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Registry No. PhSO₂CH₂Cl, 7205-98-3; PhSO₂CH₂Br, 19169-90-5; PhSO₂CH₂I, 65492-21-9; Me₂C(NO₂)₂, 595-49-3; *c*-C₆H₁₀(NO₂)₂, 4028-15-3; 9-CH₃-Fl⁻, 31468-21-0; 9-*m*-ClC₆H₄-Fl⁻, 73872-45-4; 9-C₆H₅-Fl⁻, 31468-22-1; 9-*p*-CH₃C₆H₄-Fl⁻, 42730-14-3.

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Synthesis of Quaternary Carbon Compounds¹

Summary: A general synthesis of quaternary carbon compounds RR'R''CCH₂NO₂ which gives excellent yields of pure products is described. Of special interest is the preparation of quaternary aldehydes by permanganate oxidation of these nitro compounds.

Sir: A number of simple and effective procedures are now available for the synthesis of tertiary nitroparaffins.²⁻¹² Most of them are carbon-carbon bond forming processes, and they enable one to prepare highly branched compounds which are virtually unobtainable by other means. Another attractive feature of these reactions is their capability for providing tertiary nitro compounds in which other functional groups are present, e.g., keto, ester, and cyano.

Of the common functional groups, a tertiary nitro group is the most susceptible to electron-transfer substitution, and this has enabled us to devise a general procedure for converting tertiary nitro compounds into quaternary carbon compounds.^{13,14} Equation 1 is illustrative, and

(1) This is paper 25 in the series "Substitution Reactions Which Proceed via Radical Anion Intermediates". For the preceding paper see N. Kornblum, P. Ackermann and R. T. Swiger, *J. Org. Chem.*, 45, 5294 (1980).

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


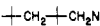



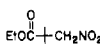

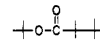

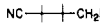

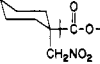

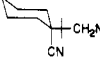

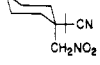

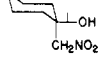

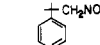

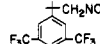

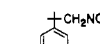

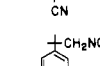

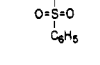

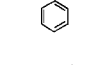

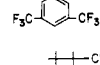
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(13) Previously the conversion of tertiary nitro compounds to quaternary carbon compounds has only been possible with systems in which the intermediate free radical of eq 3 and 4 is resonance stabilized, e.g., with Me₂C(NO₂)COOEt. Now, by employment of NaH in Me₂SO, it is possible to achieve this transformation even with compounds such as *tert*-nitrobutane and *tert*-nitrooctane (Table I).

(14) A recent review by S. F. Martin [*Tetrahedron*, 36, 419 (1980)] describes the problems associated with the construction of quaternary carbon centers.

Table I. Replacement of NO₂ by CH₂NO₂^a

tertiary nitro compd	reaction time, h	primary nitro compd	yield, ^b %
	4		60
	4		60
	4		75
	16 ^c		88 ^d
	5		95
	2		91
	3		81
	2		91
	2		89
	5		85
	18 ^e		84
	18 ^e		87
	18 ^e		95
	140 ^e		83
	4		89
	3		76
	42 ^e		60 ^f

^a All reactions were carried out at 25 °C in Me₂SO with exposure to two 20-W fluorescent lights. Unless otherwise noted the molar ratio of tertiary nitro compound to nitromethane to NaH is 1:4:8. ^b Pure, isolated product. ^c No free NaH present. ^d This experiment first carried out by Dr. R. Boss. ^e Less than the standard amount of NaH was employed (25% to 100% excess relative to the tertiary nitro compound). ^f This product contains ca. 5% *p*-NCC₆H₄C(Me)₂CH₂NO₂ which derives from fragmentation of the β-nitroaryl radical anion [cf. eq 18 of N. Kornblum, J. Widmer, and S. C. Carlson, *J. Am. Chem. Soc.*, 101, 661 (1979)].

Tables I and II summarize our results; yields refer to pure, isolated products.

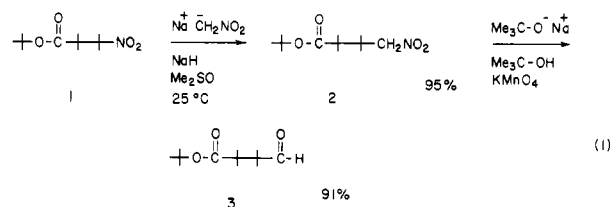
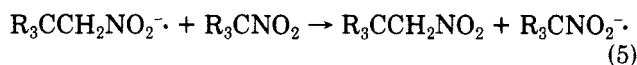
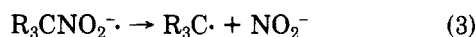
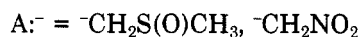


Table II. Conversion of Primary Nitro Compounds to Aldehydes

primary nitro compd	aldehyde	yield, ^a %
		96
		91
		81
		88
		83
		91
		88

^a Pure, isolated aldehyde.

The procedure for effecting the first step of eq 1 invokes the use of more sodium hydride than is needed to convert nitromethane to its salt. Although excess sodium hydride is effective in facilitating these reactions when Me₂SO is used as the solvent, in DMF, despite excess sodium hydride, there is no reaction. Presumably, in Me₂SO a catalytic amount of dimethyl sodium is formed, and this acts as a potent one-electron-transfer agent,¹⁵ thereby inducing electron-transfer chain substitution of nitro by nitromethyl.¹⁶ In accord with this view, the replacement of a tertiary nitro group by nitromethyl is inhibited by di-*tert*-butyl nitroxide, by nitrobenzene, and by *m*-dinitrobenzene; these are the attributes of an electron-transfer chain-substitution process.¹⁰ Presumably these reactions proceed via the mechanistic sequence of eq 2-5.



Our synthesis of quaternary carbon compounds incorporates a CH₂NO₂ group into the molecule. In principle, these primary nitroparaffins should be capable of undergoing a variety of transformations, one of the most useful of which is conversion to aldehydes. The standard procedure for achieving this transformation has been the Nef reaction¹⁷ which simply involves acidification of the ni-

troparaffin salt. But although the Nef reaction has repeatedly been employed to advantage, there are a number of reports of its inadequacy or downright failure, and, consequently, numerous alternatives have been devised.¹⁸

Our initial attempts to prepare aldehydes by the Nef reaction and by procedures employing TiCl₃ were unpromising, and attention was therefore directed to the use of potassium permanganate. We were encouraged to do so by the ready availability of this reagent and because Shechter and Williams,¹⁸ following the early work of Nametkin,¹⁸ had reported that neutral permanganate provides an effective means for converting the salts of primary nitroparaffins to aldehydes; but most important was the fact that Schechter and Williams emphasized the extraordinary ease with which nitroparaffin salts are oxidized at 0 °C by potassium permanganate. On the other hand, even though nearly 20 years have elapsed since potassium permanganate was proposed as an effective reagent for converting primary nitroparaffin salts to aldehydes, it has not achieved the status of a synthetically useful means of accomplishing this transformation. Indeed, the numerous alternatives to the Nef reaction have all been described since the Shechter-Williams paper appeared.¹⁸

In our hands the original permanganate procedure^{18a} gave erratic results but, by making some simple modifications, it has proved possible routinely to transform primary nitroparaffins into pure aldehydes in excellent yields (Table II).¹⁹

The general procedure is illustrated by the sequence of eq 1. A 51% oil dispersion of NaH²⁰ (0.750 g, 16 mmol) is washed with hexane, and the oil-free sodium hydride is transferred to a N₂-filled flask with 20 mL of Me₂SO.^{21,22} The mixture is stirred, a positive pressure of N₂ is maintained, and nitromethane (0.488 g, 430 μL, 8 mmol) is injected by syringe. After the foaming subsides, an addition tube²³ containing *tert*-butyl 3-nitro-2,2,3-trimethylbutanoate (1; 0.462 g, 2 mmol) is attached to the flask, and the system is purged by evacuating and then bleeding in N₂; this purge is repeated a total of three times. Then the nitro ester 1 is added without opening the system,²³ and the stirred reaction mixture is exposed to two 20-W ordinary fluorescent lights for 5 h.²⁴ The reaction mixture is acidified with 3 mL (42 mmol) of glacial acetic acid, stirred for 20 min, and then poured into 200 mL of 3-5% aqueous NaCl. The product is extracted repeatedly

(18) (a) KMnO₄: H. Shechter and F. T. Williams, *J. Org. Chem.*, **27**, 3699 (1962); S. S. Nametkin and A. S. Zabrodina, *Ber. Dtsch. Chem. Ges.*, **69**, 1789 (1936). (b) Modified Nef reactions: D. St. C. Black, *Tetrahedron Lett.*, 1331 (1972); R. M. Jacobson, *ibid.*, 3215 (1974); E. Keinan and Y. Mazur, *J. Am. Chem. Soc.*, **99**, 3862 (1977). (c) Ozonolysis: J. E. McMurry, J. Melton, and H. Padgett, *J. Org. Chem.*, **39**, 259 (1974). (d) TiCl₃: J. E. McMurry and J. Melton, *J. Am. Chem. Soc.*, **93**, 5309 (1971); *J. Org. Chem.*, **38**, 4367 (1973). (e) VCl₂: R. Kirchhoff, *Tetrahedron Lett.*, 2533 (1976). (f) *t*-BuOOH: P. A. Bartlett, F. R. Green III, and T. R. Webb, *ibid.*, 331 (1977). (g) Ce(NH₄)₂(NO₃)₆: G. A. Olah and B. G. B. Gupta, *Synthesis*, 44 (1980).

(19) A single experiment in which 1-nitrodecane was converted to pure *n*-decanal in 81% yield suggests that this KMnO₄ procedure may well prove to be the most useful and general method for converting primary nitroparaffins to aldehydes. This matter is being investigated.

(20) Alfa Products; for best results NaH from a can which has not been opened repeatedly must be used.

(21) Me₂SO may contain traces of impurities, and in a few instances these retard the desired reaction. In that event, the Me₂SO is allowed to stand overnight in contact with type 3A or 4A molecular sieves which have been activated by heating for 4 h at 320 °C.

(22) We are indebted to the Crown Zellerbach Corp. for a generous supply of Me₂SO.

(23) See N. Kornblum, S. C. Carlson, J. Widmer, M. J. Fifolt, B. N. Newton, and R. G. Smith, *J. Org. Chem.*, **43**, 1397 (1978).

(24) Reactions conducted in total darkness proceed about half as fast as those carried out with exposure to daylight fluorescent lights. The matter of yields for "dark" reactions has not been investigated.

(15) G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Am. Chem. Soc.*, **86**, 1807 (1964).

(16) N. Kornblum, R. T. Swiger, G. W. Earl, H. W. Pinnick, and F. W. Stuchal, *J. Am. Chem. Soc.*, **92**, 5513 (1970).

(17) J. U. Nef, *Justus Liebigs Ann. Chem.* **280**, 263 (1894); E. E. van Tamelen and R. F. Thiede, *J. Am. Chem. Soc.*, **74**, 2615 (1952); W. E. Noland, *Chem. Rev.*, **55**, 137 (1955); D. J. Cook and O. R. Pierce, *J. Am. Chem. Soc.*, **76**, 84 (1954); F. Kienzle, G. W. Holland, J. L. Jernow, S. Kwah, and P. Rosen, *J. Org. Chem.*, **38**, 3441 (1973).

with methylene chloride; the methylene chloride solution is washed repeatedly with dilute aqueous NaCl and then dried (MgSO₄). The solvent is removed under reduced pressure, and the residual oil on Kugelrohr distillation at 70 °C (0.005 mm) gives 0.466 g (95% yield) of pure 2.²⁵

A 60% oil dispersion of NaH²⁰ (0.100 g, 2.5 mmol) is washed with pentane, and the oil-free hydride is transferred to a nitrogen-filled flask with the aid of 10 mL of *tert*-butyl alcohol. The mixture is stirred for 10 min under N₂, and then a solution of nitro ester 2 (0.245 g, 1 mmol) in 10 mL of *tert*-butyl alcohol is added. One minute later, 200 mL of ice-cold pentane^{26,27} is added, and this is followed at once by 25 g of ice and an ice-cold solution of KMnO₄ (0.115 g, 0.73 mmol, 110% of the required amount) in 40 mL of water. The resulting mixture is stirred vigorously for 10 min, and then 1 mL (1 mmol) of 1 M sodium metabisulfite is added; this is followed by 2 mL (2 mmol) of 1 M H₂SO₄ whereupon the brown mixture is rapidly decolorized. The pentane phase is isolated, and the aqueous layer is extracted with more pentane. The combined pentane solutions are washed thoroughly with ice-cold water and dried (MgSO₄) under N₂. Removal of the pentane under N₂²⁸ gives 0.195 g (91% yield) of pure,²⁵ colorless aldehyde 3.²⁹

There are well-defined methods for converting CH₂NO₂ into a variety of other functions, e.g., COOH, CN, and CH₂NH₂, and, consequently, quaternary carbon compounds with a wide range of functions now become readily available. And if, as seems quite possible, the replacement of tertiary nitro groups by the anions of higher primary nitroparaffins proves feasible, this will provide a further demonstration of the synthetic utility of electron-transfer substitution reactions.

Acknowledgment. We are indebted to the National Science Foundation for support of this investigation.

Registry No. 1, 68896-18-4; 2, 76173-36-9; 3, 76173-37-0; 2-methyl-2-nitropropane, 594-70-7; 1,1,3,3-tetramethyl-1-nitrobutane, 5342-78-9; 2-methyl-2-nitrotridecane, 76173-38-1; ethyl 2-methyl-2-nitropropanoate, 5342-77-8; 2-cyano-2,3-dimethyl-3-nitrobutane, 29770-62-5; *tert*-butyl 2-methyl-2-(1-nitrocyclohexyl)propanoate, 76173-39-2; 1-(2-nitro-2-propyl)-1-cyanocyclohexane, 76173-40-5; 1-(2-cyano-2-propyl)-1-nitrocyclohexane, 29770-63-6; 1-(1-(tetrahydropyran-2-yl)ethyl)-1-nitrocyclohexane, 76173-41-6; 2-nitro-2-phenylpropane, 3457-58-7; 2-nitro-2-(3,5-bis(trifluoromethyl)phenyl)propane, 58324-86-0; 2-nitro-2-(*p*-cyanophenyl)propane, 58324-82-6; 2-nitro-2-(*p*-(phenylsulfonyl)phenyl)propane, 58324-84-8; 2,3-dimethyl-2-nitro-3-phenylbutane, 65638-49-5; 2,3-dimethyl-2-nitro-3-(3,5-bis(trifluoromethyl)phenyl)butane, 65338-72-9; 2,3-dimethyl-2-nitro-3-(*p*-cyanophenyl)butane, 65253-37-4; 2,2-dimethyl-1-nitropropane, 34715-98-5; 2,2,4,4-tetramethyl-1-nitrobutane, 76173-42-7; 2,2-dimethyl-1-nitrotridecane, 76173-43-8; ethyl 2,2-dimethyl-3-nitropropanoate, 76173-44-9; 2-cyano-2,3,3-trimethyl-4-nitrobutane, 76173-45-0; *tert*-butyl 2-methyl-2-(1-(nitromethyl)cyclohexyl)propanoate, 76173-46-1; 2-(1-cyanocyclohexyl)-2-methyl-1-nitropropane, 76173-47-2; 2-cyano-2-(1-(nitromethyl)cyclohexyl)propane, 76173-48-3; 1-(1-(nitromethyl)cyclohexyl)ethanol, 76173-49-4; 2-methyl-1-nitro-2-phenylpropane, 76173-50-7; 2-methyl-1-nitro-2-(3,5-bis(trifluoromethyl)phenyl)propane, 76173-51-8; 2-(*p*-cyanophenyl)-2-methyl-1-nitropropane, 76173-52-9; 2-

methyl-1-nitro-2-(*p*-(phenylsulfonyl)phenyl)propane, 76173-53-0; 2,2,3-trimethyl-1-nitro-3-phenylbutane, 76173-54-1; 2,2,3-trimethyl-1-nitro-3-(3,5-bis(trifluoromethyl)phenyl)butane, 76173-55-2; 3-(*p*-cyanophenyl)-2,2,3-trimethyl-1-nitrobutane, 76173-56-3; 2,2-dimethyltridecane, 76173-57-4; 2-(1-cyanocyclohexyl)-2-methylpropanal, 76173-58-5; 2-methyl-2-(3,5-bis(trifluoromethyl)phenyl)propanal, 76173-59-6; 2-(*p*-cyanophenyl)-2-methylpropanal, 76173-60-9; 2-(*p*-(phenylsulfonyl)phenyl)-2-methylpropanal, 76173-61-0; 2,2,3-trimethyl-3-phenylbutanal, 76173-62-1.

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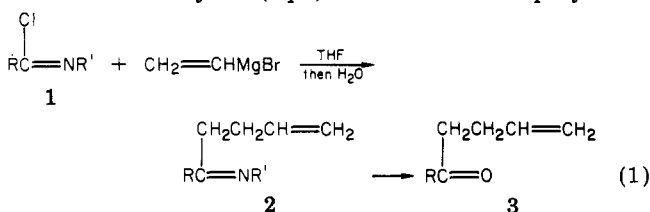
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Coupling Reactions of Vinylmagnesium Bromide with Imidoyl Chlorides and with Amides. Synthesis of Enol Imines, γ,δ -Unsaturated Ketones, and Ketimines

Summary: Vinylmagnesium bromide undergoes successive addition to imidoyl chlorides and to amides to give unsaturated ketones, imines, enol imines, or enamines, depending on the reaction conditions.

Sir: One of us has recently described several coupling reactions of imidoyl chlorides with transition-metal organometallics resulting in the formation of mesoionic compounds² and 1,4-diaza-1,3-butadienes.³ Related to the latter are 1-aza-1,3-butadienes, substituted derivatives of which can be generated by treatment of alkenylmagnesium halides with imidoyl chlorides.⁴ We expected the very reactive alkenyl Grignard vinylmagnesium bromide to undergo successive additions to an imidoyl chloride to produce a metallo enamine, which could be intercepted by reaction with appropriate acylating and alkylating reagents. Some elegant synthetic applications of metallo enamines have recently been described.⁵ We now report that imidoyl chloride (and amide)-vinylmagnesium bromide reactions provide an entry into a variety of useful organic compounds. The observation of an unusual N-alkylation of a metallo enamine is also described.

Treatment of 1 (R = Ph, R' = *p*-ClC₆H₄) with 2 equiv of vinylmagnesium bromide in tetrahydrofuran (THF) for 30 min at room temperature affords the γ,δ -unsaturated imine 2 in 75% yield (eq 1). Reaction workup by chro-



matography on silica gel or acidic alumina gave the unsaturated ketone 1-phenyl-4-penten-1-one (3, R = Ph) in 70-75% yield. Compounds 2 and 3 (R = *p*-BrC₆H₄, *p*-ClC₆H₄; R' = Ph, *p*-ClC₆H₄) were similarly obtained in very good yields (80-86%, Table I). Repetition of these experiments in the presence of catalytic amounts of tetrakis(triphenylphosphine)palladium resulted in little change in product yields.

(1) E. W. R. Steacie Fellow, 1980-1982.

(2) Alper, H.; Tanaka, M. *J. Am. Chem. Soc.* 1979, 101, 4245.

(3) Alper, H.; Tanaka, M.; Hachem, K. *J. Organomet. Chem.* 1980, 190, 95.

(4) Normant, H.; Martin, G. *Bull. Soc. Chim. Fr.* 1957, 429.

(5) See: Martin, S. F.; Phillips, G. W.; Puckette, T. A.; Colapret, J. *A. J. Am. Chem. Soc.* 1980, 102, 5866 and references cited therein.

(25) Satisfactory elemental analyses and NMR spectra were obtained for all new compounds.

(26) Pentane usually contains small amounts of impurities which KMnO₄ oxidizes to compounds that are not easily separated from low-boiling aldehydes. The pentane is purified by being stirred with concentrated H₂SO₄ containing Na₂Cr₂O₇ at 25 °C; cooling may be necessary. This is followed by distillation from CaH₂.

(27) When, as in several of our cases, the aldehyde is not soluble in pentane, ethyl acetate is substituted for pentane.

(28) There are indications that the aldehydes of Table II are rather sensitive to oxygen. They are stable for at least 1 week under N₂ at -78 °C.

(29) For some of the aldehydes passage through a short column of silica gel was required to give a pure product.