a silica gel column gave pure D1-D9.3,6 The yields of D1-D9 ranged from 15% for D2 to 60% for D1. No dimer could be obtained by heating 10 under the same conditions.

Acknowledgment. Financial support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and The University of Connecticut Research Foundation are gratefully acknowledged.

Registry No.-1, 53198-79-1; 2, 53198-80-4; 3, 5076-51-7; 4, 5076-52-8; 5, 53198-81-5; 6, 5076-53-9; 7, 53198-82-6; 8, 53198-83-7; 9, 53198-84-8; 10, 53198-85-9; phenylacetylene, 536-74-3.

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A Convenient, High-Yield Conversion of Aldehydes to Nitriles

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Received July 15, 1974

We wish to report a new method for accomplishing the conversion of aldehydes to nitriles. There have been a number of methods reported for this transformation;¹⁻⁶ ours differs from these in the fact that the experimentalist need not isolate and purify the intermediate oxime or related aldehyde derivative, although he may do so if he wishes; the method therefore saves one step in the aldehyde-to-nitrile conversion. The method additionally features relatively mild reaction conditions as well as a convenient internal indicator for the extent of reaction.

The development of efficient amino protecting groups has facilitated the synthesis of a variety of sensitive com-

pounds, including O-substituted hydroxylamines.7 Although a number of these are highly unstable,⁸ others have significant synthetic utility. Their electrophilic character has been exploited in their increasing use as aminating agents.^{9,10} Their nucleophilicity has been demonstrated by their reaction with ketones to form substituted oximes which undergo facile Beckmann and Neber rearrange $ments.^{11}$

Our method makes use of one of these reagents, O-2,4dinitrophenylhydroxylamine (1), and proceeds according to eq 1 and 2.



The O-2,4-dinitrophenyloxime is formed by simply warming an alcoholic suspension of equivalent amounts of the aldehyde and 1 until the solution becomes homogeneous, followed by the addition of a few drops of mineral acid. The O-2,4-dinitrophenyloximes of aromatic aldehydes immediately precipitate from the reaction mixture and can be isolated by filtration after cooling. High yields of these materials have been obtained; their sharp melting points indicate that only one isomer is probably formed. Others have reported similar observations, and have presented evidence that the isomer formed is the Z isomer (syn isomer) about the C=N bond.¹² Higher yields of 2 can often be obtained by the addition of 1 vol of water to the reaction mixture before cooling. Elimination to form the nitrile is accomplished by warming a suspension of the Osubstituted oxime in alcohol with excess base until the mixture becomes homogeneous (method A). The development of a deep, yellow-to-red color of the 2,4-dinitrophenolate ion indicates the extent of completion of the reaction.

The aliphatic oxime derivatives in our hands do not precipitate from the reaction mixture; however, subsequent

Table I

Results of Synthesis of O-2,4-Dinitrophenyloximes of Variou	us Aldehydes and Their Conversion to Nitriles
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Aldehyde (method)								Nitrile			
	Registry No.	Sol- vent	Mp, °C	Lit. mp, ^a °C	Yield, %	Registry No.	Sol- vent	Mp, °C	Lit. mp, ^a °C	Yield, %	Registry No.
Benzaldehyde (A)	100-52-7	EtOH	143-145	145	93	53188-15-1	MeOH			84	100-47-0
<i>p</i> -Methoxybenz- aldehyde (A)	123-11-5	EtOH	185-187	187	91	53188-16-2	MeOH	61-62	60-62	91	874-90-8
<i>p</i> -Bromobenz- aldehyde (A)	1122-91-4	EtOH	213-214	207	85	53188-17-3	MeOH	110–113	113	89	623-00-7
p-Nitrobenz- aldehyde (A)	555-16-8	EtOH	215-216	216	91	53188-18-4	EtOH	147-150	147-148	94	619-72-7
Piperonal (A) Heptaldehyde (B)	120-57-0 111-71-7	EtOH MeOH	194-195	196	.98	53188-19-5	EtOH MeOH	92-93	92-93	91^{b}	629-08-3
Undecylenic aldehyde (B)	112-45-8	EtOH					EtOH			93	53179-04-7

^a For oximes, the melting point data are from ref 12a; for nitriles, the data are from Beilstein.^b The product contained a trace of the starting aldehyde, as shown by infrared and by the diagnostic reaction with 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole.12

Notes

The choice of base for the elimination reaction to form nitriles is arbitrary, except for that of the oxime derived from p-nitrobenzaldehyde. In this case, potassium or sodium hydroxide gives a mixture of products, among which are the desired nitrile to the extent of about 50%, and smaller amounts of p-nitrobenzaldehyde and N-p-nitrophenylformamide. The use of triethylamine in absolute ethanol, however, affords p-nitrobenzonitrile cleanly.

The results of execution of these procedures with various aldehydes are given in Table I.

Experimental Section

The melting points were determined on a Büchi melting point apparatus and are corrected. The infrared spectra were taken on a Perkin-Elmer infracord spectrophotometer, and in all cases were identical with those of melting points of various derivatives are listed in Table I.

Synthetic Procedures. O-2,4-Dinitrophenylhydroxylamine was prepared either by the method of Sheradsky^{9d} or that of Tam-ara;^{10b} we found the latter method more convenient for our purposes.

Nitrile Preparation. Method A. O-2,4-Dinitrophenylhydroxylamine (0.995 g, 5 mmol) was dissolved in 50 ml of ethanol by warming on a steam bath. Piperonal (0.75 g, 5 mmol) was added, and the solution swirled until it was homogeneous. Two drops of concentrated HCl were added. A precipitate began to form immediately. Cooling followed by filtration gave a light yellow solid (1.3 g, mp 193-195°). Cooling the filtrate in a freezer (-23°) overnight gave, after filtration, 0.33 g of fine needles, mp 194-195°. The total yield of piperonal O- 2,4-dinitrophenyloxime was 98%.

This oxime derivative (0.5 g, 1.51 mmol) was suspended in 50 ml of 95% ethanol. KOH (20 ml, 0.2 N in 95% ethanol) was added and the solution heated slowly to a gentle reflux. Reflux was maintained for 3 hr, although the color of the phenolate ion developed instantaneously, and the solution was concentrated to 15 ml under reduced pressure. Water (75 ml) and 5% NaOH (15 ml) were added and the resulting suspension extracted with chloroform. Drying, evaporation, and recrystallization from hexanes yielded a white solid in 81% yield; mp 91.5-93.5°; ir 2270 cm⁻¹.

In another preparation of the same material, warming of the solution (to effect dissolution of the O-2,4-dinitrophenyloxime) for 10 min followed by work-up as described above afforded essentially the same yield of nitrile. Stirring the O-substituted oxime with triethylamine in tetrahydrofuran for 12 hr, however, gave no reaction.

Method B. O-2,4-Dinitrophenylhydroxylamine (0.199 g, 1 mmol) was dissolved in 30 ml of ethanol by warming on a steam bath. 10-Undecylenic aldehyde (Aldrich, 0.168 g, 1 mmol) was added followed by one drop of concentrated HCl. The solution was allowed to cool, and it was stirred at room temperature for 30 min. Two equivalents of triethylamine was added, and the solution was heated to gentle reflux; a dark yellow color developed. After 5 min the solution was poured into 75 ml of 5% aqueous sodium bicarbonate and extracted with ether. Drying and evaporation of the ethereal solution left a light yellow liquid. Bulb-to-bulb distillation gave a colorless liquid (153 mg, 93%): ir 2260 cm⁻¹.

Acknowledgment. This work was supported by the National Institute of General Medical Sciences. Marvin Miller would like to acknowledge support by a National Institutes of Health Training Grant.

Registry No.---1, 17508-17-7.

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A Reagent for the α,β Reduction of Conjugated Nitriles

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The reduction of α,β -unsaturated nitriles 1 to saturated nitriles 2 often proceeds with concomitant reduction of the nitrile moiety,¹ decyanation,² hydrodimerization,³ and po-lymerization.⁴ Those procedures reported to afford predominantly the nitrile 2 suffer from poor yields⁵ and limited⁶ or uncertain⁷ scope. We now wish to report a general procedure for effecting the transformation $1 \rightarrow 2$ in high yield.



The reduction of 1 to 2 using magnesium in methanol was compatible with various substitution patterns and, in the limited cases examined, with other functional groups (see Table I). A particular advantage of this method over catalytic hydrogenation was the regioselective reduction of a conjugated double bond in the presence of a nonconjugated double bond. The principal side reaction observed in only a few instances was decyanation to afford olefins.⁸

Experimental Section

Infrared spectra were determined on a Perkin-Elmer Infracord spectrometer. Nmr spectra were determined on a Varian A-60A spectrometer. Mass spectra were determined on a Varian-Mat CH5 mass spectrometer. Elemental analyses were performed by Atlantic Microlabs, Atlanta, Ga.

The following is a typical experimental procedure.

3-Phenylbutyronitrile. To 188 mg (1.31 mmol) of 3-phenyl-2-'butenitrile⁹ (E/Z = 9/1) in 13.1 ml of methanol was added 1.27 g (52.4 mmol, 40 equiv) of magnesium turnings. The exothermic reaction which ensued after 10 min was moderated with an ice bath. The reaction was stirred 1 hr at 0° and 5 hr at 25°. To the reaction at 0° was added 24 ml of 6 N hydrochloric acid over a 1-hr period to afford a clear solution which was extracted with three 20-ml portions of ether. The ether solutions were combined, washed with 20 ml of brine, dried over anhydrous magnesium sulfate, and evaporated to afford 196 mg of oil. The oil was chromatographed on a 20 \times 20 cm preparative layer Merck silica gel F254 plate in 1:9 ether-hexane to afford 183 mg (96%) of 3-phenylbutyronitrile ($R_{\rm f}$ 0.20): ir (TF) 4.48 (CN) and 6.25 μ (arom); nmr (CCl₄) δ 1.42 (d, J = 7 Hz, 3, CHCH₃), 2.35–2.55 (m, 2, CH₂CN), 2.80–3.35 (m, 1, CHCH₃), and 7.23 (5, s, ArH); mass spectrum (70 eV) m/e(rel intensity) 51 (12), 77 (32), 78 (8), 79 (16), 103 (15), 104 (6), 105 (100), 106 (11), and 145 (22).