Thermal Stability of 1,2-Diazetidinones.—In small test tubes were placed 0.03 g of each of the 1,2-diazetidinones together with 0.3 g of paraffin wax. These tubes were then immersed for 20 min in a preheated oil bath. A small portion of the wax was removed from each tube and pressed between salt plates, and the infrared spectrum was obtained. If there was no isocyanate peak at *ca.* 2270 cm^{-1}, the tube was placed back in a bath at a higher temperature and the process was repeated. The decomposition temperatures listed in Table I are the lowest temperature at which an isocyanate peak was observable.

The Solvolysis of Alkyl Diazotates. I. Partition between Carbonium Ions and Diazoalkanes in Aqueous Base

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A series of alkyl diazotates, obtained by basic cleavage of N-alkyl-N-nitrosourethans, afforded, upon hydrolysis, carbonium ion products and/or diazoalkanes. Partition was dependent on alkyl-group structure. This dependence is discussed in some detail. Alkyl diazotates appear to be a source of carbonium ions in aqueous base.

N-Nitrosourethans have long been employed as precursors of diazoalkanes.[1] Intermediacy of diazotate salts, I, in the preparation of diazomethane and phenyldiazomethane was demonstrated by Hantzsch.[2,3]

$$\underset{\text{I}}{\mathrm{R{-}N{=}N{-}\overset{-}{O}\overset{+}{M}}} \qquad \underset{\text{II}}{\mathrm{R{-}N{=}N{-}OH}}$$

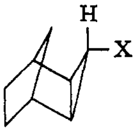
Much later, Huisgen suggested their occurrence as an intermediate in the basic decomposition of nitrosocaprolactam.[4] Under conditions similar to those of Hantzsch,[2] we decomposed a series of N-alkyl-N-nitrosourethans, observing facile formation of ether-insoluble, proton-sensitive substances, presumably alkyl diazotates. Aqueous quenching of these substances very rapidly affords diazoalkanes, and/or nitrogen, and products commonly associated with carbonium ions. The relation between diazo and ionic decomposition pathways, the common origin of these pathways in another intermediate, possibly II, and the relation between alkyl-group structure and decomposition pathway will be discussed.

Results

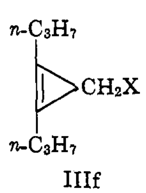
Preparation of Starting Materials.—Urethans IIIa–f, (X = $NHCOOC_2H_5$) were selected for nitrosation. Urethans IIIa,[5] b,[6] c,[7] and d[8] were known. The last compound was prepared by addition of ethanol to the commercially available allyl isocyanate, the first three *via* reaction of ethylchloroformate with the requisite amine.[9] Urethans IIIe and f were unknown. The former was obtained from Curtius rearrangement in refluxing ethanol of acid azide IVc, itself obtained, *via* acid chloride IVb, from the known acid IVa.[10] The latter was obtained from the requisite ester[11] (Chart I). Some apparent shortcuts failed, for example, ammonolysis of starting ester directly to amide. Also lithium aluminum hydride reduction of amide to amine was effected only with simultaneous double-bond reduction.[12] Urethans were characterized by infrared and nmr spectra.[13] Satisfactory elemental analyses were obtained for the new compounds.

n-C_4H_9X IIIa n-$C_8H_{17}X$ IIIb cyclo-$C_6H_{12}X$ IIIc

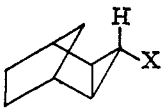
$CH_2{=}CH{-}CH_2X$ IIId



IIIe

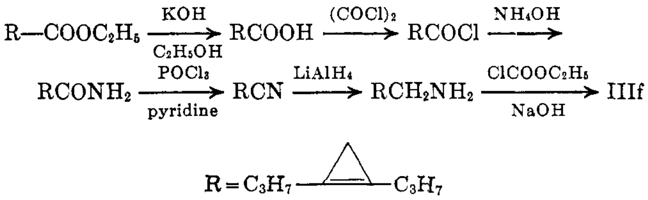


IIIf



IVa, X = COOH
b, X = COCl
c, X = CON$_3$

Chart I



$$\mathrm{R{-}COOC_2H_5 \xrightarrow[C_2H_5OH]{KOH} RCOOH \xrightarrow{(COCl)_2} RCOCl \xrightarrow{NH_4OH}}$$

$$\mathrm{RCONH_2 \xrightarrow[pyridine]{POCl_3} RCN \xrightarrow{LiAlH_4} RCH_2NH_2 \xrightarrow[NaOH]{ClCOOC_2H_5} IIIf}$$

Nitrosation of urethans IIIa–f was accomplished with ethereal nitrogen tetroxide,[14] care being taken, in the case of IIIf, to keep the reaction temperature below −55° (above this temperature, destruction of the double bond was dominant[15]). Nitrosourethans IIIe

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[1] H. v. Pechmann, *Ber.*, **28**, 855 (1895), and references therein.

[2] A. Hantzsch and M. Lehmann, *ibid.*, **35**, 897 (1902).

[3] See also H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961, p 44 ff.

[4] R. Huisgen and J. Reinertshofer, *Ann.*, **575**, 174 (1952). See also G. Nischk and E. Müller, *ibid.*, **576**, 232 (1952).

[5] A. L. Wilds and A. L. Meader, Jr., *J. Org. Chem.*, **13**, 763 (1948).

[6] D. W. Adamson and J. Kenner, *J. Chem. Soc.*, 181 (1939).

[7] F. W. Bollinger, F. N. Hayes, and S. Siegel, *J. Am. Chem. Soc.*, **72**, 5592 (1950).

[8] C. D. Hurd and S. C. Lui, *ibid.*, **57**, 2656 (1935).

[9] A. H. Blatt, Ed., "Organic Synthesis," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p 278.

[10] R. R. Sauers and P. E. Sonnet, *Tetrahedron*, **20**, 1029 (1964).

[11] R. Breslow, H. Hover, and H. W. Chang, *J. Am. Chem. Soc.*, **84**, 3168 (1962).

[12] See, in this regard, B. Franzus and E. I. Snyder, *ibid.*, **87**, 3423 (1965).

[13] Nmr spectra for urethans and their N-nitroso derivatives are discussed in detail in a separate publication: R. A. Moss, *Tetrahedron Letters*, 711 (1966).

[14] E. H. White, *J. Am. Chem. Soc.*, **77**, 6008 (1955).

[15] W. M. Jones and J. M. Denham, *ibid.*, **86**, 944 (1964). It proved impossible to obtain pure nitroso compound. Some attack, *ca.* 20%, on the double bond always occurred.

and IIIf [X = $N(NO)COOC_2H_5$] have been prepared for the first time; IIIa,[5] b,[6] and d[8] were known, but were previously prepared by other methods. Nitroso compounds were characterized by nmr spectra[13] and by quantitative liberation of nitrogen (see below). Nitrosourethan IIIc has been reported to be rather unstable,[14] and one report of its synthesis[7] was questioned by Heyns.[16] No difficulties were encountered in the present study.

Decomposition of N-Nitrosourethans.—Decomposition was effected by addition of 1 equiv of nitrosourethan to a cooled (*ca.* −30°) ethereal slurry of 2 equiv of potassium *t*-butoxide. After 20 min (*ca.* −20°), quenching was effected by rapid addition of water.

Depending on structure, nitrosourethans displayed three kinds of decomposition behavior: (1) quantitative and rapid (complete within 4 sec) elimination of nitrogen; (2) no gas evolution, but immediate formation of diazoalkane; and (3) rapid, but less than quantitative, gas evolution, accompanied by formation of diazoalkane.

Decomposition products are summarized in Table I.

TABLE I

PRODUCTS OF DECOMPOSITION OF N-NITROSOURETHANS

N-Nitrosourethan	Products (yield, %)[a]
IIIa	N_2 (40), *n*-diazobutane (60)[b,c]
IIIb	N_2 (61), *n*-diazooctane (31),[c,d] 1-octene (8), 1-octanol (28), 2-octanol (3)
IIIc	N_2 (110), cyclohexene (18), cyclohexanol (22)
IIId	Vinyldiazomethane[e]
IIIe	N_2 (93), *exo*-bicyclo[3.2.1]oct-2-en-3-ol (40)
IIIf	N_2 (60+),[f] *cis*- and *trans*-2-propyl-3-methylhex-2-enal, 3-propyl-1,3,4-heptatriene[g]

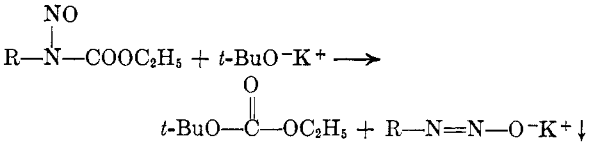
[a] Yields of N_2 were measured by displacement of water at *ca.* 25° and 760 mm. They are not corrected for partial pressure of water. Products were isolated by vpc and identified by comparison (nmr, infrared, and vpc retention time) with authentic samples. Yields were determined by vpc with added internal standards, previously calibrated against authentic products for relative detector response. In all cases except urethan IIId, nondistillable residues were observed. [b] Other products were not investigated. [c] Diazoalkanes were stable under reaction conditions; identified by intense infrared band at 4.87 μ [see P. Yates, B. L. Shapiro, N. Yoda, and J. Fugger, *J. Am. Chem. Soc.*, **79**, 5756 (1957)] and orange color, both of which disappeared upon quenching with 6 *N* HCl. Gas evolution accompanying acid quench was used to estimate diazoalkane yield. [d] Diazooctane was thermally destroyed prior to analysis of other products. A trace of normal C_{16} hydrocarbon identified in the products could have arisen here. [e] See text. [f] It was impossible to obtain pure nitrosourethan IIIf.[15] Nmr estimations gave a purity of 60–80%. Nitrogen evolution based on this was 60–80% of the theoretical. No evidence for diazoalkane formation was noted. [g] Specific yields were not obtained. Except for carbonates, no other major products were observed in vpc traces.

Not described in Table I, but common to all decompositions, was the formation of di-*t*-butyl carbonate, ethyl *t*-butyl carbonate, and (trace) diethyl carbonate.

Quenching of the IIId decomposition slurry afforded no nitrogen. Instead, there resulted a red ethereal phase, which, with copious gas evolution, was decolorized upon addition of acid and upon all attempts at manipulation. Taken with the results of Hurd,[8] the properties of this solution leave little doubt that vinyldiazomethane is a principal product in this experiment. Since, however, vinyldiazomethane is known to be more stable than saturated diazoalkanes (to both thermal and protolytic decomposition),[17] the present instability is surprising.

Discussion

Diazotates.—The initial action of *t*-butoxide on the nitrosourethans produces alkyl diazotates I (eq 1).



$$R-\overset{\overset{\large NO}{|}}{N}-COOC_2H_5 + t\text{-}BuO^-K^+ \longrightarrow t\text{-}BuO-\overset{\overset{\large O}{\|}}{C}-OC_2H_5 + R-N=N-O^-K^+\downarrow \quad (1)$$

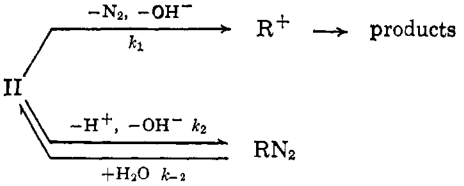
Hantzsch isolated and obtained elemental analyses for I (R $=CH_3$, $C_6H_5CH_2$) prepared in a similar manner.[2] Later, Huisgen pointed out that compounds containing the nitrosamide grouping were powerful acylating agents[18] and was promoted to suggest a reaction analogous to (1) as the initial step in the base-catalyzed decomposition of nitrosocaprolactam.[4]

In the present case, it was easy to show that (1) held. Thus, suction filtration, under nitrogen, of a 20-min-old slurry of 1 equiv of nitrosourethan IIIb, with 2 equiv of *t*-butoxide in ether, followed by ethereal washing, yielded a filtrate containing the carbonates,[19] but virtually no diazooctane, and none of the products of aqueous quenching. The precipitate, however, could be suspended in fresh ether and quenched with water, the resulting gas evolution and product analysis being identical with those shown in Table I, except that only traces of carbonates were now found.[20]

Diazotic Acids.—Addition of water to the diazotate slurry probably involves rapid proton transfer (2), affording the diazotic acid II.[3,21] Previous authors[2–4]

$$\underset{\text{I}}{R-N=N-O^-K^+} + H_2O \rightleftharpoons \underset{\text{II}}{R-N=N-OH} + K^+OH^- \quad (2)$$

(also, see below) have suggested two fates for II in basic media,[22] outlined in (3). That carbonium ions are in-



(3)

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[16] K. Heyns and A. Heins, *Ann.*, **604**, 133 (1957).

(17) D. W. Adamson and J. Kenner, *J. Chem. Soc.*, 1551 (1937). See also ref 3 and below.

(18) See R. Huisgen and G. Horeld, *Ann.*, **562**, 137 (1949), and later papers in this series. N-Nitrosoureas have been found to take a different course: W. M. Jones, D. L. Muck, and T. K. Tandy, Jr., *J. Am. Chem. Soc.*, **88**, 68 (1966); W. M. Jones and D. L. Muck, in press.

(19) Under reaction conditions, *t*-butyl ethyl carbonate and excess *t*-butoxide are involved in a set of transesterification equilibria, yielding the three carbonates described above.

(20) Some manipulative loss accounted for only 82% nitrogen balance in this experiment. A trace of diazooctane in the initial filtrate may have appeared *via* atmospheric moisture during filtration, an imperfect nitrogen blanket being provided through an inverted funnel.

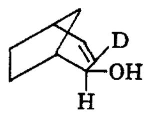
(21) We will not distinguish between i or ii or an equilibrium of i and ii for representation of II. Present observations are consistent with either or both formulations.

$$\underset{\text{i}}{R-N=N-OH} \qquad \underset{\text{ii}}{R-\overset{+}{N}\equiv N\overset{-}{O}H}$$

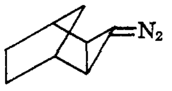
(22) Similar quantities of nitrosourethans, *ca.* 15 mmoles, were employed in all experiments. Decompositions were effected with 100% excess butoxide, quenching with 5 ml of water. Thus, assuming that (1) goes to completion, aqueous phase was at least 3 *M* in hydroxide ion.

volved in these decompositions is suggested by comparison of the products (Table I) with those of nitrous acid deamination of the corresponding amines. A qualitative parallel is observed. Thus, 1-octylamine yielded 44% 1-octanol, 2.3% 2-octanol, and 24.4% 1-octene; cyclohexylamine yielded 68% cyclohexanol and 20% cyclohexene.[23] Deamination of IV (X = NH$_2$) in acetic acid yielded the acetate ester of the bicyclic octenol cited in Table I.[10] Products from IIIf are analogous to those found in reactions attributed to the cyclopropenylcarbinyl cation.[24–26] It seems probable, that, from II, one continuation leads to a carbonium ion. Of course, some product alcohol could arise *via* direct collapse of II or *via* S$_N$2 attack of solvent or hydroxide on diazonium ion. For present purposes, k_1 is taken as including these possibilities.[27] A second pathway involves formation of diazoalkane, isolable in the cases of IIIa, b, and d. Since no diazoalkane forms until I has been protonated, it seems simplest that II is the immediate diazoalkane precursor. Carbonium ions and diazoalkanes would thus appear to have a common precursor in II.

It is of interest to learn whether these two pathways are truly independent [*i.e.*, whether, in (3), hydration of diazoalkane is slow relative to the forward processes]. When I (R = *n*-octyl) was quenched with heavy water, the aqueous phase was removed, diazooctane was thermally destroyed (in the presence of excess magnesium sulfate, which appeared to catalyze the decomposition), and octanol O–D was converted to octanol O–H (washing with 10% sodium bicarbonate solution), it was found that the product 1-octanol contained less than 2% carbon-bound deuterium (mass spectral analysis). A similar experiment with IIIc, with analysis by nmr, showed that no carbon-deuterated cyclohexanol had formed. Thus, in these cases, and *presumably* for IIIa and IIIf, partition between carbonium ion and diazoalkane is not complicated by reversible formation or direct decomposition of diazoalkane. However, when the diazotate derived from IIIe was subjected to deuterium quenching, isolated alcohol was completely deuterated (V).[28] This observation is compatible with intervention of diazocyclopropane (VI).



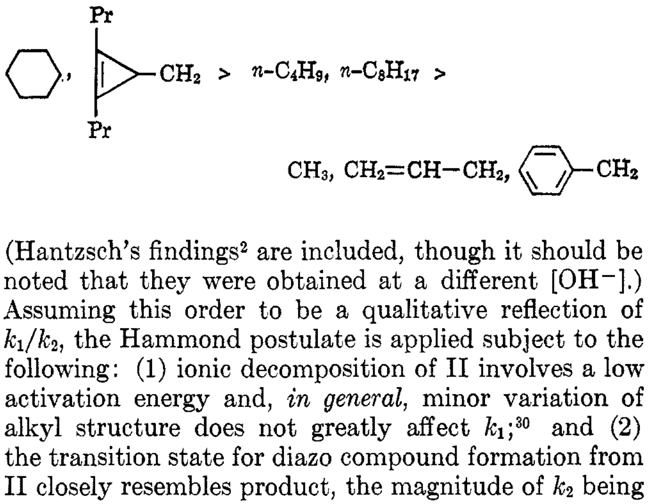
V



VI

Partition of II.—If both processes in (3) were unimolecular in II, product partition, in all examples, save IIIe, could be equated with k_1/k_2. Unfortunately, diazoalkane formation is very likely dependent on [OH$^-$]. Product partition is also, then, so dependent. Nevertheless, under the essentially constant [OH$^-$] maintained in these experiments[22] and admitting a present lack of knowledge of partition at other [OH$^-$], a naive equation of partition with k_1/k_2, and hence with ΔE_a, leads to a not unattractive rationale for the observed trends.

In order of observed decreasing product ratio (carbonium ion/diazoalkane) the alkyl systems may be ordered



(Hantzsch's findings[2] are included, though it should be noted that they were obtained at a different [OH$^-$].) Assuming this order to be a qualitative reflection of k_1/k_2, the Hammond postulate is applied subject to the following: (1) ionic decomposition of II involves a low activation energy and, *in general*, minor variation of alkyl structure does not greatly affect k_1;[30] and (2) the transition state for diazo compound formation from II closely resembles product, the magnitude of k_2 being strongly dependent on those structural factors which stabilize diazoalkane.[3,31,32]

With reference to the observed ordering, systems with primary alkyl groups occupy a central position.

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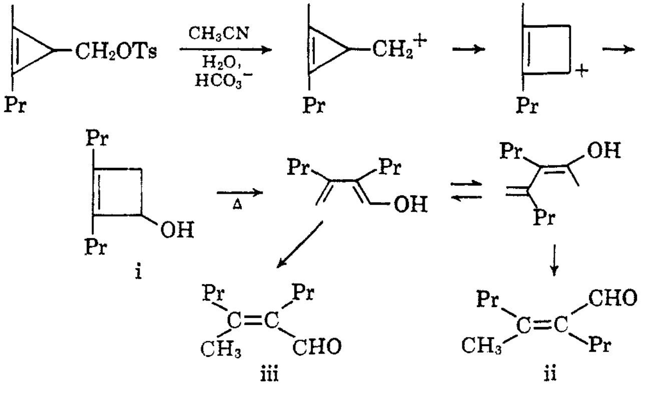
[23] H. Söll, in Houben-Weyl, "Methoden der Organischen Chemie," 4th Ed., XI/2, G. Thieme Verlag, Stuttgart, 1958, p 133 ff.

[24] P. Wolf, Ph.D. Thesis, Columbia University, 1964.

[25] R. Breslow, J. Lockhart, and A. Small, *J. Am. Chem. Soc.*, **84**, 2793 (1962).

[26] The aldehydes cited in Table I are not primary products. Thus Wolf[24] writes



We have also observed that initial product mixtures contain no ii or iii, these probably resulting *via* pyrolysis of i during vpc. Wolf also records a speculative pathway for heptatriene formation from dipropylcyclopropenylcarbinyl cation.[24]

[27] Studies of the stereochemistry attending decomposition of asymmetric diazotates, as well as decomposition studies in H_2O^{18}, may elucidate this problem. Such studies are in progress. The possibility of S$_N$2 reactions in these systems has been suggested by A. Streitwieser [*J. Org. Chem.*, **22**, 861 (1957)] and disputed by J. H. Ridd [*Quart. Rev.* (London), **15**, 418 (1961)].

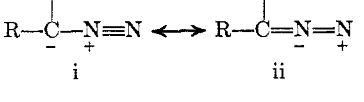
[28] Determined by nmr spectroscopy. The nondeuterated alcohol exhibited vinyl multiplets at *ca.* 6.0 and 5.4 ppm (downfield from internal TMS). The high-field resonance was assigned to the vinyl proton vicinal to the carbinol.[29] The alcohol isolated from deuterium oxide quench showed only a broadened doublet at 5.92 ppm. Controls established exchange stability of deuterated alcohol.

[29] N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, p 87.

[30] See the discussion in ref 3, p 123 ff.

[31] R. Huisgen, *Angew. Chem.*, **67**, 439 (1955).

[32] Diazoalkanes are usually represented as a resonance hybrid (i ⟷ ii). Their protolytic and thermal stability is qualitatively correlated with the



$$\overset{\mathrm{H(R)}}{\underset{-}{\mathrm{R{-}C}}}{-}\underset{+}{\mathrm{N}}{\equiv}\mathrm{N} \longleftrightarrow \overset{\mathrm{H(R)}}{\mathrm{R{-}C}}{=}\underset{-}{\mathrm{N}}{=}\underset{+}{\mathrm{N}}$$

ability of C-1 to bear the negative charge in i. Thus stability of R=N$_2$ increases in the order: R = secondary, primary, methylene, allyl ~ benzyl.[3,31]

When R becomes secondary, *e.g.*, cyclohexylidene, k_2 is reduced, while any contribution from enhanced carbonium ion stability must increase k_1. Therefore, k_1/k_2 increases, relative to primary R, so that no diazoalkane is observed. When, on the other hand, R is altered from primary to methyl, allyl, and benzyl, k_2 is sufficiently enhanced so that k_1/k_2 is too small to permit observation of solvolysis of II.[33]

The cyclopropenyl (IIIf) and the tricyclooctyl (IIIe) systems are now seen to represent special cases. The former, though primary, gives rise to no diazoalkane. Presumably II (R = cyclopropenylcarbinyl) solvolyzes with participation, directly and irreversibly, to a nonclassical cation,[25] k_1/k_2 being large for a primary R. The latter, though secondary, may involve diazocyclopropane (VI).[34] Diazocyclopropanes are no doubt highly strained and evidence for their formation rests on interception, rather than isolation.[35] Thus, k_2 (R = cyclopropyl) should be smaller than k_2 (R = cyclohexyl). Since, for R = cyclohexyl, diazoalkane does not intervene, we can account for its possible intervention here, with R = cyclopropyl, only if k_1 (cyclopropyl) is far less than k_1 (cyclohexyl). This, however, is not unlikely, even if the structural dependence of k_1 is ordinarily small, since the depression of solvolytic rate constants for cyclopropyl derivatives, relative to cyclohexyl, is very large indeed.[36] Formation of the highly reactive VI would presumably be followed by very rapid protolysis, k_{-2} being large.

Solvent change should be reflected in k_1/k_2, in the effective basicity of reaction medium, and therefore in product partition. Thus, diazocyclohexane, as well as cyclohexylmethyl ether, cyclohexane, and cyclohexanol, is observed when methanol, rather than water, is used as a quench for I (R = cyclohexyl).[7,16,37] Similar results were recorded by Applequist,[38] who found that the action of methanolic sodium methoxide on N-nitroso-N-cyclobutylurea gave products owing to cyclobutylcyclopropylcarbinyl cations, as well as diazocyclobutane. Presumably, in aqueous solution, cyclobutyl diazotate would not give diazocyclobutane.

Basic Amine Deamination.—The reaction described here is formally equivalent to an amine deamination, but unique in being a probable source of carbonium ions in basic media. This aspect may have synthetic applications.[39] Its closest analogy would appear to be the deoxidation reaction.[40]

Experimental Section[41]

Urethans III (X = $NHCOOC_2H_5$). ***n*-Butylurethan (IIIa)**[5] was obtained from *n*-butylamine and ethyl chloroformate[9] and had bp 49° (0.05 mm), infrared (CCl_4), 5.78 μ (C=O).

***n*-Octylurethan (IIIb)**[6] was obtained from *n*-octylamine and ethyl chloroformate[9] and had bp 91° (0.15 mm), infrared (CCl_4), 5.78 μ (C=O).

Cyclohexylurethan (IIIc)[7] was obtained from cyclohexylamine and ethyl chloroformate[9] and had mp 53–55°, infrared (CCl_4), 5.81 μ (C=O).

Allylurethan (IIId).[8]—Allyl isocyanate (Aldrich Co.), 30.0 g, was dissolved in 150 ml of absolute ethanol. The solution was heated to reflux and so maintained for 23 hr. Ethanol was removed by simple distillation. Vacuum distillation over a short Vigreux column gave a product, 36.7 g of water-white liquid, bp 40–42° (0.05 mm), 79%, infrared (CCl_4), 5.81 μ (C=O).

***exo*-Tricyclo[3.2.1.0^{2,4}]octane-3-*anti*-urethan (IIIe).**—Carboxylic acid IVa,[10] 21.5 g, was dissolved in 70 ml of dry ether and treated with 84 g of freshly distilled thionyl chloride. After addition, the solution was refluxed for 18 hr. Volatile constituents were stripped on a rotary evaporator, and the residue was distilled over a small Claisen head, yielding 23.3 g of colorless liquid (IVb), bp 55° (0.3 mm), 88%, infrared (CCl_4), 5.60 μ (C=O).

To a solution of 40.0 g of sodium azide in 110 ml of water, cooled to −5 to −10° and stirred mechanically, was added, dropwise, a solution of 23.3 g of acid chloride IVb in 40 ml of acetone.[42] After addition, the cooling bath was removed, and stirring was continued for 0.5 hr. Water (90 ml) was added, then 50 ml of ether. The organic phase was separated, combined with two 50-ml ethereal extracts of the aqueous, and dried over magnesium sulfate. The drying agent was filtered and the ether was stripped. The residue, 25.5 g, was acid azide IVc, *ca.* 100%, infrared (CCl_4), 4.67 (N_3) and 5.86 μ (C=O). No carboxylic acid IVa was present.

Acid azide IVc was dissolved in 150 ml of absolute ethanol; the solution was filtered through magnesium sulfate and refluxed 22 hr. Ethanol was removed *via* simple distillation, and the residue was distilled over a Claisen head, affording 20.1 g of highly viscous, clear liquid, bp 103–105° (0.08 mm). The yield of urethan IIIe was 82% based on acid chloride IVb; infrared (CCl_4), 5.78 μ (C=O).

Anal. Calcd for $C_{11}H_{17}NO_2$: C, 67.66; H, 8.78; N, 7.17. Found: C, 67.32; H, 8.62; N, 7.18.[43]

2,3-Dipropylcyclopropenylcarbinylurethan (IIIf).—The carboxylic acid[11] (see Chart I), 25.0 g, was treated with 100 g of oxalyl chloride, with stirring under nitrogen. After addition, the resulting solution was refluxed 2 hr. Volatile material was stripped by aspiration of the still hot solution, and the residue was vacuum distilled over a small Vigreux column, affording 26.3 g of water-white acid chloride, bp 42–50° (0.08 mm), 95%, infrared (CCl_4), 5.61 μ (C=O).

The acid chloride, 26.3 g, was added dropwise to 150 ml of ammonium hydroxide, cooled in an ice bath and stirred mechanically. The resulting white precipitate was filtered and taken up in chloroform; the solution was washed with water and dried. Removal of solvent, followed by vacuum drying, yielded 20.1 g of amide, mp 105–106°, 85%, infrared (CCl_4), 5.96 μ (C=O).

Anal. Calcd for $C_{10}H_{17}NO$: C, 71.81; H, 10.25; N, 8.38. Found: C, 71.87; H, 10.44; N, 8.19.

The amide, 20.1 g, was dissolved in 100 ml of pyridine (distilled from BaO). To the mechanically stirred solution, at 0°, was added dropwise a 7% excess of phosphorus oxychloride. Stirring was continued for 1 hr after addition. The reaction mixture was diluted with 1 l. of water and extracted four times with 100-ml portions of ether. Combined ether was dried and stripped. Residue was distilled, yielding 11.0 g of colorless nitrile, bp 42–45° (0.05 mm), 62%, infrared (neat), 4.50 (medium, $C\equiv N$) and 5.28 μ (weak, cyclopropene).

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[33] Failure of solvolysis in the latter two cases clearly indicates that k_1/k_2 dependence on carbonium ion structure is small, both allyl and benzyl cations being stabilized.

[34] Alternative explanations for deuterium incorporation, not involving VI, can be devised. These are not less speculative than the present (see below), which has the advantage of demonstrating the flexibility of eq 3.

[35] W. M. Jones, M. H. Grasley, and D. G. Baarda, *J. Am. Chem. Soc.*, **86**, 912 (1964), and references therein.

[36] Cyclopropyl tosylate solvolyzes some 400,000 times more slowly than does cyclohexyl tosylate (acetic acid, 60°): see A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 94 ff. Inordinate solvolytic resistance of II is further suggested by the observation that I (R = 2,2-diphenylcyclopropyl) is stable to basic water–tetrahydrofuran for 16 hr at 0°: T. K. Tandy, Jr., and W. M. Jones, *J. Org. Chem.*, **30**, 4257 (1965). Recently, application of Woodward–Hoffmann criteria suggests that solvolysis in a fused-ring system, such as IIIe, should be even slower than in the parent cyclopropyl system: C. H. DePuy, L. G. Schhack, J. W. Hausser, and W. Wiedemann, *J. Am. Chem. Soc.*, **87**, 4006 (1965).

[37] Repetition of these experiments gave similar results.

[38] D. E. Applequist and D. E. McGreer, *J. Am. Chem. Soc.*, **82**, 1965 (1960). See also, C. D. Gutsche and H. E. Johnson, *ibid.*, **77**, 109 (1955).

[39] M. S. Newman and A. Kutner, *ibid.*, **73**, 4199 (1951).

[40] P. S. Skell and I. Starer, *ibid.*, **81**, 4117 (1959).

[41] Melting points and boiling points are uncorrected. Infrared spectra were determined with a Beckman IR-5A instrument. Nmr spectra were determined on Varian A-60 equipment. All urethans and N-nitrosourethans exhibited nmr spectra consistent with structural assignments. These spectra will be discussed in a separate publication.[13] Vpc determinations were performed on a Wilkens A-90-P instrument.

[42] E. C. Horning, Ed., "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, pp 846, 847.

[43] All elemental analyses were by Micro-Tech Laboratories, Skokie, Ill.

Anal. Calcd for $C_{10}H_{15}N$: C, 80.48; H, 10.13; N, 9.39. Found: C, 80.49; H, 10.09; N, 9.47.

Nitrile, 9.4 g, was added slowly to 2.2 g of lithium aluminum hydride in 50 ml of ether. The reaction mixture was cooled in an ice bath and stirred magnetically. Stirring was continued 10 min after addition. Excess reductant was decomposed with water. About 200 ml excess water was added and the resultant slurry was extracted with 40-ml portions of ether to a total of 150 ml. The ether extract was dried over magnesium sulfate. The drying agent was filtered and the solvent was stripped. The residue, 10 g, had an ammoniacal odor: infrared (neat), 2.9–3.2 (broad, NH_2) and 5.45 μ (very weak, cyclopropene).

Amine was not purified but was directly converted to urethan IIIf with ethyl chloroformate.[9] The final product, 9.2 g, had bp, 76–77° (0.1 mm), 65% (based on nitrile), infrared (CCl_4), 5.81 μ (C=O).

Anal. Calcd for $C_{13}H_{23}NO_2$: C, 69.29; H, 10.29; N, 6.22. Found: C, 69.46; H, 10.33; N, 6.39.

N-Nitrosourethans III (X = $N(NO)COOC_2H_5$).—Nitrosation was, essentially, carried out according to White.[14] *n*-Butylurethan (IIIa) is presented as an example. *n*-Butylurethan, 3.0 g, was dissolved in 20 ml of dry ether in which 2.8 g of sodium bicarbonate had been suspended. The suspension was stirred under nitrogen and cooled to −30°. A solution of 4.0 g of nitrogen tetroxide (Matheson) in 5 ml of ether was slowly injected through a septum. During addition, temperature was maintained at −30°. The resultant suspension was stirred 1.25 hr (temperature not exceeding −5°) and then poured into 50 ml of 10% sodium bicarbonate solution. The ethereal phase was washed with water and dried over magnesium sulfate. After filtration, the solvent was stripped, and the residual golden oil, 3.12 g, was stored over Dry Ice until use.[13,41]

Exceptions to the generality of this procedure include IIIc, prepared as directed by Heyns,[16] and maintenance of reaction temperature at −55° (maximum) in the case of IIIf. Sodium acetate was used as the suspended buffer in the latter reaction.

Decomposition of N-Nitrosourethans.—The decomposition of IIIb and IIIf will be described in detail. Procedure and product identification was quite similar in all other cases. (See Discussion and Table I.)

N-Nitroso-*n*-octylurethan, 2.64 g (11.5 mmoles), was injected through a septum into a stirred, nitrogen-covered, cooled (−30°) slurry of potassium *t*-butoxide, 2.6 g (23 mmoles), in 30 ml of ether. No gas evolution was observed. After 20 min, during which time temperature rose to −18°, 5 ml of water was injected. Within *ca.* 4 sec, 220 cc of gas had evolved and was collected over water (measured at 760 mm and 25°).[44] No further gas evolution occurred over 5 min.

The aqueous phase was discarded; the ethereal phase was washed with water and dried over magnesium sulfate. Addition of the drying agent catalyzed decomposition of the diazooctane present, as evidenced by rapid gas evolution and bleaching of the orange color. The solid was filtered, ether was stripped, and the residue, 2.95 g, was submitted to vpc.

At 148°, on a 7 ft × 0.25 in. 5% Carbowax 20M on 60–80 mesh Chromosorb G column, He flow 60 cc/min, five major products were observed. The earliest eluted was a mixture of carbonates (see below). The second was identified as 2-octanol, and the third as 1-octanol, both by comparison of retention times and infrared spectra with authentic samples. The fourth peak was apparently a carbonate [infrared (CCl_4), 5.72 μ], its infrared spectrum being extremely similar to that of the initial carbonate mixture (see below). From its retention time, it probably contained two octyl groups. The fifth peak appeared to be *n*-hexadecane on the basis of retention time and infrared comparison.

Ratio of trace weights was 2.8:26:2.8:1.0 for 2-octanol:1-octanol:carbonate:hexadecane. Calibration of product 1-octanol against phenol permitted determination of its yield, in crude product, as 28% (based on nitrosourethan). Yield of 2-octanol was then 3%.

Octene-1 was identified by its retention time on a QF-1 column at 70°.[45] Analysis against a benzene standard gave its over-all yield as 8%.

The foregoing decomposition was repeated with 2.6 g of nitrosourethan IIIb. This time, however, the 20-min-old slurry was filtered under nitrogen. The solid was washed with an additional 50 ml of ether.

The ethereal filtrate evolved 15 cc of gas upon addition of 5 ml of 6 *N* HCl. Removal of all solvents afforded a residue containing only diethyl, ethyl *t*-butyl, and di-*t*-butyl carbonates (vpc).

The solid was suspended in *ca.* 50 ml of ether and quenched with 5 ml of water, 130 cc of gas being evolved. The now orange ethereal layer was removed. Infrared indicated an intense absorption at 4.87 μ. Addition of 5 ml of 6 *N* HCl to the ether caused evolution of 80 cc of gas, disappearance of the orange color, and loss of the 4.87-μ infrared band. Total gas evolution was *ca.* 82% of theoretical, of which *ca.* 61% came from aqueous quenching, the remainder from *n*-diazooctane. A vpc trace of products from the solid after quenching (with thermal decomposition of diazooctane) was identical with that described for the nonfiltration experiment, except that only traces of carbonates were present.

Decomposition of IIIf was carried out as described for IIIb. Crude product showed no nmr absorption in the region of aldehydic protons. Preparative vpc on an SE-30 column at 140° indicated the presence of five major components. The first in order of elution was identified as *t*-butyl alcohol. The second was ethyl *t*-butyl carbonate: infrared (CCl_4), 5.71 (C=O) and 11.1 μ (tertiary C–O);[46] nmr (CCl_4), quartet centered at 4.1 ppm from internal TMS (J = 7 cps), singlet at 1.47 ppm, and triplet centered at 1.24 ppm (J = 7 cps). The third component was a solid, identified as di-*t*-butyl carbonate: infrared (CCl_4), 5.74 (C=O) and 11.1 μ (tertiary C–O);[46] nmr (CCl_4), singlet, 1.47 ppm from TMS. The fourth component present to about 30% of the fifth component was a yellow oil. Its infrared and nmr spectra were identical with those of the product obtained in good yield by Wolf from treatment of 2,3-dipropylcyclopropenylcarbinol with tosyl chloride in pyridine and designated 3-propyl-1,3,4-heptatriene:[24] infrared (CCl_4), 3.28 (weak, vinyl C–H), 5.18 (weak, allene), 6.21 (medium, C=C), and 11.17 μ (strong, terminal methylene); nmr (CCl_4), a four-component multiplet from 6.42 to 5.95 ppm from TMS (1.0 proton, vinyl), a multiplet from 5.46 to 4.72 ppm (3.1 protons, terminal methylene and allenic), a multiplet from 2.31 to 1.87 ppm (4.1 protons, allylic), and multiplets at 1.87–1.17 and 1.17–0.78 ppm, together weighing 8.9 protons (methylene and methyl) (the theoretical intensities are 1:3:4:8).[47] The fifth component was an oil which was identical in spectral qualities with the product of solvolysis of 2,3-dipropylcyclopropenylcarbinyl tosylate, and identified as a mixture of *cis*- and *trans*-2-propyl-3-methyl-hex-2-enal:[24] infrared (CCl_4), 3.64 (weak, aldehydic C–H), 5.99 (strong, conjugated C=O), 6.14 μ (medium, C=C); nmr (CCl_4), 10.08 ppm from TMS (singlet, aldehydic proton), 10.05 ppm (singlet, aldehydic proton), singlets at 2.18 and 1.97 ppm (allylic), singlets at 2.18 and 1.97 ppm (allylic methyl), multiplet at 1.97–1.19 ppm (methylene), and a crude triplet centered at 0.97 ppm (methyl). Integral intensities were not in good agreement with theoretical predictions. It was considered that the aldehyde was contaminated. Derivatization with 2,4-dinitrophenylhydrazine afforded a solid, which, after five recrystallizations from methanol, had mp 120–130°.

Anal. Calcd for $C_{16}H_{22}N_4O_4$: C, 57.45; H, 6.63; N, 16.75. Found: C, 57.93; H, 6.91; N, 16.93.

Deuterium Oxide Decompositions.—Deuterium oxide decompositions for IIIb, c, and e were carried out as described for ordinary aqueous decompositions. Products were isolated by vpc and had proper infrared spectra. For IIIc, the experiment was repeated three times. In each case, the C-1 proton was integrated with respect to the remaining ring protons. Three integrals were taken for each experiment. The percent average deviation for integrals in each experiment was less than 5%. Results of the experiments (expressed as per cent deviation from the expected 0.10 ratio) were −2, −7, and +7%. (Positive sign indicates ratio was *less* than 0.1.)

Results for duplicate deuterium quenching of IIIe are summarized in the Discussion.[28]

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(44) Nitrogen evolution was about 80% of theory. This value ranged from a low of 61% (cited in Table I) to a high of 80% over four experiments.

(45) Octene-1 was the only product not identified spectroscopically. In the IIIc series, for example, cyclohexene was identified by both retention time and infrared comparisons.

(46) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p 26.

(47) This spectrum is reproduced in ref 24.

Results for IIIb are also summarized in the Discussion. Because diazooctane was stable under reaction conditions, only one deuterium quench was carried out.

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Organoboron Compounds. II. The Preparation of Ethyl-Substituted Boranes by Hydrogenation of 2-Chlorovinyl- and 2-Chlorovinylethylboranes[1a]

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The 2-chlorovinyl- and 2-chlorovinylethylboranes have been hydrogenated to the corresponding ethyl-substituted boranes with the liberation of hydrogen chloride. The reaction takes place at 50–100° in the gas phase with palladium black as catalyst. Reduction to the desired product becomes more difficult with increasing number of chlorovinyl groups in the molecule.

Although the preparation and reactions of 2-chlorovinyl-substituted compounds have been examined in some detail,[2–7] hydrogenation of the 2-chlorovinyl group has never been reported. In connection with our studies into the preparation of alkylboranes without metallic reagents,[7] the catalytic hydrogenation of 2-chlorovinyl- and 2-chlorovinylethylboranes was investigated as a method for preparing 2-chloroethyl-substituted boranes.

This reaction did not yield the expected products but gave instead the corresponding ethyl-substituted boranes and hydrogen chloride. Thus, hydrogenation of (2-chlorovinyl)dichloroborane (I), bis(2-chlorovinyl)-chloroborane (II), and tris(2-chlorovinyl)borane (III) was found to give ethyldichloroborane (IV), diethylchloroborane (V), and triethylborane (VI), respectively, in yields of 97, 51, and 25%. Presumably reduction to the desired products becomes more difficult as the number of chlorovinyl groups in the molecule increases. This was confirmed by the hydrogenation of (2-chlorovinyl)ethylchloroborane (VII) and bis(2-chlorovinyl)ethylborane (VIII), which give diethylchloroborane and triethylborane, respectively, in 90 and 30% yields.

The reaction, which was found to be very exothermic, occurs readily at 50 to 100° in the gas phase with palladium black as catalyst. Degradative side reactions occur owing to the liberated hydrogen chloride. These side reactions increase above 100°, especially with the more highly substituted chlorovinyl compounds. Thus, hydrogenation of I at 150 to 200° gives ethane and boron trichloride primarily while ethyldichloroborane is the major product at 50°. Although better yields were obtained for II, III, and VIII at the lower temperatures, side reactions could not be eliminated.

Other reaction conditions were investigated in order to improve the yields. Hydrogenation in the liquid phase resulted in extensive disproportionation of the starting materials. The use of ethylboranes as solvents produced no improvement in the yields. The inclusion of granular zinc for the purpose of removing hydrogen chloride as formed did not result in any improvement. A solution of tris(2-chlorovinyl)borane in bis(2-methoxyethyl) ether containing sufficient 2,6-lutidine to react with all the liberated hydrogen chloride resulted only in the formation of unidentified black tars. Pressures up to 100 psi permitted the reaction to proceed at temperatures below 50°, but the yields were not improved because of the increased solubility of hydrogen chloride in the reactants and products. Of the many catalysts investigated, palladium black was the most active at low temperatures and furthermore was unaffected by hydrogen chloride. It is interesting to note that the attempted platinum-catalyzed hydrogenation of these compounds was unsuccessful.

One can visualize the side reactions that might take place, as outlined in Scheme I, according to known reactions of alkylboranes with hydrogen chloride.[8,9] Moreover, we have been able to isolate and identify all these products. Using this diagram, the best yields can be expected with I, VII, and IX, since these compounds contain only one chlorovinyl group. In fact, we found this to be true experimentally.

Hawthorne, *et al.*,[10] have found that chloroethylboranes are exceedingly unstable, giving ethylene and other products. We were unable to find any chloroethylboranes or ethylene. We did, however,

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(1) This research was performed under Contract AF 33(600)-33920 for the Wright Air Development Center. (b) To whom correspondence should be sent: IBM Research Laboratory, San Jose, Calif.

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(7) E. Gipstein, P. R. Kippur, M. A. Higgens, and B. F. Clark, *J. Org. Chem.*, **26**, 943, 2947 (1961).

(8) Dialkylboron halides have been prepared by the reaction of hydrogen chloride with trimethyl- and triethylboranes at 150–180° for 1 hr: E. Wiberg, A. Boltz, and P. Bucheit, unpublished work cited by J. Goubeau, *FIAT Rev. Ger. Sci., Inorg. Chem.*, **1**, 218 (1948).

(9) The reaction of hydrogen chloride with tri-*n*-butylborane in the presence of aluminum chloride has been used to prepare *n*-butyldichloroborane. Two-thirds of the alkyl groups are lost as hydrocarbon: R. C. Booth and C. A. Kraus, *J. Am. Chem. Soc.*, **74**, 1415 (1952).

(10) M. F. Hawthorne and J. A. Dupont, *ibid.*, **80**, 5830 (1958).