chloroform (225 ml) was added 15 drops of absolute ethanol. After the solution was cooled to −15 to −20° (Dry Ice–CCl_4) the oxime (2.8–4.0 g) was added and then chlorine gas was bubbled through the solution at a moderate rate for 25–35 min. The reaction mixture was allowed to stand at −20° for 2 hr, and then at room temperature for 6–8 hr. The solution was flushed with nitrogen gas to remove excess chlorine. Filtration and subsequent evaporation of the filtrate gave an oil. The benzohydroxamoyl chloride was crystallized by adding pentane and immersing the solution in a Dry Ice–acetone bath for 15 min. The crystals were filtered and dried in a vacuum desiccator. Yields of pure **5** follow: R = C_6H_5, 56%; R = 4-ClC_6H_4, 79%; R = 4-$C_6H_5C_6H_4$, 42%; R = 4-$NO_2C_6H_4$, 84%; R = 2,6-$Cl_2C_6H_3$, 62% [mp 92–93° (lit.[12] mp 93–94°). *Anal.* Calcd for $C_7H_4Cl_3NO$: C, 37.44; H, 1.80; N, 6.24. Found: C, 37.44; H, 1.76; N, 6.31 (Dondoni and coworkers[12] claimed that this compound could not be prepared by direct chlorination of the oxime)]; R = 4-FC_6H_4, 74% (mp 72–73°. *Anal.* Calcd for C_7H_5ClFNO: C, 48.44; H, 2.90; N, 8.07. Found: C, 48.09; H, 2.73; N, 8.29.).

Compound **5**, R = 2,4,6-$(CH_3O)_3C_6H_2$, was prepared from the nitrile oxide following the procedure of Grundmann and Dean.[13]

General Procedures for Conversion of Benzohydroxamoyl Chlorides to Nitriles. A. $Fe(CO)_5$.—To a dried, deoxygenated solution to THF (40–50 ml) was added the benzohydroxamoyl chloride (5.0–8.7 mmol) followed by $Fe(CO)_5$ [2:1 mole ratio of $Fe(CO)_5$:5]. The mixture was refluxed (expect for **5**, R = 4-$NO_2C_6H_4$, where a reaction temperature of 60° was used) with stirring for 18–24 hr, cooled, and filtered, and pentane (100 ml) was then added to the filtrate. After standing in the refrigerator overnight, the solution was filtered, and the filtrate was flash evaporated. The residual nitrile (**10**) obtained from flash evaporation was then purified, if necessary, by sublimation, recrystallization (*n*-heptane), or distillation. The yields of nitrile are given in Table I.

B. $Fe_3(CO)_{12}$–CH_3OH.—A mixture of $Fe_3(CO)_{12}$ (2.92 g, 4.3 mmol) and methanol (1.0 ml) in benzene (55 ml) was refluxed with stirring for 8 hr. The solution was cooled, the benzohydroxamoyl chloride (4.52 mmol) was added, and the resulting mixture was refluxed for 17–22 hr. The solution was cooled and filtered, and the filtrate was evaporated to afford reasonably pure nitrile. Further purification, if required, could be effected as described in A. The two products obtained from 4-nitrobenzohydroxamoyl chloride were separated by chromatography on Florisil or by trituration with hexane. 2,6-Dichlorobenzaldoxime failed to react with $Fe_3(CO)_{12}$–methanol under these conditions.

Reaction of 2,6-Dichlorobenzohydroxamoyl Chloride with $Fe_2(CO)_9$.—A mixture of $Fe_2(CO)_9$ (1.72 g, 4.72 mmol) and 2,6-dichlorobenzohydroxamoyl chloride (0.825 g, 3.60 mmol) in benzene (50 ml) was stirred at room temperature for 2 hr. The solution was filtered and evaporation of the filtrate gave 2,6-dichlorobenzonitrile and the nitrile oxide. The benzene-insoluble solid apparently was an iron tetracarbonyl complex (see Results and Discussion) but was of low stability and could not be isolated in analytically pure form. Reactant **5**, R = 4-$C_6H_5C_6H_4$, behaved similarly when treated with $Fe_2(CO)_9$.

2,5-Diphenyl-1,3,4-dioxazole.—The general procedure described for the reaction of **5** and $Fe(CO)_5$ was repeated for **5**, R = C_6H_5, in the presence of a fivefold excess of benzaldehyde. Work-up as above gave 2,5-diphenyl-1,3,4-dioxazole, mp 38–40° (lit.[9] mp 41–42°), in 40% yield and benzonitrile in 14% yield.

General Procedure for Deoxygenation of Nitrile Oxides by $Fe(CO)_5$.—An equimolar mixture of nitrile oxide[13] (0.5–4.0 mmol) and $Fe(CO)_5$ in THF (20–50 ml) was refluxed with stirring for 1–2 hr. The reaction was worked up as described for the benzohydroxamoyl chloride–$Fe(CO)_5$ reaction. The nitriles were identified by comparison with authentic samples and by comparison with melting points and spectral data. Rearrangement of nitrile oxides to isocyanates[13] does not occur to a significant extent under these reaction conditions.

Acknowledgments.—Acknowledgment is made to the Research Foundation of the State University of New York, and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We are indebted to Hoffmann-La Roche, Inc., for carrying out the microanalytical determinations. Ms. R. Cartmell was kind enough to run some nmr spectra on the HA-100 spectrometer.

Registry No.—$Fe(CO)_5$, 13463-40-6; $HFe_3(CO)_{11}^-$, 25948-56-5.

(12) A. Dondoni, G. F. Pedulli, and G. Barbaro, *J. Org. Chem.*, **37**, 3564 (1972).

(13) C. Grundmann and J. M. Dean, *J. Org. Chem.*, **30**, 2809 (1965).

A New Method for the Conversion of Nitro Groups into Carbonyls

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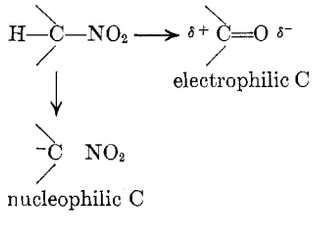
When a primary or secondary nitro compound is treated with aqueous $TiCl_3$, reduction occurs yielding an imine which hydrolyzes to the corresponding ketone or aldehyde. A study of the scope and mechanism has been carried out. A variety of functional groups including ketone, ester, nitrile, ketal, and hydroxyl survive the reaction conditions. Yields range between 45 and 90%. The reaction probably proceeds through a nitroso intermediate which then tautomerizes to an oxime and is further reduced to imine. Evidence in support of this mechanism is presented. The use of the reaction in organic synthesis is illustrated by a synthesis of *cis*-jasmone.

The nitro group is a function of great synthetic potential in organic chemistry because of the versatility with which it may react.[1] Acting as a strong electron withdrawer, a nitro group can activate a neighboring C–H bond for aldol or Michael-type additions to suitable acceptors. Conversely, nitro olefins can themselves act as excellent Michael acceptors. Nitro groups β to carbonyls can also act as leaving groups in β-elimination reactions—a property which we recently took advantage of in our synthesis of α-methylenebutyrolactones.[2] Acting in yet other ways, nitro groups can be converted into other useful functional groups such as amines or carbonyls. This latter conversion is of considerable interest and utility because it in effect reverses



(1) For a review of the chemistry of nitro groups, see H. Feuer, Ed., "The Chemistry of the Nitro and Nitroso Groups," Wiley-Interscience, New York, N. Y., 1969.

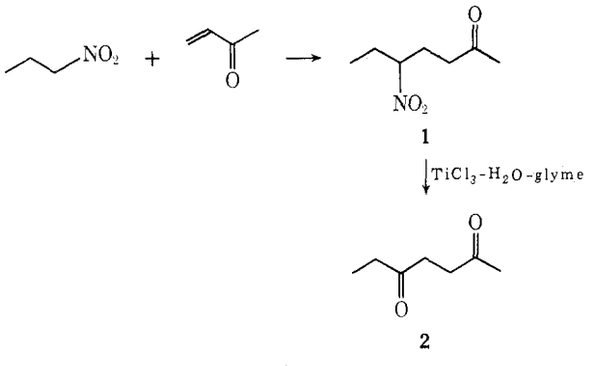
(2) J. W. Patterson and J. E. McMurry, *Chem. Commun.*, 488 (1971).

the polarity of the neighboring carbon from nucleophilic to electrophilic, thus allowing a wide range of transformations to be carried out.

Current methods for effecting this conversion, however, are either incompatible with the presence of other sensitive functionality within the molecule or proceed in low yield. Thus the Nef reaction[3] is an acidic method which is incompatible with the presence of a ketal function; permanganate oxidation of nitronate anions[4] is incompatible with other easily oxidized functional groups; persulfate oxidation of nitronates[5] proceeds in low yield. We therefore sought an effective, mild method for performing the nitro → carbonyl transformation.

In a recent communication, Timms and Wildsmith reported[6] that oximes are rapidly reduced by aqueous titanium trichloride to imines which are then hydrolyzed to carbonyl compounds in high overall yield. Since oximes might be expected to occur as intermediates in the reduction of primary and secondary nitro compounds, we investigated the action of aqueous Ti^{III} on aliphatic nitro compounds in the hope that they too might be reduced to imines, and thence, by hydrolysis, to ketones.

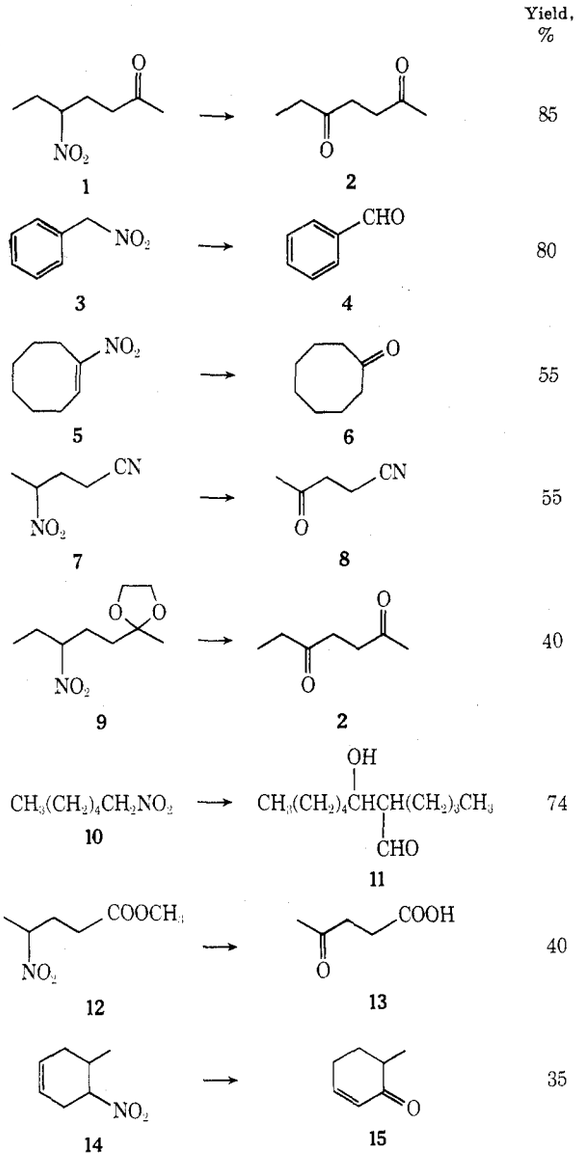
For a model system, we examined the reduction of 5-nitroheptan-2-one (1) prepared by diisopropylamine-catalyzed addition of 1-nitropropane to methyl vinyl ketone (MVK). Addition of an aqueous solution of 4 equiv of $TiCl_3$ to a solution of **1** in glyme at room temperature resulted in the slow disappearance of the deep purple Ti^{III} color. After 6 hr, vpc analysis indicated the absence of starting material and the presence of a single new product. After work-up, 2,5-heptanedione was isolated in 85% yield.[7]



The feasibility of this new method had therefore been established and we began a study of the reaction's scope.

It quickly became apparent that, although simple nitro compounds underwent ready transformation to the corresponding ketones in good yields (**1** → **2**, 85%; α-nitrotoluene → benzaldehyde, 80%; nitrocyclooctene → cyclooctanone, 55%), our conditions were still too vigorous (pH <1) for acid-sensitive functional groups to survive. For example, nitro ketal **9** was reduced and hydrolyzed to diketone **2** in the course of the reaction; hexanal (from 1-nitrohexane) aldolized during the reaction to give the dimer **11**; nitro ester **12** was reduced and hydrolyzed to the corresponding keto acid **13**; nitro olefin **14** was reduced and isomerized to α,β-enone **15** under the reaction conditions. These transformations are summarized in Table I.

TABLE I
REACTION OF NITRO COMPOUNDS WITH AQUEOUS $TiCl_3$ SOLUTIONS (pH <1)



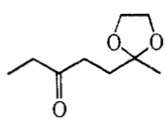
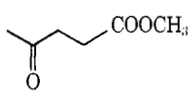
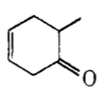
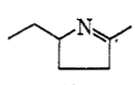
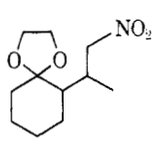
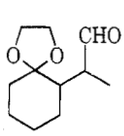
Because of these difficulties, we therefore sought milder conditions under which we could carry out the reaction. The obvious solution was to raise the pH of the reaction medium, and we chose to do this by adding ammonium acetate as a buffer. In the proportion $NH_4OAc:TiCl_3$ of 6:1, the pH of the reaction was approximately 6 and reduction still occurred at a rate similar to that at pH <1. We immediately found that under these near neutral conditions a marked improvement in some of the reactions could be made. For example, the nitro ketal **9** now gave the desired keto ketal **16** in 70% yield. Similarly, the nitro ester **12** gave the desired keto ester **17** (35%) and nitro olefin **14** gave β,γ-enone **18** (30%), although yields were still not acceptable.

(3) For a review of the Nef reaction, see W. E. Noland, *Chem. Rev.*, **55**, 137 (1955).
(4) H. Shechter and F. T. Williams, *J. Org. Chem.*, **27**, 3699 (1962).
(5) A. H. Pagano and H. Shechter, *J. Org. Chem.*, **35**, 295 (1970).
(6) G. H. Timms and E. Wildsmith, *Tetrahedron Lett.*, 195 (1971).
(7) A preliminary account of this work has already appeared: J. E. McMurry and J. Melton, *J. Amer. Chem. Soc.*, **93**, 5309 (971).

Much to our surprise, however, several nitro compounds gave worse results under these neutral conditions than under acidic conditions. For example, nitro ketone **2** gave none of the expected diketone **3** but gave rather, as the only isolable organic compound, the pyrroline **19** (20%). Similarly, 1-nitrohexane now gave aldol dimer plus azoxy-*n*-hexane. These results are given in Table II.

TABLE II

REACTION OF NITRO COMPOUNDS WITH $TiCl_3$–NH_4OAc (1:6) AT pH 6

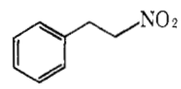
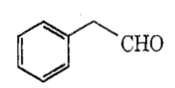
			Yield, %
5	→	6	70
9	→	 **16**	70
12	→	 **17**	35
14	→	 **18**	30
10	→	**11** (45%) + $C_6H_{13}N{=}NC_6H_{13}$ (O↑)	20
1	→	 **19**	20
 **23**	→	 **24**	70

These unexpected results are saying something about the mechanism of the reduction but, leaving this aside for the moment, it is still clear that better conditions are needed in some cases. After considering the possible mechanism of the reaction (*vide infra*), and after further experimentation, we found that, if we first formed the sodium salt of the nitro compound (1 equiv of $NaOCH_3$ in CH_3OH) and then added this salt to an aqueous solution of $TiCl_3$–NH_4OAC (1:3, pH ~ 5–6), reaction occurred within minutes at room temperature and the desired carbonyl compounds could be isolated in good yields in all cases.

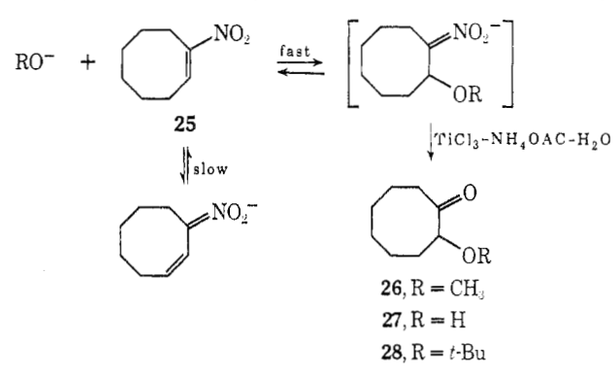
Thus, to dwell on only the more delicate cases, the nitro ester **12** could be transformed into methyl levulinate (**17**, 90%); nitro nitrile **7** similarly was converted in 90% yield to keto nitrile **8**; β-nitrophenylethane was converted to phenylacetaldehyde (70%); 1-nitrohexane gave hexanal (45%); and nitro olefin **14** was transformed into the β,γ-unsaturated ketone **18** in 60% yield. This last case is particularly noteworthy, because, in effect, a nitro olefin has served as a ketene equivalent in the Diels–Alder reaction with butadiene. This simple synthesis of β,γ-unsaturated cyclohexenones is thus complementary to the well-known Birch reduction of anisoles. These and other examples are shown in Table III.

TABLE III

REACTION OF NITRONATE ANIONS WITH $TiCl_3$–NH_4OAc (1:3) AT pH 6

			Yield, %
9	→	16	70
12	→	17	90
7	→	8	90
14	→	18	60
10	→	$CH_3(CH_2)CHO$ **22**	45
 **20**	→	 **21**	70
23	→	**24**	90

One further point we wanted to investigate was the reaction of conjugated nitro olefins with Ti^{III}. *A priori*, one might expect to obtain an α,β-unsaturated ketone from such a reaction. In fact, however, when we treated 1-nitrocyclooctene (**25**) with 1 equiv of $NaOCH_3$ in CH_3OH followed by treatment with 1:3 $TiCl_3$–NH_4OAc in water, a 70% yield of 2-methoxycyclooctanone (**26**) was formed. Similarly, if we used hydroxide in aqueous dioxane as the base, a 90% yield of 2-hydroxycyclooctanone could be isolated. Presumably the alkoxide adds to the olefin to give the 2-alkoxynitronate anion, which then reduces normally.



26, R = CH_3
27, R = H
28, R = *t*-Bu

Synthetically, this appears to be quite an attractive way to generate these rather difficultly accessible systems.

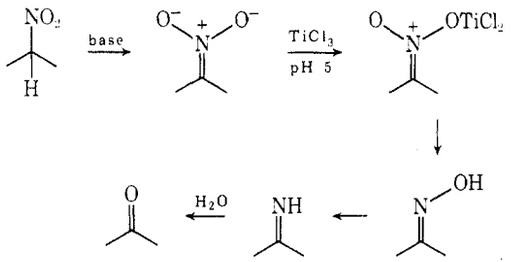
Mechanistically, however, this was a most unexpected result, since it has been reported[8] that treatment of a nitro olefin with ethoxide leads to the conjugated nitronate anion, not to the addition product. Interestingly, however, we have been able to show that the product obtained by treating a nitro olefin with alkoxide depends on the conditions used. When we treated 1-nitrocyclooctene with 1 equiv of $NaOCH_3$ in methanol followed rapidly by quenching the dilute acetic acid–sodium acetate buffer at 0°, we isolated 2-methoxy-1-nitrocyclooctane in near-quantitative yield. If, on the other hand, we allowed the base to react with 1-nitrooctene overnight followed by quenching, we recovered largely 1-nitrocyclooctene. Evidently the

(8) A. T. Neilsen, *J. Org. Chem.*, **27**, 2001 (1962).

addition product is kinetically formed whereas the conjugated nitronate anion is thermodynamically favored.

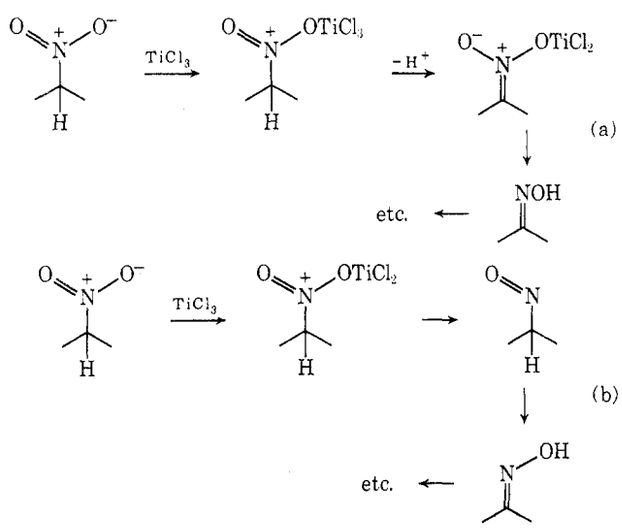
Mechanism.—As reported above, we have carried out two basic kinds of reactions: reactions on free nitro compounds at different pH's and reactions on nitronate anions. These two cases may well proceed by different mechanisms and we will consider them separately.

Reduction of Nitronate Anions.—Since Timms and Wildsmith have conclusively shown[6] that oximes reduce rapidly to imines with aqueous $TiCl_3$, we see no reason to assume that the reduction of nitronate anions is anything other than analogous. It can be written in the following way.



The details of the N–O bond cleavage steps are not clear (although radicals are probably involved since Ti^{III} is a one-electron reducing agent) but the general picture seems secure.

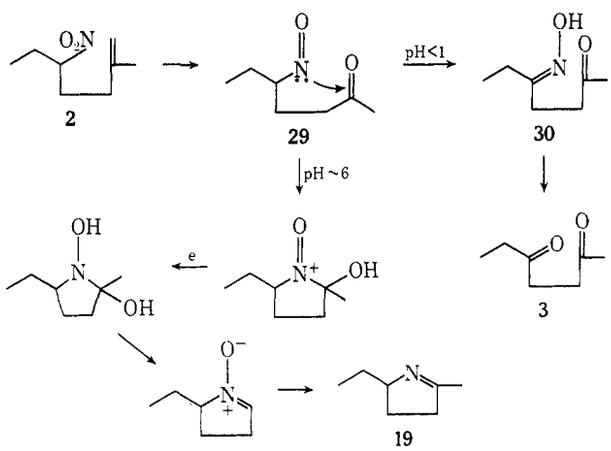
Reduction of Free Nitro Compounds.—The mechanism of reduction of free nitro groups is considerably less obvious, since one must deal with the question of when the C=N double bond is formed. Assuming that at some stage the titanium is covalently bound to nitro oxygen, we can conceive of two routes, a and b.



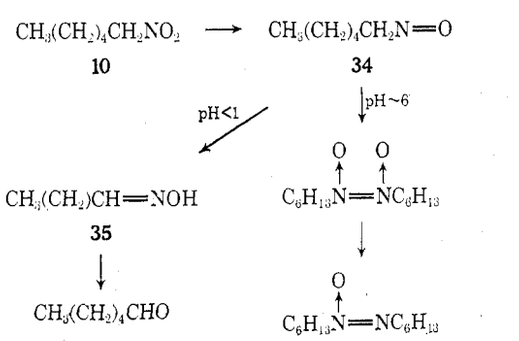
The major difference between the two concerns the timing of C=N double bond formation. In a, C=N double bond formation takes place while the titanium is still bound to oxygen, whereas in b the C=N double bond is formed *via* tautomerization of a discrete nitroso intermediate. We have found evidence pointing to b as the correct mechanism, and we believe that a nitroso compound is in fact an intermediate in the reaction. Our evidence is the following.

(1) The initial step in a is simply a Lewis acid (Ti^{III}) catalyzed tautomerization of the nitro compound to its acidform. It has been shown, however, that acid-catalyzed tautomerizations of nitro compounds are extremely slow.[9] Thus this mechanism is probably incorrect.

(2) As shown in Tables I and II, 5-nitroheptan-2-one (**2**) reduces normally to the diketone **3** at low pH, but gives only pyrroline **19** at neutral pH. We feel that this is best explained by assuming that nitroso compound **29** is an intermediate. At low pH, tautomerization to the oxime **30** would be rapid[10] and further reduction to the diketone would occur normally. At neutral pH, however, tautomerism of **29** to oxime **30** is slower,[10] and the nitroso group can therefore be trapped internally by the ketone carbonyl. Further reduction of the N–O bond followed by dehydration gives the observed pyrroline (**19**).



(3) The third piece of evidence in support of a nitroso intermediate comes from reduction of 1-nitrohexane. At pH <1, reaction occurs normally and hexanal is produced. At neutral pH, however, a mixture of hexanal (as the aldol dimer) and azoxy-*n*-hexane is formed. It is well known that nitroso compounds, particularly primary ones, dimerize quite readily to azodioxy compounds.[11] Evidently, 1-nitrosohexane (**34**) is an intermediate in the reduction of **10**. At low pH, **34** tautomerizes rapidly to oxime **35**, but, at neutral pH where tautomerization is slow, dimerization intervenes and further reduction occurs. It is interesting that only in the case of a primary nitro compound does this dimerization of the nitroso intermediate occur, but this is just what one would expect on steric grounds.

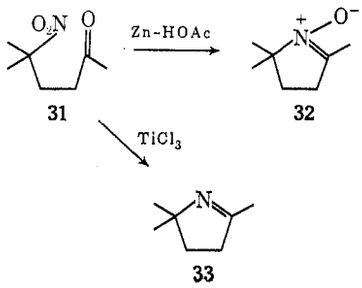


(9) A. T. Neilsen in "The Chemistry of the Nitro and Nitroso Groups," Vol. 1, H. Feuer, Ed., Wiley-Interscience, New York, N. Y., 1969, pp 370–372.

(10) M. H. Palmer and E. R. R. Russell, *Chem. Ind. (London)*, 157 (1966).

(11) J. H. Boyer in "The Chemistry of the Nitro and Nitroso Groups," Vol. 1, H. Feuer, Ed., Wiley-Interscience, New York, N. Y., 1969, pp 252–255.

There is good analogy in the literature for this cyclization. Zinc–acetic acid reduction of 5-methyl-5-nitrohexan-2-one (**31**) has been reported to yield the pyrroline 1-oxide **32**, presumably also through the intermediacy of a nitroso ketone.[12] Aqueous $TiCl_3$ is evidently able to carry the reduction one step further, for, when **31** is treated with $TiCl_3$, pyrroline **33** is the sole product isolated.



31 **32** **33**

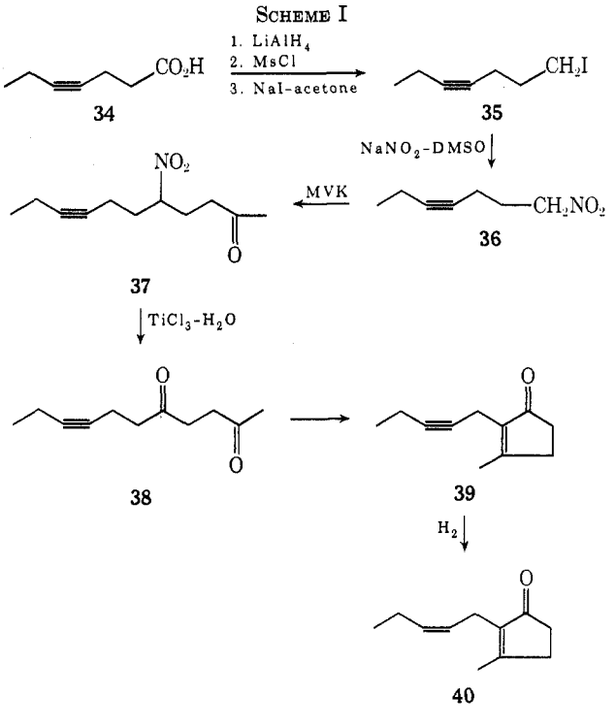
(4) Finally, one further point which should be made is that we have shown that hexanal oxime reduces normally to hexanal at pH ~6 and does not dimerize. Thus it cannot be an intermediate in the formation of azoxyhexane at this pH.

Synthesis of *cis*-Jasmone.—As stated at the outset, the nitro → carbonyl conversion is of great synthetic importance because it allows one to alter the polarity of the neighboring carbon atom. One consequence of this is the ability of a primary nitro compound to serve as a "carbonyl anion" equivalent.[13] We decided to demonstrate this process in a simple synthesis of the naturally occurring *cis*-jasmone (**40**).

4-Heptynoic acid[14] was reduced ($LiAlH_4$), and the resulting alcohol was mesylated. This mesylate was converted into the iodide by treatment with NaI in acetone, and the iodide was readily converted into the required primary nitro compound **36** with $NaNO_2$ in DMSO.[15] Taking advantage of the nucleophilic character of the nitro-bearing carbon, the diisopropylamine-catalyzed addition of **36** to MVK gave the desired nitro ketone **37** in 83% yield. Treatment of **37** in glyme with 4.5 equiv of aqueous $TiCl_3$ then gave the desired diketone **38** (85%), which was cyclized to dehydrojasmone (**39**) in 90% yield by treatment with refluxing 5% NaOH in aqueous ethanol. Hydrogenation of **39** over Lindlar catalyst[16] gave pure *cis*-jasmone (**40**, 95%), identified by comparison with an authentic sample[17] (Scheme I).

Summary.—In summary, we have developed, and refined conditions on, a new method of transforming a nitro group into a carbonyl. If the specific case is not acid sensitive, the simplest procedure is to treat the nitro compound with an unbuffered aqueous solution of $TiCl_3$. For sensitive cases, however, one should first form the nitronate anion, and then treat it with a buffered $TiCl_3$ solution.

SCHEME I



34 **35** **36** **37** **38** **39** **40**

Experimental Section

Preparation of Nitro Compounds.—4-Nitrovaleronitrile and methyl 4-nitrovalerate were prepared by the procedure of von Schickh.[18] 1-Nitrocyclohexene and 1-nitrocyclooctene were prepared according to Seifert.[19]

5-Nitroheptan-2-one (**1**).—1-Nitropropane (0.2 mol, 17.8 g) and diisopropylamine (10 ml) in 200 ml of chloroform were stirred at 60° under a nitrogen atmosphere. Methyl vinyl ketone (0.1 mol, 7.0 g) was added dropwise to this solution. After 3 hr, another portion of MVK (0.1 mol, 7.0 g) was added and the reaction was further stirred for 24 hr. The solution was then washed sequentially with water, 10% aqueous HCl, 5% $NaHCO_3$, and saturated brine, then dried (Na_2SO_4), concentrated, and distilled to yield nitro ketone **1** (17.0 g, 55%): bp 120° (10 mm); ir (neat) 1715, 1545 cm^{-1}; nmr (CCl_4) δ 0.97 (t, 3 H, J = 7 Hz), 2.7–2.5 (m, 6 H), 2.13 (s, 3 H), 4.38 (m, 1 H).

5-Nitroheptan-2-one Ethylene Ketal (**9**).—The nitro ketone **1** (10 mmol, 1.59 g) was dissolved in 5 ml of benzene, and ethylene glycol (12 mmol, 0.75 g) and 5 mg of *p*-toluenesulfonic acid monohydrate were added. The mixture was refluxed for 5 hr in a flask fitted with a Dean–Stark trap. The reaction solution was cooled and diluted with ether. After washing with 5% aqueous $NaHCO_3$ and brine, the organic phase was dried (Na_2SO_4) and concentrated, giving 1.98 g (98%) of crude nitro ketal **9**: ir (neat) 1545, 1040 cm^{-1}; nmr (CCl_4) δ 0.93 (t, 3 H, J = 7 Hz), 1.20 (s, 3 H), 2.2–1.3 (m, 6 H), 3.75 (s, 4 H), 4.5–4.0 (m, 1 H).

4-Nitro-5-methylcyclohexene (**14**).—A thick-walled glass tube was charged with 1-nitropropene[20] (9.0 g, 0.10 mol) and butadiene (4.5 ml). The tube was sealed and heated on a steam bath for 4 days to yield 6.54 g (46%) of **14**: bp 90° (10 mm); ir (neat) 3050, 1650, 1545 cm^{-1}; nmr (CCl_4) δ 0.95 (d, 3 H, J = 5.5 Hz), 3.0–1.5 (m, 4 H), 4.30 (m, 1 H), 5.53 (d, 2 H, J = 1.5 Hz). *Anal.* Calcd for $C_7H_{11}NO_2$: C, 59.56; H, 7.85. Found: C, 59.64; H, 7.87.

Nitro Ketal 23.—1-Nitropropene (2.0 g, 27.5 mmol) in 20 ml of acetonitrile was added dropwise to a stirred solution of morpholinocyclohexene (6.0 g) in 20 ml of acetonitrile at −20° and the reaction was let stir for 1 hr under a nitrogen atmosphere. Hydrolysis of the enamine was effected by addition of 30 ml of 1.5 *M* HCl. After extraction with ether, distillation gave 2.64 g (65%) of nitro ketone corresponding to **23**: bp 90° (7 mm); ir (neat) 1710, 1545 cm^{-1}; nmr (CCl_4) δ 1.00 (d, 3 H, J = 6 Hz), 3.5–1.30 (m, 9 H), 4.33 (d, 2 H, J = 6 Hz). The 2,4-DNP had

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mp 139–140°. *Anal.* Calcd for $C_{15}H_{19}N_5O_6$: C, 49.31; H, 5.24. Found: C, 49.41; H, 5.21.

General Procedures for $TiCl_3$ Reduction of Nitro Compounds. A. Reductions with Aqueous $TiCl_3$ at pH 1.—The alkyl nitro compound in an appropriate solvent (THF or dimethoxyethane, 0.2 *M*) was treated with 4 equiv of $TiCl_3$ (20% aqueous solution) and stirred under nitrogen at room temperature for the indicated time. The reaction mixture was then poured into ether and separated into phases. The aqueous phase was extracted several times with ether; the organic extracts were combined, washed with 5% $NaHCO_3$ and with brine, then dried (Na_2SO_4), concentrated, and distilled. The following examples were run.

α-Nitrotoluene (3).—Benzaldehyde was isolated in 80% yield after allowing α-nitrotoluene (**3**) to react for 18 hr in THF.

5-Nitroheptan-2-one (1).—Dione **2** was isolated in 66% yield after allowing **1** to react for 24 hr in THF: ir (neat) 1710 cm^{-1}; nmr (CCl_4) δ 2 60 (s, 4 H), 3.41 (q, 2 H, J = 7 Hz), 2.10 (s, 3 H), 1.00 (t, 3 H, J = 7 Hz). Dione **2** was further identified by cyclization with 5% aqueous NaOH to the known 2,3-dimethylcyclopentenone (85%), 2,4-DNP mp 226–227° (lit.[21] mp 226–227°).

1-Nitrohexane (10).—Hexanal aldol dimer (**11**) was isolated in 74% yield after allowing **10** to react for 18 hr in THF: ir ($CHCl_3$) 2730, 1680, 1640 cm^{-1}; nmr (CCl_4) δ 9.35 (s, 1 H), 6.4 (t, 1 H, J = 7.5 Hz), 2.5–2.0 (m, 4 H), 1.8–1.1 (m, 6 H), 1.1–0.8 (m, 6 H).

4-Nitrovaleronitrile (7).—Levulinonitrile (**8**) was isolated in 55% yield after allowing **7** to react for 2 days in THF, 2,4-DNP mp 146° (lit.[22] mp 146°).

Methyl 4-Nitrovalerate (12).—Methyl levulinate was isolated in 16% yield, plus 32% levulinic acid after allowing **12** to react for 12 hr in THF.

1-Nitrocyclooctene (5).—Allowing **5** to react for 2 hr in THF gave 55% **6**.

5-Nitroheptan-2-one Ethylene Ketal (9).—Keto ketal **16** was isolated in 40% yield after allowing **9** to react for 12 hr in THF.

4-Nitro-5-methylcyclohexene (14).—After reaction for 12 hr in THF, 6-methylcyclohex-2-en-1-one (**15**) was isolated in 35% yield.

B. Reduction of Nitro Compounds with Aqueous $TiCl_3$ at pH 5.—A buffered $TiCl_3$ solution was prepared by adding NH_4OAc (4.6 g, 0.06 mol) in 15 ml of H_2O to 20% aqueous $TiCl_3$ (0.01 mol) under nitrogen. Nitro compound in the appropriate solvent was added rapidly and the mixture was stirred for the indicated period at room temperature. Product isolation was carried out as in procedure A. The following examples were run.

2-Nitroheptan-2-one Ethylene Ketal (9).—Keto ketal **16** was isolated in 67% yield after reaction of **9** for 12 hr in dimethoxyethane: ir (neat) 1715, 1100, 1030 cm^{-1}; nmr (CCl_4) δ 0.97 (t, 3 H, J = 7 Hz), 1.18 (s, 3 H), 2.0–1.3 (m, 2 H), 3.6–2.0 (m, 2 H), 3.75 (s, 4 H). Ketal **16** was further identified by acidic hydrolysis to diketone **2**.

Nitro Ketal 23.—Ketal aldehyde **24** was isolated in 70% yield after stirring nitro ketal **23** for 12 hr in methanol: ir (neat) 2750, 1725 cm^{-1}; nmr (CCl_4) δ 0.96 and 1.00 (two doublets, 3 H, $J = J'$ = 7 Hz), 3.84 (s, 4 H), 9.1 and 11.1 (two doublets, 1 H, $J = J'$ = 4 Hz). *Anal.* Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.60; H, 9.14.

1-Nitrohexane (10).—After reaction of **10** for 3 hr in methanol, hexanal dimer (45%) and azoxy-*n*-hexane (20%) were isolated. Azoxy *n*-hexane had ir ($CHCl_3$) 1500 cm^{-1}; nmr ($CDCl_3$) δ 4.15 (t, 2 H, J = 7 Hz), 3.40 (t, 2 H, J = 7 Hz), 2.0–1.0 (m, 10 H), 1.0–0.6 (m, 6 H). An authentic sample was prepared for comparison purposes by the procedure of Greene,[23] and was identical in all respects.

5-Nitroheptan-2-one (1).—After 12 hr reaction in THF, 2-methyl-5-ethyl-Δ¹-pyrroline (**19**) was isolated (20%): ir (neat) 2975, 2940, 2880, 1650 cm^{-1}; nmr (CCl_4) δ 3.6 (m, 1 H), 2.20 (m, 2 H), 1.9 (d, 3 H, J = 1.5 Hz), 1.7–1.2 (m, 4 H), 1.2–0.7 (m, 3 H); picrate mp 126.5–127.5°. *Anal.* Calcd for $C_{13}H_{16}N_4O_7$: C, 45.89; H, 4.74. Found: C, 46.14; H, 4.80.

1-Nitrocyclohexene.—After reaction for 12 hr in methanol, a 42% yield of cyclohexanone was found.

1-Nitrocyclooctene (5).—After reaction for 12 hr in methanol, cyclooctanone was produced in 70% yield.

Methyl 4-Nitrovalerate (12).—After 12 hr in THF, methyl levulinate (**17**) was isolated (35%).

4-Nitro-5-methylcyclohexene (14).—After 12 hr reaction in THF, 6-methylcyclohex-3-en-1-one (**18**) was isolated (30%).

C. Reduction of Nitronate Anions with Aqueous $TiCl_3$ at pH 5.—The nitro compound was dissolved in methanol (0.5 *M*) and treated with 1 equiv of $NaOCH_3$. A buffered $TiCl_3$–NH_4OAc solution prepared as in procedure B was then added in one portion to the anion solution at room temperature under a nitrogen atmosphere. After an appropriate period, the reaction was worked up as in procedure A. The following examples were examined.

4-Nitro-5-methylcyclohexene (14).—After reaction for 45 min, 6-methylcyclohex-3-en-1-one (**18**) was isolated in 60% yield: ir (neat) 3040, 1715 cm^{-1}; nmr (CCl_4) δ 1.05 (d, 3 H, J = 6 Hz), 5.71 (m, 2 H); 2,4-DNP mp 142°. *Anal.* Calcd for $C_{13}H_{14}N_4O_4$: C, 53.79; H, 4.86. Found: C, 53.75; H, 4.77.

Methyl 4-Nitrovalerate (12).—A 90% yield of methyl levulinate was isolated after 30-min reactions, 2,4-DNP mp 141° (lit.[24] mp 141°).

4-Nitrovaleronitrile (7).—A 90% yield of levulinonitrile was isolated after 45-min reaction, 2,4-DNP mp 146° (lit.[22] mp 146°).

Nitro Ketal 23.—A 90% yield of ketal aldehyde was isolated after 45 min reaction.

β-Nitrophenylethane (20).—Phenylacetaldehyde (**21**, 70%) was isolated after 30-min reaction.

1-Nitrohexane (10).—Hexanal (45%) was isolated after 30-min reaction.

1-Nitrocyclooctene (5).—After 1 hr reaction, 2-methyoxycyclooctanone (70%) was isolated: ir (neat) 1710, 1100 cm^{-1}; nmr (CCl_4) δ 3.54 (m, 1 H), 3.28 (s, 3 H), 2.8–0.8 (12 H); 2,4-DNP mp 136°. *Anal.* Calcd for $C_{15}H_{20}N_4O_5$: C, 53.57; H, 5.99. Found: C, 53.56; H, 6.11.

When aqueous NaOAc–dioxane was used to form the nitronate anion, 2-hydroxycyclooctane (90%) was formed.

5-Nitroheptan-2-one Ethylene Ketal (9).—Keto ketal **16** was isolated in 70% yield after 2-hr reaction in methanol.

4-Heptyn-1-ol.—A slurry of lithium aluminum hydride (1.93 g, 0.051 mol) in 75 ml of dry ether was mechanically stirred in a 250-ml flask and a solution of 4-heptynoic acid (6.13 g, 0.049 mol) in 75 ml of ether was slowly added. After addition was complete, the reaction was further stirred for 30 min and then cautiously quenched by sequential addition of water (2.5 ml), 15% NaOH (2.5 ml), and water (7.5 ml). The reaction mixture was then filtered, dried (Na_2SO_4), concentrated, and distilled to yield the desired alcohol (5.18 g, 95%) as a colorless oil: bp 91° (15 mm); ir (neat) 3350, 1050 cm^{-1}; nmr (CCl_4) δ 3.58 (t, 2 H, J = 6.5 Hz), 3.6 (s, 1 H), 2.15 (m, 4 H), 1.68 (m, 2 H), 1.08 (t, 3 H, J = 7.5 Hz).

1-Iodo-4-heptyne (35).—4-Heptyn-1-ol (1.0 g, 8.9 mmol) was dissolved in 40 ml of methylene chloride and 15 ml of triethylamine at −10°. Methanesulfonyl chloride (10 mmol) was slowly added, and, after 15 min of additional stirring, the mixture was transferred to a separatory funnel and washed sequentially with water, 10% HCl, 5% $NaHCO_3$, and saturated brine. The solution was then dried (Na_2SO_4) and concentrated to yield crude mesylate (1.67 g, 100%).

Without further purification, the crude mesylate (3.54 g, 18.6 mmol) was added to a mixture of NaI (4.15 g, 28 mmol) in acetone (20 ml) and the reaction mixture was stirred overnight at room temperature. The mixture was then filtered and concentrated. The residue was taken up in ether and washed with water, 10% $NaHSO_3$, and saturated brine, and then was dried (Na_2SO_4) and concentrated. The residual oil was distilled to give iodide **35** (3.0 g, 73%): bp 91–94° (15 mm); ir (neat) 2980, 1240, 1165 cm^{-1}; nmr (CCl_4) δ 3.12 (m, 2 H), 2.7 (m, 2 H), 2.17 (m, 2 H), 1.12 (t, 3 H, J = 7.5 Hz).

1-Nitro-4-heptyne (36).—A solution of iodide **35** (2.77 g, 12.5 mmol) and $NaNO_2$ (1.52 g, 21.7 mmol) in DMSO (10 ml) was mechanically stirred for 1 hr at room temperature. The reaction mixture was diluted with 30 ml of ice water and extracted with petroleum ether (bp 30–60°) (5 × 10 ml). The combined extracts were washed with water, dried ($MgSO_4$), filtered, concentrated, and distilled to give the nitro compound **36** (0.8 g, 45%): bp 60–70° (5 mm); ir (neat) 1550 cm^{-1}; nmr (CCl_4) δ 4.25 (t, 2 H, J = 7 Hz), 2.5–1.4 (m, 6 H), 1.10 (t, 3 H, J = 7 Hz).

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5-Nitro-8-undecyn-2-one (**37**).—1-Nitro-4-heptyne (0.79 g, 5.62 mmol), diisopropylamine (0.3 ml), and methyl vinyl ketone (0.43 g, 6.1 mmol) in 6 ml of chloroform were stirred at 40° for 16 hr under nitrogen. The solution was then distilled to give 980 mg (83%) of product **37**: bp 110° (0.001 mm); ir (neat) 1715, 1545 cm^{-1}; nmr (CCl_4) δ 1.09 (t, 3 H, J = 7 Hz), 2.10 (s, 3 H), 4.6 (m, 1 H); mass spectrum m/e (rel intensity) 162 (P^+, 50), 147 (100). *Anal.* Calcd for $C_{11}H_{17}NO_3$: C, 62.53; H, 8.13. Found: C, 62.53; H, 8.10.

8-Undecyne-2,5-dione (**38**).—This compound was prepared by reduction of **37** with $TiCl_3$ according to procedure A above; an 85% yield was obtained after 18-hr reaction in dimethoxyethane as solvent.

Dehydrojasmone (**39**).—Diketone **38** (0.38 g, 2.1 mmol) was dissolved in 10 ml of 5% ethanolic KOH solution and the solution was refluxed for 2 hr under nitrogen. The solution was then poured into a separatory funnel, diluted with water, and extracted with ether. The extracts were washed with brine, dried ($MgSO_4$), concentrated, and distilled to yield dehydrojasmone (**39**, 0.34 g, 85%): bp 103–105° (0.1 mm); ir (neat) 1705, 1650 cm^{-1}; nmr (CCl_4) δ 1.13 (t, 3 H, J = 7 Hz), 2.15 (s, 3 H), 2.25 (m, 6 H), 2.95 (t, 2 H, J = 1.5 Hz); 2,4-DNP mp 165° (lit.[25] mp 166°).

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cis-**Jasmone** (**40**).—Lindlar catalyst[16] (50 mg) in 2 ml of ethyl acetate was equilibrated under 1 atm of hydrogen for 12 hr and dehydrojasmone (0.050 g, 0.003 mol) in 1 ml of ethyl acetate was added. After 5 min, hydrogen uptake stopped, and the reaction was filtered free of catalyst and concentrated to yield *cis*-jasmone (**40**, 47 mg, 95%): ir 1705, 16.50 cm^{-1}; nmr (CCl_4) δ 0.97 (t, 3 H, J = 7.5 Hz), 2.02 (s, 3 H), 2.20 (m, 6 H), 2.84 (d, 2 H, J = 5 Hz), 5.22 (triplet of doublets, 2 H, J = 4, J' = 6 Hz); 2,4-DNP mp 116° (lit.[26] mp 117.5°).

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Registry No.—**1**, 42397-25-1; **2**, 1703-51-1; **3**, 622-42-4; **5**, 1782-03-2; **7**, 16506-99-3; **9**, 42397-27-3; **10**, 646-14-0; **11**, 42397-28-4; **12**, 10312-37-5; **14**, 42397-30-8; **16**, 42397-31-9; **18**, 32863-04-0; **18** 2,4-DNP, 42397-33-1; **19**, 42397-34-2; **19** picrate 42397-12-6; **20**, 6125-24-2; **23**, 42397-13-7; **23** 2,4-DNP, 42397-14-8; **24**, 42397-15-9; **26**, 42397-16-0; **26** 2,4-DNP, 42397-17-1; **34**, 42441-83-8, and **35**, 18498-36-7 (Scheme I); **36**, 42397-19-3; **37**, 42397-20-6; **38**, 7051-43-6; **39**, 7051-37-8; **40**, 488-10-8; $TiCl_3$, 7705-07-9; 1-nitropropane, 108-03-2; methyl vinyl ketone, 78-94-4; 1-nitropropene, 3156-70-5; butadiene, 106-99-0; morpholinocyclohexene, 670-80-4; azoxy-*n*-hexane, 42441-84-9; 1-nitrocyclohexene, 2562-37-0; 4-heptyn-1-ol, 42397-24-0.

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Synthesis of *N*-(2-Triphenylstannylethyl)amines and Their Reactivities

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The reactions of seven *N*-(2-triphenylstannylethyl)amines (**3a–g**), prepared from the corresponding 2-chloroethylamines (**1a–e,g**) and triphenyltinlithium (**2**), with methyl halides (MeX) or hydrogen halides (HX) were investigated. In the case of X = I or Br, the quaternary ammonium salts or the amine hydrohalides, produced from *N*-(2-triphenylstannylethyl)alkylamines (**3a** and **3b**), were unstable and were cleaved by nucleophilic attack of X^- at tin atom which resulted in the formation of triphenyltin halides and alkylamines with the loss of ethylene. On the contrary, **3a–c** hydrochlorides were stable, but the presence of excess hydrogen chloride led quantitatively to (2-alkylaminoethyl)phenyltin dichloride hydrochlorides (**8a–c**) by electrophilic attack of H^+ on the phenyl groups. However, the reaction of *N*-(2-triphenylstannylethyl)arylamines (**3d** and **3e**) with hydrogen chloride gave a mixture of triphenyltin chloride, diphenyltin dichloride, phenyltin trichloride, and *sec*-arylamines, as a result of the competition between the nucleophilic attack of Cl^- at tin atom and the electrophilic attack of H^+ on phenyl group.

Previous investigations of aminoalkyltin compounds have dealt with the chemistry of the α-[1] and γ-amino[2] derivatives. While a few of the β-aminoalkyltin compounds have been obtained by additions of triorganotin hydrides to vinylamines[2a,3] or by carbon–carbon insertion reaction into tin–nitrogen bonds,[4] little is known about their chemical properties. We now report the preparation of several new alkylamino- and arylaminoethyltriphenyltin compounds as well as some of the reactions that they undergo.

Seven *N*-(2-triphenylstannylethyl)amines (**3a–g**) were synthesized in 60–80% yields from reactions of the corresponding 2-chloroethylamines (**1a–e,g**) with triphenyltinlithium (**2**) in tetrahydrofuran (see Table I). Their structures were confirmed by elemental and ^1H nmr spectral analyses (see Table IV). *N*-(2-Triphenylstannylethyl)aniline (**3f**) was isolated in low yield from the reaction of *N*-(2-chloroethyl)acetanilide (**1g**) with **2**. Hydrolysis of *N*-(2-triphenylstannylethyl)acetanilide (**3g**) in alcoholic potassium hydroxide also gave **3f**. The reduction of **3g** with lithium aluminum hydride gave **3f** in high yield. No *N*-(2-triphenylstannylethyl)-*N*-ethylaniline was obtained. The acetylation of **3f** with acetic anhydride led to **3g**. However, the methylation of **3f** with an equimolar amount of methyl bromide or methyl iodide in ethanol did not produce *N*-(2-triphenylstannylethyl)-*N*-methylaniline (**3d**) as expected, but gave mixtures which consisted of *N*-methylaniline, triphenyltin bromide, or triphenyltin iodide, respectively, as major products, and aniline and *N*,*N*-dimethylaniline as minor products along with unreacted **3d**. These products are regarded as resulting from the following reactions (Scheme I).

The reaction of **3f** with MeX (X = Br, I) initially gives **3d** hydrohalide (**3d**-HX). Proton transfer from **3d**-HX to **3f** affords **3f** hydrohalide (**3f**-HX) and **3d**, which subsequent reacts with additional MeX to give *N*-(2-triphenylstannylethyl)-*N*,*N*-dimethyl-*N*-phenylammonium halide (**5d**). These three ammonium

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