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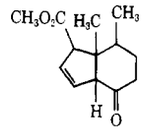
(45) Ethyl cyclopropyl acrylate undergoes addition with $(CH_3)_2CuLi$.[44c]
(46) The syn ester **27e** is stable in refluxing benzene, with or without *p*-TsOH. In the presence of ethylene glycol, a second peak (VPC) slowly appears. Hydrolysis of the ketalization mixture provides **27e** and a product which was identical with a material isolated from hydrolysis of a ketalization which had proceeded for an extended period of time. This substance's NMR spectrum was consistent with i, arising by an acid-catalyzed vinylcyclopropane rearrangement due to the steric compression of the ketal group.



i

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(60) The chromatographic properties of the two series of compounds are similar. It is unlikely that there are dramatic polarity differences between isomers. Care has been taken to analyze adjacent TLC bands. Both cyclopropyl series experiments are reproducible and the difference in product composition argues against selective loss of one isomer.

Notes

Methyldialkylcyanodiazenecarboxylates as Intermediates for Transforming Aliphatic Ketones into Nitriles

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Several years ago we described[3] a method for converting aliphatic ketones into nitriles by the base-induced decomposition of methyl dialkylcyanodiazenecarboxylates. The method permits the in situ methylation and carbomethoxylation of the intermediate nitrile anions, thereby constituting a method for geminal substitution at the α carbonyl carbon.[4] This Note provides the experimental details for this reaction. The diazenes **1b–4b** were readily prepared as outlined in Scheme I. Generation of hydrogen cyanide in situ (KCN–NH_4Cl) gave somewhat lower yields than liquid HCN, due to water solubility of the products.

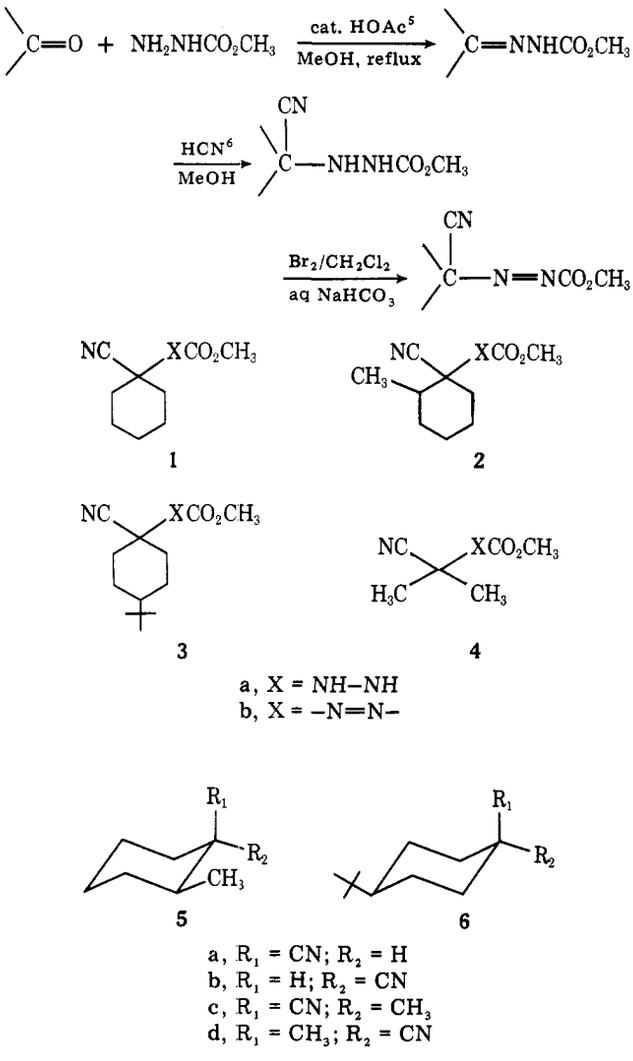
The decomposition of diazene **1b** with catalytic NaOMe in MeOH at 0 °C provided cyclohexylnitrile in 94% yield (VPC). When MeOH-d_1 was employed, cyclohexylnitrile-d_1 was obtained. The cleavage with methoxide also undergoes a degenerate methoxide exchange with the substrate. Evidence for this process was obtained by employing a two-phase system of ether and water, the yellow diazene being soluble in the former phase. When dilute aqueous NaOH was added slowly to the mixture at 0 °C, the aqueous phase turned yellow (diazenecarboxylate salt) as gas was evolved from the same phase. When gas evolution had ceased, the reaction mixture was colorless.

Diazene **2b** provided approximately an equal mixture of *cis*- (**5a**) and *trans*-2-methylcyclohexylnitrile (**5b**), while the 4-*tert*-butyldiazene **3b** gave rise to two nitriles in a ratio of 58/42 by VPC analysis. Rickborn and Jensen[7a] have shown that the equilibrium (*t*-BuOK/*t*-BuOH) of 4-*tert*-butylcyclohexylnitrile favors the equatorial nitrile **6b** over the axial isomer **6a** (**6b/6a** = 56/44). Subjection of the mixture to these conditions provides a thermodynamic mixture, the major component now becoming the minor component. Thus, the catalytic decomposition provides a kinetic mixture, wherein the axial nitrile **6a** predominates.

In order to permit alkylation of the nitrile anion, it was necessary to perform the reaction with stoichiometric quantities of methoxide and to employ an aprotic solvent. Anhydrous lithium methoxide was prepared in situ from anhydrous methanol and butyllithium (hexane) or methyllithium (ether) in dimethoxyethane (DME). When the diazene in the presence of an excess of methyl iodide was added dropwise at 0 °C to the base, the yellow diazene color was discharged and gas evolution occurred providing from diazene **1b** an 84% yield of products consisting of 1-methylcyclohexylnitrile 77%) and 1-carbomethoxycyclohexylnitrile (13%). This method of addition of the methyl iodide is necessary, since, if the diazene is added first and then the methyl iodide, upwards of 70% of the reaction mixture consists of 1-carbomethoxycyclohexylnitrile. This arises from the nitrile anion reacting with generated dimethyl carbonate or unreacted diazene. The concomitant addition procedure allows the alkylation to favorably compete with the acylation. An efficient procedure for the preparation of 1-carbomethoxycyclohexylnitrile was achieved by adding the diazene to the $LiOCH_3$/DME containing excess dimethyl carbonate.

The in situ methylation of the nitrile anion from diazene **2b** provided a diastereomeric mixture (**5c/5d** = 73/27) of methylated nitriles (63%) and a diastereomeric mixture of carbomethoxylated nitriles (25%). The identity of the minor methylated nitrile was confirmed by synthesis from the Diels–Alder adduct of tiglic acid and butadiene.[4b,7] A similar decomposition of diazene **3b** provided 1-methyl-4-*tert*-butylcyclohexylnitrile as a mixture of diastereomers (**6c/6d** = 76/24) in 70% yield along with 23% of carbomethoxylated product. House and Bare[8] have obtained a similar ratio (71/29)

Scheme I



by treating 4-*tert*-butylcyclohexylnitrile with lithium diethylamide followed by methyl iodide.

Since methylation is among the least sterically demanding of alkylation procedures, and in view of the fact that approximately 25% of carbomethoxylated product is obtained in the in situ process, it is more efficient to generate the nitriles by the protic sequence followed by alkylation using dialkylamide bases.[8]

Experimental Section

Vapor-phase chromatography (VPC) analyses were determined on an Aerograph A-90-P or Varian Aerograph Model 90-P instrument employing a 20 ft × ⅜ in. 20% SE-30 on Chromosorb W (45/60) column. Cyclohexylnitrile, cyclohexanone, or biphenyl were used as internal standards. Infrared spectra (IR) were determined on a Perkin-Elmer Model 421 or 337 spectrometer. Nuclear magnetic resonance spectra (NMR) were recorded on a Jeolco Model JNM-MH-100 or Varian A-60A spectrometer using Me_4Si as an internal standard. Melting points were determined on a Fisher–Johns apparatus and are corrected. Microanalyses were performed by Galbraith Laboratories or Atlantic Microlabs and are within 0.3% of the theoretical composition. Cyclohexanone, 2-methylcyclohexanone, 4-*tert*-butylcyclohexanone, methyl carbazate, *n*-butyllithium, and methyllithium were obtained commercially. Organic extracts were dried over anhydrous magnesium sulfate. Dimethoxyethane (DME) was distilled from sodium benzophenone ketyl and methanol from $Mg(OCH_3)_2$.

Hydrazine 1a (via liquid HCN). To a solution of 4.5 g (50.0 mmol) of methyl carbazate in 10 mL of methanol containing a drop of acetic acid was added 4.9 g (50.0 mmol) of cyclohexanone. The solution was refluxed for 30 min, concentrated in vacuo, taken up in ether, and dried. Filtration and concentration of the solution gave light yellow oil which was dissolved in 10 mL of methanol, cooled to 0 °C with stirring, and treated with 6 mL (~150 mmol) of liquid hydrogen cyanide[9] (HOOD!) at such a rate that the temperature remained below 10 °C. After 15 min a heavy, white precipitate formed, requiring the addition of 10 mL of methanol to facilitate stirring. After 30 min, the mixture was filtered and washed with methanol to afford 7.0 g of white crystalline solid. Concentration of the mother liquors provided an additional 2.5 g (97.5%). Recrystallization (methanol/pentane) provided a sample of hydrazine **1a:** mp 135–136 °C IR ($CHCl_3$) 3600–3200, 2235, and 1740 cm^{-1}; NMR ($CDCl_3$) δ 3.82 (3 H, s), 4.46 (1 H, br s), and 6.82 (1 H, br s).

Anal. ($C_9H_{15}N_3O_2$): C, H, N.

Hydrazine 2a: 90% yield; mp 138 °C (methanol/pentane); IR ($CHCl_3$) 3700–3250, 2235, and 1735 cm^{-1}; NMR ($CDCl_3$) δ 1.14 (3 H, d, J = 6 Hz), 3.82 (2 H, s), 4.62 (1 H, br d, J = 4 Hz), and 6.76 (1 H, br d, J = 4 Hz).

Anal. ($C_{10}H_{17}N_3O_2$): C, H, N.

Hydrazine 3a: 90% yield; mp 132–133.5 °C (methanol/pentane); IR ($CHCl_3$) 3700–3225, 2230, and 1730 cm^{-}; NMR ($CDCl_3$) δ 0.90 (9 H, s), 3.80 (3 H, s), 4.54 (1 H, br s), and 6.92 (br s).

Anal. ($C_{13}H_{23}N_3O_2$): C, H, N.

Hydrazine 4a: 98% yield; mp 99.5–101 °C (methanol/pentane); IR ($CHCl_3$) 3700–3200, 2230, and 1730 cm^{-1}; NMR ($CDCl_3$) δ 1.50 (6 H, s), 3.80 (3 H, s), 4.46 (1 H, br d, J = 4 Hz), and 6.80 (1 H, br s).

Anal. ($C_6H_{11}N_3O_2$): C, H, N.

Hydrazine 1a (via in situ generation of HCN). To 0.1 mol of the carbazone of cyclohexanone (vide supra) was added a solution of 15.5 g (0.3 mol) of ammonium chloride and 16 g (0.3 mmol) of potassium cyanide in 75 mL of water and 50 mL of methanol. After stirring the mixture at room temperature for 18 h, the solution was diluted with 100 mL of water and thoroughly extracted with CH_2Cl_2. After drying, concentration, and crystallization (MeOH/pentane), hydrazine **1a** was obtained in 60% yield.

Diazene 1b. To a vigorously stirred mixture of 11.7 g (0.06 mol) of hydrazine **1a** in 100 mL of CH_2Cl_2 and 15.1 g (0.18 mol) of $NaHCO_3$ in 100 mL of H_2O was added dropwise 24 mL (67 mmol) of a 2.8 M Br_2/CH_2Cl_2 solution over 10 min at room temperature. After the addition had been completed, the mixture developed a persistent orange-red color (+ KI–starch). The excess bromine was discharged by the addition of small portions of solid Na_2SO_3 to the reaction mixture. The layers were separated and the aqueous phase extracted with CH_2Cl_2 (two 50-mL portions). The combined organic fractions were washed with H_2O (50 mL), dried, filtered, and concentrated. The residue was distilled to provide 11.0 g (95%) of diazene **1b** as a bright yellow liquid: bp 115 °C (1.3 mm); IR (CCl_4) 1785 cm^{-1}; NMR ($CDCl_3$) δ 3.98 (3 H, s).

Anal. ($C_9H_{13}N_3O_2$): C, H, N.

Diazene 2b: 96% yield; bp 103 °C (0.4 mm); IR (CCl_4) 1780 cm^{-1}; NMR ($CDCl_3$) δ 1.02 (3 H, d, J = 7 Hz), and 4.20 (3 H, s).

Anal. ($C_{10}H_{15}N_3O_2$): C, H, N.

Diazene 3b: 96% yield; mp 89.5–90.5 °C (ether/pentane); IR (CCl_4) 2245 and 1775 cm^{-1}; NMR ($CDCl_3$) δ 0.96 (9 H, s) and 4.11 (3 H, s).

Anal. ($C_{13}H_{21}N_3O_2$): C, H, N.

Protic Decomposition of Diazene 1b. To a solution of 540 mg (10 mmol) of $NaOCH_3$ in 5 mL of CH_3OH maintained at 0 °C was added dropwise 3.9 g (20 mmol) of diazene **1b** in 10 mL of ether/methanol (1/1). The addition proceeded with vigorous gas evolution and required approximately 30 min for completion, during which time the temperature was maintained between 0 and 10 °C. When gas evolution had ceased, the solution was allowed to warm to room temperature and was diluted with water (10 mL). The mixture was thoroughly extracted with ether, dried, filtered, concentrated, and distilled to provide a 94% yield of cyclohexylnitrile (compared with an authentic sample).

Protic Decomposition of Diazene 3b. In the manner described *cis*- (**6a**) and *trans*-4-*tert*-butylcyclohexylnitrile (**6b**) were obtained in 96% yield (VPC). Samples collected via preparative GLC gave: **6a,** mp 57 °C (lit.[7b] 56.3–57.3 °C, IR (CCl_4) 2240 cm^{-1}, NMR ($CDCl_3$) δ 0.89 (9 H, s) and 2.96 (1 H, m); **6b,** mp 33–34 °C (lit.[7b] 33.4–34.7 °C), IR (CCl_4) 2240 cm^{-1}, NMR ($CDCl_3$) δ 0.85 (9 H, s).

Aprotic Decomposition of Diazene 1a (methylation). To solution of 1.75 mL (45 mmol) of dry methanol in 20 mL of dry DME containing a trace of triphenylmethane maintained under N_2 at 0 °C was added 20 mL (46 mmol) of 2.3 M BuLi in hexane until a pink color persisted. To the reaction mixture was added a solution of 1.95 g (10.0 mmol) of diazene **1b** and 8 mL (120 mmol) of methyl iodide in 20 mL of dry DME over a period of 1 h at 3–10 °C. After the addition was complete, the reaction mixture was stirred at 25 °C for 1 h, then diluted with 40 mL of H_2O and thoroughly extracted with ether, dried,

and concentrated. Analysis (VPC) of the residue indicated two products formed in 84% yield. The major material (86%) was identical (NMR, VPC collected) with 1-methylcyclohexylnitrile prepared by the procedure of House,[8] while the minor component was identical with 1-carbomethoxycyclohexynitrile prepared from methyl 2-cyano-6-heptenoate.[10]

Aprotic Decomposition of Diazene 2b. In the manner described (vide supra) VPC analysis indicated an overall yield of 90% consisting of *trans*-1,2-dimethylcyclohexylnitrile (**5c**, 46%) [IR (CCl_4) 2240 cm^{-1}; NMR ($CDCl_3$) δ 1.08 (3 H, d, J = 8 Hz), 1.34 (3 H, s), and 0.95–2.14 (9 H, m)], *cis*-1,2-dimethylcyclohexylnitrile (**5d**, 17%), identical with a sample prepared from butadiene and tiglic acid,[4b] diastereomeric 2-methyl-1-carbomethoxycyclohexylnitrile (25%) [IR (CCl_4) 2245 and 1730 cm^{-1}; NMR ($CDCl_3$) δ 1.04 (3 H, d, J = 6 Hz), 1.15–2.37 (9 H, m), and 3.90 (3 H, s)], and diastereomeric 2-methylcyclohexylnitrile (≤2% **5a** and **5b**), identical with material from the protic decomposition.

Aprotic Decomposition of Diazene 3b. As described (vide supra), a combined yield of 95% was obtained consisting of *trans*-1-methyl-4-*tert*-butylcyclohexylnitrile (53%, **6c**), *cis*-1-methyl-4-*tert*-butylcyclohexylnitrile (17%, **6d**),[7] diastereomeric 1-carbomethoxy-4-*tert*-butylcyclohexylnitrile (23%) [IR (CCl_4) 2240 and 1740 cm^{-1}; NMR (CCl_4) δ 0.91 (9 H, s), 0.82–2.32 (9 H, m), and 3.91 (3 H, s)], and diastereomeric 4-*tert*-butylcyclohexylnitrile (≤1%, **6a** and **6b**), identical with material from the protic decomposition.

Carbomethoxylation of Diazene 1b. To a mixture of 45 mmol of lithium methoxide (vide supra) and 10.8 g (0.120 mol) of freshly distilled dimethyl carbonate maintained under N_2 at 0–5 °C was added dropwise over 25 min 1.95 g (10.0 mmol) of diazene **1b** in 15 mL of DME. After the addition was complete, the solution was allowed to warm to 25 °C, then diluted with 25 mL of H_2O and thoroughly extracted with ether, dried, filtered, and concentrated. The residue accounted for an 84% yield (VPC) consisting of cyclohexylnitrile (7%) and 1-carbomethoxycyclohexylnitrile (77%), both spectroscopically (IR and NMR) identical with authentic samples.

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Registry No.—**1a**, 61827-29-0; **1b**, 33670-04-1; **2a**, 61827-30-3; **2b**, 33794-84-2; **3a**, 61827-31-4; **3b**, 33670-05-2; **4a**, 61827-32-5; **5a**, 25144-00-7; **5b**, 10479-61-5; **5c**, 61827-33-6; **5d**, 61827-34-7; **6a**, 15619-19-9; **6b**, 15619-18-8; **6c**, 15619-22-4; **6d**, 15619-20-2; methylcarbazate, 6294-89-9; cyclohexanone, 108-94-1; 2-methylcyclohexanone, 583-60-8; 4-*tert*-butylcyclohexanone, 98-53-3; acetone, 67-64-1; *trans*-1-carbomethoxy-4-*tert*-butylcyclohexylnitrite, 61827-35-8; *cis*-1-carbomethoxy-4-*tert*-butylcyclohexylnitrile, 61827-36-9; *trans*-2-methyl-1-carbomethoxycyclohexylnitrile, 61827-37-0; *cis*-2-methyl-1-carbomethoxycyclohexylnitrile, 61827-38-1.

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Rotational Energy Barriers in 1-(3,4,5-Trimethoxyphenyl)benz[*h*]imidazo[1,5-*a*]quinoline and Related Compounds

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During our synthetic investigations on certain benzimidazoquinoline and -isoquinoline systems,[2] it was noted that 1-aryl derivatives of benz[*h*]imidazo[1,5-*a*]quinoline gave rise to temperature-dependent NMR spectra. Hindered rotation of the aryl group about the aryl–C_1 bond would account for the observed phenomena.[3a–d] The temperature dependence of the NMR spectra of several of these compounds has now been studied in greater detail.

In the NMR spectrum of 1-(3,4,5-trimethoxyphenyl)-benz[*h*]imidazo[1,5-*a*]quinoline (1) at ambient temperature and above, the three methoxy groups appear as two singlets, a three-proton singlet at 3.79 ppm and a six-proton peak at 3.44 ppm (corresponding to the methoxy groups in the 3 and 5 positions) as shown in Figure 1.[4] The protons on the phenyl ring at the 2 and 6 positions appear as a singlet at 6.50 ppm. As the temperature is lowered the 3- and 5-methoxy groups give rise to two peaks which eventually attain chemical shifts of 2.76 and 4.13 ppm at the lowest temperature obtainable in the deuteriochloroform solvent, −67 °C. At this temperature the peak separation, $\Delta\nu$, is 124 Hz. Likewise, the two phenyl ring protons form two peaks, one at 5.49 ppm, the other buried in the aromatic envelope. Coalescence was observed to occur at −23 ± 2 °C for the peaks of the methoxy groups at the 3 and 5 positions.[5] Of the two sets of signals, those corresponding to the methoxy groups were used for the subsequent lineshape analysis.

Since $\Delta\nu$ in the absence of exchange is important both in the computer and manual calculations, it was desirable to determine whether or not the separation increased significantly at lower temperatures. A plot of $\Delta\nu$ vs. temperature approaches 125 Hz at low temperature, and $\Delta\nu$ was found to be 124.7 Hz at −79 °C in dichloromethane solution. It thus appears that $\Delta\nu$ was within 1 or 2 Hz of its maximum value and an error of a few hertz would have a negligible effect upon the calculations. To avoid residual broadening errors due to rotation of the methoxy groups, the signal at 3.79 ppm was used as a resolution standard. This was found to broaden somewhat as the temperature was lowered when checked against dichloromethane.

A Dreiding model of 1 indicates that complete rotation of the aryl group about the aryl–C_1 bond is not allowed. Consequently, in the extreme allowed conformations the 2 and 3 and then the 4 and 5 positions are alternately above and then tilted away from the π-electron cloud of the benz[*h*]quinoline ring system, as in the hexahelicene-like conformations **1a** and **1b**. The model suggests that the benz[*h*]imidazo[1,5-*a*]quinoline ring system is planar, in which case **1a** and **1b** are enantiomeric. Thus the 3- and 5-methoxy groups should give rise to two NMR signals at low temperature. A similar argument can