alkylation reactions listed in Table III, averaged 0.998 ± 0.002. Where duplicate determinations of rate constants were measured, an average deviation of ± 2% was obtained.

To demonstrate that the rate measurements applied to a reaction involving simple replacement of the α-halogen with the amino group, (Scheme II), the following experiment was carried out. 2'-t-Butyl-2-bromo-6'-ethylacetanilide (IIId, 4.0 g, 0.013 mole) was placed in a mixture containing 22.5 g of piperidine (0.26 mole) and 45 g of water. The solution was brought to a total volume of 375 ml with acetone, then permitted to stand at room temperature for 4 hr. The material was vacuum treated to remove solvent; then water was added and the white, crystalline solid was filtered off. The dried product (4.1 g, quantitative yield) possessed mp 155–155.5°, unimproved by crystallization as needles from aqueous methanol. Nmr and infrared spectra were shown to be consistent with the structural assignment as 2'-t-butyl-6'-ethyl-2-(1-piperidyl)acetanilide.

Anal. Calcd for $C_{19}H_{30}N_2O$: C, 75.45; H, 10.00; N, 9.26. Found: C, 75.18; H, 10.12; N, 9.60.

Registry No.—Ia, 13117-74-3; Ib, 13117-75-4; Ic, 13117-76-5; Id, 13117-77-6; Ie, 13117-78-7; If, 13117-79-8; Ig, 13135-43-8; Ih, 13117-80-1; Ii, 13117-81-2; IIb, 13117-82-3; IIc, 13117-83-4; IId, 13117-84-5; IIe, 13117-85-6; IIf, 13117-86-7; IIg, 13117-87-8; IIh, 13117-88-9; IIi, 13117-89-0; IIIa, 587-65-5; IIIb, 1131-01-7; IIIc, 13117-92-5; IIId, 13117-93-6; IIIe, 13143-69-6; IIIf, 13143-70-9; 6-t-butyl-o-toluidine, 13117-94-7; 6-t-butyl-o-benzotoluidide, 13117-95-8; 4'-t-butyl-o-benzotoluidide, 13117-96-9; 2-t-butyl-6-ethylaniline, 13117-97-0; 2'-t-butyl-6'-ethylbenzanilide, 13117-98-1; 4-t-butyl-2-ethylaniline, 13117-99-2; 4'-t-butyl-2'-ethylbenzanilide, 13118-00-8; 2',6'-di-t-butylbenzanilide, 13118-01-9; 6-t-butyl-N-methyl-o-toluidine, 13143-71-0; 2-t-butyl-6-ethyl-N-methylaniline, 13118-02-0; 2,6-di-t-butyl-N-methylaniline, 13118-03-1; 2'-t-butyl-6'-ethyl-2-(1-piperidyl)acetanilide, 13143-72-1, 4-t-butyl-o-toluidine, 2909-82-2; 2,6-di-t-butylaniline, 2909-83-3.

Nitration Studies. XV. Nitromercuration and the Synthesis of β-Nitromercurials[1]
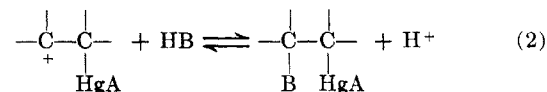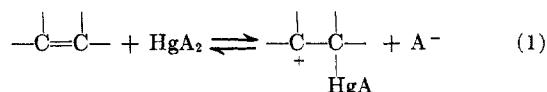
G. BRYANT BACHMAN AND MAYNARD L. WHITEHOUSE[2]

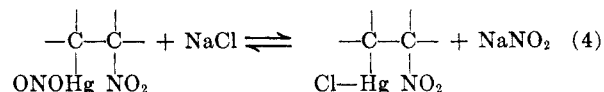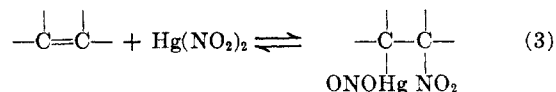*Department of Chemistry, Purdue University, Lafayette, Indiana 47907*

Olefins react with solutions containing mercuric and nitrite ions to form β-nitroalkylmercuric salts. Conversions and rates depend markedly on concentrations of the above ions, which in turn are highly dependent on the concentrations of counterions, and on the structure of the olefin. The complex and mobile equilibria involved are readily disturbed by acids, bases, reducing reagents, and other substances with regeneration of the olefin or its polymers. The remarkable predominance of the entrance of the nitrite ion into the product as a nitro group rather than as a nitrite ester group is discussed.

Addition to olefins is one of the most characteristic reactions of mercuric salts[3] but one of the least characteristic reactions of salts of other metals. No other metal approaches mercury in the ease with which such additions take place and in the stability of the products. However, the addition of the mercuric ion must also be accompanied by the addition of a negative ion, and the synthetic possibilities which this engenders have not been adequately developed. This paper is concerned with an evaluation of such possibilities in the specific case of the negative ion NO_2^-. As an ambient anion[4] NO_2^- may attach itself to a carbonium ion either *via* an oxygen atom to form a nitrite ester or *via* the nitrogen atom to form a nitro compound. A matter of interest is, therefore, the influence of the mercuric ion on the way in which the NO_2^- ion enters the molecule.

Additions of mercuric salts to olefins are normally run in hydroxylic solvents to attain adequate solubility of the mercuric salt. However, under such circumstances the solvent rather than the anion of the salt usually enters the product molecule. In this way a variety of hydroxy, alkoxy, acyloxy, and related oxymercurials have been prepared from mercuric chloride, nitrate, or acetate in water, alcohols, and carboxylic acids.[3] However, it was recently reported[5] that mercuric nitro-

$$-\overset{|}{C}=\overset{|}{C}- + HgA_2 \rightleftharpoons -\overset{|}{\underset{+}{C}}-\overset{|}{\underset{HgA}{C}}- + A^- \quad (1)$$

$$-\overset{|}{\underset{+}{C}}-\overset{|}{\underset{HgA}{C}}- + HB \rightleftharpoons -\overset{|}{\underset{B}{C}}-\overset{|}{\underset{HgA}{C}}- + H^+ \quad (2)$$

formate adds as such to olefins without involving the solvent (water). We have found that mercuric nitrite does the same and gives β-nitroalkyl mercuric salts provided that the reaction medium is sufficiently acidic to prevent oxymercuration. This novel synthesis of nitro

$$-\overset{|}{C}=\overset{|}{C}- + Hg(NO_2)_2 \rightleftharpoons -\overset{|}{\underset{ONOHg}{C}}-\overset{|}{\underset{NO_2}{C}}- \quad (3)$$

$$-\overset{|}{\underset{ONOHg}{C}}-\overset{|}{\underset{NO_2}{C}}- + NaCl \rightleftharpoons -\overset{|}{\underset{Cl-Hg}{C}}-\overset{|}{\underset{NO_2}{C}}- + NaNO_2 \quad (4)$$

compounds may be termed *nitromercuration*. Since the reaction seems to be peculiarly sensitive to conditions, we have studied various factors influencing conversions and yields, including the formulation of the nitromercurating reagent, the structure of the olefin, the nature of the solvent, the pH, the effects of other anions and cations, and the changes produced by changes in the concentrations of the reactants. From these data it has been possible to formulate a mecha-

(1) From the Ph.D. Thesis of M. L. Whitehouse, Purdue University, Aug 1966.

(2) Commercial Solvents Corp. Research Assistant.

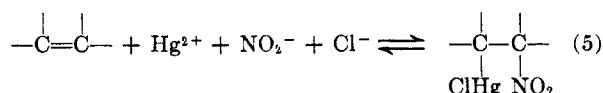(3) J. Chatt, *Chem. Rev.*, **48**, 7 (1951).

(4) N. Kornblum, R. A. Smiley, R. K. Blackwood, D. D. Mooberry, E. P. Oliveto, and G. E. Graham, *J. Am. Chem. Soc.*, **78**, 1497 (1956).

(5) S. S. Novikov, T. I. Godovikova, and V. A. Tartakovskii, *Proc. Acad. Sci. USSR*, **124**, 89 (1959); S. S. Novikov, V. A. Tartakovskii, T. I. Godovikova, and G. B. Gribov, *Bull. Acad. Sci. USSR*, 249, 254 (1962); V. A. Tartakovskii, S. S. Novikov, and T. I. Godovikova, *ibid.*, 963 (1961); V. A. Tartakovskii, I. A. Savost'yanova, and S. S. Novikov, *ibid.*, 1204 (1963); V. A. Tartakovskii, I. A. Savost'yanova, and B. G. Gribov, *ibid.*, 1206 (1963).

nism for the reaction and to explain some of the properties of the products.

The Nitromercuration Reagent.—Mercuric nitrite has been prepared in aqueous solution and in the pure form with the aid of the reaction between mercuric chloride and silver nitrite.[6] However a very satisfactory nitromercurating reagent may be prepared by simply dissolving mercuric chloride in an aqueous solution of sodium or potassium nitrite. The resulting pale yellow solution may be brought into contact with the olefin, in gaseous or liquid form, and in a short time precipitation of the solid white adduct begins and is generally complete in a day at room temperature.

$$-\overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}}- + Hg^{2+} + NO_2^- + Cl^- \rightleftharpoons -\overset{|}{\underset{ClHg}{C}}-\overset{|}{\underset{NO_2}{C}}- \quad (5)$$

The solubilities of mercuric halides are increased by the presence of nitrite anions as shown in Table I.

TABLE I

MOLAL SOLUBILITIES OF MERCURIC SALTS
IN SOLUTIONS OF SODIUM NITRITE[a]

Sodium nitrite, m	$HgCl_2$, m	$HgBr_2$, m	HgI_2, m
None[b]	0.25	0.017	0.00013
2.0	2.12	0.372	0.009

[a] Sodium nitrite was dissolved in 50 ml of distilled water, then the appropriate mercuric salt was added with stirring until the solution was saturated. Measurements were made at 23°. [b] Data from J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. II, Longmans, Green and Co., London, (1923), pp 695–1049.

The increase is greatest for mercuric iodide, less for the bromide, and still less for the chloride. It is so great as to indicate complex formation, perhaps of the type shown in eq 6. The color change from colorless to

$$Hg^{2+} + 2Cl^- + 2Na^+ + 2NO_2^- \rightleftharpoons 2Na^+ + [Hg(NO_2)_2Cl_2]^{2-} \quad (6)$$
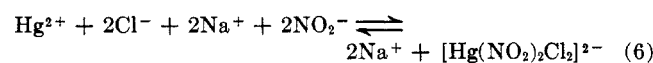
yellow which accompanies these dissolutions is in accord with this concept of complexation. However, no ultraviolet or infrared absorption spectral changes were noted in the regions which could be examined in aqueous solutions.[7] Continuous ether extraction yielded only mercuric chloride and no mercuric nitrite. Addition of dioxane to the aqueous nitromercurating reagent precipitated only the dioxane–mercuric chloride complex.[8]

Other salts of mercury, such as mercuric nitrate and acetate, may also be used in nitromercuration. Results obtained in these cases will be discussed later.

Nitromercurating reagents must be used fairly promptly since they decompose slowly on standing with precipitation of mercurous salts. The pH of the solu-

$$2Hg^{2+} + NO_2^- + 2OH^- \longrightarrow Hg_2^{2+} + NO_3^- + H_2O \quad (7)$$
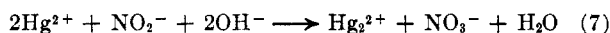
tion changes from about 6.0–6.5 to lower values as a result of the consumption of hydroxide ion.

(6) P. C. Ray, *J. Chem. Soc.*, **85**, 523 (1904).

(7) M. LePostellec [*Compt. Rend.*, **254**, 2988 (1962)] has demonstrated that certain complex nitrites are distinguished from simple double salts containing nitrite anions by increases in the asymmetric stretching frequency of the NO₂ group in the infrared region.

(8) A. Luyken and H. Schmittmann, *J. Prakt. Chem.*, **149**, 42 (1937); S. G. K. Nair and S. S. Moosath, *Proc. Indian Acad. Sci.*, **47A**, 344 (1958); H. Rheinboldt, A. Luyken, and H. Schmittmann, *J. Prakt. Chem.*, **149**, 30 (1937).

Structure of Olefin.—Olefin reactivity in nitromercuration is highly dependent on structure. Both steric and electrical effects are involved, and changes in both reaction rates and product stabilities are observed. Since addition proceeds with Markovnikov-like orientation it is presumed that the rate-controlling step is the combination of the olefin with a cation, in this case XHg^+. Therefore, the presence of electron-supplying substituents should increase the rates, while electron-withdrawing substituents should decrease them. This was found to be true within limits. The rates of reaction increase from ethylene through propylene to cyclohexene, but trialkylated ethylenes give low yields because of steric hindrance, while tetra-alkylated ethylenes do not react. Negatively substituted ethylenes, such as vinyl halides and dichloro-ethylenes (*cis* and *trans*) do not react. However, mesityl oxide and methyl acrylate react readily, though diethyl maleate and dimethyl itaconate do not react. Styrene gives a mixture of products probably containing ring-substituted derivatives. The olefin, 4-methyl-2-pentene, reacts readily in its *cis* form but not in its *trans* form. Stabilities of the products are inversely proportional to the extent of alkyl substitution with the product from ethylene being the most stable, but poorly purified products decompose easily regardless of structure.

Effects of Other Solvents.—Simple olefins exhibit very low solubilities in water and in nitromercurating solutions. This diminishes the rate of the nitromercuration reaction and indirectly promotes oxymercuration. A number of different solvents were added to the nitromercurating reagent or employed alone in efforts to overcome this difficulty. Water-miscible solvents tried included methanol, acetone, acetonitrile, tetrahydrofuran, dimethylformamide, and dimethyl sulfoxide. Water-immiscible solvents tried included benzene, chloroform, and cyclohexane. Both groups of solvents (water miscible and water immiscible) were found to be undesirable for the following reasons. (a) Conversions were not more than half so great as those observed for water alone. Nitromercuration was slowed considerably and in some cases it was halted altogether. Acetone, acetonitrile, dimethylformamide, and dimethyl sulfoxide form complexes with the mercuric salt which effectively hinders its reaction with the olefin. When employed with little or no water, the above-mentioned solvents suppress all mercuration reactions. (b) The one alcoholic solvent studied, methanol, proved to be a strong competitor of nitrite ions for the olefin, giving rise to methoxymercuration instead of nitromercuration. (c) On prolonged standing, some of the water–solvent nitromercuration mixtures were observed to be unstable and underwent decomposition (an acetone–water mixture containing mercuric chloride and sodium nitrite deposited metallic mercury on standing). (d) And finally such solvents as tetrahydrofuran produce a by-product resin which coats the nitromercurial product, making purification difficult. For these reasons the normally employed aqueous nitromercuration mixture was found to be the best system investigated.

Effects of Other Ions.—Nitromercuration can occur satisfactorily only when there are adequate concentrations of both mercuric cations and nitrite anions pres-
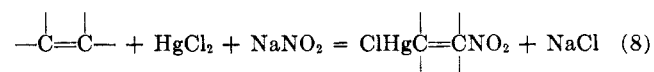
TABLE II
β-NITROALKYLMERCURIAL SALTS[a]

Compound (source)	Time, hr	Molality[b]	Convn,[c] %	Mp,[d] °C	Calcd, %				Found, %			
					C	H	N	Cl	C	H	N	Cl
1-Chloromercuri-2-nitroethane (from ethylene)[e]	12.0	0.40	69	103–105	7.75	1.30	4.52	11.44	7.70	1.54	4.55	11.66
1-Chloromercuri-2-nitropropane (from propylene)[e,f]	18.0	0.46	80	74–75	11.12	1.87	4.32	10.94	11.45	1.88	4.10	10.64
1-Chloromercuri-2-methyl-2-nitrobutane (from 2-methyl-1-butene)	12.5	0.40	75	68–69	17.05	2.86	3.98	10.07	17.31	3.08	3.87	9.97
2-Chloromercuri-4-methyl-3-nitropentane (from cis-4-methyl-2-pentene)	144.0	0.50	12	117–118	19.68	3.30	3.82	9.68	19.50	3.38	3.61	9.80
1-Chloromercuri-2-nitrocyclohexane (from cyclohexene)[g]	28.0	0.53	79	91–93	19.79	2.77	3.84	9.74	19.76	2.91	3.72	9.52
1-Bromomercuri-2-nitrocyclohexane (from cyclohexene)[h]	168.0	0.38	45	80–82	17.64	2.47	3.43	19.56	18.11[i]	2.72	3.45	19.05
Methyl 2-chloromercuri-3-nitropropionate (from methyl acrylate)	24.0	0.27	69	149–152	13.05	1.64	3.81	9.63	13.18	1.74	3.69	9.40
2-Nitro-2-methyl-3-chloromercuri-4-pentanone (from mesityl oxide)	3.00	0.25	25	85–87	18.85	2.65	3.68	9.33	19.05	2.91	3.72	9.32

[a] Each experiment was carried out at room temperature employing 0.04 mole of mercuric chloride, 0.08 mole of sodium nitrite, and 0.04 mole of olefin unless stated otherwise. [b] Molal concentration of nitromercuration mixture based on mercuric salt. [c] Conversions are based on mercuric salt. [d] Gaseous decomposition accompanies melting in all cases. [e] Gaseous olefins were passed into the nitromercuration mixture until optimum conversions were realized. [f] Calcd: mol wt, 324. Found: mol wt, 368. [g] Calcd: mol wt, 364. Found: mol wt, 412. [h] Reaction mixture consisted of 0.019 mole of mercuric bromide, 0.10 mole of sodium nitrite, and an excess (ca. 10 ml) of cyclohexene. [i] The instability of this compound prevented obtaining a sample pure enough to give very accurate elemental analyses.

ent. However, other ions present may influence the concentrations of these two ions and so determine the degree of success of the reaction. The pH of the solution is of considerable importance since nitrite ion is readily protonated and so *inactivated* to addition. Furthermore, undissociated nitrous acid decomposes to nitrogen oxides fairly rapidly at room temperature. Also any nitromercuration product formed is decomposed by strong acid since the product is apparently in mobile equilibrium with the reactants from which it is formed. These effects become substantial below a pH of about 4.5. On the other hand, too high a pH promotes oxymercuration which can easily become the predominant process above a pH of about 7.[3]

Mercuric chloride and mercuric nitrate are the salts of choice in nitromercuration. Mercuric chloride has the advantage of yielding the nitromercurial as an easily handled, solid product, while mercuric nitrate yields a liquid product, but the rate of production of the nitromercurial from a mercuric nitrate–sodium nitrite mixture is about five times as fast as that found when a mercuric chloride–sodium nitrite mixture is used. Also, the liquid product can be readily converted to the solid chloride salt by treatment with an aqueous alkali chloride solution. As might be anticipated from the data in Table I, the solubility of mercuric iodide is very low, even with nitrite ions present, and it gives little or no nitromercuration. Mercuric bromide is more effective than the iodide but less so than the chloride. Mercuric acetate leads predominantly to oxymercuration. However, oxymercuration can be suppressed by acidifying the solution moderately, for example, by adding acetic acid. Oxymercuration is likely to occur in nitromercurating solutions which have stood too long before use, because of the decrease in nitrite ion concentration as a result of the spontaneous reaction illustrated in eq 7 (above). For the same reason, slow or unduly prolonged nitromercurations are always accompanied by some oxymercuration.

Relative Concentrations of Reagents.—The stoichiometric ratios of reactants required by eq 8, are 1:1:1.
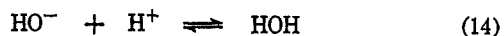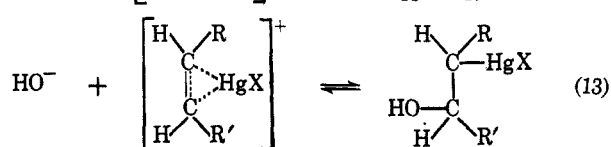
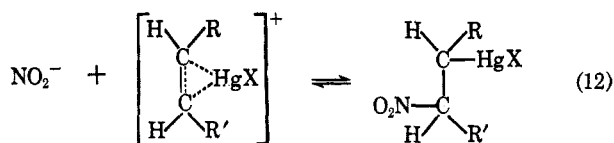$$-\overset{|}{C}=\overset{|}{C}- + HgCl_2 + NaNO_2 = ClHg\overset{|}{C}-\overset{|}{C}NO_2 + NaCl \quad (8)$$
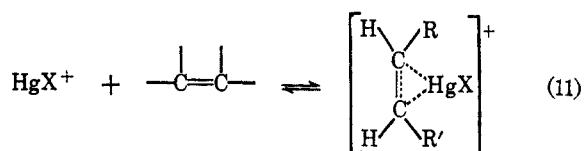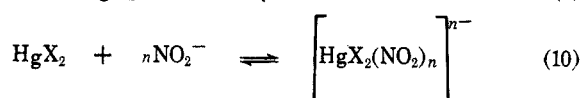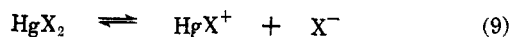
Any variations in these ratios affected conversions based on any one reactant according to the law of mass action. In general a 1:1:2 ratio worked quite satisfactorily, and conversions based on HgCl$_2$ given in Table II were obtained using these ratios. However, conversions also depend on total concentrations of reactants in an inverse relationship, so that better conversions were obtained with more dilute solutions. This probably arises from the effect of dilution in reversing eq 6, indicating that Hg^{2+} or ClHg$^+$ and NO$_2^-$ ions are necessary for the reaction to occur. The results of Table II were obtained using 0.25–0.53 m solutions of mercuric salts. With 2.5 m solutions of reagents no nitromercuration occurs and any preformed nitromercurial is decomposed with regeneration of olefin. More concentrated solutions are also more unstable to the decomposition of eq 7 and rapidly begin to deposit mercurous chloride and become acidic.

Reactions of Nitromercurials.—Aliphatic mercurials exhibit a tendency to regenerate the olefin from which they are derived on treatment with a wide variety of reagents.[3] Nitromercurials appear to be even more sensitive in this respect. Acids (including 5% hydrochloric acid and acetic acid), bases (including 5% aqueous sodium hydroxide, pyridine, aqueous ammonia, and dimethylformamide), salts (including those supplying ions which complex strongly with either mercuric or nitrite ions), and solvents (which complex readily with mercuric salts) decompose them, usually with regeneration of the olefin. Even essentially neutral reducing agents, such as diborane, Raney nickel, and ethyl phosphite react to give mercury and olefin. The Hg–C bond has been cleaved selectively in many cases

with halogens or halogenating agents[9] to give CX products, where X is halogen. When 1-chloromercuri-2-nitropropane was chlorinated, the reaction was slow, and some dozen different products were formed with no one of them predominating. Better success was obtained in the action of bromine on 1-chloromercuri-2-nitrocyclohexane, which yielded 1-bromo-2-nitrocyclohexane. Most of these reactions indicate the ease with which the equilibrium reactions involved in formation of nitromercurials are reversed.

Mechanism of Nitromercuration.—The following equilibria play significant roles in nitromercuration and offer rational explanations of the observed facts.

$$HgX_2 \rightleftharpoons HgX^+ + X^- \tag{9}$$

$$HgX_2 + nNO_2^- \rightleftharpoons \left[HgX_2(NO_2)_n\right]^{n-} \tag{10}$$

$$HgX^+ + -\overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}}- \rightleftharpoons \left[\begin{array}{c} H \diagdown \diagup R \\ C \\ \vdots \diagup HgX \\ C \\ H \diagup \diagdown R' \end{array}\right]^+ \tag{11}$$

$$NO_2^- + \left[\begin{array}{c} H \diagdown \diagup R \\ C \\ \vdots \diagup HgX \\ C \\ H \diagup \diagdown R' \end{array}\right]^+ \rightleftharpoons \begin{array}{c} H \diagdown \diagup R \\ C—HgX \\ O_2N—C \\ H \diagup \diagdown R' \end{array} \tag{12}$$

$$HO^- + \left[\begin{array}{c} H \diagdown \diagup R \\ C \\ \vdots \diagup HgX \\ C \\ H \diagup \diagdown R' \end{array}\right]^+ \rightleftharpoons \begin{array}{c} H \diagdown \diagup R \\ C—HgX \\ HO—C \\ H \diagup \diagdown R' \end{array} \tag{13}$$

$$HO^- + H^+ \rightleftharpoons HOH \tag{14}$$

X is an anion such as halide, nitrate, or nitrate and n is 1 or 2

Mercuration has been shown to follow second-order kinetics[3] (first order in mercuric salt and first order in olefin), to give Markovnikov orientation[3] (signifying electrophilic attack on the olefin in the rate-controlling step), to be stereospecific[3] (signifying an intermediate not free to rotate about the C–C bond), to produce *trans* adducts[10] (signifying rearward attack by the anion) except in strained bicyclic olefin systems,[10,11] and probably to involve a cyclic mercurinium ion[12] as an intermediate.[3]

The evidence obtained indicates that nitromercuration proceeds similarly to other mercurations of olefins. However, the fact that nitro compounds are produced

rather than nitrites requires further consideration. The mercurinium ion may be represented as a complex involving partial positive charges on each atom in the ring. Since HgX$^+$ possesses a low degree of electro-

$$\begin{array}{c} X \\ | \\ \delta^+ Hg \\ \delta^+ \diagup \diagdown \delta^+ \\ R\overset{|}{C}\text{---}\overset{|}{C}R' \\ | \quad | \\ H \quad H \end{array}$$
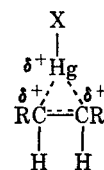
negativity,[13] the partial positive charges on the carbon atoms will also be low, and there will be little carbonium ion character developed on either of them. As a consequence, attack by the ambident nitrite anion is slow and reversible, and thermodynamically rather than kinetically controlled.[14] The situation is analogous to the previously discussed C acylation of nitronate anions.[15] In both cases C–O bond formation, which is usual in faster irreversible reactions, is overcome by formation of a less polar bond between carbon and an atom of lower electronegativity than oxygen.

Experimental Section[16]

Nmr Spectra.—The spectra were measured on a Varian A-60 nmr spectrometer and are reported in units of τ relative to tetramethylsilane as an internal standard. Concentrated or saturated solutions were necessary in order to obtain a satisfactory signal to noise ratio for the mercury satellite peaks as well as for the proton peaks, primarily because of the low solubility of the nitromercurial products. A variety of solvents was employed to obtain suitable spectra.

Infrared Measurements.—The measurements were made with Perkin-Elmer recording spectrophotometers, Models 21, 221, and 421. The solid compounds were measured in Nujol and/or Fluorolube mulls as well as in chloroform solutions, when necessary.

Ultraviolet Measurements.—All measurements were made with a Bausch & Lomb Spectronic 505.

General Procedure for the Preparation of β-Nitromercurials.—The mercuric salt (1 mole) was dissolved with stirring in a solution of alkali nitrite (2 moles) in water (2 l.). The olefin (1 mole) was added to this pale yellow solution, and vigorous stirring at room temperature was maintained until precipitation of the adduct was apparently complete.[17,18] The product was separated by filtration and recrystallized from a dichloromethane–petroleum ether (bp 35–37°) mixture.[19] The filtrate was treated with dilute potassium iodide solution (avoiding an excess) to precipitate any oxymercurial formed as the oxymercuric iodide and any unreacted inorganic mercuric salt as mercuric iodide. The oxymercuric iodide could be separated and purified by recrystallization from chloroform–petroleum ether.

With mercuric chloride or bromide the product precipitated as a crystalline solid, but with mercuric nitrate or acetate the product precipitated as a heavy, viscous oil which was separated from the aqueous layer, dissolved in dichloromethane, shaken with an aqueous solution of an alkali chloride, and recrystallized as the nitroalkylmercuric chloride after adding petroleum ether. The oil from both mercuric nitrate and acetate appeared to be a

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(10) T. G. Traylor and A. W. Baker, *ibid.*, **85**, 2746 (1963), and references therein.

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(12) H. J. Lucas, F. R. Hepner, and S. Winstein, *J. Am. Chem. Soc.*, **61**, 3102 (1939).

(13) L. Kaplan, H. Kwart, and P. von R. Schleyer, *ibid.*, **82**, 2341 (1960).

(14) A. G. Catchpole, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 11 (1948).

(15) G. B. Bachman and T. Hokama, *J. Am. Chem. Soc.*, **81**, 4882 (1959).

(16) Melting points are uncorrected.

(17) The absence of a precipitate of mercuric oxide upon the addition of caustic alkali to a sample of the mixture is usually taken to indicate completion of mercuration reactions. However, this test does not appear to be entirely reliable: G. F. Wright, *J. Am. Chem. Soc.*, **57**, 1993 (1935).

(18) The production of nitromercuration adducts from simple olefins is initially rapid. Prolonging the reaction beyond this period appears to offer little advantage. The disadvantages include an increase in oxymercuration as well as decomposition of the nitromercuration mixture.

(19) The crude, impure nitromercurial is easily decomposed by prolonged heating in solvents which boil above 50°. When purified, it can also be recrystallized, with caution, from benzene or chloroform.

TABLE III
PROTON RESONANCE VALUES AND MERCURY–PROTON COUPLING CONSTANTS OF β-NITROMERCURIALS

Compd	Solvent	τ_{C_1H}	τ_{C_2H}	τ_{C_3H}	τ_{C_4H}	τ_{C_5H}	J_{Hg-C_1H}
O_2N–CH_2CH_2–$HgCl$ (I) 2 1	C_6H_5CN	7.72ᵃ	4.10ᵃ				b, j
	$CHBr_3$	7.60	5.18				
	Dioxane	7.91	5.38				
$CH_3CH(NO_2)CH_2$–$HgCl$ (II) 3 2 1	Dioxane	7.75ᵇ	5.06ᶜ	8.39ᵇ			227.0ᵉ,ᵏ
	$CHBr_3$	7.59	4.93	8.29			212.9ᶜ,ᵏ
	Pyridine	7.55	4.83	8.45			
	$CDCl_3$	7.69	4.95	8.43			
$CH_3CH_2C(CH_3)(NO_2)CH_2$–$HgCl$ᵈ (III) 4 3 3 1	$CDCl_3$	7.58ᵉ		8.32ᵉ	7.96ᶠ	9.05ᵃ	312.0ᵉ,ᵐ
$(CH_3)_2CHCH(NO_2)CH(HgCl)CH_3$ (IV) 5 4 3 2 1	C_6H_5CN	8.53ᵇ	7.14ᵍ	5.35ᶠ	Ca. 8ᵍ	9.04ⁱ	241.2ᵏ,ⁿ
	$CHBr_3$	8.55	7.14	5.48	Ca. 8	8.95	240.8ᵒ
	Pyridine	8.67	7.12	5.32	Ca. 8	9.13, 9.10	236.3ᵒ
	Dioxane	8.62	Ca. 7.3	5.45	Ca. 8	9.03, 8.97	
$(CH_2)_4CH(NO_2)CH$–$HgCl$ (V) 2 1	$CHBr_3$	7.06ᶜ	5.22ᶜ				l
	$CDCl_3$	7.10	5.25				

ᵃ Triplet. ᵇ Doublet. ᶜ Sextet. ᵈ For conveniences of tabulation, resonance data for C₃, and C₄ of this compound are listed under τ_{C_4} and τ_{C_5}, respectively. ᵉ Singlet. ᶠ Quartet. ᵍ Doubled quartet, partially obscured by the noise level. ʰ Poorly resolved isopropyl methine multiplet. ⁱ Apparently a triplet, though actually two overlapping, closely spaced doublets, resolvable in pyridine and in dioxane. ʲ Satellite peaks noted but poorly resolved. ᵏ Doublets. ˡ Not located. ᵐ Singlet J_{Hg-C_3H} coupling constant of 15.5 was also noted. ⁿ High-field mercury satellite peaks obtained by offsetting spectrum by 250 cps above TMS. ᵒ Coupling constants derived by doubling the distance from the resonance peak of the CH_3CHgCl group to the low-field mercury satellite doublet.

β-nitroalkylmercuric nitrite, as evidenced by positive tests for nitrite ion obtained with the alkali chloride wash water after the β-nitroalkylmercuric nitrite had been converted to its chloride derivative. Such compounds, the liquid products, are relatively unstable, and they decompose in a few hours with the evolution of oxides of nitrogen and the deposition of mercurous salts. In order to avoid oxymercuration using mercuric acetate, the pH of the solution was adjusted to 4.3–4.5 with acetic acid.

With gaseous olefins more than 1 mole equiv was needed to obtain good conversions unless the rate of addition of olefin was tediously slow. Efforts to improve this situation by the use of solvents (miscible or immiscible with water) were unsuccessful. Use of gaseous olefins under pressure also did not improve conversions, although the reaction was considerably faster. It was found necessary to flush the pressure flask at intervals to remove oxides of nitrogen generated during the reaction.

Structures of Nitromercurials.—Structures were assigned with the aid of elemental analyses and ultraviolet, infrared, and nmr spectra. Nitro group absorptions at about 280 mμ in the ultraviolet[20] and at about 6.5 and 7.3 μ in the infrared[21] were characteristically present. The nmr spectra were measured in several different solvents in each case (Table III) and revealed numerous structural details compatible only with the proposed formulas. Thus, for example, 1-chloromercuri-2-nitropropane (II) showed an Hg¹⁹⁹–H¹ satellite peak at 227.0 cps[22] centered about the methylene doublet of the CH_2HgCl group at 7.75. This proved the presence of an Hg–C σ bond and also the Markovnikov-like orientation of the addition reaction. Similar coupling constants permitted location of the Hg atom in the other products. In 1-chloromercuri-2-nitrocyclohexane (V) the two coupling constants (J_{aa} = 10.0 cps and J_{ae} = 3.6 cps) about the $CHNO_2$ sextet at τ 5.22 and the two coupling constants (J_{aa} = 10.5 cps and J_{ae} = 3.6 cps) about the $CHHgCl$ sextet at 7.06 demonstrate the *trans* configuration of the product.[23,24] In methyl 2-chloromercuri-3-nitropropionate the infrared spectrum showed a carbonyl band at 1710 while methyl propionate itself shows a carbonyl band at 1740 cm⁻¹. This shift of 30 cm⁻¹ demonstrates that the chloromercuri group was in the position α to the ester group.[25,26] Similar shifts of carbonyl frequencies in 2-nitro-2-

methyl-3-chloromercuri-4-pentanone demonstrated the α position of the chloromercuri group in this compound also. The presence of two carbonyl bands at 1683 and at 1670 cm⁻¹ may be attributed to the presence of two spatial arrangements arising from restricted rotation about the C–CO single bond. Similar effects have been observed with α-halogen-substituted aldehydes and ketones.[27]

Reactions of Nitromercurials. Bromination of 1-Chloromercuri-2-nitrocyclohexane.—To a slurry of 20.74 g (0.057 mole) of 1-chloromercuri-2-nitrocyclohexane in 100 ml of water was added dropwise 6.12 ml (0.12 mole), of bromine. Diethyl ether (50 ml) was added to the reaction mixture after about 10 min when a semisolid mass settled from solution. After 12 hr the reaction mixture was extracted with fresh diethyl ether and the extracts were dried. Addition of cold chloroform to the ethereal extract yielded 12.72 g (62.0% conversion) of mercuric bromide. The chloroform solution was concentrated to yield a viscous, red liquid, which was column chromatographed through neutral alumina with petroleum ether (60–70°). The eluent was collected and concentrated *in vacuo* to yield 10 ml (ca. 15–20 g) of a yellow, lachrymatory liquid. Vacuum distillation gave 1-bromo-2-nitrocyclohexane: bp 75–77° (0.4 mm), $n^{25}D$ 1.5113. The instability of this compound prevented obtaining very accurate elemental analyses.

Anal. Calcd for $C_6H_{10}BrNO_2$: C, 34.64; H, 4.84; Br, 38.41; N, 6.73. Found: C, 35.15; H, 5.04; Br, 38.72; N, 6.16.

The bromonitrocyclohexane was shown not to be 1-bromo-1-nitrocyclohexane by the fact that the infrared spectrum of the isolated compound showed nitro group absorption bands at 6.45 and 7.31 μ, which were not in agreement with the reported values[21] of 6.35 ± 0.02 and 7.42 ± 0.03 μ for the nitro group absorption bands of compounds containing the *gem*-halonitro system ($XCNO_2$, where X is Cl or Br). Since the bromination of *trans*-1-chloromercuri-2-nitrocyclohexane was carried out in a heterogeneous mixture of water and diethyl ether, it is probable[28] that the product was a mixture of the *cis* and *trans* isomers.

(20) R. N. Hazledine, *J. Chem. Soc.*, 2525 (1953); H. E. Ungnade and R. A. Smiley, *J. Org. Chem.*, **21**, 993 (1956); H. E. Ungnade and L. W. Kissinger, *ibid.*, **22**, 1088 (1957).

(21) J. F. Brown, *J. Am. Chem. Soc.*, **77**, 6431 (1955).

(22) S. Brownstein [*Discussions Faraday Soc.*, **34**, 25 (1962)] has found that for a series of β-methoxymercurials the spin-coupling constants between Hg¹⁹⁹ and the protons on the carbon atom directly attached to mercury are within 10 cps of the value 215 cps, regardless of the anion attached to mercury.

(23) M. M. Anderson and P. M. Henry, *Chem. Ind.* (London), 2053 (1960).

(24) A. C. Huitric, J. B. Carr, W. F. Trager, and B. J. Nist, *Tetrahedron*, **19**, 2146 (1963); W. F. Trager, F. F. Vuncenzi, and A. C. Huitric, *J. Org. Chem.*, **27**, 3006 (1962).

(25) Introduction of a mercury atom α to the carbonyl group of ketones and aldehydes shifts the carbonyl absorption band to lower frequencies by some 50–80 cm⁻¹: A. N. Nesmeyanov, L. A. Kazitsyna, I. F. Lutsenko, and G. A. Rudenko, *Proc. Acad. Sci. USSR*, **127**, 971 (1959).

(26) Introduction of a nitro group α to the carbonyl group of ketones and acid esters shifts the carbonyl absorption band to higher frequencies by some 20–30 cm⁻¹: ref 21; T. Hokama, Ph.D. Thesis, Purdue University, 1958; H. L. Finkbeiner and M. Stiles, *J. Am. Chem. Soc.*, **85**, 616 (1963); R. M. Silverstein and G. C. Bassler, "Spectrometic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, pp 62–64.

(27) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, pp 139–160.

(28) Cleavage of the Hg–C bond with bromine and other brominating agents under polar conditions occurs stereospecifically and with retention of configuration while, under free-radical conditions with molecular bromine in nonpolar solvents, a mixture of *cis* and *trans* products results: ref 9.

Chlorination of 1-Chloromercuri-2-nitropropane.—Passage of chlorine gas through a slurry of 1-chloromercuri-2-nitropropane in chloroform for 2 hr led to evolution of some NO_2 fumes and precipitation of 57% of the mercury as its dichloride. From the chloroform were recovered 21% of starting material and 10 ml of a yellow, lachrymatory liquid which contained at least 12 components as indicated by gas chromatographic analyses. None of these corresponded to the expected 1-chloro-2-nitropropane. They were not identified.

Other Reactions of 1-Chloro-2-nitropropane (II).—Triethyl phosphite in refluxing dioxane gave triethyl phosphate, nitric oxide in small amounts, and propylene. No other indentifiable products were found. Acetyl chloride[29] in excess, refluxed for 11 hr, gave no nitro ketone. Although dilute hydrochloric acid decomposes β-nitromercurials immediately to the corresponding olefins, 25% nitric acid may be warmed to about 90° with 1-chloro-2-nitropropane before rapid evolution of oxides of nitro-

gen occurs. The product contained no identifiable nitro aliphatic compound. Both dilute and concentrated solutions of sodium hydroxide decompose β-nitromercurials rapidly with deposition of metallic mercury, evolution of olefin, and formation in small amounts of gummy organic solids. Steam distillation of the solid yielded no organic product.

Many attempts were made to reduce β-nitromercurials to nitro alkanes, but without any success. Agents tried included a copper–zinc couple in water, sodium borohydride, diborane, platinum oxide and hydrogen, Raney nickel in alcohol, stannous chloride dihyrate in ethyl acetate, and mercury–mercurous chloride in chloroform.

(29) H. Gilman and G. F. Wright [*J. Am. Chem. Soc.*, **55**, 3302 (1933)] have shown that furan organomercurials can readily be converted to the corresponding furan methyl ketones by the action of acetyl chloride.


Nitrile Oxides. IX. Basic, Substituted, Stable Nitrile Oxides[1]

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Nitrile oxides of the benzene and pyrimidine series, stabilized by controlled steric hindrance and substituted by a dimethylamino group, are described, and some of their reactions are discussed. These compounds are the first isolated nitrile oxides which contain an additional different functional group.

The wide variety of organic structures which react spontaneously with nitrile oxides[2] considerably restricts the chances of obtaining nitrile oxides with functional groups. Aside from some difunctional nitrile oxides,[2b] no compounds containing another true functional group have been isolated so far.[3] Since a common procedure for the preparation of nitrile oxides consists in the dehydrohalogenation of hydroxamyl chlorides by triethylamine,[4] it can be

$$RC(NOH)Cl + NEt_3 \longrightarrow RC{\equiv}N{\rightarrow}O + HCl{\cdot}Et_3N$$
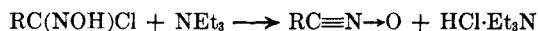
assumed that the tertiary amino group is compatible with the CNO group. There are, however, occasional observations that some hydroxamyl chlorides form rather stable quaternary salts with tertiary amines, especially pyridine.[3,5–7] The nitrile oxides described in this paper were protected from spontaneous dimerization to a furoxan (1,2,5-oxadiazole 2-oxide) by controlled steric hindrance, as previously described.[8]

The recently obtained[9] 4-dimethylamino-2,6-dimethylbenzaldehyde (I) and 4-dimethylamino-2,6-dimethylisophthaldialdehyde (II) were converted into the corresponding aldoximes and subjected to alkali hypobromite. Contrary to our experience with simple aromatic nitrile oxides, the dehydrogenation procedure worked satisfactorily only under the very specific conditions given in the Experimental Section. The oxime of I (III) was obtained in the two stereoisomeric forms (*syn* and *anti*). The structural assignment was based on the fact that by reaction with alkali or acetic anhydride, the lower melting isomer was transformed into the corresponding nitrile (VI) and was, therefore, the *anti* oxime, while the higher melting (*syn*) oxime remained unchanged, or yielded an acetate. Only the *syn* oxime reacted readily with alkaline hypobromite to yield 4-dimethylamino-2,6-dimethylbenzonitrile oxide (IV), while the *anti* isomer was converted in poor yield into 4-dimethylamino-3-bromo-2,6-dimethylbenzaldoxime (V).[10] From the outset of our studies of the hypohalogenite oxidation of aldoximes to nitrile oxides,[8] we had anticipated such steric effects, but in the case of the mesityllaldoximes, where both isomers are well known, we have failed to recognize such differences in reactivity, probably because in the alkaline environment the unfavorable (*anti*) configuration is converted rapidly into the favorable (*syn*) configuration. Apparently, it depends entirely on the rate of such alkali-induced isomerization whether steric effects will be observed. Contrary to other aromatic al-

(1) Paper VIII: C. Grundmann and H.-D. Frommeld, *J. Org. Chem.*, **31**, 4235 (1966).

(2) (a) C. Grundmann and H.-D. Frommeld, *ibid.*, **31**, 157 (1966); (b) C. Grundmann, *Fortsch. Chem. Forsch.*, **7**, 62 (1966), a review of the pertinent literature to 1965.

(3) R. H. Wiley and B. J. Wakefield [*J. Org. Chem.*, **25**, 546 (1960)] prepared 3,5-dichloro-2-hydroxy-benzonitrile oxide in carbon tetrachloride solution and identified the nitrile oxide by its infrared spectrum, but isolated only the corresponding furoxane.

(4) For a review, see C. Grundmann in Houben-Weyl, "Methoden der Organischen Chemie," Vol. X/3, 4th ed, E. Müller, Ed., Georg Thieme, Stuttgart, 1965, pp 841–870.

(5) H. Wieland and A. Höchtlen, *Ann.*, **505**, 237 (1933).

(6) A. Quilico, G. Gaudiano, and A. Ricca, *Gazz. Chim. Ital.*, **87**, 638 (1957).

(7) C. Grundmann, V. Mini, J. M. Dean, and H.-D. Frommeld, *Ann.*, **687**, 191 (1965).

(8) C. Grundmann and J. M. Dean, *Angew. Chem.*, **76**, 682 (1964); C. Grundmann and J. M. Dean, *J. Org. Chem.*, **30**, 2809 (1965).

(9) C. Grundmann and J. M. Dean, *Angew. Chem. Intern. Ed. Engl.*, **4**, 955 (1965).

(10) G. Just and K. Dahl [*Tetrahedron Letters*, 2441 (1966)] studied the oxidation of stereoisomeric aldoximes with lead tetraacetate and found that only the *syn* (*cis*) oximes gave nitrile oxides or products derived from them by secondary reactions.