salt was removed. The solvent was removed on a rotatory evaporator and the residue was recrystallized from 95% ethanol to yield 4.8 g (25%) of VIII. Further purification was obtained by sublimation at 56° *in vacuo:* mp 61–62°; ir 1825 (C=O) and 1705 cm^{-1} (C=N); nmr (CCl_4) δ 1.6 (m), 1.85 (s), and 3.55 ppm (m). The singlet was superimposed on the 1.6 multiplet. The areas were in the ratio of 2:23.

Anal. Calcd for $C_{16}H_{25}N_2OCl$: C, 64.8; H, 8.45; N, 9.46. Found: C, 64.8; H, 8.77; N, 9.40.

3-Chloro-1-isopropyl-4-isopropyliminoazetidin-2-one (IX).—A 10.1-g (0.065 mol) portion of chloroacetyl bromide in 25 ml of hexane was slowly added to a refluxing solution of 8.2 g (0.065 mol) of diisopropylcarbodiimide and 6.5 g (0.13 mol) of triethylamine in 100 ml of hexane. The reaction mixture was refluxed for 2 hr after the addition was completed. Upon removal of the salt by filtration and evaporation of the solvent, the residue was distilled to yield 2.4 g (20%) of impure IX: ir 1820 (C=O) and 1705 cm^{-1} (C=N).

3-*n*-Butyl-3-ethyl-1-isopropyl-4-isopropyliminoazetidin-2-one (X).—To a refluxing solution consisting of 9.95 g (0.079 mol) of diisopropylcarbodiimide in 50 ml of hexane was slowly added 9.95 g (0.079 mol) of butylethylketene in 50 ml of hexane. This solution was refluxed for an additional 2 hr. The solvent was evaporated and the residue was distilled at 80–89° (0.025 mm) to yield 2.3 g (12%) of impure X: ir 1810 (C=O) and 1690 cm^{-1} (C=N).

1-Isopropyl-4-isopropyliminoazetidin-2-one (XI).—An excess of ketene was bubbled into a solution of 8.1 g (0.07 mol) of diisopropylcarbodiimide over a period of 8 hr. The solvent was evaporated to yield predominantly unreacted carbodiimide with only a very small amount (5%) of XI: ir 1820 (C=O) and 1700 cm^{-1} (C=N).

7-Chloro-7-phenylbicyclo[3.2.0]hept-2-en-6-one (XII).—A 17.25-g (0.17 mol) portion of triethylamine in 30 ml of benzene was added dropwise with stirring to a solution containing 29.35 g (0.155 mol) of α-chloro-α-phenylacetyl chloride, 102.5 g (1.55 mol) of cyclopentadiene, and 100 ml of dry benzene. After the addition was complete, the mixture was refluxed for 1 hr. The amine salt was removed by filtration and the filtrate was concentrated and distilled *in vacuo* to yield 27 g (80%) of XII: bp 113–113.5° (0.9 mm); ir 1784 (C=O) and 1600 cm^{-1} (C=C); nmr (CCl_4) δ 2.55 (m, 2 H), 4.18 (m, 2 H), 5.6 (m, 2 H), and 7.4 ppm (m, 5 H).

Anal. Calcd for $C_{13}H_{11}ClO$: C, 71.40; H, 5.08. Found: C, 71.3; H, 5.07.

Registry No.—Phenylethylketene, 20452-67-9; XII, 20452-75-9.

Thermal Cleavage Reactions of N-Chloroketimines. Behavior of Imino Radicals

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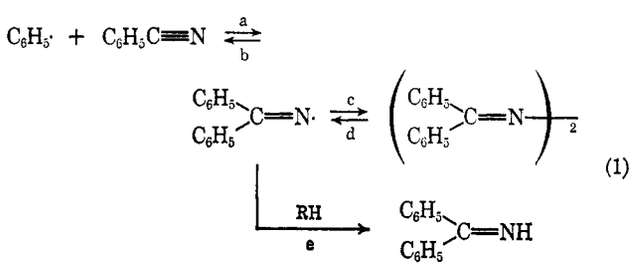
In contrast to the relatively stable diphenyl N-chloroketimine (**1**), phenyl benzyl N-chloroketimine (**2**) in chlorobenzene solution (<0.04 *M*) undergoes cleavage at 130° to form benzonitrile and benzyl chloride along with small amounts of bibenzyl. The reaction is accelerated by slow addition of benzoyl peroxide and inhibited by oxygen. A radical chain sequence is postulated involving β scission of phenyl benzyl ketimino radical (**13**) as the key step. The intermediate benzyl radical has been trapped by added 1-octene to form 1-phenyl-3-chlorononane (**12**) and by added tri-*n*-butyltin hydride (Bu_3SnH) to form toluene. At 35–40°, radical **13** can be partially intercepted by Bu_3SnH before cleavage. Phenyl α-methylbenzhydryl N-chloroketimine (**3**) gives benzonitrile, 1,1-diphenylethylene, and hydrogen chloride on thermolysis, the latter two products apparently derived from 1,1-diphenyl-1-chloroethane (**10**). In concentrated solution, additional products from the thermolysis of **2** included ammonium chloride and 2,3,4,5-tetraphenylpyrrole (**9**). The reduction of **1** with Bu_3SnH at 50–60° could be inhibited by oxygen and accelerated by di-*t*-butyl peroxyoxalate as anticipated for a radical chain process. Silver ion catalyzed Beckmann rearrangement of **2** gave N-phenylphenylacetamide (**4**) free from N-benzylbenzamide (**5**), so that chlorine appears to be *syn* to the benzyl group. Similar treatment of **3** gave no amides but only benzonitrile and 1,1-diphenylethylene. Attempts to prepare the N-chloroketimine from phenyl benzhydryl ketimine by the same procedures which were successful for **1**, **2**, and **3** gave initial chlorination on carbon rather than on nitrogen.

The methylenimino radical ($H_2C{=}N\cdot$), produced by addition of hydrogen atoms to hydrogen cyanide in a low-temperature matrix, has been observed by esr spectroscopy.[1] However, methods of formation and typical reactions of substituted ketimino radicals ($RR'C{=}N\cdot$) are not well known. We wish to report some reactions of N-chloroketimines which involve the intermediacy of such radicals.

Generation of cyclohexyl or phenyl radicals in the presence of benzonitrile gives small amounts of ketimines;[2] a ketimino radical produced by addition of the carbon radical to the nitrile group (step 1a) is a reasonable intermediate if it is assumed to be able to abstract hydrogen (step 1e) to give the observed product. Among the products from pyrolysis of benzophenone azine at 375–500° are benzene, biphenyl, benzonitrile, and benzophenone ketimine;[3] initial N–N bond homolysis (step 1d) followed by β scission of a ketimino radical (step 1b) was invoked to explain nitrile formation. A similar scheme would rationalize the



(1)

pyrolysis of acetone azine to form acetonitrile and ethane[4] as well as the use of certain azines as polymerization initiators.[5,5a] Other reactions which apparently involve radical addition to the nitrile function and the intermediacy of ketimino radicals [$R(X)C{=}N\cdot$] which either undergo β scission (X = Cl) or abstract hydrogen

(1) E. L. Cochran, F. J. Adrian, and V. A. Bowers, *J. Chem. Phys.*, **36**, 1938 (1962).

(2) J. R. Shelton and C. W. Uzelmeier, *J. Amer. Chem. Soc.*, **88**, 5222 (1966).

(3) S. S. Hirsch, *J. Org. Chem.*, **32**, 2433 (1967).

(4) J. L. Anderson, U. S. Patent 2,770,643 (1956).

(5) M. J. Roedel, U. S. Patent 2,439,528 (1948).

(5a) NOTE ADDED IN PROOF.—Photolysis of benzalazine has also been postulated to proceed through imino radicals: R. W. Binkley, *J. Org. Chem.*, **34**, 2072 (1969).

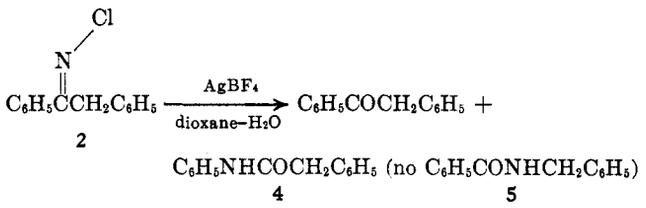
(X = CN) are the introduction of cyano groups into hydrocarbons by reaction with cyanogen chloride[6a,b] and of α-cyanoimino groups by reaction with cyanogen.[6b] A similar addition–β scission sequence may explain the addition of trifluoroacetonitrile to simple olefins.[6c]

Curtin and McCarty[7] observed free-radical halogenation of hydrocarbons by benzophenone N-halimines; the evidence did not, however, allow a clear distinction between reaction through ketimino radicals as hydrogen-abstracting chain carriers and reaction through halogen atoms in which the N-halimine only served as a halogen source by reaction with hydrogen halide. Photolysis of hexafluoroacetone N-bromimine gave hexafluoroacetone azine,[8] possibly by radical coupling (an analog of step 1c).

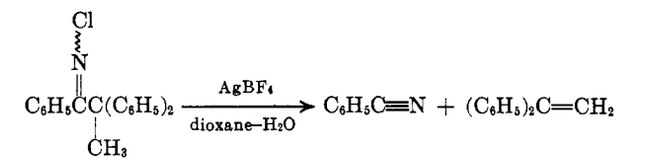
Aldimino radicals and their conversion to nitriles by donation of a hydrogen atom to molecular oxygen have been postulated[9a] in the conversion of aldehydes to nitriles by reaction with ammonia, base, oxygen, and a copper salt; the evidence seems circumstantial at best. An aldimino radical and a 1,2-hydrogen shift within it have been suggested[9b] in the base-catalyzed rearrangement of arylhydrazones of aromatic aldehydes to amidines; this proposal, however, provides no role for the base which is obviously vital to the reaction.

Results

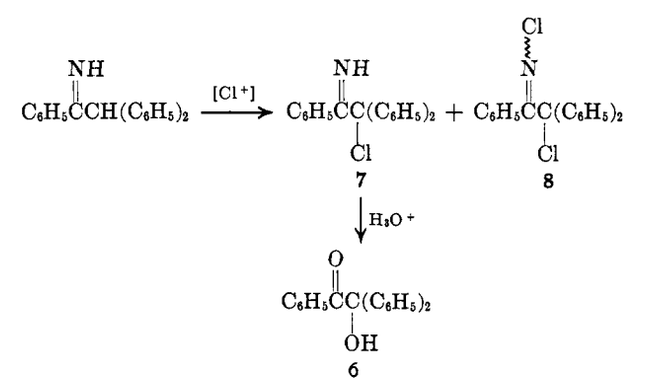
N-Chloroketimines.—Treatment of the respective ketimines with *t*-butyl hypochlorite gave diphenyl N-chloroketimine (**1**),[10] phenyl benzyl N-chloroketimine (**2**),[11] and phenyl α-methylbenzhydryl N-chloroketimine (**3**), whose purity could be determined by iodometric titration for active chlorine. The nmr spectrum of **2** showed only one singlet (4.37 ppm) for the benzylic protons in deuteriochloroform solution, even down to −60°, whereas two signals would have been expected for a mixture of *syn* and *anti* forms[12–14] in the absence of rapid interconversion. Since *syn–anti* isomerization of similarly constituted N-halimines has been shown to be slow at room temperature,[12,13] the predominance of a single isomer is suggested.[15] Treatment of **2** with silver tetrafluoroborate in dioxane–water gave, in addition to partial hydrolysis to deoxybenzoin, rearrangement only to N-phenylphenylacetamide (**4**) free from N-benzylbenzamide (**5**). Since this Beckmannlike rearrangement has been shown in similar cases to occur with concerted stereospecific migration of the group *trans* to chlorine,[13] we assign **2** with the chlorine *syn* to the benzyl group.



This argument would not be valid if the migratory aptitude of phenyl was considerably greater than that of benzyl in this particular reaction; then the isomer with chlorine *trans* to phenyl could have given **4** while that with chlorine *trans* to benzyl was being hydrolyzed. However, the migratory aptitudes of phenyl and *s*-butyl have been shown to be quite similar;[13] this fact, coupled with the nmr evidence, makes the assignment reasonable. The nmr spectrum of **3** showed only a single methyl group. Treatment with silver tetrafluoroborate in dioxane–water gave no amide formation, but rather conversion to benzonitrile and 1,1-diphenylethylene. Apparently the normal Beckmannlike rearrangement[13] is superseded by the "abnormal Beckmann rearrangement"[16] when a leaving cation as stable as 1,1-diphenylethyl is possible. Thus this reaction cannot be used to assign configuration to **3**.



Treatment of phenyl benzhydryl ketimine with positive chlorine donors gave both a monochloride and a dichloride. The monochloride gave erratic values for active chlorine and failed to show the expected benzhydrylic proton in the nmr spectrum. Hydrolysis gave phenyl α-hydroxybenzhydryl ketone (**6**) rather than the parent ketone. Therefore, we formulate the monochloride as **7** and suggest that the initial attack of positive chlorine occurred on carbon of an enamine tautomer of the imine rather than on nitrogen of the imine itself. As a precedent, we note that the imine of diphenylacetaldehyde seems to be more stable in its enamine tautomeric form.[17] The dichloride would



(6) (a) E. Müller and H. Huber, *Chem. Ber.*, **96**, 670, 2319 (1963). (b) D. D. Tanner and N. J. Bunce, *J. Amer. Chem. Soc.*, **91**, 3028 (1969). (c) B. Hardman and G. J. Janz, *ibid.*, **90**, 6272 (1968); J. B. Flannery and G. J. Janz, *ibid.*, **88**, 5097 (1966).

(7) D. Y. Curtin and C. G. McCarty, *J. Org. Chem.*, **32**, 223 (1967).

(8) W. J. Middleton and C. G. Krespan, *ibid.*, **30**, 1398 (1965).

(9) (a) W. Brackman and P. J. Smit, *Rec. Trav. Chim.*, **82**, 757 (1963); (b) I. I. Grandberg, Y. A. Naumov, and A. N. Kost, *J. Org. Chem. USSR* (Engl. Trans.), **1**, 809 (1965).

(10) P. P. Peterson, *Am. Chem. J.*, **46**, 325 (1911).

(11) K. N. Campbell, *J. Amer. Chem. Soc.*, **59**, 2058 (1937).

(12) D. Y. Curtin, E. J. Grubbs, and C. G. McCarty, *ibid.*, **88**, 2775 (1966).

(13) R. N. Loeppky and M. Rotman, *J. Org. Chem.*, **32**, 4010 (1967).

(14) G. J. Karabatsos, F. M. Vane, R. A. Taller, and N. Hsi, *J. Amer. Chem. Soc.*, **86**, 3351 (1964), and references therein.

(15) A single form may have preferentially crystallized. A dilute solution of **2** in carbon tetrachloride was heated at reflux for 1 hr; after the solution was cooled and concentrated, no changes in the nmr spectrum were observed. If the rate of interconversion is similar to that for diaryl cases,[12] this may still have not been drastic enough treatment to effect isomerization. However, more severe thermal treatment was precluded by the thermal instability discussed below.

(16) C. A. Grob and P. W. Shiess, *Angew. Chem. Intern. Ed. Engl.*, **6**, 9 (1967).

(17) D. Y. Curtin, J. A. Kampmeier, and B. R. O'Connor, *J. Amer. Chem. Soc.*, **87**, 863 (1965).

TABLE I

THERMAL DECOMPOSITION OF PHENYL BENZYL N-CHLOROKETIMINE

Entry	Temp, °C	Concn, solvent[a]	Conditions	$t_{1/4}$, min[b]	$t_{1/2}$, min[c]	t_f, min[d]	Yield, % C_6H_5CN	Yield, % $C_6H_5CH_2Cl$
1	81	0.020, B	N_2	>2800				
2	105	0.020, C	N_2	>1500[e]				
3	131	0.020, C	N_2	70	200	<1500	97	92
4[f]	131	0.020, C	N_2	200[g]	280[g]	<1500	97	91
5[f]	131	0.020, C	N_2	40	85	~250	97	78[h]
6	131	0.010, C	N_2	90	120	<1500	100	69
7	131	0.040, C	N_2	65	140	360	95	90
8	131	1.03, C	N_2			<105	22[i]	17[i]
9	131	0.020, C	O_2	>360		<1500	95	20[j]
10	131	0.020, C	O_2	>330		<1500	77	25[k]
11	131	0.020, C	*l*		75	240	80	34
12	131	0.020, C	Bz_2O_2,[m]	18	42	180	100	73
13	131	0.020, C	Bz_2O_2[n]		15	120	84	68
14	81	0.020, B	Bz_2O_2[o]	>360				
15	131	0.020, C	*p*	45	100		99	80
16	28	0.020, C	$h\nu$[q]	~150		<1500	9	4

[a] Molarity in benzene (B) or chlorobenzene (C). [b] Time for 25% loss of active chlorine. [c] Time for 50% loss of active chlorine. [d] Time for total loss of active chlorine; "<1500" signifies reactions incomplete after ~400 min but complete after standing overnight at the stated conditions. [e] Increasing temperature to 131° at this point led to decomposition with $t_{1/2}$ ~200 min. [f] These entries represent extremes of behavior with respect to inhibition periods; different batches of **2** were used. [g] Significant inhibition period observed. [h] 0.065 mol of bibenzyl formed per mol of chlorimine. [i] 0.27 mol of ammonium chloride and 0.165 mol of 2,3,4,5-tetraphenylpyrrole formed per mol of chlorimine. [j] 16% unknown product. [k] 25% unknown product. [l] 10 mol % 4-*t*-butylcatechol added. [m] 10 mol % Bz_2O_2 (benzoyl peroxide) added at steady rate over 120-min period. [n] 11 mol % added at steady rate over 50-min period. [o] 12 mol % present initially. [p] 10 mol % *t*-butyl peroxide present initially. [q] Three 275-W sun lamps through Pyrex at ~6 in.

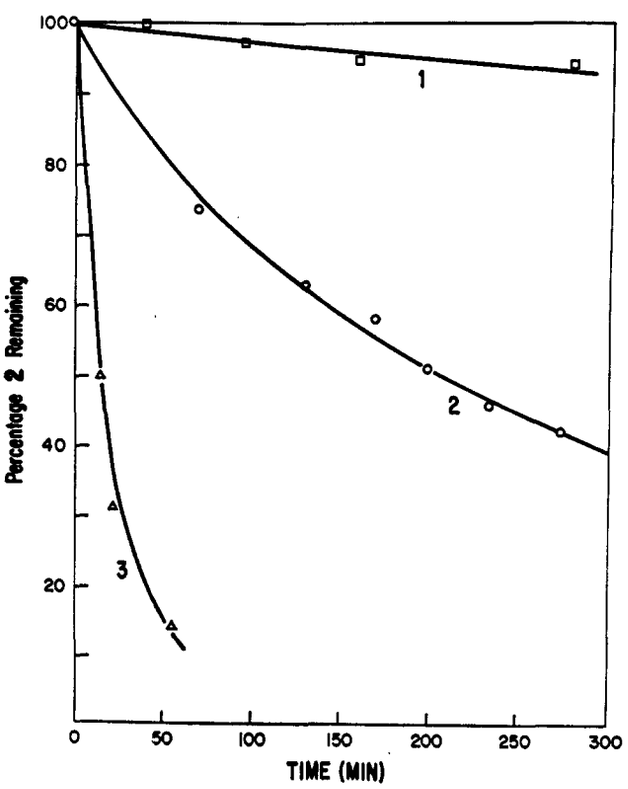
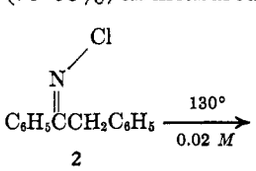


Figure 1.—Typical rate profiles for thermal decomposition of phenyl benzyl N-chloroketimine (**2**) at 131° (0.02 *M* solution in chlorobenzene): curve 1 (□), oxygen atmosphere, entry 9, Table I; curve 2 (○), nitrogen atmosphere; curve 3 (△), slow addition of benzoyl peroxide, entry 13, Table I.

appear to be **8**, but this material was not investigated extensively.

Thermal Stability.—Diphenyl N-chloroketimine (**1**) was heated in chlorobenzene solution (0.02 *M*) at 130–131° under nitrogen for 6 hr without detectable loss of active chlorine; such thermal stability of diaryl N-chloroketimines has been noted previously.[12,13]

In contrast, heating a dilute solution (<0.04 *M*) of the phenyl benzyl analog **2** in chlorobenzene under comparable conditions led to loss of active chlorine after occasionally observed induction periods. The products were benzonitrile (95–100%) and benzyl chloride (70–95%) as measured by glpc analysis; minor amounts

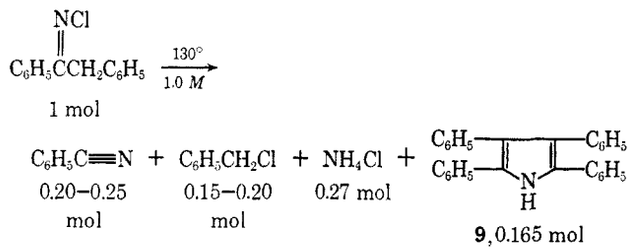


$$C_6H_5C{\equiv}N + C_6H_5CH_2Cl + C_6H_5CH_2CH_2C_6H_5$$
95–100% 70–95% ~5%

of bibenzyl were detected. Results under a variety of conditions are shown in Table I and typical data are plotted in Figure 1. Although individual concentration *vs.* time plots for runs under nitrogen were impossible to reproduce exactly (different batches of **2** were used and variable amounts of oxygen may have been present since rigorous degassing techniques were not used), the inhibition by added oxygen was so marked as to be unmistakable; runs under oxygen carried to total loss of active chlorine gave benzonitrile in good yield but gave benzyl chloride in diminished amounts (20–25%). Slow addition of benzoyl peroxide solution ($t_{1/2}^{130°}$ <5 min) led to considerable enhancement of initial rates. Thermal cleavage at low concentration could also be conveniently carried out by slow addition of **2** to refluxing chlorobenzene at a rate such that the concentration never exceeded 0.04 *M*. Reaction was extremely slow at 80°; loss of active chlorine did occur on photolysis at 28°, but <10% of benzonitrile and benzyl chloride were produced.

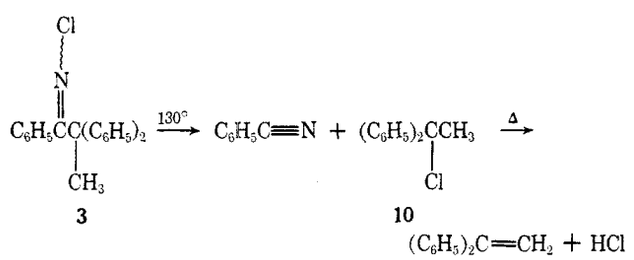
Thermal decomposition of **2** at 130–131° under nitrogen in 1.0 *M* chlorobenzene solution was much more rapid than that in dilute solution, but produced only 20–25% of benzonitrile and 15–20% of benzyl chloride. A new set of products was formed: ammonium chloride

(27% based on nitrogen and chlorine; 54% based on available hydrogen in 2) and 2,3,4,5-tetraphenylpyrrole (9) (16.5% based on nitrogen; 33% based on



phenyl groups in 2). This obviously rather complex condensation at higher concentrations was not explored further; however, it may be noted that pyrrole 9 has been prepared from treatment of the ketazine of phenyl benzyl ketone with hydrogen chloride at 180°.[18]

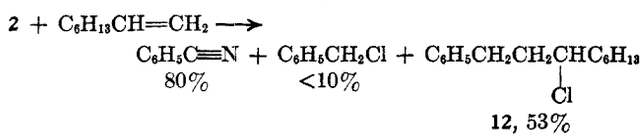
Thermal cleavage of the phenyl α-methylbenzhydryl analog 3 in dilute chlorobenzene solution at 130–131° gave benzonitrile (84%), 1,1-diphenylethylene (95%), and hydrogen chloride (70.5%), which was constantly swept out of solution with a stream of nitrogen. Based on the known thermal instability of 1,1-diphenyl-1-chloroethane (10) toward dehydrochlorination,[19] we propose a decomposition scheme parallel to that of 2; in particular, no 1,1-diphenylethane was produced.



Reactions with 1-Octene.—When N-chlorimine 1 in a refluxing 1:1 mixture of 1-octene and chlorobenzene under nitrogen (internal temperature ~124°) was subjected to slow addition of benzoyl peroxide, loss of active chlorine did occur, but nmr spectra of the crude product failed to reveal significant absorption in the δ 2.5–5.0 region expected for protons α to chlorine or doubly bonded nitrogen[20] in the hoped-for adduct, 11. Some allylic chlorination of the olefin is suspected on the basis of glpc evidence but has not been rigorously confirmed.

$$(C_6H_5)_2C{=}NCH_2CHClC_6H_{13}$$
11

Slow addition of 2 to a refluxing 1:1 mixture of chlorobenzene and 1-octene under nitrogen gave smooth decomposition to produce benzonitrile in 80% yield but benzyl chloride in <10% yield. The new product isolated (53% yield) was 1-phenyl-3-chlorononane (12).



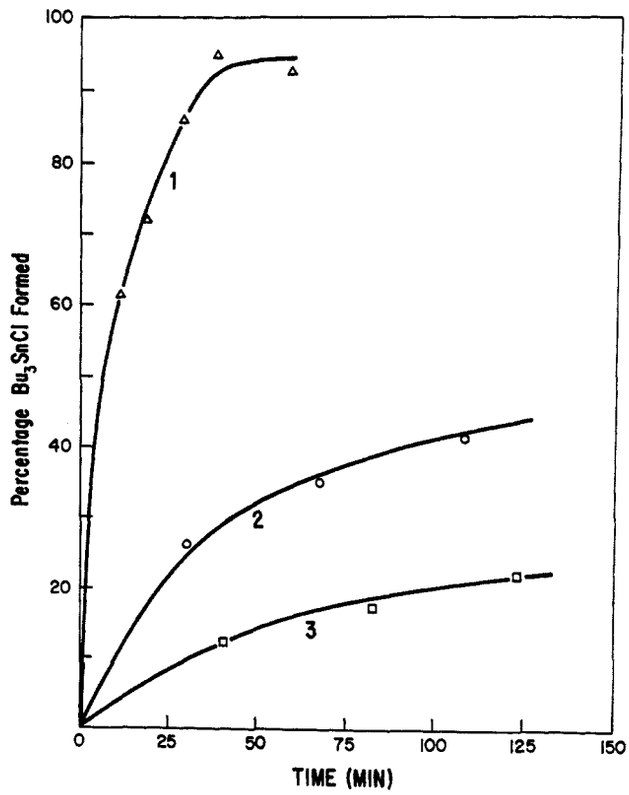


Figure 2.—Typical rate profiles for reaction of diphenyl N-chloroketimine (1) with tri-*n*-butyltin hydride at 55° (each 0.02 *M* in benzene): curve 1 (△), 10 mol % di-*t*-butyl peroxyoxalate added over 30-min period; curve 2 (○), nitrogen atmosphere; curve 3 (□), oxygen atmosphere.

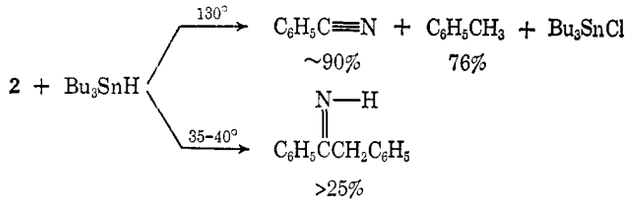
Reductions with Tri-*n*-butyltin Hydride.—Treatment of a 0.02 *M* solution of 1 in benzene at 80° with an equimolar amount of tri-*n* butyltin hydride (Bu_3SnH)[21] led to 100% conversion into tri-*n*-butyltin chloride (Bu_3SnCl) after 2 hr as judged by titration of aliquots with standard base.[22] (Iodometric titration for active chlorine could not be used in the presence of Bu_3SnH since it consumed the iodine liberated in the usual procedure.) Treatment of the residue with hydrogen chloride gave benzophenone imine hydrochloride in 80% yield. This reduction of 1 by Bu_3SnH was studied at 55 ± 1° under a variety of conditions; results obtained by titration for Bu_3SnCl formed are shown in Figure 2. Under nitrogen with 0.02 *M* concentrations of each reagent, reaction was complete in 16–24 hr and

$$\underset{1}{(C_6H_5)_2C{=}N{-}Cl} + Bu_3SnH \longrightarrow (C_6H_5)_2C{=}NH + Bu_3SnCl$$

imine hydrochloride was isolated in 90% yield. However, under oxygen, the reaction was initially slower and proceeded to only 50–60% completion after 48 hr. In contrast, slow addition of 10 mol % of di-*t*-butyl peroxyoxalate[23] ($t_{1/2}$ = 10–15 min in benzene at 55°[23]) in benzene solution over a 30-min period led to essentially complete reaction at the end of the addition period. Individual values shown for this run in Figure 2 may be slightly high, since the initiator was shown to consume some base during a typical titration, but the dramatic effect of this radical initiator is unmistakable.

(18) G. M. Robinson and R. Robinson, *J. Chem. Soc.*, **113**, 639 (1918).
(19) C. S. Schoepfle and J. D. Ryan, *J. Amer. Chem. Soc.*, **52**, 4021 (1930); **54**, 3687 (1932).
(20) D. Y. Curtin and J. W. Hausser, *ibid.*, **83**, 3474 (1961).
(21) H. G. Kuivila, *Advan. Organometal. Chem.*, **1**, 47 (1964).
(22) D. H. Lorenz, P. Shapiro, A. Stern, and E. I. Becker, *J. Org. Chem.*, **28**, 2332 (1963).
(23) P. D. Bartlett, E. P. Benzing, and R. E. Pincock, *J. Amer. Chem. Soc.*, **82**, 1762 (1960).

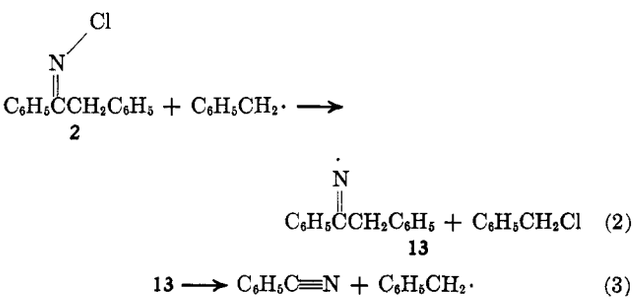
Slow addition of equimolar solutions of **2** and Bu_3SnH at identical rates to refluxing chlorobenzene under nitrogen gave reaction essentially as fast as the reagents were introduced, as judged by glpc analysis for toluene product. At the end of the addition period, titration revealed the appropriate amount of Bu_3SnCl formed and glpc analysis showed benzonitrile (90–100%) and toluene (76%). Reduction could also be carried out at



35–40° with photolytic initiation, although much less efficiently; toluene was found in only minor amounts and phenyl benzyl ketimine became a significant product.

Discussion

The thermal cleavage of N-chloroketimine **2** to benzonitrile and benzyl chloride seems best explained by a radical chain decomposition (steps 2 and 3) involving formation and β scission of ketimino radical **13**.



$$\mathbf{13} \longrightarrow C_6H_5C{\equiv}N + C_6H_5CH_2\cdot \qquad (3)$$

This chain mechanism, in contrast to possible intramolecular rearrangements or heterolytic rearrangements related to the "abnormal Beckmann reaction,"[16] is supported by the initiation and inhibition data depicted in Figure 1 (as well as by the tendency of the reaction to exhibit variable inhibition periods). The isolation of bibenzyl speaks for involvement of benzyl radicals. Since the oxygen-inhibited reaction eventually produced benzonitrile but little benzyl chloride, oxygen apparently traps benzyl radical more effectively than radical **13** under the conditions of our experiment.

The sequence outlined in steps 2 and 3 is analogous to the well-documented[24] decomposition of *t*-alkyl hypochlorites to ketones and alkyl chlorides; in this reaction, cleavage of alkoxy radicals gives the most stable possible departing radical. Similarly, cleavage of **13** proceeds as in step 3 rather than to produce the less stable phenyl radical and phenylacetonitrile. The much greater stability of N-chlorimine **1** can then be related to the absence of a good leaving radical, and the facile decomposition of **3** is as predicted.

In the presence of a large excess of 1-octene, the benzyl radical is trapped by the olefin before reacting with **2**, so that step 2 is replaced by the combination of steps 4 and 5; thus steps 3–5 constitute the major

$$C_6H_5CH_2\cdot + CH_2{=}CHC_6H_{13} \longrightarrow C_6H_5CH_2CH_2\dot{C}HC_6H_{13} \qquad (4)$$

$$C_6H_5CH_2CH_2\dot{C}HC_6H_{13} + \mathbf{2} \longrightarrow \mathbf{12} + \mathbf{13} \qquad (5)$$

chain. The addition of benzyl radicals to terminal olefins has been observed previously.[25] No products derived from addition of ketimino radical **13** to 1-octene were observed. Even in the diphenyl case where β scission is insignificant, a radical addition of **1** to 1-octene could not be achieved.

The reduction of **2** by Bu_3SnH is also apparently a radical chain reaction[26] analogous to the reduction of alkyl halides (see below for more conclusive evidence for the case of **1**). Since reduction at 130° is much faster than thermal decomposition, the reaction must be more complex than simply secondary reduction of benzyl chloride to toluene, and steps 6 and 7 seem reasonable. Thus, the chain is now steps 6, 7, and 3 with the combination of steps 6 and 7 being less of a

$$C_6H_5CH_2\cdot + Bu_3SnH \longrightarrow C_6H_5CH_3 + Bu_3Sn\cdot \qquad (6)$$

$$Bu_3Sn\cdot + \mathbf{2} \longrightarrow Bu_3SnCl + \mathbf{13} \qquad (7)$$

barrier to reaction than step 2. In contrast to the run at 130° where the average concentration of Bu_3SnH was low, the run at 35–40° where the concentration of Bu_3SnH was surely higher gave mainly ketimine, rather than toluene, apparently through step 8. Thus, at low

temperatures and high concentrations of chain-transfer agent, bimolecular step 8 is faster than unimolecular step 3, whereas at high temperatures and low concentrations, the reverse is true. Such an effect is reasonable for the sequence proposed.

In summary, then, both radical species proposed in steps 2 and 3 for the thermal cleavage of **2** have been trapped by added reagents: the benzyl radical as adduct **12** and as toluene (as well as by itself to form bibenzyl) and radical **13** as the ketimine.

The reduction of N-chloroketimine **1** with Bu_3SnH was studied as a model reaction for the more complex reduction of **2** discussed above. The occurrence of both marked initiation and moderate inhibition support a radical chain (steps 9 and 10) pathway and demonstrate that trialkyltin radicals can abstract chlorine from nitrogen as well as from carbon. Although radical addition of trialkyltin hydrides to certain >C=N–

$$\mathbf{1} + Bu_3Sn\cdot \longrightarrow (C_6H_5)_2C{=}N\cdot + Bu_3SnCl \qquad (9)$$

$$(C_6H_5)_2C{=}N\cdot + Bu_3SnH \longrightarrow (C_6H_5)_2C{=}NH + Bu_3Sn\cdot \qquad (10)$$

bonds has been reported,[27] the good yields of both benzophenone imine and Bu_3SnCl preclude any significant contribution from such a potential secondary reaction.

Experimental Section

All melting and boiling points are uncorrected. Infrared spectra were recorded on a Beckman IR-10 spectrometer. Nmr spectra were recorded on a Varian A-60 spectrometer in carbon tetrachloride solution unless otherwise specified, and results are expressed in parts per million downfield from internal tetramethylsilane. Glpc analyses were performed on a Micro-Tek

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(25) R. L. Huang, H. H. Lee, and L. Y. Wong, *J. Chem. Soc.*, 6730 (1965).

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(27) W. P. Neumann and E. Heymann, *Ann.*, **683**, 24 (1965).

2500R instrument equipped with a flame ionization detector. All quantitative results compared to internal standards were based on measured molar response factors determined from known mixtures of authentic materials. Chlorobenzene was distilled from calcium hydride, and benzene from Drierite.

Ketimine Hydrochlorides.[11,28]—To a 2.2 *M* solution of phenylmagnesium chloride in ether was added the appropriate nitrile: benzonitrile, diphenylacetonitrile (Matheson Coleman and Bell), or 2,2-diphenylpropionitrile.[29] After 24–48 hr at reflux, the mixture was treated with excess gaseous ammonia. The solids were removed by filtration and the filtrate was treated with gaseous hydrogen chloride after partial evaporation to remove excess ammonia. The precipitated hydrochlorides were stored in a freezer after drying *in vacuo* over phosphorus pentoxide. Phenyl benzyl ketimine hydrochloride was prepared from benzylmagnesium chloride and benzonitrile in analogous fashion.[11]

N-Chloroketimines.—A stirred suspension of 11.85 g (51 mmol) of phenyl benzyl ketimine hydrochloride in 140 ml of benzene was treated with gaseous ammonia at 0° for 30 min. The solids were removed by filtration and the filtrate was partially evaporated *in vacuo* without heating to remove excess ammonia. The resulting solution of ketimine was treated dropwise with a solution of 6.0 g (55 mmol) of *t*-butyl hypochlorite (Frinton Laboratories) in 15 ml of benzene at 0° and then stirred for 1 hr. The solvent was evaporated *in vacuo* at room temperature to give an oil which crystallized in the freezer. The product was dissolved in chloroform at room temperature and precipitated with two volumes of hexane to give after cooling 6.37 g of phenyl benzyl N-chloroketimine (**2**), mp 78–79° (lit.[11] mp 78°); a second crop (1.25 g) had mp 77.5–78.5°. The nmr spectrum showed a singlet at 4.37 ppm and a multiplet at 7.15–7.75 ppm in the ratio of 1.9:10.1; two protons of the latter multiplet were rather cleanly separated at ~7.65 ppm from the higher field portion. The singlet remained sharp and no new peaks appeared at −60° in deuteriochloroform solution. A 0.02 *M* solution in carbon tetrachloride was heated at reflux for 1 hr, cooled, and evaporated *in vacuo* to a suitable concentration to determine the nmr spectrum; no significant changes occurred in the spectrum. Iodometric titration of the product in a methylene chloride–aqueous acetic acid mixture consistently showed >95% active chlorine.

Anal. Calcd for $C_{14}H_{12}ClN$: C, 73.20; H, 5.27; N, 6.10; Cl, 15.44. Found: C, 73.15; H, 5.28; N, 6.10; Cl, 15.44.

Analogous reaction gave diphenyl N-chloroketimine (**1**), mp 35.5–37° (lit.[6] mp 35–36°), 100% pure by iodometric titration. A 0.02 *M* solution in chlorobenzene was refluxed under nitrogen for 6 hr with no loss of active chlorine and only slight development of a yellow color. Phenyl α-methylbenzhydryl N-chloroketimine (**3**), mp 164–166°, showed the expected nmr singlet at 1.75 ppm and showed 95% active chlorine by iodometric titration.

Anal. Calcd for $C_{21}H_{18}ClN$: C, 78.87; H, 5.63; N, 4.38; Cl, 11.11. Found: C, 78.72; H, 5.85; N, 4.64; Cl, 11.19.

Reactions of Phenyl Benzhydryl Ketimine with Chlorinating Agents.—The crude ketimine hydrochloride (1.80 g, *ca.* 5.8 mmol) was converted into the free ketimine with ammonia in benzene as above and treated with 0.73 g (6.7 mmol) of *t*-butyl hypochlorite for 1 hr at 0°. Evaporation at room temperature and crystallization from chloroform–hexane gave 1.08 g of product A, mp 91–95° (slight residue); normal iodometric titration indicated *ca.* 40% active chlorine. Repetition with 1.50 g (*ca.* 4.9 mmol) of ketimine hydrochloride and 1.0 g (9.2 mmol) of *t*-butyl hypochlorite gave, after crystallization, 0.58 g of a new product B, mp 141–142°, and several lower melting subsequent crops. Normal iodometric titration gave erratic values; replacement of methylene chloride as the cosolvent by ethanol gave values of *ca.* 150% for active chlorine content. A third run with 1.19 g (*ca.* 3.8 mmol) of hydrochloride and 0.54 g (4.0 mmol) of N-chlorosuccinimide was carried out in benzene solution. Over a 2-hr period at 0°, a precipitate was gradually formed. Filtration after partial evaporation gave succinimide (ir identification). Evaporation of the filtrate and crystallization several times from chloroform–hexane gave 200 mg of product, mp 90–94°, which showed 95% active chlorine by iodometric titration in ethanol and which was the same material by infrared analysis as product A above. Nmr spectra of A and B showed aromatic absorption but no singlet ascribable to the benzhydrylic proton.

Anal. Calcd for $C_{20}H_{16}ClN$ (A): C, 78.56; H, 5.24; N, 4.58; Cl, 11.62. Found: C, 76.30; H, 5.26; N, 4.70; Cl, 11.66.

Anal. Calcd for $C_{20}H_{15}Cl_2N$ (B): C, 70.59; H, 4.41; N, 4.11; Cl, 20.88. Found: C, 71.00; H, 4.51; N, 3.82; Cl, 20.79.

Product A (300 mg) was treated with 40 ml of refluxing 6 *N* hydrochloric acid for 3.5 hr. Extraction with ether, drying, and evaporation gave 287 mg of white solid, mp 81–86°. The ir spectrum showed both hydroxyl and carbonyl absorption as expected for phenyl α-hydroxybenzhydryl ketone (**6**) (lit.[30] mp 87–88°) but was quite different from that of the parent ketone. Similar hydrolysis of B gave an oily residue with a similar infrared spectrum. Therefore we assign A as phenyl α-chlorobenzhydryl ketimine (**7**) and B as phenyl α-chlorobenzhydryl N-chloroketimine (**8**).

Refluxing a 0.02 *M* solution of **7** in chlorobenzene under nitrogen led to total loss of active chlorine after 5 hr, but glpc analysis revealed <7% benzonitrile formation (internal standard technique as described below). Parallel treatment of **8** gave 82% benzonitrile.

Silver Ion Catalyzed Rearrangement of Phenyl Benzyl N-Chloroketimine.—Authentic N-phenylphenylacetamide (**4**), mp 114–116° (lit.[31] mp 117°), and N-benzylbenzamide (**5**), mp 104–105.5° (lit.[32] mp 105–106°), were prepared from the corresponding acid chlorides and amines. The benzylic resonances in the nmr spectrum (deuteriochloroform solution) occurred at 3.62 ppm (s) and 4.54 ppm (d, J = 6 cps), respectively. To a solution of 2.00 g (10.3 mmol) of silver tetrafluoroborate in 25 ml of 3:1 dioxane–water (v/v) at 60° was added 1.07 g (4.66 mmol) of N-chloroketimine **2**. The mixture was held at reflux for 4 hr as precipitation occurred. Cooling and filtration gave 0.655 g (98%) of silver chloride. The filtrate was poured into a solution of 2.5 g of sodium chloride in 100 ml of water, and the newly formed precipitate was recovered by filtration and dried. Digestion of this solid in 50 ml of boiling ligroin and evaporation of the liquid phase gave 0.39 g (43%) of low-melting solid whose ir spectrum was consistent with that of deoxybenzoin. The ligroin-insoluble residue was digested in 50 ml of boiling acetone, and evaporation of the liquid phase gave 0.26 g (26%) of solid, mp 97–105°, whose ir spectrum was consistent with that of amide **4**; crystallization from ethanol raised the melting point to 113–115°. Extraction of the original aqueous filtrate with chloroform and evaporation of the chloroform gave 0.20 g of a mixture whose ir spectrum suggested the presence of both deoxybenzoin and amide **4**. The experiment was repeated with 0.46 g of **4** and proportional quantities of other reagents; all of the organic product was collected in chloroform solution by a combination of extraction of the aqueous layer and digestion of the inorganic precipitates. Drying and evaporation of the chloroform gave 0.42 g of product whose nmr spectrum (deuteriochloroform solution) showed the expected singlets for deoxybenzoin (4.25 ppm) and amide **4** (3.63 ppm) in comparable amounts as well as a singlet at 3.67 ppm assigned to dioxane; no signal could be observed near 4.5 ppm for amide **5**, whereas 5% of the amount of **4** should have been easily detected.

Silver Ion Catalyzed Rearrangement of Phenyl α-Methylbenzhydryl N-Chloroketimine.—The above experiment was repeated with 3.25 g (16.8 mmol) of silver tetrafluoroborate, 1.43 g (4.45 mmol) of N-chloroketimine **3**, and 40 ml of dioxane–water (3:1). The nmr spectrum of the total organic residue (1.17 g) showed no absorption from 0.0–3.5 ppm expected for the methyl groups in rearranged amides, but instead showed (in addition to a small singlet for dioxane) a singlet at 5.47 ppm and aromatic absorption at 7.0–7.7 ppm in the ratio of 1.0:8.5; the position of the singlet corresponded to that of 1,1-diphenylethylene. Glpc analysis revealed benzonitrile (66% compared to *o*-dichlorobenzene as internal standard) and 1,1-diphenylethylene (90.5% compared to diphenylmethane as internal standard) based on retention times and coinjection with authentic samples.

Thermal Decomposition of Phenyl Benzyl N-Chloroketimine (2) at Low Concentration.—An appropriate amount of benzene or chlorobenzene (usually 25 ml) containing a known amount of *o*-dichlorobenzene(*ca.* 0.01 *M*) was heated to reflux; the mixture was flushed with nitrogen. The N-chloroketimine **2** was added

(28) P. L. Pickard and D. J. Vaughan, *J. Amer. Chem. Soc.*, **72**, 876 (1950).

(29) P. L. Pickard and E. F. Engles, *ibid.*, **73**, 864 (1951).

(30) A. Werner, *Ber.*, **39**, 1278 (1906).

(31) A. W. Hofmann, *ibid.*, **13**, 1223 (1880).

(32) E. Beckmann, *ibid.*, **23**, 3331 (1890).

in one portion and refluxing was continued under a positive nitrogen pressure. For runs under oxygen, the solvent was first saturated with oxygen in similar fashion. For runs with slow addition of benzoyl peroxide, the solution of peroxide in 2 ml of chlorobenzene was added at a constant rate from a syringe driven by a variable-speed syringe pump. Aliquots were removed periodically with a syringe through a serum cap and quenched in excess potassium iodide in 40% aqueous acetic acid; liberated iodine was titrated with standard sodium thiosulfate solution. When reaction was complete as judged by total disappearance of active chlorine, glpc analysis was used to determine the yields of benzonitrile and benzyl chloride based on the *o*-dichlorobenzene as internal standard. Results are summarized in Table I; plots of **2** remaining *vs.* time were made to estimate $t_{1/4}$ and $t_{1/4}$ (times for $^1/_4$ and $^1/_2$ reaction) which are listed *only* to indicate the general progress of the reaction and have no exact kinetic significance because the exact nature of the curves varied somewhat from run to run and probably depended on the purity of **2** as well as the exact degree of oxygen exclusion.

A slow-addition procedure was also successful. A solution of 28.9 mg (0.197 mmol) of *o*-dichlorobenzene in 15 ml of chlorobenzene was flushed with nitrogen and brought to reflux. A solution of 221 mg (0.963 mmol) of **2** in 5 ml of chlorobenzene was added in 5 hr at a constant rate from the motor-driven syringe. Iodometric titration showed that at 54% addition, 20% of the added **2** had disappeared; at 100% addition, 50% of **2** had disappeared, so that the concentration at this point was 0.024 *M*. After 16-hr reflux, titration was negative. Glpc analysis showed 100% benzonitrile and 92% benzyl chloride.

Partial decomposition to benzonitrile and benzyl chloride also occurred whenever solutions contaning **2** were injected into the heated glpc inlet.

Thermal Decomposition of Phenyl Benzyl N-Chloroketimine (2) at High Concentration.—A solution of 951 mg (4.14 mmol) of **2** and 96.5 mg of *o*-dichlorobenzene in 4.0 ml of chlorobenzene was flushed with nitrogen and heated under reflux. Almost immediately a flocculent precipitate appeared; iodometric titration after 1.75 hr was negative. After cooling to room temperature, the solid (60.8 mg, 1.14 mmol) was collected by centrifugation; it did not melt below 315° and had an ir spectrum (KBr) consistent with that for ammonium chloride. Additional cooling and concentration of the mother liquor gave 252.5 mg (0.68 mmol) of new solid in several crops melting in the range 205–212°. The ir spectrum[33] identified the product as 2,3,4,5-tetraphenylpyrrole (**9**) (lit.[24] mp 214–215°). Glpc analysis of the final mother liquor showed 22% benzonitrile and 17% benzyl chloride.

Thermal Decomposition of Phenyl α-Methylbenzhydryl N-Chloroketimine (3).—A solution of 165 mg (0.514 mmol) of N-chloroketimine **3** and 30.7 mg of *o*-dichlorobenzene in 25 ml of chlorobenzene was heated at reflux. A slow stream of nitrogen was fed over the reaction surface, through the condenser, and into a known volume of standard base. Iodometric titration of aliquots indicated complete reaction after 3 hr. Titration of the base trap with standard acid indicated the formation of 0.362 mequiv (70.5%) of volatile acid, presumably hydrogen chloride. Glpc analysis revealed 84% benzonitrile compared to the *o*-dichlorobenzene internal standard (after correction for aliquots taken) and a peak of retention time equal to that of 1,1-diphenylethylene in 95% yield compared to a diphenylmethane internal standard added after reaction; this identity was confirmed by nmr spectroscopy (singlet at 5.47 ppm). No 1,1-diphenylethane was detected either by glpc or nmr analysis.

Thermal Decomposition of Diphenyl N-Chloroketimine (1) in the Presence of 1-Octene.—To a solution of 1.168 g (5.42 mmol) of N-chloroketimine **1** in a mixture of 50 ml of chlorobenzene and 50 ml of 1-octene at reflux under nitrogen was added a solution of 135 mg (0.56 mmol) of benzoyl peroxide in 17 ml of chlorobenzene from a motor-driven syringe over a 5-hr period. At the end of the addition, 58% of active chlorine had disappeared, which increased to 82% overnight. Another 15.5 mg of benzoyl peroxide in 6 ml of chlorobenzene was added in 2 hr. After another 5-hr reflux, the active chlorine content had decreased to zero. Evaporation *in vacuo* gave 1.88 g of residue whose nmr spectrum showed 170 units of absorption intensity in the aromatic region, <4 units between 5.0 and 2.3 ppm, and 116 units between 2.3 and 0.6 ppm. Chromatography over alumina gave a large number of ill-defined fractions.

(33) "The Sadtler Standard Spectra Catalog," Sadtler Research Laboratories, Philadelphia, Pa., compound no. 14152.

Thermal Decomposition of Phenyl Benzyl N-Chloroketimine (2) in the Presece of 1-Octene.—A solution of 24.9 mg of *o*-dichlorobenzene in a mixture of 7.5 ml of chlorobenzene and 7.5 ml of 1-octene was flushed with nitrogen and brought to reflux (solution temperature 124°). A solution of 226 mg (0.98 mmol) of N-chloroketimine **2** in 5 ml of chlorobenzene was added from a motor-driven syringe at a constant rate in 5 hr. After 70% addition, iodometric titration indicated that 54% of the added **2** had disappeared; after 100% addition, 89% had reacted. The solution was held under reflux for 16 additional hr; glpc analysis showed 78% benzonitrile and <10% benzyl chloride. The solution was evaporated at 40° and *ca.* 1 Torr. The residue (236 mg) was dissolved in benzene and passed through a short column of Woelm neutral alumina. Benzene eluted 123 mg (53%) of clear liquid whose ir and nmr spectra coincided with those of 1-phenyl-3-chlorononane (**12**).

1-Phenyl-3-nonanol.—Condensation of 2-phenylethyl Grignard reagent and heptanal in ether gave, after acidic work-up and distillation, a center cut (63%), bp 95–97° (0.5 mm), n^{24}D 1.4986. The nmr spectrum showed a broadened singlet at 7.18 ppm (C_6H_5), a very broad band at 3.58 ppm ($-CH_2-\underset{\displaystyle H}{\underset{|}{C}}OHCH_2-$), a singlet at 3.10 ppm (OH), a multiplet at 2.70 ppm ($C_6H_5CH_2-CH_2-$), and complex absorption at 1.9–0.8 ppm with a terminal methyl group clearly visible; the relative areas were 5.0:1.05:1.1:1.95:14.9.

3-Chloro-1-phenylnonane (12).—Several attempts to convert the related alcohol into **12** were accompanied by olefin formation; the best attempt follows. To a stirred mixture of 6.12 g (0.028 mol) of the alcohol and 4.48 g (0.056 mol) of pyridine was slowly added 6.22 g (0.052 mol) of thionyl chloride as the temperature gradually rose to 60°. The mixture was heated at 100–110° for 1.5 hr before cooling and quenching with water. The organic material was collected in pentane to give 4.6 g of residue after drying and evaporation. Distillation gave two fractions with indistinguishable ir spectra: 1.48 g, bp 60–68° (0.03 mm), and 1.55 g, bp 68° (0.03 mm). The nmr spectrum showed absorption at 7.17 ppm, a broad band at 3.72 ppm, a multiplet at 1.95 ppm, and complex absorption at 1.8–0.8 ppm; the spectrum was analogous to that of the parent alcohol, as expected.

Anal. Calcd for $C_{15}H_{23}Cl$: C, 75.44; H, 9.71; Cl, 14.85. Found: C, 76.25; H, 9.87; Cl, 14.28.

Reduction of Diphenyl N-Chloroketimine (1) with Tri-*n*-butyltin Hydride (Bu_3SnH).—Quantitative runs were conducted at 0.02 *M* concentrations of each reagent in benzene. A solution of N-chloroketimine **1** in the bulk of the benzene required was flushed with nitrogen and heated to the desired temperature. The Bu_3SnH in a small volume of benzene was then added in one portion. Reaction was followed by titration of aliquots in aqueous ethanol for tri-*n*-butyltin chloride (Bu_3SnCl) formed with standard base.[22] Control experiments showed that neither N-chlorimines nor Bu_3SnH consumed base under these titration conditions. Iodometric titration could not be used to follow N-chlorimine loss, since control experiments showed that the iodine produced was consumed by Bu_3SnH. To determine the yield of diphenyl ketimine formed, selected reaction mixtures were evaporated at room temperature *in vacuo*, taken up in ether, and treated with dry hydrogen chloride to precipitate the ketimine hydrochloride; its ir spectrum was compared to that of authentic material. This procedure could be performed only when titration indicated complete reaction, since N-chloroketimines also can react with hydrogen chloride to give ultimately ketimine hydrochlorides.[10]

At reflux (81°), reduction was complete in 2 hr (100% yield of Bu_3SnCl by titration) and ketimine hydrochloride was obtained in 80% yield after correction for aliquots taken for titration. At 55 ± 1°, reaction proceeded smoothly with a first half-life of *ca.* 1.5 hr, but required standing overnight for complete reaction; ketimine hydrochloride was isolated in 90% yield. Under an oxygen atmosphere, reaction proceeded to only 50–60% conversion after 48 hr. Addition of 10 mol % di-*t*-butyl peroxyoxalate[23] in 1 ml of benzene over a 30-min period to a 50-ml initial reaction mixture led to complete reaction at the end of the addition period; each point in this run may be *ca.* 10% high, since the initiator was shown to consume some base during titration. Typical runs at 55 ± 1° are shown in Figure 2 to demonstrate the effects of oxygen and the peroxyoxalate. At 42 ± 1°, reduction proceeded through a first half-life in *ca.* 4 hr, but then the rate fell off sharply and only 70–75% of the theo-

retical amount of Bu_3SnCl was formed after 24 hr. A run under oxygen proceeded to only *ca.* 15% conversion in 4 hr and *ca.* 35% in 24 hr.

Reduction of Phenyl Benzyl N-Chloroketimine (2) with Bu_3SnH. A. 130–131°.—A solution of 30.3 mg (0.206 mmol) of *o*-dichlorobenzene in 10 ml of chlorobenzene was flushed with nitrogen and heated to reflux. Separate solutions of 227 mg (0.99 mmol) of N-chlorimine 2 in 5 ml of chlorobenzene and 303 mg (1.04 mmol) of Bu_3SnH in 5 ml of chlorobenzene were added under nitrogen at the same rate from motor-driven syringes over a 5-hr period. A cold trap was placed in the system to trap any volatile material which escaped the reflux condenser. Glpc analysis of aliquots indicated that toluene was formed essentially as fast as the reagents were added. At the end of the addition period, titration of an aliquot indicated 1.10 mmol of Bu_3SnCl formed. Glpc analysis revealed 76% toluene and 90–100% benzonitrile formed.

B. 35–40°.—To a solution of 235 mg (1.03 mmol) of N-chloroketimine 2 and 20 μl (0.196 mmol) of chlorobenzene in 15 ml of benzene was added a solution of 308 mg (1.06 mmol) of Bu_3SnH in 5 ml of benzene from a motor-driven syringe over 5 hr under N_2. The solution was irradiated throughout with a 275-W sun lamp at *ca.* 6 in., and the temperature was maintained at 35–40° by cooling with an air stream. Titration of an aliquot after 3-ml addition (0.64 mmol Bu_3SnH added) showed that 0.41 mmol of Bu_3SnCl had formed. At the end of the addition, 0.70 mmol had formed, and, after 1.3 hr additional, 0.75 mmol. Glpc analysis then showed 4% toluene, 8% benzyl chloride (apparently from inlet decomposition of residual 2), and 15% benzonitrile, by comparison to the chlorobenzene internal standard. Addition of dry hydrogen chloride to the residual reaction mixture and chilling overnight gave a solid, mp 215–216°, whose infrared spectrum agreed with that of phenyl benzyl ketimine hydrochloride; the yield corrected for the aliquots removed for titration was 0.57 mmol, *at least* one-half of which must have been derived from ketimine in the reaction mixture rather than residual 2 based on the final titration for Bu_3SnCl.

Registry No.—1, 7699-76-5; 2, 20453-02-5; 3, 20452-77-1; 1-phenyl-3-nonanol, 20452-78-2; 12, 20452 79-3; Bu_3SnH, 688-73-3.

Autoxidation of 1-Octene with *t*-Butyl Hydroperoxide and Chromium(III) Acetylacetonate. I. Kinetics

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The system chromium(III) acetylacetonate–*t*-butyl hydroperoxide has been used to initiate autoxidation of 1-octene in 1-chlorooctane solvent in the temperature range 0–60°. Emperical kinetic equations are presented based upon spectrophotometrically determined disappearance rates of chromium(III) acetylacetonate, titrimetrically determined *t*-butyl hydroperoxide decomposition rates, and oxygen absorption data. Activation parameters for the kinetic data have been calculated. The data are interpreted in terms of two superimposed chain reactions, one involving peroxide decomposition through chromium complexes, the other involving chain autoxidation of the 1-octene. Products of the autoxidation are compared with azo-initiated olefin autoxidation products.

Recently, metal acetylacetonates have been studied in terms of their ability to promote olefin epoxidation,[2,3] amine oxidation,[4] styrene polymerization,[5] and autoxidation[6] in the presence of hydroperoxide. This paper and subsequent ones[7] describe in some detail the use of chromium(III) acetylacetonate and *t*-butyl hydroperoxide as an autoxidation initiator for 1-octene. Reaction mixtures from the 1-octene autoxidation have been chromatographed and compared with azo-initiated autoxidation.[8] The effects of solvents and free-radical inhibitors on the reaction are described in part II.[7]

Experimental Section

Chemicals.—The chemicals for these experiments have been described previously.[6]

Kinetics.—Oxygen absorption measurements and *t*-butyl hydroperoxide decomposition studies for these experiments are as previously described.[6] The rate of chromium(III) acetylactonate disappearance was measured by observing the disappearance of the absorption peak at 336 mμ (ε 15,500 l./mol-cm).[9] Samples for analysis were taken from the same evacuated tubes as for *t*-butyl hydroperoxide decomposition studies and diluted in chlorobenzene. Measurements were done on a Cary Model 14 or a Perkin-Elmer Model 202 spectrophotometer. The reference cell contained chlorobenzene. It was observed that the presence of *t*-butyl hydroperoxide in chromium(III) acetylacetonate solutions caused deviations in Beer's law plots of absorbance *vs.* concentration. Corrections were made either by including *t*-butyl hydroperoxide in the reference cell or from calibration curves of absorption *vs. t*-butyl hydroperoxide concentration.

Rates in all cases were taken from initial portions of the kinetic curves. Rates of autoxidation and *t*-butyl hydroperoxide decomposition showed considerable curvature (lowering) after the initial portions. Chromium(III) acetylacetonate disappearance was linear. The reproducibility of duplicate rate measurements was *ca.* ±5% for chromium(III) acetylacetonate disappearance, *ca.* ±3% for autoxidation, and *ca.* ±6% for *t*-butyl hydroperoxide decomposition.

Product Analysis.—Product analysis was done by vapor phase chromatography on a Perkin-Elmer Model 154 gas chromatograph using a glass 88-in. Carbowax 20M column, helium pressure 10 psi, column temperature 150°, block temperature 74°. Retention times of products from previously described systems were used to correlate products from this work. Retention times of significant compounds are given in Table I for the above column conditions.

Preparation of 3-*t*-Butylperoxy-1-octene, 1-*t*-Butylperoxy-3-octene, and 3-Octenal.—Following the method of Kharasch and Fono[10] 0.033 g of cuprous chloride, 10 ml of 1-octene, and 2 ml of *t*-butyl hydroperoxide were mixed under nitrogen for *ca.* 5 hr at 60–70°. Four products peaks were observed gas chromatographically. Products of long retention time were assigned to the dialkyl peroxides, *t*-butyl alcohol was identified by comparison to an authentic sample, and octenal was assigned the remaining peak.

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