concentration of **18a** by GC using thermal conductivity detection (24 in. × $^1/_4$ in. column of 5% OV-101 at 160 °C, and the peak areas were measured on a digital integrator. The samples for the kinetic determinations were prepared from a stock solution of approximately 0.05–0.1 M **16a** in benzene containing heptadecane as internal standard. These samples were degassed using three freeze–thaw cycles and sealed in glass ampoules. Appropriate calibration solutions were employed in the GC analysis. The kinetics were studied at two different concentrations with identical rate constants (within experimental error) being measured. The average rate constant obtained from three different runs was 1.5×10^{-4} s^{-1}. The maximum error in this value is estimated to be ±8%. Detailed procedures and a representative kinetic plot are given in the supplementary material.

Acknowledgment. We thank the National Science Foundation and The Ohio State University Investigators Fund for support of this work.

Registry No. **6**, 15791-03-4; **9b**, 135614-81-2; **12**, 935-50-2; **13a**, 135614-71-0; **13b**, 135639-18-8; **14a**, 135614-72-1; **14b**, 135614-65-2; **15a**, 135614-73-2; **15b**, 135614-66-3; **16a**, 135614-74-3; **16b**, 135614-67-4; **17a**, 135614-92-5; **17b**, 135639-20-2; **18a**, 52727-26-1; **18b**, 52727-32-9; **19**, 135639-21-3; **20**, 135614-75-4; **21**, 66629-00-3; (*E*)-**22**, 135614-70-9; (*Z*)-**22**, 135614-76-5; (*E*)-**23**, 135614-82-3; (*Z*)-**23**, 135614-77-6; **24**, 135639-22-4; **25**, 135614-78-7; **26**, 135614-79-8; **27**, 92-69-3; **28**, 135639-23-5; **29**, 135614-80-1; **32**, 135639-24-6; **33**, 135614-83-4; **34**, 135614-84-5; **35**, 135639-25-7; **36**, 135614-85-6; **36** 2,4-DNP hydrazone, 135614-68-5; **37**, 135614-86-7; **38**, 135614-87-8; **39**, 135614-88-9; **40**, 135614-89-0; **41**, 135614-90-3; **44**, 135614-91-4; $[(COD)Ir(PPh_2Me)_2]PF_6$, 38465-86-0; 4-hydroxy-4-phenylcyclohexa-2,5-dienone, 135639-19-9; ethylene acetal benzoquinone monoethylene ketal, 35357-34-7; 4-hydroxy-4-(4-phenyl-3-butynyl)cyclohexa-2,5-dienone dimethyl acetal, 135614-69-6; 1-butyne, 107-00-6; 1-pentyne, 627-19-0.

Supplementary Material Available: Experimental procedures for reactions of **9a**, **39**, **29**, **37**, and **38** and kinetic studies; NMR spectra of products (43 pages). Ordering information is given on any current masthead page.

Phase-Transfer Catalyzed Formation of α-Cyano Ketones from Ketone Aroylhydrazones in NaCN(aq)–Inert Organic Solvent System

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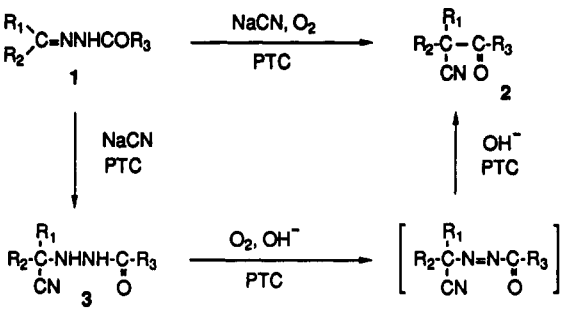
α-Cyanoalkyl aryl ketones can be obtained from ketone aroylhydrazones by heterogeneous reaction with aqueous sodium cyanide, an inert organic solvent, and acetic acid in the presence of air and a catalytic amount of a quaternary ammonium salt. The initially formed HCN adducts undergo air oxidation followed by alkaline-induced decomposition affording the α-cyanoalkyl ketones. The phase-transfer catalyst promotes all three reactions.

Previously, we reported the preparation of 1-(cyanoalkyl)-2-acylhydrazines from ketone hydrazones utilizing phase-transfer catalysis (PTC). These reactions were carried out in a stoppered flask in all cases.[1] Subsequently, it was found that the identical reaction run in an open flask in contact with air afforded α-cyanoalkyl aryl ketones (**2**). The cyano ketones were presumed to arise from the decomposition of the corresponding diazene generated by the oxidation of the HCN adduct (**3**). The formation of **2** from **1** involving carbon–carbon bond formation under mild conditions appears to be an attractive synthetic process.

The application of PTC for the oxidation of organic compounds has widely been investigated by using anionic oxidants such as permanganate, chromate, hypochlorite, periodate, or super oxide or by the combined use of metal catalysts;[2,3] however, examples of air oxidation promoted by quaternary ammonium salts seem to be limited.[4] Therefore, we have investigated phase-transfer catalysis of the present reaction and have applied the procedure to the synthesis of various α-cyanoalkyl aryl ketones **2** (Scheme I).

Scheme I



Results and Discussion

Addition of HCN to Ketohydrazones and Air Oxidation of the Resulting HCN Adducts. The reaction progress in the presence or absence of air was examined

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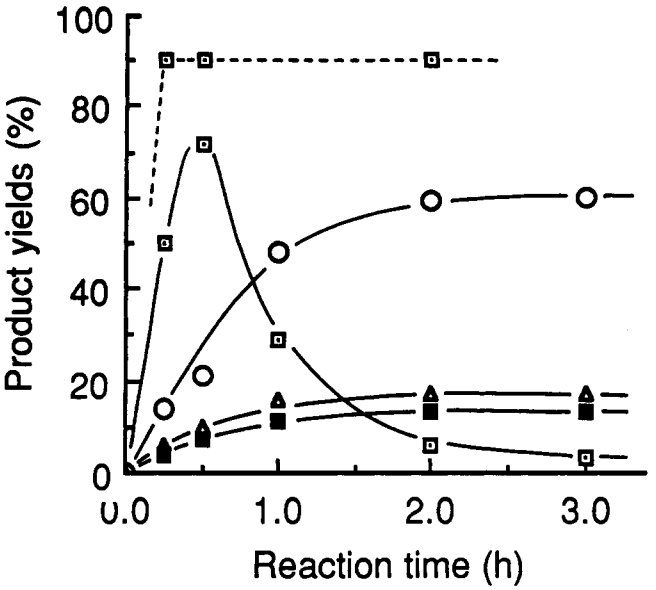


Figure 1. Relationships between the product yields and reaction time in the reaction of **1f** (5.0 mmol) in NaCN (10 mmol)–H_2O (20 mL)–cyclohexane (20 mL)–AcOH (7.5 mmol)–TOMAC (1.0 mmol) in the absence of air (---□---, HCN adduct **3f**) and in the presence of air (–□–, HCN adduct **3f**; –○–, α-cyano ketone **2f**; –△–, 4-heptanone; and –■–, 2-*n*-propylpentanenitrile).

Table I. Catalytic Ability of Quaternary Ammonium Salts to the Air Oxidation of 3f in Two-Phase Mixture of NaCN(aq) and Cyclohexane[a]

		% yield of products[b]		
catalyst	% recovery of **3f**	**2f**	4-heptanone	2-*n*-propylpentanenitrile
$(C_4H_9)_4N^+Br^-$	90	3	2	1
$(C_6H_5CH_2)N^+(C_2H_5)_3Cl^-$	94	trace	trace	trace
$C_5H_5N^+C_{12}H_{25}Cl^-$	75	2	2	trace
$C_{12}H_{25}N^+(CH_3)_3Cl^-$	38	25	12	10
$(C_{12}H_{25})_2N^+(CH_3)_2Br^-$	10	47	16	13
$(C_8H_{17})_3N^+CH_3Cl^-$	0	60	18	13

[a] Reaction conditions: **3f** (2.5 mmol), NaCN (2.5 mmol), cat. (0.5 mmol), cyclohexane–H_2O (10 mL–10 mL) at rt for 3 h. [b] GLC yield.

by using 4-heptanone benzoylhydrazone (**1f**) as the starting material. A two-phase mixture consisting of aqueous sodium cyanide/cyclohexane containing **1f** and trioctylmethylammonium chloride (TOMAC) was vigorously stirred in the presence of acetic acid in a stream of air or N_2.

The relationship between the product yield and reaction time is illustrated in Figure 1. Under a nitrogen atmosphere, hydrazone **1f** was converted into the HCN adduct (**3f**) almost quantitatively within 20 min, and the amount of **3f** remained constant. However, in the reaction conducted in contact with air, the initially formed HCN adduct underwent further reaction giving the α-cyano ketone (**2f**) along with small amounts of 2-*n*-propylpentanenitrile and 4-heptanone. Analogous results were obtained when the HCN adduct **3f** itself was treated with air in the above two-phase reaction. In the absence of TOMAC, however, **3f** was recovered unchanged. Apparently, the PTC is required for the oxidative conversion of **3f** into **2f** with air, as well as the addition of HCN to **1f**.

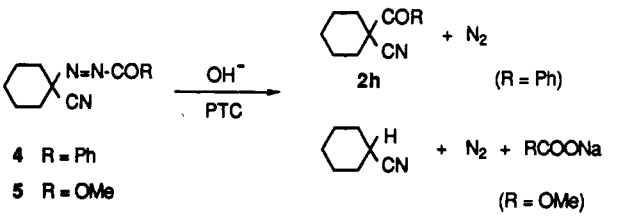
The catalytic activity of other phase-transfer catalysts for the air oxidation of **3f** was examined. The results shown in Table I indicate that quaternary ammonium salts with highly lipophilic cations catalyze the oxidation, while the more hydrophilic catalysts such as benzyltriethyl- or tetrabutylammonium salts are ineffective. A variety of mixtures of water and organic solvents were also examined for their suitability in promoting this reaction in the presence of TOMAC (Table II). Aprotic nonpolar solvents such as hexane or cyclohexane were appropriate for the formation of **2f**, whereas reactions run in more polar solvents were prone to side reactions.

Table II. Solvent Effect in the Air Oxidation of 3f in the Presence of TOMAC[a]

		% yield of products[b]		
solvent system	% recovery of **3f**	**2f**	4-heptanone	2-*n*-propylpentanenitrile
hexane–H_2O	trace	56	16	10
cyclohexane–H_2O	0	60	18	13
benzene–H_2O	8	43	15	9
CH_2Cl_2–H_2O	21	20	11	7
MeCN–H_2O	27	16	14	4
MeOH–H_2O	24	30	27	12
MeOH	74	7	8	5

[a] Reaction conditions: **3f** (2.5 mmol), NaCN (2.5 mmol), TOMAC (0.5 mmol), organic solvent (10 mL), H_2O (10 mL) at rt for 3 h. [b] GLC yield.

Scheme II



Decomposition of the Diazene Intermediate. The oxidation of 1,2-disubstituted hydrazines of type **3** to the corresponding diazenes is known; however, the resulting diazenes are generally susceptible to thermal or alkaline-induced decomposition.[5] Accordingly, it seemed likely that the diazene would be an intermediate product in the present reaction. The appearance of the characteristic yellow color of diazenes, which faded after the reaction was completed, is consistent with this assumption.

In order to examine the reactivity of diazenes under the present conditions, we subjected the known 1-(1-cyanocyclohexyl)-2-benzoyldiazene (**4**)[6] and 1-(1-cyanocyclohexyl)-2-carbomethoxydiazene (**5**)[7] to the two-phase reaction. Benzoyldiazene **4** immediately decomposed with evolution of N_2 in the presence of the catalyst and afforded α-cyano ketone **2h** as the main product. In contrast, a similar treatment of carbomethoxydiazene **5** gave cyclohexanecarbonitrile exclusively. The difference in behavior between **4** and **5** seems to stem from the stability of the acyl radicals generated by their decompositions. The relatively stable benzoyl radical is captured by recombination with cyanoalkyl radical[5] (Scheme II).

Preparation of Keto Nitriles from Ketoaroylhydrazones. By the present method, various ketoaroylhydrazones **1** were converted into the corresponding α-cyano ketones **2**. The results are summarized in Table III. In all cases, almost pure **2** could be obtained in moderate

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Table III. Preparation of α-Cyanoalkyl Aryl Ketones from Ketone Aroylhydrazones Using Phase-Transfer Catalysis[a]

	hydrazone 1			molar ratio of catalyst to 1	reaction time, h	% yield of 2[b]
	R_1	R_2	R_3			
1a	Me	Me	Ph	0.4	8	28
1b	*i*-Bu	Me	Ph	0.4	5	47
1c	*t*-Bu	Me	Ph	0.8	8	41
1d	*i*-Pr	*i*-Pr	Ph	0.8	9	38
1e	*n*-Hex	Me	Ph	0.4	4	50
1f	*n*-Pr	*n*-Pr	Ph	0.4	4	58
1g	$-(CH_2)_4-$		Ph	0.4	8	45
1h	$-(CH_2)_5-$		Ph	0.4	3	46
1i	*n*-Pr	*n*-Pr	2-pyridyl	0.4	3	53
1j	*n*-Pr	*n*-Pr	2-furyl	0.4	3	47
1k	*n*-Pr	*n*-Pr	2-ClPh	0.4	2	58
1l	*n*-Pr	*n*-Pr	4-ClPh	0.4	3	56
1m[c]	*n*-Pr	*n*-Pr	2-MeOPh	1.6	15	48
1n	*n*-Pr	*n*-Pr	4-MeOPh	0.4	6	50
1o	*n*-Pr	*n*-Pr	2-NO_2Ph	0.4	2.5	56

[a] Reaction conditions: hydrazone (10 mmol), NaCN (40 mmol), AcOH (30 mmol), cyclohexane (40 mL), H_2O (40 mL), catalyst = TOMAC. [b] Isolated yield based on 1. [c] NaCN (60 mmol), AcOH (40 mmol) was used.

yields, including sterically hindered α-cyano ketones such as **2c** and **2d**. The required amount of catalyst and reaction time varied depending upon the reactivity of 1. Generally, substituted benzoylhydrazones with electron-withdrawing groups such as $-NO_2$ or –Cl on the benzene ring were readily converted into **2**, whereas those with an electron-donating group such as –OMe on the benzene ring showed low reactivity in the oxidation. In the case of *o*-methoxy derivative (**1m**), a considerable amount of the HCN adduct (**3m**) still remained after the lengthy reaction time, in spite of the use of excess amounts of catalyst and NaCN.

α-Cyano ketones are usually prepared by acylation of nitriles with esters by means of sodium amide in liquid ammonia,[8] by reaction of ketones with *N*-(chlorosulfonyl)isocyanate followed by treatment of the resulting *N*-(chlorosulfonyl)-β-ketoamide with DMF,[9] and by substitution of α-bromo ketones with tetraalkylammonium cyanide.[10] For the preparation of cyclic α-cyano ketones, cyanation of the corresponding ketone enamine with cyanogen chloride has been utilized.[11]

The present method affords the α-cyano ketones in one pot from ketone aroylhydrazones which can be prepared in nearly quantitatively yields from readily accessible aroylhydrazines and ketones. In addition, the reaction is simple to carry out, and the conditions are mild compared to the above methods. A limitation of the reaction is that only aromatic cyano ketones can be made.

Experimental Section

General. Melting and boiling points are uncorrected. The ^1H NMR spectra were measured at 200 MHz in $CDCl_3$. GLC analyses were performed using glass columns packed with FFAP on Chromosorb W AW with N_2 as carrier gas and an FID detector.

Materials. Aroylhydrazones were prepared from the corresponding aroylhydrazine and ketone by the methods described earlier.[12] The HCN adducts of the hydrazones were prepared by our procedure using PTC.[1] 1-(1-Cyanocyclohexyl)-2-benzoyldiazene (**4**) and 1-(1-cyanocyclohexyl)-2-carbomethoxydiazene (**5**) were prepared by oxidation of the corresponding HCN adduct with HgO or Br_2 according to the procedures of Lynch and Ziegler.[6,7,13] Their spectral data are consistent with those in the literature. Commercially available quaternary ammonium salts were used without further purifications.

Preparation of α-Cyano Ketones (2a–o) from Ketone Aroylhydrazones (1a–o). General Procedure. A 200-mL round-bottomed flask was equipped with a large magnetic stirring bar, a gas-inlet tube, and an efficient reflux condenser fitted with a gas-outlet tube connected to a water aspirator. The flask was charged with the hydrazone (10 mmol), NaCN (40 mmol), cyclohexane (40 mL), water (40 mL), and trioctylmethylammonium chloride (TOMAC) (4 mmol). The mixture was stirred vigorously, a gentle stream of air was passed through the two phases with slight aspiration, and acetic acid (30 mmol) was added dropwise through a syringe over 5 min. Stirring was continued for several hours at rt.

After the reaction was complete, the water layer was removed, and the organic layer was washed with water (20 mL × 2), dried with Na_2SO_4, and concentrated. The residue was purified by flash chromatography on a short column of silica gel (15 cm height × 2 cm diameter, Merk Kieselgel 60, 230–400 mesh) with benzene as eluant. The first fraction (ca. 75 mL) usually contained almost pure α-cyano ketone together with small amounts of the parent ketone and nitrile. The starting hydrazone, the HCN adduct, and TOMAC were not eluted with benzene. The isolated yields are shown in Table III. Analytical samples were obtained by micro-distillation or recrystallization.

2-Benzoyl-2-methylpropanenitrile (2a): bp 103–105 °C (3 mm) [lit.[10] bp 124–126 °C (10 mm)]; IR ($CHCl_3$) ν 2230 (CN), 1690 cm^{-1} (CO); ^1H NMR δ 1.72 (s, 6 H), 7.4–7.6 (m, 3 H), 8.1–8.2 (m, 2 H). Anal. Calcd for $C_{11}H_{11}NO$: C, 76.27; H, 6.40; N, 8.09. Found: C, 76.37; H, 6.47; N, 8.03.

2-Benzoyl-2,3,3-trimethylbutanenitrile (2c): bp 123–124 °C (2.5 mm); IR ($CHCl_3$) ν 2225 (CN), 1680 cm^{-1} (CO); ^1H NMR δ 1.17 (s, 9 H), 167 (s, 3 H), 7.4–7.6, 8.0–8.1 (total 5 H). Anal. Calcd for $C_{14}H_{17}NO$: C, 78.10; H, 7.96; N, 6.51. Found: C, 78.00; H, 7.95; N, 6.44.

2-Benzoyl-3-methyl-2-isopropylbutanenitrile (2d): bp 132–133 °C (2.5 mm); IR ($CHCl_3$) ν 2225 (CN), 1680 cm^{-1} (CO); ^1H NMR δ 1.08 (d, J = 6.8 Hz, 6 H), 1.56 (d, J = 7.3 Hz, 6 H), 2.4–2.7 (m, 2 H), 7.4–7.7, 8.0–8.2 (total 5 H). Anal. Calcd for $C_{15}H_{19}NO$: C, 78.56; H, 8.35; N, 6.11. Found: C, 78.39; H, 8.31; N, 6.06.

2-Benzoyl-2-*n*-propylpentanenitrile (2f): bp 139–140 °C (3 mm); IR ($CHCl_3$) ν 2220 (CN), 1690 cm^{-1} (CO); ^1H NMR δ 0.95 (t, J = 7.3 Hz, 6 H), 1.3–1.7 (m, 4 H), 1.8–2.0 (m, 2 H), 2.05–2.25 (m, 2 H), 7.4–7.7, 8.0–8.1 (total 5 H). Anal. Calcd for $C_{15}H_{19}NO$: C, 78.56; H, 8.35; N, 6.11. Found: C, 78.46; H, 8.44; N, 6.17.

2-Benzoylcyclohexanecarbonitrile (2h): bp 146–144 °C (2 mm), mp 43–45 °C; IR ($CHCl_3$) ν 2225 (CN), 1690 cm^{-1} (CO); ^1H NMR δ 1.1–1.5 (br, 1 H), 1.7–2.0 (br, 7 H), 2.2–2.4 (br, 2 H), 7.4–7.7, 8.1–8.2 (total 5 H). Anal. Calcd for $C_{14}H_{15}NO$: C, 78.84; H, 7.09; N, 6.57. Found: C, 79.06; H, 7.11; N, 6.59.

2-Picolyl-2-*n*-propylpentanenitrile (2i): bp 145–146 °C (2 mm); IR ($CHCl_3$) ν 2230 (CN), 1695 cm^{-1} (CO); ^1H NMR δ 0.92 (t, J = 7.3 Hz, 6 H), 1.2–1.7 (m, 4 H), 2.03 (dt, J = 13, 5.1 Hz, 2 H), 2.62 (dt, J = 13, 5.1 Hz, 2 H), 7.52 (t?, 1 H), 7.88 (dt, J = 7.3, 1.5 Hz, 1 H), 8.01 (d, J = 7.3 Hz, 1 H), 8.7 (d, J = 5.1 Hz, 1 H). Anal. Calcd for $C_{14}H_{18}N_2O$: C, 73.01; H, 7.88; N, 12.17. Found: C, 72.89; H, 8.03; N, 12.01.

2-(2-Furoyl)-2-*n*-propylpentanenitrile (2j): bp 127–128 °C (3 mm); IR ($CHCl_3$) ν 2230 (CN), 1670 cm^{-1} (CO); ^1H NMR δ 0.94 (t, J = 7.3 Hz, 6 H), 1.2–1.7 (m, 4 H), 1.86 (dt, J = 13, 5.1 Hz, 2 H), 2.05–2.25 (m, 2 H), 6.60 (dd, J = 3.7, 1.5 Hz, 1 H), 7.64 (d, J = 3.7 Hz, 1 H), 7.68 (d, 1.5 Hz, 1 H). Anal. Calcd for $C_{13}H_{17}NO_2$: C, 71.20; H, 7.82; N, 6.31. Found: C, 71.31; H, 7.99; N, 6.28.

2-(2-Chlorobenzoyl)-2-*n*-propylpentanenitrile (2k): bp 155–156 °C (2 mm); IR ($CHCl_3$) ν 2225 (CN), 1715 cm^{-1} (CO); ^1H NMR δ 0.99 (t, J = 7.3 Hz, 6 H), 1.4–1.7 (m, 4 H), 1.75–1.95 (m, 2 H), 2.0–2.2 (m, 2 H), 7.3–7.5 (m, 4 H). Anal. Calcd for $C_{15}H_{18}NOCl$: C, 68.30; H, 6.88; N, 5.31; Cl, 13.44. Found: C, 68.31; H, 6.99; N, 5.41; Cl, 13.04.

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(13) For the preparation of **4**, the reaction time of 0.5 h, described in the literature, was too short to reach completion. A satisfactory yield of **4** was obtained after 4 h.

2-(2-Methoxybenzoyl)-2-*n*-propylpentanenitrile (2m): bp 153-154 °C (2.5 mm); IR ($CHCl_3$) ν 2225 (CN), 1690 cm^{-1} (CO); ^1H NMR δ 0.96 (t, J = 7.3 Hz, 6 H), 1.4-1.7 (m, 4 H), 1.7-1.9 (m, 2 H), 2.0-2.2 (m, 2 H), 3.90 (s, 3 H), 6.9-7.1 (m, 2 H), 7.2-7.3 (m, 1 H), 7.4-7.5 (m, 1 H). Anal. Calcd for $C_{16}H_{21}NO_2$: C, 74.10; H, 8.16; N, 5.40. Found: C, 74.19; H, 8.15; N, 5.33.

2-(2-Nitrobenzoyl)-2-*n*-propylpentanenitrile (2o): mp 80-81 °C (from cyclohexane); IR ($CHCl_3$) ν 2230 (CN), 1720 cm^{-1} (CO); ^1H NMR δ 1.01 (t, J = 7.3 Hz, 6 H), 1.4-1.7 (m, 4 H), 1.8-2.2 (m, 2 H), 2.0-2.3 (m, 2 H), 7.35 (dd, J = 7.3, 1.5 Hz, 1 H), 7.6-7.9 (m, 2 H), 8.28 (dd?, J = 8.1, 1.5 Hz, 1 H). Anal. Calcd for $C_{15}H_{18}N_2O_3$: C, 65.67; H, 6.61; N, 10.21. Found: C, 65.69; H, 6.61; N, 10.15.

Kinetic Experiments with Hydrazone (1f). The reaction progress in a stream of air or N_2 was examined under conditions indicated in the caption in Figure 1. The reaction was stopped at various times, and the organic layer was passed immediately through a short column of silica gel. The fractions eluted with benzene were analyzed by GLC, and the product yields were determined by the internal standard method using a 1-m FFAP column for **2f** (t_R = 2.3 min; 190 °C, 67 mL/min) and a 2-m FFAP column for 4-heptanone and 2-*n*-propylpentanenitrile (t_R = 1.8 min and 5.1 min; 90 °C, 38 mL/min). Continued elution with benzene-Et_2O (2:1) afforded **3f** as a white solid (R_f = 0.44, benzene-Et_2O (2:1), which was identified by a mixed melting point test with an authentic sample.

Oxidative Conversion of HCN Adduct (3f) into 2f. HCN adduct **3f** (0.65 g, 2.5 mmol) was stirred vigorously in a heterogeneous mixture of aqueous NaCN (0.12 g, 2.5 mmol in 10 mL of H_2O) and the organic solvent in the presence of a quaternary ammonium salt (0.5 mmol) for 3 h in a stream of air. The product yields indicated in Table II and III were determined by the internal standard method as described above.

Decomposition of Diazenes (4, 5). Freshly prepared **4** (0.96 g, 4 mmol) was treated in a mixture of aqueous Na_2CO_3 (0.21 g, 2 mmol in 20 mL H_2O) and cyclohexane (20 mL) at rt. Addition of TOMAC (0.4 g, 1 mmol) brought about vigorous evolution of N_2, and the yellow mixture became colorless. From the organic layer, **2h** was isolated by flash chromatography on silica gel eluting with benzene (0.37 g, 43%), which was identified by spectroscopic comparison with an authentic sample.

Similar treatment of **5** (1.95 g, 10 mmol) gave 0.97 g of cyclohexanecarbonitirle [yield, 87% based on **5**, bp 85-87 °C (23 mm)] and was identified by comparison with an authentic sample prepared previously.[12]

Registry No. **1a**, 3408-16-0; **1b**, 124243-18-1; **1c**, 128721-91-5; **1d**, 124243-16-9; **1e**, 124243-17-0; **1f**, 124243-15-8; **1g**, 24214-78-6; **1h**, 24214-79-7; **1i**, 135664-40-3; **1j**, 135664-41-4; **1k**, 135664-42-5; **1l**, 135664-43-6; **1m**, 135664-44-7; **1n**, 135664-45-8; **1o**, 135664-46-9; **2a**, 7391-73-3; **2b**, 135664-47-0; **2c**, 135664-48-1; **2d**, 135664-49-2; **2e**, 135664-50-5; **2f**, 135664-51-6; **2g**, 135664-52-7; **2h**, 135664-53-8; **2i**, 135664-54-9; **2j**, 135664-55-0; **2k**, 135664-56-1; **2l**, 135664-57-2; **2m**, 135664-58-3; **2n**, 135664-59-4; **2o**, 135664-60-7; **3f**, 128721-94-8; **4**, 27702-92-7; **5**, 33670-04-1; sodium cyanide, 143-33-9; trioctylmethylammonium chloride, 5137-55-3; cyanocyclohexane, 766-05-2; 4-heptanone, 123-19-3; 2-propylpentanenitrile, 13310-75-3; tetrabutylammonium bromide, 1643-19-2; triethylbenzylammonium chloride, 56-37-1; *N*-dodecylpyridinium chloride, 104-74-5; trimethyldodecylammonium chloride, 112-00-5; didodecyldimethylammonium bromide, 3282-73-3.

Supplementary Material Available: ^1H NMR and IR spectral data and elemental analyses for compounds **2b**, **2e**, **2g**, **2l**, and **2n** (1 page). Ordering information is given on any current masthead page.

Catalytic Aminomercuration Reactions of 3-Alken-1-ynes: An Improved Method for the Synthesis of 2-Amino-1,3-butadienes and 1-Aza-1,3-butadienes[1]

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Catalytic aminomercuration of 3-alken-1-ynes leads to 1-aza-1,3-butadienes and 2-amino-1,3-butadienes. Under appropriate reaction conditions it is possible to prepare these compounds via mercuration of 3-alken-1-ynes in the presence of either aromatic or aliphatic primary and secondary amines. Depending on the substituents in the starting 3-alken-1-yne, the mercuration reaction may afford γ-amino enamines instead of 2-amino-1,3-butadienes and 3-imino amines or 4-amino-1-aza-1,3-butadienes instead of 1-aza-1,3-butadienes.

The increasing development of the Diels-Alder reaction in the last 20 years has made 1,3-dienes very important starting materials in organic synthesis through [4 + 2] cycloaddition processes.[2] However, 1-aza-1,3-butadienes[3] and 2-amino-1,3-butadienes[4] have not been studied as extensively as their oxygen analogues.[5] While the preparation of these compounds via condensation reactions between amines and α,β-unsaturated carbonyl compounds is successful in some specific instances,[6] Michael-type addition of the amine often occurs.[6c,7,8]

For many years we have studied the catalytic aminomercuration of terminal C≡C triple bonds leading to en-

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