Oxidations of Amines. XI. Kinetics of Fragmentation of Triethylenediamine Chlorammonium Cation in Aqueous Solution[1]

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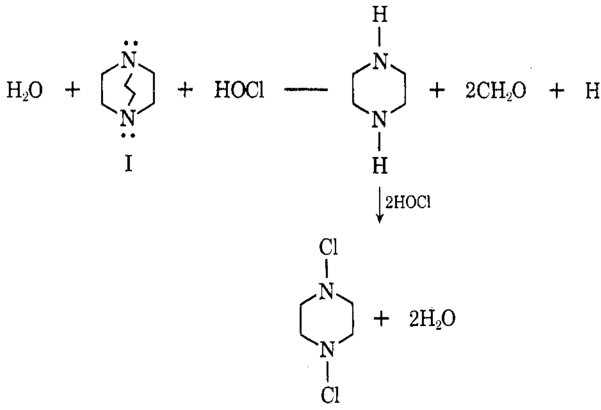
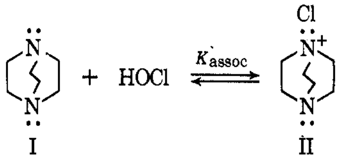
The reaction of hypochlorous acid with triethylenediamine has been studied by stopped-flow kinetics. A species identified as the chlorammonium cation was rapidly formed and detected by its ultraviolet absorption. Pre-steady-state and steady-state kinetics were obtained for the occurrence of the triethylenediamine cation radical. The data were analyzed in terms of two mutually exclusive mechanisms, either of which may be plausible, using the molar absorptivity of the cation radical obtained in previous work.[1] Related decompositions of aliphatic chlorammonium cations are discussed, as well as observations concerning the Hofmann-Loeffler reaction, in the light of these results and previous results of this series.

The action of hypochlorous acid on TED (triethylenediamine) differs markedly from its action on either simple aliphatic tertiary amines (such as triethylamine) or quinuclidine (which it resembles in important respects). With triethylamine, an aldehyde results without any carbon-carbon bond breaking.[2-4] With quinuclidine, the highly stable *N*-chloroquinuclidinium ion is formed[5] and reaction proceeds no further. By contrast, TED undergoes both carbon-carbon and carbon-nitrogen bond scission in an oxidative fragmentation reaction.[6]

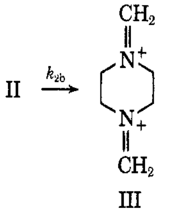
Oxidative fragmentation of TED can occur both by two-electron processes, as most likely happens with perchloryl fluoride,[7] and by one-electron processes, as with chlorine dioxide.[1] By whatever process, the stoichiometry of the hypochlorous acid reaction is expressed by eq 1. The simplest *mechanism* for the first step of reaction 1 would be the two-electron process (eq 2). Such a formulation is insufficient to explain one observed aspect of the reaction, namely, the appearance of the cation radical corresponding to the loss of a single electron by TED.[8] This was tentatively identified[8] as a minor side reaction (eq 3).



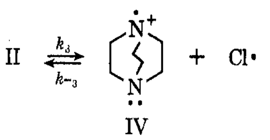
(1)



(2a)



(2b)



(3)

In the present study, our previous investigations have been extended through the use of a stopped-flow spectrophotometric technique for kinetics, which has permitted experiments at higher pH levels and temperature. The objective was to explore more closely the role of the cation radical in reaction 1.

Results

A species, observable at 357 nm,[9] arose too rapidly (within 5 msec) for its rate of appearance to be followed. From its behavior, this ultraviolet absorber, a partial spectrum of which is shown in Figure 1, was postulated as the chloroammonium cation of triethylenediamine. Its absorptivity was proportional to the initial analytical concentration of hypochlorous acid and independent of amine concentration provided that the amine was in stoichiometric excess; therefore, the maximum ("instantaneous") concentration of this new species was assumed to be equal to the introduced concentration of hypochlorous acid. On this basis, the molar absorptivity of the chloroammonium species at 357 nm was estimated as 139 M^{-1} cm^{-1}. Attempts

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[1] Previous paper of this series: G. T. Davis, M. M. Demek, and D. H. Rosenblatt, *J. Amer. Chem. Soc.*, **94**, 3321 (1972).

[2] H. Böhme and W. Krause, *Angew. Chem.*, **63**, 531 (1951).

[3] A. J. Ellis and F. G. Soper, *J. Chem. Soc.*, 1750 (1954).

[4] L. Horner and G. Podschus, *Angew. Chem.*, **63**, 531 (1951).

[5] T. Higuchi, A. Hussain, and I. Pitman, *J. Chem. Soc. B*, 626 (1969); T. Higuchi, A. Hussain, K. Ikeda, and A. Hurwitz, Final Report on Contract DA18-108-AMC-209(A), University of Wisconsin, Sept 27, 1966.

[6] W. H. Dennis, Jr., L. A. Hull, and D. H. Rosenblatt, *J. Org. Chem.*, **32**, 3783 (1967).

[7] D. M. Gardner, R. Helitzer, and D. H. Rosenblatt, *ibid.*, **32**, 1115 (1967).

[8] L. A. Hull, W. P. Giordano, D. H. Rosenblatt, G. T. Davis, C. K. Mann, and S. B. Milliken, *J. Phys. Chem.*, **73**, 2147 (1969).

[9] The ascending portion of the absorption curve at 357 nm was arbitrarily used with no attempt to locate a peak, because the absorptions of Cl(I) species were known to be negligible at this wavelength and the signal-to-noise ratio was less than at lower wavelengths.

were made to determine the dissociation constant[10] for this ion.

$$K_{\text{assoc}} = \frac{[\text{II}][\text{OH}^-]}{[\text{I}][\text{HOCl}]} = \frac{[\text{II}][\text{OH}^-]}{([\text{I}]_0 - [\text{II}])([\text{HOCl}]_0 - [\text{II}])} \times \frac{[\text{H}^+] + 5.89 \times 10^{-8}}{[\text{H}^+]} \frac{[\text{H}^+] + 1.18 \times 10^{-9}}{[\text{H}^+]}$$

The values obtained at pH 9.22–10.47 were poor, *i.e.*, $K_{\text{assoc}} = 3.22 \pm 1.28$, but support the view that hypochlorous acid is completely converted to II in the presence of excess amine in the pH range of the kinetic experiments, 8.92–9.09.

A second species, the cation radical IV, could be monitored at 465 nm[1] without interference from other species; it has a molar absorptivity,[1] ϵ_{IV}, of $2104 \pm 231\ M^{-1}\ \text{cm}^{-1}$. Under stopped-flow conditions, it was observed not only at steady state (*i.e.*, about 500–20,000 msec after mixing), but also under applicable pre-steady-state conditions[11] (*i.e.*, about 5–50 msec after mixing).

The formation of II was complete in <5 msec. Its disappearance, over periods of 150–20,000 msec from the time of mixing, followed first-order kinetics, with the first-order rate constants, k_t, shown in Table I.

TABLE I

CONSTANTS FOR FIRST-ORDER DISAPPEARANCE OF II AT 357 mμ ($\mu = 0.200$; $T = 25.0°$)

[Total amine], M	[Initial HOCl], M	pH	k_t, sec^{-1}
0.0500	3.48×10^{-3}	8.925	0.313
0.1000	7.49×10^{-4}	9.06	0.316
0.1000	7.49×10^{-4}	9.06	0.356
0.1000	3.75×10^{-3}	8.97	0.354
0.1000	3.75×10^{-3}	8.97	0.296
0.0100	7.54×10^{-4}	9.09	0.416
0.0100	7.54×10^{-4}	9.09	0.398
0.0100	6.95×10^{-4}	8.99	0.457[a]
0.544	3.48×10^{-3}	9.05	0.266[b]
0.544	3.48×10^{-3}	9.05	0.285[b]
0.0100	7.54×10^{-4}	9.09	0.525[a]
0.0100	7.54×10^{-4}	9.09	0.443[a]
		Mean	0.350 ± 0.036

[a] Scale expansion was made to cover 70–100 or 80–100% transmittancy. Not used in calculation of mean value. [b] $\mu = 0.544$. Amine and conjugate acid functioned as the buffer. Nitrate salt was used instead of perchlorate. Not used in calculation of mean value.

The pre-steady-state formation of IV over 5–50 msec was essentially linear and could be calculated as pseudo zero order for each experiment, *i.e.*, $\Delta[\text{IV}]/\Delta t = k_0\ M\ \text{sec}^{-1}$, where $[\text{IV}] = A_{\text{IV}}/\epsilon_{\text{IV}}$ and A_{IV} was the absorptivity of IV at any particular time. Data are shown in Table II.

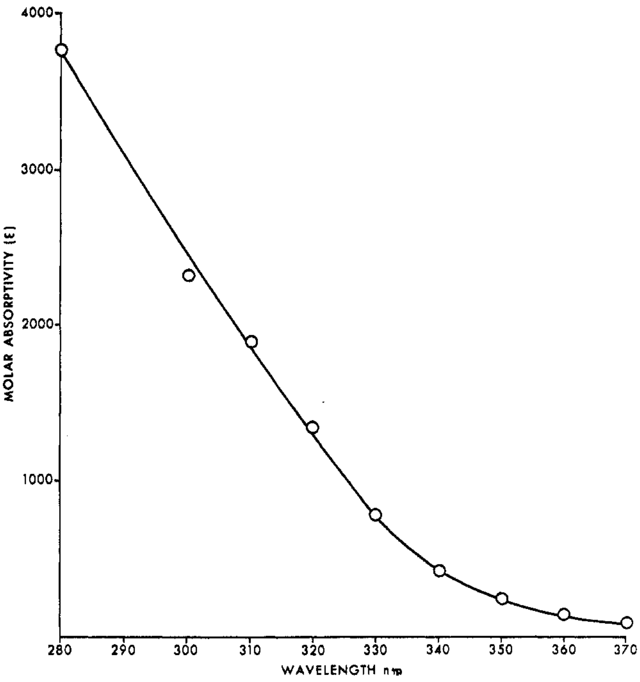

Figure 1.—Partial absorption spectrum of chlorammonium cation of triethylenediamine obtained in stopped-flow apparatus.

TABLE II

PRE-STEADY-STATE DATA FOR FORMATION OF IV ($\mu = 0.200$; $T = 25.0°$)

[Total amine], M	[Initial HOCl], M	pH	k_0, M sec^{-1}
0.050	3.48×10^{-3}	8.925	0.989
0.100	7.49×10^{-4}	9.06	0.235
0.100	3.80×10^{-3}	8.97	1.269
0.0100	6.95×10^{-4}	8.99	0.235
0.544[a]	3.48×10^{-3}	9.05	0.981
0.100	7.54×10^{-4}	9.09	0.188

[a] $\mu = 0.544$. Amine and conjugate acid functioned as the buffer. Nitrate salt was used instead of perchlorate.

When data for the concentrations of II and IV were plotted in various ways, for the time frame 500–20,000 msec, a linear relationship was found only when [IV] was plotted against $[\text{II}]^{1/2}$. The slopes for these plots are shown in Table III.

Discussion

The disappearance of II can be attributed to either or both pathways shown in eq 2b and 3. Under pre-steady-state conditions, k_{-1}, even if real, may be ignored. For each of the pre-steady-state experiments reported in Table II, a first-order rate constant can be calculated by dividing k_0 by $[\text{HOCl}]_0$; this would be k_3, provided that there is no other process for production of IV. For steady-state kinetics, the experimental $k_t = k_{2b}$ (Table I). If we now add the steady-state assumption for processes 2 and 3, then $d[\text{IV}]/dt \sim k_3[\text{II}] - k_{-3}[\text{IV}][\text{Cl}\cdot]$, and, since $[\text{Cl}\cdot] \equiv [\text{IV}]$, $k_3[\text{II}] = k_{-3}[\text{IV}]^2$, whence $(k_3/k_{-3})^{1/2} = [\text{IV}]/[\text{II}]^{1/2}$. We identify these values with the values shown in Table III. From k_3 and $(k_3/k_{-3})^{1/2}$, k_{-3} can be calculated (see Table IV). Although the mechanism requires remarkable selectivity of the chlorine atom for exclusive reaction with the cation radical, we do not feel that it can be ruled out in the absence of detailed knowledge of the stability of solvated chlorine radicals in aqueous media, and in the absence of such knowledge concerning the patterns of chlorine atom reactivity

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[10] The acid association constants for hypochlorous acid and monoprotonated TED at 0.200 M ionic strength were estimated as 5.89×10^{-8} and 1.18×10^{-9}, respectively, from thermodynamic data by R. Caramazza, *Gazz. Chim. Ital.*, **87**, 1507 (1957), and from ref 1.

[11] Ordinarily, a reaction observable at steady state reaches this condition too rapidly for the initial process to be studied. Only when chemical behavior can be followed over many orders of magnitude on the time scale, as with the stopped-flow apparatus, can both pre-steady- and steady-state kinetics readily be determined.

TABLE III

CONSTANTS FROM SQUARE ROOT PLOT FOR DECOMPOSITION OF CHLORAMMONIUM CATION OF TRIETHYLENEDIAMINE ($\mu = 0.200$; $T = 25.0°$)

[Total amine], M	[Initial HOCl], M	pH	$[IV]/[II]^{1/2}$	$10^6k_3/k_{-3} = 10^6k_{4a}/k_{4c}$	$10^{-4}k_{-3}/2 = 10^{-4}k_{4c}$
0.0500	3.475×10^{-3}	8.925	2.83×10^{-3}	8.01	0.89
0.1000	7.49×10^{-4}	9.06	2.51×10^{-3}	6.30	1.13
0.1000	7.49×10^{-4}	9.06	2.67×10^{-3}	7.12	1.00
0.1000	3.746×10^{-3}	8.97	2.49×10^{-3}	6.20	1.15
0.1000	3.746×10^{-3}	8.97	2.84×10^{-3}	8.07	0.88
0.0100	7.536×10^{-4}	9.09	2.648×10^{-3}	7.01	1.01
0.0100	7.536×10^{-4}	9.09	2.751×10^{-3}	7.57	0.94
0.0100	7.536×10^{-4}	9.09	2.48×10^{-3}	6.16	1.16
				Mean	1.02 ± 0.09

TABLE IV

CONSTANTS DERIVED FROM MECHANISTIC MODELS CONSIDERED

$k_t = 0.350 \pm 0.036\ \text{sec}^{-1}$

$k_3 = 0.141 \pm 0.13\ \text{sec}^{-1}$

$k_{2b} = 0.371\ \text{sec}^{-1}$ (if pathway 3 is followed)

$k_{-3} = 2.04 \pm 0.18 \times 10^4\ M^{-1}\ \text{sec}^{-1}$

$k_{4a} = 0.0713 \pm 0.0068\ \text{sec}^{-1}$

$k_{2b} = 0.279\ \text{sec}^{-1}$ (if pathway 4 is followed)

$k_{4c} = 1.02 \pm 0.09 \times 10^4\ M^{-1}\ \text{sec}^{-1}$

in water. Solvent effects on chlorine atom reactivity are known,[12] an increase in specificity being observed with charge transfer type solvation, but the cited studies have not included examination of aqueous media.

An alternative mechanism includes pathway 2b and, in place of pathway 3, takes cognizance of the more appealing concept that the electrophilic chlorine free radical is a very reactive species, and should not react with IV, which is present in quite low concentration, but should react rapidly with I, which is much more abundant. In this case there is no reverse reaction as in eq 3 and we represent the overall process as

$$\text{II} \xrightarrow{k_{4a}} \text{IV} + \text{Cl}\cdot \tag{4a}$$

$$\text{I} + \text{Cl}\cdot \xrightarrow{\text{fast}} \text{IV} + \text{Cl}^- \tag{4b}$$

Accordingly, $k_t = k_{2b} + k_{4a}$. We calculate k_{4a} as $k_0/2[\text{HOCl}]_0$. The final organic product, III, must be formed by the reaction

$$2\,\text{IV} \xrightarrow{k_{4c}} \text{I} + \text{III} \tag{4c}$$

Under the steady-state assumption, $d(\text{IV})/dt = 2k_{4a}[\text{II}] - 2k_{4c}[\text{IV}]^2$. Hence $k_{4a}/k_{4c} = [\text{IV}]/[\text{II}]^{1/2}$. The disappearance of II by pathway 4, then, leads to results indistinguishable from those of pathway 3, and the data do not inherently indicate which is correct.

The constants obtained for the pathways discussed above are summarized in Table IV.

Mechanisms 3 and 4 cannot operate simultaneously, since according to eq 3 the dissociation of II must be reversible and according to eq 4 it must be irreversible (since [I] has no rate effect).

Identification of the ultraviolet-absorbing intermediate species as the chlorammonium ion follows by chemical analogy with the work of Böhme and Krause[2] and Ellis and Soper.[3] In their work, the chloroammonium ion of trimethylamine showed no ultraviolet absorption. However, some ultraviolet absorption has been observed for the stable chloroquinuclidinium ion.[5]

While our work does not serve to establish a definite mechanism for the reaction of hypochlorous acid with triethylenediamine, it does show that *substantial* homolytic cleavage of the nitrogen–chlorine bond occurs, either in a competing equilibrium or in a process which leads to products. Also, a far *greater* amount of heterolytic cleavage occurs than homolytic cleavage in either of the postulated models; *i.e.*, mechanism A shows $k_{2b} > k_{4a}$ (Table IV), and mechanism 2 requires complete heterolytic cleavage for *product* generation. These results tend to increase confidence in the heterolytic mechanisms of Böhme and Krause[2] and Ellis and Soper[3] as being more important than the homolytic one proposed by Horner and Podschus[4] for reaction of HOCl with aliphatic amines. It is interesting to note that all of the findings of Horner and Podschus[4] which were interpreted as support for a free-radical mechanism, *except* for *polymerization initiation* by the chlorine radical, are equally accommodated by the heterolytic process described by Ellis and Soper.[3] Thus, the chlorine radicals detected by Horner and Podschus in reaction of hypochlorous acid with triethylamine are very likely a minor contributor to the overall reaction. Nevertheless, they are evidence for the corresponding production of small amounts of aminium cation radicals. It is further noteworthy that, in the hypochlorous acid–triethylenediamine system, the homolytic route would be unusually favored over the heterolytic route. There is additional thermodynamic stabilization of the cation radical due to delocalization[1] as well as kinetic stability conferred by the bridgehead structure which prevents proton loss (normal decomposition), since the latter would violate Bredt's rule. Further, the disproportionation (eq 4c) would be unusually favored, since the charge delocalization would allow easier approach of two cation radicals.

The fate of radicals generated from chloroammonium ions is an important consideration in the Hofmann–Loeffler reaction to form cyclic amines.[13] The need for *strongly acidic media* with light, heat, or free-radical initiators has been demonstrated for the reaction[14] and more recently reemphasized by Neale and coworkers.[15] The latter workers also found *addition* of aminium radicals to unsaturated hydrocarbons to be more facile and characteristic of aminium radicals than hydrogen-atom abstractions (such as postulated for the Hofmann–Loeffler rearrangement).[13] Aminium rad-

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(12) G. A. Russell, *J. Amer. Chem. Soc.*, **80**, 4987, 4997 (1958).

(13) M. E. Wolff, *Chem. Rev.*, **63**, 55 (1963).

(14) S. Wawzonek and J. D. Nordstrom, *J. Org. Chem.*, **27**, 3726 (1962).

(15) R. S. Neale, M. R. Walsh, and N. L. Marcus, *J. Org. Chem.*, **30**, 3683 (1965), and preceding papers.

icals have, in fact, been photolytically generated from secondary amines in strongly acidic media.[16] Parallelling our present results, spontaneous production of aminium radicals from protonated chloramines *under mild conditions* was observed,[15] and subsequent fast addition to unsaturated hydrocarbons. If ordinary aliphatic aminium radicals are generated in weakly basic, neutral, or weakly acidic aqueous media, we have found,[17] rapid loss of α protons occurs with subsequent oxidative dealkylation. Hence, the characteristic reactions of aminium ions near neutrality are different from those in strongly acidic media.

Experimental Section

Water and triethylenediamine perchlorate were purified as previously described.[1] Aqueous hypochlorous acid solutions were prepared by the procedure of Higuchi and Hasegawa.[18] The mononitrate salt was prepared analogously to the perchlorate salt, and recrystallized thrice from ethanol. It was transferred to stoppered containers in a drybox prior to weighing due to its hygroscopicity. Other salts and buffers used were of the purities previously described.[1]

For determination of hypochlorous acid, stock solutions were diluted and analyzed spectrophotometrically in the presence of excess iodide ion, as previously described,[2] using the molar absorptivity reported by Awtrey and Connick.[19]

Stopped-flow kinetics were obtained in the apparatus of ref 1, employing procedures used there. Hypochlorous acid solutions of known concentration were mixed in the apparatus 1:1 with known concentrations of triethylenediamine in buffered salt solutions to give final ionic strengths after mixing of 0.2. The chlorammonium species was observed at 357 nm and the cation radical[1] was followed at 465 nm.

Registry No.—II, 35666-89-8; IV, 35666-90-1.

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(16) W. C. Danen and R. C. Rickard, *J. Amer. Chem. Soc.*, **94**, 3254 (1972).

(17) L. A. Hull, G. T. Davis, D. H. Rosenblatt, H. K. R. Williams, and R. C. Weglein, *ibid.*, **89**, 1163 (1967).

(18) T. Higuchi and J. Hasegawa, *J. Phys. Chem.*, **69**, 796 (1965).

(19) A. D. Awtrey and R. E. Connick, *J. Amer. Chem. Soc.*, **73**, 1842 (1951).

Steric Crowding in Organic Chemistry. VI. Reactivity of Tri-*tert*-butylethylene and Related Compounds[1]

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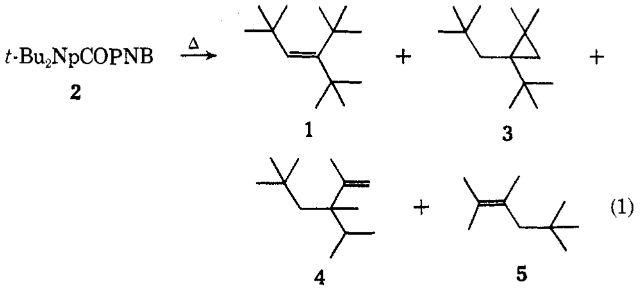
Pyrolysis of di-*tert*-butylneopentylcarbinyl *p*-nitrobenzoate (**2**) or benzoate (**7**) gives tri-*tert*-butylethylene (**1**), 1-*tert*-butyl-1-neopentyl-2,2-dimethylcyclopropane (**3**), and 2,3,5,5-tetramethyl-3-*tert*-butyl-1-hexene (**4**). A pathway to these products involving initial formation of an ion pair is proposed. Hydrogenation and bromination of **1** are relatively slow, presumably due to steric shielding of the double bond. Ozonation of **1** leads to cleavage of the double bond without formation of an epoxide. Hydroboration of **1** is slow and after oxidation with alkaline hydrogen peroxide gives 4-*tert*-butyl-2,2,5,5-tetramethyl-3-hexanone (**9**), *trans*-2,3-di-*tert*-butyl-4,4-dimethyltetrahydrofuran (**10**), and the expected 4-*tert*-butyl-2,2,5,5-tetramethyl-3-hexanol (**11**). Oxidation of the hydroboration product with *m*-chloroperbenzoic acid yields **10** and **11′** but none of **9**. It is proposed that **9** arises from a free-radical oxidation route which competes with the retarded normal ionic oxidation by alkaline hydrogen peroxide but not with the faster ionic oxidation by *m*-chloroperbenzoic acid, while **10** is derived from cyclization of the initially formed borane to give a boron heterocycle **13** which leads to **10** on oxidation. Reaction of di-*tert*-butylacetyl chloride with *tert*-butyllithium leads to the formation of **9,11**,tri-*tert*-butylcarbinol, 4-*tert*-butyl-4-hydroxy-2,2,5,5-tetramethyl-3-hexanone (**19**), 3,6-di-*tert*-butyl-5-hydroxy-2,2,7,7-tetramethyl-4-octanone (**20**), and 3,6-di-*tert*-butyl-2,2,7,7-tetramethyl-4,5-octadione (**21**). A mechanism involving radical and radical anion intermediates is proposed for this transformation.

There is a continuing intense interest in the influence of steric strain on the properties of olefins.[2b,3] These studies have involved olefins that are strained by their incorporation in rings[3a–c,e] and those strained by the presence of bulky substituents.[2b,4]

As part of a study of the effects of extreme steric crowding on the physical and chemical properties of organic compounds, tri-*tert*-butylethylene (**1**) has been prepared in this laboratory. Its synthesis has been described,[2b,4] as well as some aspects of its chemical reactivity[4] and studies of the effect of crowding on the Raman,[4] ultraviolet,[2b] and ^{13}C nmr[2c] spectra of olefins. This report contains a description of a number of chemical reactions of **1** and some related compounds which are potential precursors to a compound which is an as yet unrealized synthetic goal in this laboratory: tetra-*tert*-butylethylene. The unusual course taken in some of these reactions illustrates the remarkable influence of extreme steric crowding in affecting chemical reactivity.

Preparation of Tri-*tert*-butylethylene (1).—This synthesis was accomplished by the pyrolysis of di-*tert*-


t-Bu$_2$NpCOPNB $\xrightarrow{\Delta}$

2

1

3

4

5

(1)

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(1) Acknowledgment is made to the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. Part V, ref 2a; part IV, ref 2b; part VII, ref 2c.

(2) (a) G. J. Abruscato and T. T. Tidwell, *J. Amer. Chem. Soc.*, **94**, 672 (1972); (b) G. J. Abruscato, R. G. Binder, and T. T. Tidwell, *J. Org. Chem.*, **37**, 1787 (1972); (c) G. J. Abruscato, P. D. Ellis, and T. T. Tidwell, *Chem. Commun.*, 988 (1972).

(3) (a) C. C. Levin and R. Hoffmann, *J. Amer. Chem. Soc.*, **94**, 3446 (1972); (b) G. L. Buchanan and G. Jamieson, *Tetrahedron*, **28**, 1123, 1129 (1972); (c) W. L. Mock, *Tetrahedron Lett.*, 475 (1972); (d) L. Radom, J. A. Pople, and W. L. Mock, *ibid.*, 479 (1972); (e) R. Keese and E.-P. Krebs, *Angew. Chem., Int. Ed. Engl.*, **11**, 518 (1972).

(4) G. J. Abruscato and T. T. Tidwell, *J. Amer. Chem. Soc.*, **92**, 4125 (1970).