed by gas chromatography on one of the following columns: (a) 6 ft, 20% SE-30 silicone rubber on 100/120-mesh Chromosorb W; (b) 6 ft, 10% DEGS on 100/120-mesh Chromosorb W; (c) 6 ft, 15% Carbowax 20M on 100/120-mesh Chromosorb W; (d) 6 ft, 10% OV-101 on Chromosorb W. Reaction products were identified by comparison of their retention times with those of authentic samples on at least two different columns.

Reaction of CSI with Cyclohexane. A 2-mL sample of a 1.16 M solution of CSI in cyclohexane was placed into each of 30 tubes. Into two sets of 10 tubes each was placed a small amount of either benzoyl peroxide or AIBN. The third set of tubes had no added thermal initiator. The tubes were degassed, sealed, and placed in a constant-temperature bath at 42.0 ± 0.5 °C. The tubes containing the thermal initiators were wrapped with foil to protect them from the light before being placed in the bath. The bath was irradiated by two 150-W lamps for 2 months.

The tubes were opened, and an accurately weighed amount of a standard, bromocyclohexane, was added. An aliquot was removed and added to methanol. This solution was allowed to stand for 30 min before GC analysis on column d. The remaining solution was added to water to destroy any unreacted CSI and then extracted with ether. The ether extract was dried with sodium sulfate before GC analysis. The aqueous solution was titrated with standard base, and then barium chloride was added to precipitate the sulfate present. The amount of sulfate present was determined gravemetrically.

Table V. Tertiary to Primary Selectivity as a Function of Temperature for the Hydrogen Abstracting Radical from CSI toward 2,3-Dimethylbutane

	selectivity	
temp, °C	photochemical	thermal
42.0	140 ± 21	137 ± 17
49.2	117 ± 8	115 ± 11
52.8	82 ± 9	74 ± 7
57.0		64 ± 6
62.5	78 ± 2	53 ± 3

Two tubes in each set were opened and poured directly into concentrated ammonia. The solution was evaporated to dryness and the resulting cyclohexylurea identified by melting point, after recrystalization from methanol.

In all the reactions, a white insoluble material was formed on the inside of the tubes. This was washed from the sides of the tubes, and the solvent was evaporated. The resulting solid was weighed. The infrared spectrum of the solid was identical with that reported for cyanuric acid[22] $(HNCO)_3$. The neutralization equivalent of the solid was found to be 128 ± 2 (calculated for $(HNCO)_3$ 129). Typical percentage yields are reported in Table IV.

Competitive Reactions. Relative rates of reactions were determined by the methods previously reported by this Laboratory[11] for both the thermal and the photochemical reactions. The values are reported in Tables II and III. All values are the results of at least four independent competitions.

Reaction of 2,3-Dimethylbutane with CSI. In a set of experiments similar to those with cyclohexane and CSI, no solid organic material could be detected after treatment of the reaction mixtures with ammonia and evaporation of the solutions to dryness.

Selectivity as a Function of Percent Conversion. A 1-mL sample of a 0.66 M solution of CSI in sodium-dried 2,3-dimethylbutane was placed into each of 20 ampules. Ten of the ampules contained small amounts of benzoyl peroxide. All the samples were degassed and sealed. The ampules containing benzoyl peroxide were foil wrapped. All of the ampules were placed in a constant-temperature bath maintained at 41.2 ± 0.5 °C, and the tubes were irradiated with two 150-W tungsten lamps. At various times the tubes were removed and opened, and an accurately weighted amount of standard was added. The selectivity and the percent conversion were determined on GC column c. Typical values are reported in Table I.

Selectivity as a Function of Temperature. Into each of 30 ampules was placed 1 mL of a 0.66 M solution of CSI in sodium-dried 2,3-dimethylbutane. Fifteen of the ampules contained several milligrams of benzoyl peroxide. All of the tubes were degassed and sealed, and the ampules containing benzoyl peroxide were wrapped in foil to protect them from the light. Sets of a minimum of three of each type of ampule were placed in constant-temperature baths maintained at 42.0 ± 0.5, 49.2 ± 0.5, 52.8 ± 0.7, and 62.5 ± 1.0 °C. The tubes were irradiated with two 150-W lamps for a minimum of 3 weeks. The tubes were opened, and an accurately weighted amount of chlorobenzene was added as a standard. The selectivities and the percent yields were determined by GC analysis of column c. The values are reported in Table V.

An addition temperature was used for the benzoyl peroxide initiated reactions. A solution of CSI (0.25 M) and benzoyl

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peroxide (0.006 M) in 2,3-dimethylbutane was refluxed overnight in a 100-mL round-bottomed flask equipped with a magnetic stirring bar, a reflux condenser, and a calcium chloride drying tube. The products were determined as above. These values are also included in Table V.

Acknowledgment is made for a Faculty Development Grant for research from Missouri Southern State College for support of this project.

Registry No. Cyclohexane, 110-82-7; toluene, 108-88-3; cycloheptane, 291-64-5; cyclooctane, 292-64-8; cyclopentane, 287-92-3; 2,3-dimethylbutane, 79-29-8; 2,2,3,3-tetramethylbutane, 594-82-1; perdeuteriocyclohexane, 1735-17-7; 1-chlorobutane, 109-69-3; p-xylene, 106-42-3; m-xylene, 108-38-3; p-chlorotoluene, 106-43-4; m-cyanotoluene, 620-22-4; m-nitrotoluene, 99-08-1; p-nitrotoluene, 99-99-0; chlorosulfonylisocyanate, 1189-71-5.

Coupling of Enolates of Phenones with 2-Chloro-2-nitropropane[1]

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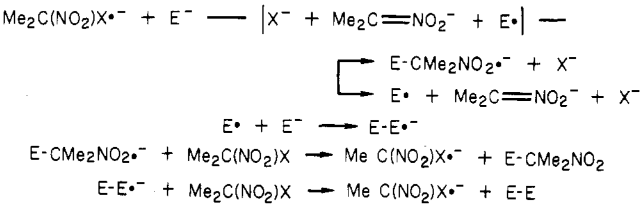
Lithium enolates of acetophenone, α-methoxyacetophenone, propiophenone, meta- or para-substituted propiophenones, butyrophenone, isovalerophenone, 1-phenyl-1-hexanone, 1-indanone, 1-tetralone, or 1-benzosuberone react with 2-chloro-2-nitropropane in THF by free radical chain processes to produce $\mathrm{ArCOCH(CMe_2NO_2)R}$ or $\mathrm{ArCOC(R){=}CMe_2}$ and when $R \neq H$ the product of oxidative dimerization, $\mathrm{[ArCOC(R){-}]_2}$. The enolate anion of deoxybenzoin yields in a free radical chain process only the dimerization product.

The radical chain substitution process of Scheme I,[2,3] which has been labeled $S_{RN}1$,[4] has been reported for geminal halo nitroalkanes ($\mathrm{R_2C(NO_2)X}$) and N^- = nitroalkane anions,[2,5] enolates of β-dicarbonyl or β-cyano carbonyl compounds,[6,7] malonitriles,[6] aryl thiolates and sulfinates,[8–10] and dialkyl phosphite or thiophosphite anions.[11,13] Similar reactions have been reported in most instances with $X = NO_2$[5,6,10,12,13] or $\mathrm{ArSO_2}$.[9,11,13,14] Lithium enolates of monoketones in THF will also participate in free radical chain substitutions of geminal halo nitroalkanes.[15,16]

Scheme I

$$\begin{aligned}
&\mathrm{R_2C(NO_2)X^{-\cdot} \longrightarrow R_2\dot{C}NO_2 + X^-}\\
&\mathrm{R_2\dot{C}NO_2 + N^- \longrightarrow R_2C(NO_2)N^{-\cdot}}\\
&\mathrm{R_2C(NO_2)N^{-\cdot} + R_2C(NO_2)X \longrightarrow}\\
&\qquad\qquad \mathrm{R_2C(NO_2)N + R_2C(NO_2)X^{-\cdot}}
\end{aligned}$$

Scheme II



The coupling product 1 (eq 1) is accompanied by the elimination product 2 (eq 2) and the enolate dimerization product (3) which is also formed by a free radical chain process (eq 3).[16] The ratio of (1 + 2)/3 depends not only

$$\mathrm{Me_2C(NO_2)X + R'C(OLi){=}CHR \rightarrow \underset{\textstyle 1}{R'COCH(R)CMe_2NO_2} + LiX} \qquad (1)$$

$$\mathrm{1 + B^- \rightarrow \underset{\textstyle 2}{R'COC(R){=}CMe_2} + NO_2^- + HB} \qquad (2)$$

$$\mathrm{Me_2C(NO_2)X + R'C(OLi){=}CHR \rightarrow \underset{\textstyle 3}{[R'COCHR{-}]_2} + Me_2C{=}NO_2Li + LiX} \qquad (3)$$

upon R and R′ but also on the nature of X, with $X = NO_2$

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