[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY, NEW HAVEN, CONNECTICUT]

The Preparation and Decomposition of Certain N-Nitroamides and N-Nitrocarbamates

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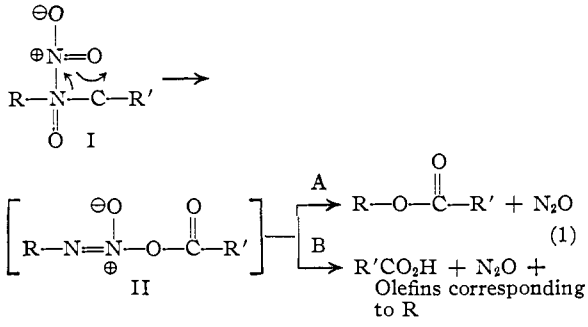
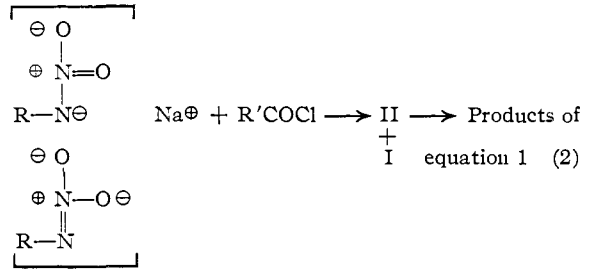
A number of N-nitroamides have been prepared and decomposed at 25–75° to yield the corresponding esters and nitrous oxide; a diazoxyester [RN=N(O)—O—C(O)R'] is an intermediate in this reaction. The same diazoxyester was prepared *in situ* by the reaction of the appropriate acid chloride (R'COCl) with the sodium salt of an N-nitroamine (RN–$NO_2\ominus Na\oplus$) and an isomeric intermediate [RN(O)=N—O—C(O)R'] was prepared by the reaction of the acid chloride with the sodium salt of an N-nitrosohydroxylamine [RN(NO)O⊖Na⊕]. Nitrous oxide and the corresponding ester were also formed in the decomposition of the latter intermediate. A few N-nitrocarbamate esters were prepared and decomposed. The infrared spectra of the nitrocarbamates are anomalous in that two peaks are observed in the carbonyl region; the splitting is attributed to rotational isomerization.

The nitrosoamide decomposition is a useful reaction for the conversion of aliphatic amines into alcohols and their derivatives,[2] and it has been the subject of a number of investigations.[3] This paper is concerned with the related nitroamide decomposition.[4] The N-alkyl-N-nitro-3,5-dinitrobenzamides used were prepared by the nitration of the appropriate amides with a mixture of 100% nitric acid and sulfur trioxide. Copper nitrate–acetic anhydride mixtures[5] and nitric acid–acetic anhydride mixtures[6] led to incomplete nitration, although the latter reagent was suitable for the nitration of N-alkylacetamides. The nitroamides proved to be slightly more stable thermally than the corresponding nitrosoamides, the order of stability being the same, however; *i.e.*, primary alkyl > secondary alkyl. The organic reaction products formed on decomposition were the same as those obtained from the nitrosoamides[3] (equation 1).



The results for several decompositions are given in Table I.

The similarity in rate ratios and products for the nitrosoamide[2] and nitroamide reactions suggests that the mechanisms are similar. Diazoesters are intermediates in the nitrosoamide reaction; the analogous intermediate here would be diazoxyester II. To confirm this, II was synthesized by an independent route, a route involving the reaction of an acid chloride with the salt of a nitroamine.



The expected ester and nitrous oxide were obtained (presumably *via* the unstable intermediate II) and in the run with the salt of isobutylnitroamine, the nitroamide I was also isolated. The ester yields were rather low because of several side-reactions. The sodium salt of the nitroamine reacts with the 3,5-dinitrobenzoic acid formed in the elimination step (eq. 1, path B) to form the free nitroamine and sodium 3,5-dinitrobenzoate. The latter salt in turn reacts with 3,5-dinitrobenzoyl chloride to form the anhydride. Both reactions effectively remove starting material.

As further support for II as a common reaction intermediate, it was shown that the amount of isomerization which occurred in the "salt" reaction (R = *iso*-butyl), and the configurational changes observed (R = L-*sec*-butyl) were comparable with the corresponding quantities measured for the "thermal" reaction (eq. 1). The decomposition of L-N-(*sec*-butyl)-N-nitro-3,5-dinitrobenzamide in

TABLE I

DECOMPOSITION OF N-ALKYL-N-NITROAMIDES $\left(\begin{array}{c} NO_2 \\ | \\ RN-C-R' \\ \| \\ O \end{array}\right)$ IN CCl_4 AT 77°

R	R'	Concn., *M*	Yields[a] Path A (eq. 1) $R'CO_2R$ (%)	Yields[a] Path B (eq. 1) $R'CO_2H$ (%)
n-Butyl[b]	Methyl	0.2	75	23
n-Butyl	3,5-Dinitrophenyl	.5	71	24
iso-Butyl	3,5-Dinitrophenyl	.2	40	49
sec-Butyl[c]	3,5-Dinitrophenyl	.1	9	65

[a] Nitrous oxide and the olefins were identified from infrared spectra. [b] Taken from ref. 2. [c] In this run, the nitroamide was held at 25° for five days in chloroform; Ester yields of 15 and 25% have been obtained under other conditions (ref. 4).

(1) Taken in part from a thesis submitted by Daniel W. Grisley, Jr. to the faculty of the Graduate School of Yale University in partial fulfillment of the requirements for the Ph.D. degree.

(2) E. H. White, THIS JOURNAL, **77**, 6011 (1955).

(3) For leading references see (a) E. H. White and C. A. Aufdermarsch, Jr., *ibid.*, **83**, 1179 (1961); (b) R. Huisgen and C. Ruchardt, *Ann.*, **601**, 21 (1956); K. Heyns and W. von Bebenburg, *Ber.*, **89**, 1303 (1956).

(4) (a) E. H. White, THIS JOURNAL, **77**, 6014 (1955). (b) Preliminary results were given in ref. 2 and 4a.

(5) W. Davey and J. R. Gwilt, *J. Chem. Soc.*, 204 (1950).

(6) W. E. Bachmann, *et al.*, THIS JOURNAL, **72**, 3132 (1950).

chloroform at 25° yielded *sec*-butyl 3,5-dinitrobenzamide containing 59% of the L form (retention of configuration)[4] whereas the reaction of 3,5-dinitrobenzoyl chloride with the sodium salt of L-N-nitro-*sec*-butylamine in chloroform at 25° yielded *sec*-butyl 3,5-dinitrobenzoate containing 60% of the L form. The isomerization data is given in Table II; the two reactions (runs 2 and 3) gave esters having approximately the same isomer content. Isomerizations of this type have been noted in a number of reactions of nitrosoamides, nitroamides and diazoalkanes.[2,7a] It is worth noting that in an SN2 reaction (run 5) under approximately the same conditions, no isomerization occurred.

TABLE II

ISOMERIZATION IN VARIOUS ESTER-FORMATION REACTIONS IN CCl_4

Run	Reaction (R = isobutyl, R′ = 3,5-dinitrophenyl)	Temp., °C.	Isomeric esters formed ($R'CO_2R''$) in addition to $R'CO_2R$ (%): R'' = *sec*-butyl[a]	R'' = *tert*-butyl
1	$R-N(NO_2)-C(=O)-R'$	76	16	1-3
2	$R-N(NO_2)-C(=O)-R'$	55	9	1-3
3	$R-N^{\ominus}(NO_2)\,Na^{\oplus} + R'COCl$	30	12	
4	$R-N(NO)-O^{\ominus}Na^{\oplus} + R'COCl$	0	10	1-3
5	$RBr + (Bu)_4N^{\oplus}\,R'CO_2^{\ominus}$	65[b]	[c]	[c]

[a] Error = ± 2%. [b] The solvent was chloroform in this run. [c] None detected (0-1%).

Diazoalkanes have been established as reaction intermediates for the nitrosoamide reaction of primary carbinamines,[7] and an analogous α-elimination is probable for the corresponding nitroamide reaction.

$$R''CH_2N^{\oplus}(=O)-O-C(=O)-R' \longrightarrow [R''CH=N-N=O \leftrightarrow R''CH=N^{\oplus}=N-O^{\ominus}] \text{ (III)} + R'CO_2H \longrightarrow \text{Products of equation 1} \quad (3)$$

The oxygen-18 results are consistent with this reaction path.[7a] For diazoxyesters derived from secondary carbinamines, the reaction would be that of equation 4, a path established for nitrosoamides of secondary carbinamines.[3]

$$II \longrightarrow [RN_2^{\oplus}\,{}^{\ominus}O_2CR'] \longrightarrow N_2O + [R^{\oplus}\,{}^{\ominus}O_2CR'] \longrightarrow \text{Products of equation 1} \quad (4)$$

This mechanism accounts for the predominant retention of configuration observed (R = *sec*-butyl) and also for the finding that II (R = cyclohexyl) labelled in the carbonyl groups with O-18 yielded the ester containing all of the O-18 (mostly in the carbonyl position)[3a] and nitrous oxide containing 0.0 atom per cent. O-18.[3a]

N-Nitrocarbamate Esters.—Several N-nitrocarbamate esters were prepared by the nitration of the corresponding carbamates with fuming nitric acid.

$$R-N(H)-CO_2Et \longrightarrow R-N(NO)CO_2Et \xrightarrow{HNO_3} R-N(NO_2)CO_2Et\ (V) \quad (5)$$

When the ordinary colored acid (containing nitrogen oxides) was used, it was found that N-nitrosocarbamates were formed as reaction intermediates. At low temperatures (−80°), the nitroso derivatives were formed principally, whereas at higher temperatures, the nitrosocarbamates were converted rapidly into the N-nitrocarbamates. This behavior is reminiscent of phenol nitrations with nitric acid containing nitrous acid. The nitrosophenol is an intermediate in the reaction, and it is subsequently oxidized to the nitrophenol.[8] A similar oxidation may be involved in our case; on the other hand, a rapid denitrosation[9] followed by an essentially irreversible nitration can also account for the results.

The infrared spectra of V(R = *n*-butyl, *n*-hexyl, isobutyl and *tert*-butyl) and the spectrum of methyl N-nitro-N-(*n*-butyl)-carbamate are unusual in that two peaks are found in the carbonyl region (*ca.* 5.65 and 5.75 μ). In contrast, the N-nitroacetamides, N-nitro-3,5-dinitrobenzamides and N-nitrosocarbamates that we have prepared have only a single peak in this region of the spectrum. The N-nitrocarbamates were analytically pure and fractionation gave no evidence that isomers were present. Molecular weight measurements and the fact that dilution had no effect on the spectra show that the nitrocarbamates are not associated in solution. Fermi resonance was then considered as an explanation for the double peaks; the double carbonyl bands of certain cyclopentanones have been accounted for on this basis.[10a] Overtones of bands near 11.4 μ lie sufficiently close to the carbonyl bands to account for the band-splitting of our compounds (with the possible exception of methyl N-nitro-N-(*n*-butyl)-carbamate). Other evidence is not in accord with this explanation, however. Methyl N-nitro(N-15)-N-(*n*-butyl) carbamate[11] showed exactly the same band splitting as the unlabelled compound, and furthermore, the effect of solvent on the doublet was not consistent with the observations of Bellamy on solvent shifts with ethylene carbonate, the split peaks of which have been accounted for in terms of Fermi Resonance.[10b] An examination of the infrared spectra at different

(7) (a) E. H. White and C. A. Aufdermarsh, Jr., THIS JOURNAL, **83**, 1174 (1961); (b) A. Streitwieser, Jr., and W. D. Schaeffer, *ibid.*, **79**, 2893 (1957).

(8) (a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 286. (b) Similarly N-nitrosoamines have been converted into N-nitroamines with peroxy trifluoroacetic acid (W. D. Emmons, THIS JOURNAL, **76**, 3468 (1954)), and with nitric acid (P. Van Romburgh, *Ber.*, **29**, 1015 (1896)).

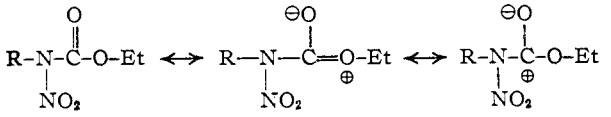
(9) E. H. White, THIS JOURNAL, **77**, 6008 (1955).

(10) (a) P. Yates and L. L. Williams, *ibid.*, **80**, 5896 (1958); (b) L. J. Bellamy and R. L. Williams, *Trans. Faraday Soc.*, **55**, 14 (1959); (c) R. N. Jones, P. Humphries, F. Herling and K. Dobriner, THIS JOURNAL, **73**, 3215 (1951).

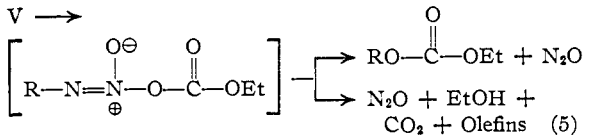
(11) We are indebted to Dr. L. P. Kuhn for this compound.

temperatures provided a clue since the intensity ratio of the two carbonyl peaks of methyl N-nitro-N-(*n*-butyl)carbamate showed progressive changes in spectra run at 25°, −75° and −196°. The splitting of the carbonyl peaks, therefore, is probably a matter of rotational isomerization[10c]; the two coplanar isomers formed by rotation about the N–C bond to the carbethoxy group are most likely involved.

The N-nitrourethanes are considerably more stable than the N-nitroamides, presumably because of deactivation of the carbonyl group.

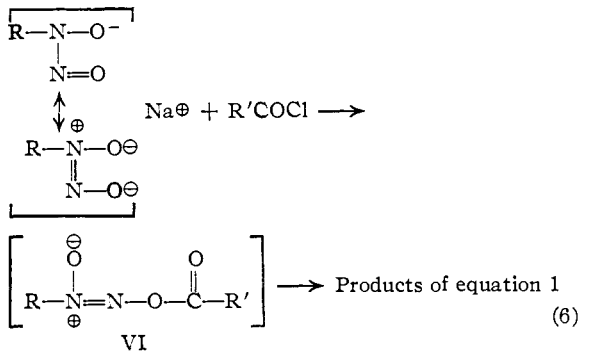


At the temperatures required for a reasonable rate of decomposition, the elimination path is quite important[2] and consequently the yields of carbonate



esters are low. The decomposition of ethyl N-(isobutyl)-N-nitrocarbamate in dodecane at 140° yielded ethyl isobutyl carbonate (44%) and the decomposition of ethyl N-(*tert*-butyl)-N-nitrocarbamate in *iso*-octane at 75° yielded ethyl *tert*-butyl carbonate (2%). The corresponding olefins, nitrous oxide and carbon dioxide were also identified as reaction products.

N-Nitrosohydroxylamines.—An isomer of II was prepared *in situ* by the reaction of 3,5-dinitrobenzoyl chloride with the sodium salt of N-isobutyl-N-nitrosohydroxylamine.



It yielded nitrous oxide and essentially the same mixture of isomeric esters as was obtained from II (Table II)[12]; the coördinate-covalent oxygen atoms of II and VI apparently do not have an important effect on the ester formation reaction.

Experimental[13]

Optically Active N-(*sec*-butyl) Amides.—*sec*-Butylamine was resolved with the aid of tartaric acid.[14] The salt was recrystallized seven times from 20% alcohol, $[\alpha]^{25}D$ + 18.2° (*c* 5.0 in H_2O).[14a] The benzamide was prepared directly from the optically pure salt, m.p. 97–98.5°, $[\alpha]^{25}D$ + 31.4° (*c* 1.25 in EtOH). Lit.[14b] m.p., 92–92.5°, $[\alpha]^{25}D$ + 30.74° (*c* 4.0 in EtOH).

Anal. Calcd. for $C_{11}H_{15}NO$: C, 74.54; H, 8.53; N, 7.90. Found: C, 74.76; H, 8.35; N, 7.85.

N-*sec*-butyl-3,5-dinitrobenzamide (optically pure) was prepared from the same tartrate, m.p. 174–174.5°, $[\alpha]^{25}D$ + 24.8° (*c* 0.972 in EtOH) (lit.[9] m.p. 173–174° (for DL)).

Anal. Calcd. for $C_{11}H_{13}N_3O_5$: C, 49.44; H, 4.90; N, 15.72. Found: C, 49.65; H, 4.97; N, 15.41.

Isomer Determinations.—Isobutylamine was fractionated and a middle cut used in the synthesis of derivatives. Analysis by gas–liquid chromatography indicated that the amine contained less than 2% of the *sec*-butyl isomer; standard mixtures of the amines were run to establish this figure. The amides and nitroamides prepared from this amine were further purified by recrystallization and they contained no detectible amounts of the *sec*-butyl isomer (infrared spectra). The nitroamides of *sec*-butylamine and *tert*-butylamine are very unstable; thus, any present would have decomposed during the preparation and purification of the isobutyl derivative. The isomer contents of the product esters were determined by comparing the spectra in CCl_4 with the spectra of mixtures of the esters of known composition. The *sec*-butyl 3,5-dinitrobenzoate was determined in particular by bands at 8.90, 9.13 and 11.60 μ and the *tert*-butyl isomer by a band at 12 μ.

Preparation of the N-Nitroamides. (a) **N-(Isobutyl-N-nitro-3,5-dinitrobenzamide.**—Liquid sulfur trioxide[15] (12 ml.) was added cautiously to 40 ml. of 100% fuming nitric acid at −80° under anhydrous conditions; the mixture was then allowed to warm to 0°. To this mixture was added N-(isobutyl) 3,5-dinitrobenzamide (10.7 g., 0.04 mole). The reaction mixture was kept at 0° for 20 hr. in a flask protected by a drying tube. The mixture was poured onto ice and the resulting solid extracted into 1:1 benzene–ether. The organic phase was washed with dilute sodium carbonate solution and then with saturated salt solution until the aqueous layer remained neutral. The organic layer was dried and evaporated *in vacuo* at room temperature. The solid obtained was dissolved in benzene, and hexane was added until the solution became cloudy. Cooling yielded yellowish-white crystals of the nitroamide. Recrystallization gave 7.24 g. (57%), m.p. 90.2–93.5° dec., infrared: C=O, 5.83 μ; N–NO_2, 6.33 μ.

Anal. Calcd. for $C_{11}H_{12}N_4O_7$: C, 42.30; H, 3.88; N, 17.91. Found: C, 42.42; H, 4.09; N, 17.74.

(b) **N-(*n*-Butyl)-N-nitro-3,5-dinitrobenzamide.**—The *n*-butyl derivative was prepared in 71% yield by the procedure used for the isobutyl derivative, m.p. 95–97° dec.

Anal. Calcd. for $C_{11}H_{12}N_4O_7$: C, 42.30; H, 3.88; N, 17.91. Found: C, 42.52; H, 3.87; N, 17.92.

(c) **L-N-(*sec*-Butyl)-N-nitro-3,5-dinitrobenzamide.**—Fourteen g. (52 mmoles) of (+)-N-(*sec*-butyl)-3,5-dinitrobenzamide {$[\alpha]^{25}D$ + 23.7° (*c* 0.996 in EtOH); 95.5% optically pure} was added to a mixture of 100% fuming nitric acid (55 ml.) and liquid sulfur trioxide (15 ml.) at 0°. After 60 hr. at 0° (anhydrous conditions), the reaction mixture was poured onto ice and the resulting mixture extracted with chloroform. The organic layer was washed successively with dilute sodium carbonate solution and water at 0°. The organic layer was dried and evaporated at room temperature *in vacuo*. Yellowish-white crystals were obtained; these were dissolved in chloroform, hexane was added and the solution cooled to 0°. White crystals of (+)-N-(*sec*-butyl)-N-nitro-3,5-dinitrobenzamide separated; 8.98 g. (28 mmoles, 54%), m.p. 87° dec., $[\alpha]^{25}D$ + 12.3° (*c* 3.01 in $CHCl_3$). The optically pure nitroamide, therefore, has $[\alpha]^{25}D$ + 12.9°.

Thermal Decomposition of the N-Nitro-3,5-dinitrobenzamides.—The nitroamides of *n*-butylamine and isobutylamine were decomposed at 77° for *ca.* 8 hr. and the nitroamide of *sec*-butylamine was decomposed at 25° for five days. An equal volume of *n* pentane was then added to each reaction mixture and the mixture cooled to 0°. The solid, 3,5-dinitrobenzoic acid, m.p. 204–205° (lit.[16] m.p. 204–205°) was filtered off and washed with *n*-pentane. The acid was determined by titration of a dioxane–water solution. The

(12) Similarly, N-nitroso-O,N-diacetylhydroxylamine at 25° yielded nitrous oxide, acetic anhydride, acetic acid and ketene.

(13) Analyses were by the Schwartzkopf Microanalytical Laboratory, Woodside 77, New York.

(14) (a) L. G. Thome, *Ber.*, **36**, 582 (1903); (b) N. J. Leonard and E. W. Nommensen, THIS JOURNAL, **71**, 2810 (1949).

(15) Sulfan B, The Baker Chemical Company.

(16) H. Hübner, *Ann.*, **222**, 75 (1884).

organic soluble fraction of the reaction mixture was washed with dilute sodium hydroxide solution to remove the last traces of the acid and with water until the aqueous phase remained neutral. The organic layer was dried and evaporated *in vacuo* to yield the 3,5-dinitrobenzoate esters. The esters were quantitatively sublimed at 100° (0.6 mm.), and the isomer contents and the optical activities were determined with these samples.

In the case of the *sec*-butyl derivatives, (+)-N-(*sec*-butyl)-N-nitro-3,5-dinitrobenzamide ($[\alpha]^{25}D$ + 12.3°, *c* 3.01 in $CHCl_3$; 95.5% optically pure) yielded 9% of (+)-*sec*-butyl 3,5-dinitrobenzoate, $[\alpha]^{25}D$ + 6.58° (*c* 1.2 in $CHCl_3$). Since the optically pure ester has $[\alpha]^{21}D$ + 38.3° ($CHCl_3$),[4a] the product ester has an optical purity of 17%. The nitroamide decomposition, therefore, proceeded with 18% retention of configuration.

Preparation of the Nitroamine Salts. (a) **The Sodium Salt of N-nitroisobutylamine.**—Ethyl N-nitro-N-isobutylcarbamate (*vide infra*) was saponified[6] at 25° and the N-nitroisobutylamine, m.p. 32°, was liberated using the procedures of Bachmann,[6] (lit.[17] m.p. 32°), infrared: 6.35 μ (N-NO_2). Ultraviolet: λ_{max} 230 mμ (ϵ 5370 in EtOH).

Anal. Calcd. for $C_4H_{10}N_2O_2$: C, 40.79; H, 8.47; N, 23.73. Found: C, 40.57; H, 8.54; N, 23.98.

A suspension of N-nitroisobutylamine (6.94 g., 58 mmole) in water was titrated with 0.1 *N* sodium hydroxide solution (phenolphthalein end-point). The aqueous solution was extracted with ether and the water solution was evaporated *in vacuo* to yield a white powder, the sodium salt of N-nitroisobutylamine (6.67 g., 48 mmole, 83% yield). Ultraviolet: λ_{max} 229 mμ (ϵ 9333 in H_2O[18]).

(b) **(+)-N-Nitro-*sec*-butylamine and its Sodium Salt.**—A solution of 2 *M* sodium hydroxide (25 ml., 50 mmole) was added to a suspension of 95.5% optically pure (+)-N-(*sec*-butyl)-N-nitro-3,5-dinitrobenzamide {$[\alpha]^{25}D$ + 12.3° ± 0.1° (*c* 3.01 in $CHCl_3$)} (3.74 g., 12 mmole) in methanol (70 ml.) at 0° with vigorous stirring. After 3 hr. at 0°, 6 *N* hydrochloric acid was added to the mixture until a *p*H of 4 was reached. The resulting mixture was saturated with salt and the aqueous phase extracted repeatedly with chloroform. The organic layers were combined, dried and evaporated at room temperature. The oily solid obtained was triturated with carbon tetrachloride (25 ml.) and the triturate filtered and evaporated. The product was distilled in an evaporative still (5 mm., oil-bath at 75°) to give (+)-N-(*sec*-butyl)-N-nitroamine, 0.77 g., (6.5 mmole, 54% yield), m.p. −7° to −2° (lit.[19] m.p. for DL − 32.5° to − 31.5°), $[\alpha]^{25}D$ + 36.9° (*c* 6.7 in EtOH). The optically pure nitroamine, therefore, has $[\alpha]^{25}D$ + 38.6°; lit.[20] $[\alpha]^{21}D$ + 40° (*c* 4.1 in EtOH). The infrared spectrum had bands at 6.35μ (N-NO_2) and 3.10μ (N-H).

A solution of the nitroamine in 50% ethanol-water (19 ml.) was titrated with 0.1 *N* sodium hydroxide solution (phenolphthalein end-point). The resulting solution was evaporated *in vacuo* to yield a white solid, the sodium salt of (+)-N-*sec*-butylamine (0.68 g., 4.8 mmole, 74%), $[\alpha]^{25}D$ + 38.9° (*c* 5.24 in H_2O).

Anal. Calcd. for $C_4H_9N_2O_2Na$: C, 34.28; H, 6.47; N, 19.99. Found: C, 34.72; H, 6.30; N, 19.70.

The Reaction of the Sodium Salt of N-Nitroisobutylamine with 3,5-Dinitrobenzoyl Chloride.—A mixture of the sodium salt of N-nitroisobutylamine (1.08 g., 7.7 mmoles) and 3,5-dinitrobenzoyl chloride (1.76 g., 7.6 mmoles) in 15 ml. of carbon tetrachloride was stirred at 30° in a flask protected by a drying tube. After 18 hr., the solid phase was filtered and dried to yield a white solid I whose infrared spectrum indicated a mixture of 3,5-dinitrobenzoic anhydride (infrared 5.5μ and 5.75μ) and 3,5-dinitrobenzoic acid (infrared 5.85μ). The solid was triturated thoroughly with water to yield a water solution A and a solid B. Solid B (largely anhydride) was dissolved in a mixture of dioxane and water and titrated with 0.1 *N* NaOH; 3.8 meq. of the 3,5-dinitrobenzoate moiety was found. The water solution A was acidified, and the 3,5-dinitrobenzoic acid which separated (0.3 mmole) was removed. The acidified solution A was extracted with chloroform. The chloroform solution was dried and evaporated to yield N-nitroisobutylamine (0.7 mmole) identified from its infrared spectrum.

The carbon tetrachloride solution II from the reaction mixture was extracted with sodium bicarbonate solution to remove N-nitroisobutylamine (2.9 mmoles) and the neutral organic phase was chromatographed on silica gel[21] with pentane–ether mixtures. The 3% ether eluate contained the ester, 0.107 g. (0.4 mmole, 5%). The product contained 12% of *sec*-butyl 3,5-dinitrobenzoate. The ether eluate yielded N-(isobutyl)-N-nitro-3,5-dinitrobenzamide (0.06 g., 0.2 mmole, 2%).

A similar reaction carried out in the presence of an excess of anhydrous potassium carbonate yielded 3,5-dinitrobenzoic acid (32% as the potassium salt + anhydride), isobutyl 3,5-dinitrobenzoate (8.5%) and N-(isobutyl)-N-nitro-3,5-dinitrobenzamide (9%).

A similar reaction carried out on the silver salt of N-nitroisobutylamine yielded isobutyl 3,5-dinitrobenzoate (7.4%). No nitroamide was detected in this run.

The Reaction of the Sodium Salt of (+)-N-Nitro-*sec*-butylamine with 3,5-Dinitrobenzoyl Chloride.—The sodium salt of (+)-N-nitro-*sec*-butylamine (0.63 g., 4.5 mmoles) (95.5% optically pure) was reacted with 3,5-dinitrobenzoyl chloride (1.04 g., 4.5 mmoles) in chloroform (15 ml.) at 25° (cooling required). The mixture was protected from moisture by a drying tube. After 3.5 hr., the reaction mixture was filtered to yield a solid (1.04 g.) containing infrared bands characteristic of 3,5-dinitrobenzoic acid (5.85μ) and of sodium 3,5-dinitrobenzoate (6.14μ). A mixture of the solid in hot ethanol water was titrated with 0.1 *N* sodium hydroxide solution (phenolphthalein end-point). Base was required equivalent to 2.3 mmole of 3,5-dinitrobenzoic acid. The remainder of the solid, sodium 3,5-dinitrobenzoate, therefore, amounted to (~0.55 g., ~2.3 mmole).

The chloroform filtrate was evaporated to yield an oil (0.37 g.), which was chromatographed on silica gel (Davison mesh 20–200). There was obtained a fraction (eluted with 3% ether–97% pentane) which, after sublimation at 1 mm. and 100°, yielded (0.083 g., 0.3 mmole, 6.6% yield) of (+)-*sec*-butyl 3,5-dinitrobenzoate. The ester had $[\alpha]^{25}D$ + 6.97° ± 0.05° (*c* 3.93 in $CHCl_3$). Since the optically pure ester has $[\alpha]^{21}D$ + 38.3°,[4a] the ester in this experiment has an optical purity of 18.2%. In the conversion of the sodium salt to the ester, there was, therefore, 19.0% retention of configuration. The ether eluate from the chromatography yielded (+)-N-nitro-*sec*-butylamine (0.19 g., 1.6 mmole, 35%); no N-(*sec*-butyl)-N-nitro-3,5-dinitrobenzamide was detected in this run.

Tetrabutylammonium 3,5-Dinitrobenzoate.—Moist silver oxide from the reaction of an aqueous solution of sodium hydroxide (1.6 g., 40 mmoles) with an aqueous solution of silver nitrate (6.8 g., 40 mmoles) was added in portions to a stirred solution of recrystallized tetra *n*-butylammonium iodide (4.77 g., 13 mmoles; m.p. 147–148°) at 70°. The suspension was stirred for 15 minutes, filtered through Celite and extracted with ether. The aqueous phase was then added slowly to a solution of 3,5-dinitrobenzoic acid (2.12 g., 10 moles) in 50% ethanol until the solution became slightly basic. The solution was extracted thoroughly with chloroform and the organic phase was dried and evaporated at room temperature *in vacuo* to yield a yellow crystalline solid. This was recrystallized from a chloroform–ether mixture at 0° to yield yellow rhomboids of tetra (*n*-butyl) ammonium 3,5-dinitrobenzoate (3.10 g., 6.9 mmoles, 69%), m.p. 107–109°.

Anal. Calcd. for $C_{23}H_{39}N_3O_6$: C, 60.90; H, 8.67; N, 9.26. Found: C, 60.88; H, 8.54; N, 9.09.

Tetramethylammonium 3,5-dinitrobenzoate was prepared in a similar fashion. The crude product was recrystallized from methanol, m.p. 284–285°.

Anal. Calcd. for $C_{11}H_{15}N_3O_6$: C, 46.66; H, 5.31; N, 14.73. Found: C, 46.93; H, 5.51; N, 14.57.

The Reaction of Tetra-*n*-butylammonium 3,5-Dinitrobenzoate with Isobutyl Bromide.—Isobutyl bromide was

(17) H. Van Erp, *Rec. trav. chim.*, **14**, 32 (1895).

(18) For ultraviolet measurements on other aliphatic nitroamine salts see (a) R. Jones and G. Thorn, *Can. J. Research*, **27B**, 828 (1949); (b) H. M. Curry and J. P. Mason, THIS JOURNAL, **73**, 5449 (1951); (c) M. Carmack and J. J. Leavitt, *ibid.*, **71**, 1221 (1949).

(19) G. M. R. Smart and G. F. Wright, *Can. J. Research*, **26B**, 284 (1948).

(20) P. Bruck, I. N. Denton and A. H. Lamberton, *J. Chem. Soc.*, 921 (1956).

(21) A mixture of the isobutyl and *sec*-butyl esters of 3,5-dinitrobenzoic acid was shown to be stable under these conditions.

purified[22] and then fractionated from anhydrous potassium carbonate. A fraction, b.p. 91–91.2°, $n^{20}D$ 1.4362 was used; it was free of *sec*-butyl and *tert*-butyl isomers as shown by the absence of bands at 7.82, 8.25 and 8.74μ in the infrared spectrum. A solution of this isobutyl bromide (6.3 g., 46 mmoles) and tetrabutylammonium 3,5-dinitrobenzoate (0.09 g., 0.2 mmole) in chloroform (5 ml.) was refluxed for 26 hr. The solvent was removed and the resulting yellow oil was extracted with ether. The ether was removed and the product was sublimed at 100° and 0.1 mm. The infrared spectrum was identical with that of pure isobutyl 3,5-dinitrobenzoate (*i.e.*, < 1% *sec*-isomer).

Nitrosation of Ethyl N-Isobutylcarbamate with Fuming Nitric Acid.—Ethyl N-(isobutyl)-carbamate (0.25 g., 1.9 mmole) was added dropwise to 100% fuming nitric acid (16 g., specific gravity, 1.6) at −70°. After 1 hr., carbon tetrachloride (6.5 ml.) was added, the mixture was shaken vigorously and the layers were separated. The organic layer was washed successively with dilute sodium carbonate solution and then with water until the aqueous phase remained neutral. The infrared spectrum of the dried solution showed ethyl N-(isobutyl)-N-nitrosocarbamate (90%) and ethyl N-(isobutyl)-N-nitrocarbamate (10%). Ethyl N-(isobutyl)-N-nitrosocarbamate (from the urethane, sodium nitrite, acetic acid and acetic anhydride) and a pure sample of the nitrourethane were used as standards.

When the pure N-nitrosourethane (0.5 g.) was treated with 100% fuming nitric acid (30 g.) at −13° for 30 minutes, it was converted quantitatively to the N-nitrourethane.

Ethyl N-Isobutyl-N-nitrocarbamate.—Ethyl N-(isobutyl) carbamate (0.28 g., 1.9 mmole) was added dropwise to 100% fuming nitric acid (16 g.) at such a rate that the temperature was maintained (acetone-Dry Ice cooling) between −15° and −20°. The addition was accomplished within a few seconds, and the mixture was allowed to react for an additional five minutes at this temperature. It was then poured over cracked ice. The mixture was extracted with ether and the extract was washed with sodium bicarbonate, dried and evaporated *in vacuo* to an oil. This was distilled at 59.5–60.5° (0.3 mm.) to yield the nitrourethane with $n^{25}D$ 1.4398 (lit.[23] $n^{21}D$ 1.4433), infrared in CCl_4: 5.64μ, 5.75μ (C=O); 6.32μ (N-NO_2).

Anal. Calcd. for $C_7H_{14}N_2O_4$: C, 44.44; H, 7.35; N, 14.73; mol. wt. 190. Found: C, 44.55; H, 7.51; N, 14.38; mol. wt. 197,[24] 193.[25]

Ethyl N-Nitro-N-(*t*-butyl)carbamate.—Nitric acid (100° fuming) (16.48, 0.26 mole) was added dropwise to acetic anhydride (36 g., 0.35 mole) at 0°. After the addition was complete, the temperature of the mixture was allowed to rise to 20°. Ethyl N-(*t*-butyl)carbamate (24.6 g, 0.17 mole) was added to the stirred mixture at 20–25°. After the addition, the mixture was stirred for thirty minutes at 25–30°. The mixture was poured into ice and water to yield an oil which was extracted into ether. The organic layer was separated and washed with cold, dilute sodium carbonate solution until the acetic anhydride had been hydrolyzed. The organic phase was washed with water until the aqueous phase remained neutral, then it was dried and evaporated *in vacuo*. The oil which was obtained was distilled to yield 22.7 g. (0.12 mole, 70%) of the nitrourethan, b.p. 53–56° (0.5 mm.) (lit.[26] b.p. 56°, 2 mm.), $n^{20}D$ 1.4364, (lit.[26] $n^{20}D$ 1.4331). Ultraviolet spectrum: λ_{max} 2.33 mμ (ϵ 2344 in EtOH) (lit.[27] λ_{max} 2.39 mμ (ϵ 2690 in EtOH)). The infrared spectrum in CCl_4 had peaks at 5.66μ and 5.74μ (C=O), and 6.27μ and at 6.44μ (N-NO_2).

Anal. Calcd. for $C_7H_{14}N_2O_4$: C, 44.44; H, 7.35; N, 14.73; mol. wt. 190. Found: C, 44.57; H, 7.53; N, 14.70; mol. wt. 171,[24] 176.[25]

A sample of the ethyl N-nitro-N-(*t*-butyl)carbamate was fractionated with a Piros–Glover Spinning Band Micro-Still (Martin No. 8480). The maximum efficiency of the column is rated by the manufacturer at twenty theoretical plates at 1 mm. of pressure. The nitrourethane had a b.p. of 54–56° (1.2 mm.). The material was completely volatile and the infrared spectrum of the first two drops to distill was identical with that of the last fraction (containing 20% of the sample).

Infrared Spectra of the Carbamate Derivatives.—Without exception, the nitrosoamides, nitroamides and nitrosocarbamates that we have synthesized showed only a single carbonyl peak in the infrared spectra. All of the N-nitrocarbamates that we have prepared (the ethyl esters of the N-*n*-butyl, N-isobutyl, N-*t*-butyl and N-*n*-hexyl derivatives and the methyl ester of the N-*n*-butyl derivative) show two peaks in the carbonyl region of the infrared spectra at *ca.* 5.65 and 5.75μ. In carbon tetrachloride or in heptane, the 5.75 peak is the more intense whereas in the pure liquid and in chloroform or methylene dichloride, the 5.65 peak is the more intense of the two. For the methyl ester of the *n*-butyl derivative, the splitting is about 36 $cm.^{-1}$ in heptane and 30 $cm.^{-1}$ in chloroform and in the pure liquid. Two peaks are also observed in the nitro region of the spectrum (6.27 and 6.44μ) for the *t*-butyl derivative; the single band observed for the other compounds is wide enough to indicate an unresolved doublet.

Methyl N-nitro-N-(*n*-butyl)-carbamate was prepared by the method given for the *tert*-butyl derivative, ($n^{21}D$ 1.4488; lit.[23] $n^{22}D$ 1.4486). The spectrum of the N-15 (NO_2 group) analog was almost the same[11]; the carbonyl bands were in the same position with the same relative intensity. However, the nitro band had been shifted from 1580 to 1546 $cm.^{-1}$ and a band at 750 $cm.^{-1}$ had decreased in intensity with a proportionate gain in the spectrum at 730 cm^{-1}. The spectra of 0.2, 0.04 and 0.004 *M* solutions in carbon tetrachloride in 0.1, 0.5 and 5 mm. cells, respectively, showed identical ratios of peak heights.

Compared to our other nitrocarbamates, the splitting of the carbonyl peak of methyl N-(*n*-butyl)-N-nitrocarbamate (1775 and 1744 $cm.^{-1}$) could be accounted for the *least* satisfactorily on the basis of Fermi resonance (which would require a band near 880 $cm.^{-1}$). The closest significant band of medium intensity for this compound is one at 920 $cm.^{-1}$. The infrared spectrum of the pure liquid showed a ratio of optical densities for the 5.63 μ and 5.75 μ peaks of 1.9 at 25°, 2.4 at −75°, and 3.6 at −196°. At the lower temperatures, bands at 7.95 μ and 10.5 μ increase in intensity, new bands appear at 8.95 μ and 9.5 μ, and a band at 8.12 μ decreases in intensity. Similar changes are observed for spectra taken in polar solvents (see above).

Thermal Decomposition of Ethyl N-Nitro-N-(*t*-butyl) Carbamate.—A solution of ethyl N-nitro-N-(*t*-butyl) carbamate, (0.95 g., 5 mmole) in heptane (10 ml.) was refluxed for 65 hr. Dry nitrogen was slowly bubbled through the reaction mixture. The effluent gas was passed through a Dry Ice trap, an ascarite tube (protected on either side by drierite tubes) and finally through two liquid nitrogen traps. The liquids which collected in the Dry-Ice trap and the first liquid nitrogen trap were titrated with a 0.35 *M* bromine in carbon tetrachloride solution; 3.4 mmoles of bromine reacted corresponding to 3.4 mmoles of isobutylene (68%). The infrared spectrum of the bromination product was identical with that of the bromination product of pure isobutylene. The liquid in the second liquid nitrogen trap was identified as N_2O from its infrared spectrum (in chloroform) which contained the characteristic N_2O bands at 4.59, 7.29 and 7.83μ. The ascarite tube increased in weight by 0.2637 g. corresponding to 5.9 mmole (119%) of carbon dioxide. In another run, ethyl N-nitro-N-(*t*-butyl)-carbamate (16.3 g., 95 mmoles) was decomposed in 50 ml. of spectrograde isoöctane at 75° for 258 hr. in a flask fitted with a reflux condenser and a drying tube. The volatiles were distilled at atmospheric pressure (b.p. 71–98°) to yield a liquid residue (I) (1.42 g). A vapor phase chromatograph of (I) yielded by weight, isoöctane (69%), *t*-butyl ethyl carbonate (20%, 0.28 g.) (a 2% yield) and ethyl N-(*t*-butyl)-carbamate (11%, 0.156 g.) (a 1% recovery). The samples were collected and identified by the comparison of their infrared spectra with those of authentic samples. The chromatogram[28] was run on a Perkin–Elmer Vapor Fractometer Model 154-C at T = 83°, 10 lb. He, flow rate of 80 ml./min. on a 2 meter column on a substrate of Dow-Corning Silicon Fluid 550 (10% on C-22 fire brick).

(22) M. L. Dhar, E. D. Hughes, C. K. Ingold and S. Masterman, *J. Chem. Soc.*, 2055 (1948).

(23) J. W. Brühl, *Z. physik. Chem.*, **22**, 390 (1897).

(24) Signer–Barger method in benzene (ref. 13).

(25) We wish to thank Mrs. G. Kratzer, Monsanto Analytical Laboratory, Dayton, Ohio, for determining these molecular weights by freezing point depression of benzene.

(26) H. M. Curry and J. Mason, THIS JOURNAL, **73**, 5043 (1951).

(27) H. M. Curry and J. Mason, *ibid.*, **73**, 5449 (1951).

(28) We wish to thank Mr. W. Ross and Mr. J. Schlater of the Monsanto Chemical Company, Dayton, Ohio, for this analysis.

Thermal Decomposition of Ethyl N-Nitro-N-isobutylcarbamate.—A solution of ethyl N-(isobutyl)-N-nitrocarbamate (0.95 g., 5 mmole) in dodecane (20 ml.) was kept at 140° for 89 hr. in a flask fitted with a reflux condenser which was connected to the absorption train used for the rearrangement of ethyl N-nitro-N-(*t*-butyl)-carbamate. For the last fifteen minutes of the reaction, nitrogen was swept through the reaction mixture. The liquid in the dry ice trap was titrated with a carbon tetrachloride solution of bromine (0.35 *M*); 2.2 ml. were required equivalent to 16% isobutylene (0.8 mmole). Nitrous oxide was found in the liquid nitrogen trap. It was identified by its infrared spectrum in chloroform. The Ascarite tube increased in weight by 0.060 g. corresponding to 1.4 mmole (28%) of carbon dioxide. The dodecane solution was distilled at 70° (10 mm.) in a short path distillation apparatus to yield isobutyl ethyl carbonate (0.323 g., 2.2 mmole, 44%) identified by means of its infrared spectrum.

The Copper Salt of N-(Isobutyl)-N-nitrosohydroxylamine.[29]—Isobutyl magnesium bromide in 150 ml. of ether was prepared under nitrogen from isobutyl bromide (54.8 g., 0.4 mole) in a three-necked flask fitted with stirring motor, condenser and pressure-equalized addition funnel. The condenser was attached to a glass tube the end of which was immersed in a few cm. of mercury. The solution was cooled to −10° and nitric oxide, which had been passed through conc. sulfuric acid and then drierite, was introduced at such a rate that a slight positive pressure was maintained. The temperature rose suddenly to 35°, then fell slowly to 0°. The nitric oxide atmosphere was maintained over the stirred mixture at this temperature for 3 hr. The ether solution was decanted from a gummy residue. The residue was triturated with water (750 ml.) and the triturate was filtered. To the clear aqueous filtrate (slightly basic) was added a saturated copper sulfate solution until the solution reached a *p*H of 5. The aqueous phase was extracted with carbon tetrachloride until the extracts were no longer colored blue. The organic layers were combined, dried, filtered and the solution evaporated *in vacuo* at room temperature. The deep blue solid which remained weighed 32.6 g. (0.11 mole, 55%). The solid was dissolved in warm ether, *n*-pentane was added and the solution cooled to yield blue crystals, m.p. 80–82.5°.

Anal. Calcd. for $C_8H_{18}N_4O_4Cu$: C, 32.26; H, 6.09; N, 18.82; mol. wt., 298. Found: C, 32.50; H, 6.22; N, 18.63; mol. wt., 272.[24]

(29) The preparation is a modification of that of J. Sand and F. Singer, *Ann.*, **329**, 190 (1903). See also E. Muller and H. Metzger, *Ber.*, **89**, 396 (1956).

The Sodium Salt of N-(Isobutyl)-N-nitrosohydroxylamine.—A 0.1 *N* sodium hydroxide solution (330 ml., 33 mmole) was added to a solution of the copper salt of N-(isobutyl)-N-nitrosohydroxylamine (4.94 g., 17 mmole) in 95% ethanol (200 ml.) and the mixture was allowed to stand for one half hour at room temperature. A light blue precipitate formed leaving a light blue, alkaline solution. The solid was filtered and the filtrate neutralized with 6 *N* hydrochloric acid; approximately 3 ml. (18 mmole) was required. The resulting solution was evaporated at room temperature *in vacuo* to yield a light blue solid. The solid was triturated with ether (60 ml.), the blue color entering the ether phase. The white crystalline solid obtained weighed 3.02 g., and it consisted of sodium chloride and the sodium salt of N-(isobutyl)-N-nitrosohydroxylamine (68%) as determined from the band at 245 mμ in the ultraviolet spectrum, (lit. λ_{max} 249 mμ, ε 8730[18c]; λ_{max} 243 mμ, ε 8300).[30]

The Reaction of the Sodium Salt of N-(Isobutyl)-N-nitrosohydroxylamine with 3,5-Dinitrobenzoyl Chloride.—A mixture of potassium carbonate (4.14 g., 30 mmole), the sodium salt of N-isobutyl-N-nitrosohydroxylamine (2.90 g., 14 mmole) (corrected for NaCl content) and 3,5-dinitrobenzoyl chloride (2.90 g., 13 mmole) was suspended in carbon tetrachloride (25 ml.). The mixture was stirred with a magnetic stirrer in a flask protected by a drying tube. The temperature of the mixture was lowered to 0° while stirring. After forty-five minutes of stirring, the solids were filtered and washed with ether (30 ml.). The ether wash was combined with the filtrate and the solvents were removed *in vacuo* at room temperature to yield a white solid (1.59 g.) which was essentially isobutyl 3,5-dinitrobenzoate. The solid was chromatographed on a silica-gel column (Davison-mesh 28–200) and the esters were quantitatively eluted with 3% ether–97% pentane for a yield of 0.49 g., 1.8 mmoles, 14%. The esters contained 10 ± 2% *sec*-butyl 3,5-dinitrobenzoate as shown by the infrared spectrum. Elution of the column with ether yielded a yellow oil which was probably crude N-(isobutyl)-N-nitroso-O-3,5-dinitrobenzoylhydroxylamine. The oil gave a positive Lieberman's nitroso test and the infrared spectrum contained bands at 5.69, 6.45 and 6.67μ.

Acknowledgment.—We wish to thank the Research Corporation for its support of this work.

(30) G. Kortüm and B. Finckh, *Z. physik. Chem.*, **48B**, 32 (1940).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENTS OF NORTHWESTERN UNIVERSITY, EVANSTON, ILL., AND THE UNIVERSITY OF WISCONSIN, MADISON 6, WIS.]

Carbanion Rearrangements. II[2]

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2,2-Diphenylpropyllithium has been found to rearrange with phenyl migration to yield 1,2-diphenyl-1-methylethyllithium, The analogous magnesium and mercury compounds have been prepared. Unlike the lithium derivative, the Grignard reagent does not rearrange. Preparation of the organopotassium derivative leads directly to the rearranged carbanion. 2-Phenyl-2-(*p*-tolyl)-propyllithium has been found to rearrange with preferential phenyl migration. This and other results are interpreted as support for a carbanion rather than a free radical rearrangement mechanism. A molecular orbital treatment of the chemistry of 1,2-shifts is presented.

In our previous publication[2c] dealing with carbanion rearrangements, we noted that while 1,2-carbon to carbon rearrangements of carbonium ions, in which a group migrates from one carbon atom to an adjacent and positively charged carbon atom, have been known for a very long time, and while the analogous 1,2-shifts of free radicals are known and have received considerable study, there has been little evidence for the reality of a parallel 1,2-carbon to carbon shift of carbanions.

In this previous publication the rearrangement of 1,1,1-triphenyl-2-chloroethane (I), on treatment

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(2) (a) Taken largely from the Ph.D. thesis of Arnold Zweig, Northwestern University. A portion of the calculations were completed at the University of Wisconsin. (b) The material described in the present publication was presented in part, April, 1960, at the Cleveland, Ohio, A.C.S. Meeting, Abstracts p. 170. (c) Paper I, H. E. Zimmerman and F. J. Smentowski, *J. Am. Chem. Soc.*, **79**, 5455 (1957).