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Thermal and Base-Catalyzed Decomposition of Ester and Nitrile Derivatives of 2-(2,2-Dicarboxyvinyl)-1,1,1-trimethylhydrazinium Hydroxide Inner Salt

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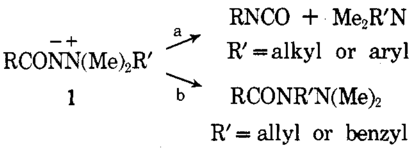
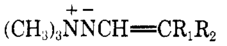
Curtius (path a) or Stevens (path b) rearrangements may be initiated by thermal decomposition of appropriately substituted aminimides derived from carboxylic acids (**1**).[1]



$$\underset{\mathbf{1}}{\text{RCO}\overset{-}{\text{N}}\overset{+}{\text{N}}(\text{Me})_2\text{R}'}\;\begin{cases}\xrightarrow{a}\ \text{RNCO} + \text{Me}_2\text{R}'\text{N} \quad \text{R}' = \text{alkyl or aryl}\\ \xrightarrow{b}\ \text{RCONR}'\text{N(Me)}_2 \quad \text{R}' = \text{allyl or benzyl}\end{cases}$$

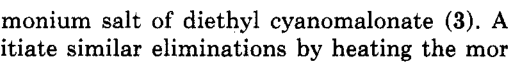
This note reports the results of our study of the thermal and base-catalyzed decomposition of three vinylogous aminimides (**2**) which were first synthesized by Brown[2] in 1967.



$$(\text{CH}_3)_3\overset{+}{\text{N}}\overset{-}{\text{N}}\text{CH}{=}\text{CR}_1\text{R}_2$$

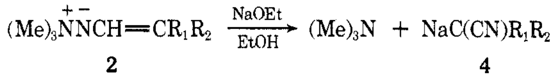
2a, $R_1 = R_2 = CO_2Et$
b, $R_1 = CN$; $R_2 = CO_2Et$
c, $R_1 = R_2 = CN$

Brown[2] reported that the diester **2a** decomposes in refluxing chloroform to give trimethylamine and unidentified products. The latter observation was of interest to us since **2a** is incapable of undergoing a Curtius-type rearrangement and the unidentified products could therefore derive from the vinyl nitrene, $NCH{=}C(CO_2Et)_2$. Although the odor of trimethylamine was apparent during the thermolysis of **2a** in refluxing chloroform, we have established that the major pathway for the thermal decomposition of **2a** is β elimination of trimethylammonium ion to give the trimethylammonium salt of diethyl cyanomalonate (**3**). Attempts to initiate similar eliminations by heating the more stable nitrile derivatives **2b** and **2c** in *N,N*-dimethylformamide at 140° gave recovered starting materials and tarry, unidentified products.



$$\underset{\mathbf{2a}}{(\text{Me})_3\overset{+}{\text{N}}\overset{-}{\text{N}}\text{CH}{=}\text{C}(\text{CO}_2\text{Et})_2} \longrightarrow \underset{\mathbf{3}}{(\text{Me})_3\overset{+}{\text{N}}\text{H}\ \text{NC}\overset{-}{\text{C}}(\text{CO}_2\text{Et})_2}$$

When treated with 1 equiv of sodium ethoxide in refluxing ethanol, **2a** eliminated trimethylamine and was converted to diethyl sodiocyanomalonate (**4a**). Similar treatment of **2b** and **2c** afforded ethyl sodiodicyanoacetate (**4b**) and sodium tricyanomethide (**4c**), respectively.



$$\underset{\mathbf{2}}{(\text{Me})_3\overset{+}{\text{N}}\overset{-}{\text{N}}\text{CH}{=}\text{CR}_1\text{R}_2} \xrightarrow[\text{EtOH}]{\text{NaOEt}} (\text{Me})_3\text{N} + \underset{\mathbf{4}}{\text{NaC(CN)R}_1\text{R}_2}$$

a, $R_1 = R_2 = CO_2Et$
b, $R_1 = CO_2Et$; $R_2 = CN$
c, $R_1 = R_2 = CN$

These nitrile-forming β-eliminations find precedence in our previously reported base-catalyzed conversion of aldehyde quaternary hydrazones to nitriles.[3]

Experimental Section

Melting points are uncorrected and were determined with a Mel-Temp apparatus. NMR spectra were determined on a Perkin-Elmer R-20 spectrometer utilizing hexamethyldisiloxane as an internal standard.

Thermolysis of 2-(2,2-Dicarbethoxyvinyl)-1,1,1-trimethylhydrazinium Hydroxide Inner Salt (2a) in Chloroform. A solution containing 2.5 g of **2a**[2] in 50 ml of chloroform was heated under reflux for 10.5 hr. Removal of the chloroform in vacuo afforded 2.5 g of the crude semisolid trimethylammonium salt of diethyl cyanomalonate. Recrystallization from ethanol–ether gave hygroscopic white crystals: mp 109–110°; NMR ($CDCl_3$) δ 2.86 (s, 9), 1.15 (t, 6, J = 8 Hz), 4.05 (q, 4, J = 8 Hz); ir (KBr) 2170 (CN, m), 1690 cm^{-1} (CO, s).

Anal. Calcd for $C_{11}H_{20}N_2O_4$: N, 11.5. Found: N, 11.3.

The salt was identical (ir, NMR) with that precipitated by addition of anhydrous ether to a solution prepared by adding diethyl cyanomalonate[4] to methanolic trimethylamine.

Reaction of Aminimides with Ethanolic Sodium Ethoxide. Ten percent ethanolic solutions of **2a**, **2b**, and **2c** containing 1 equiv of sodium ethoxide were heated under reflux for 5, 18, and 15 hr, respectively. Trimethylamine was evolved and was identified (from **2b**) by conversion to its picrate, mp 220–225° (ir identical with that of an authentic sample). The ethanol was evaporated in vacuo to give the crude sodium salts (**4a**, **4b**, and **4c**).

Crude diethyl sodiocyanomalonate (**4a**) from 2.0 g of **2a** was acidified with 10 ml of 6 *N* HCl and the resultant solution extracted with chloroform. Evaporation of the dried extract gave 1.0 g (66%) of pure diethyl cyanomalonate, which was identified by comparison of its NMR and ir spectra with those of an authentic sample.[4]

Crude ethyl sodiocyanoacetate (**4b**) obtained from 4.0 g of **2b** was recrystallized from ethanol–ether, affording 1.5 g (54%) of product whose structure was established to be **4b** by comparison of its NMR and ir spectra (KBr) with those of an authentic sample.[5] The NMR spectrum (CD_3COCD_3) indicated contamination with <5% of **4b**.

The crude sodium tricyanomethide (**4c**) obtained from 2.0 g of **2c** displayed an ir spectrum identical with that of an authentic sample.[6]

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Registry No.—**2a**, 18248-91-4; **2b**, 18248-92-5; **2c**, 18248-93-6; **3**, 57196-67-5; **4a**, 22466-42-8; **4b**, 4513-68-2; **4c**, 36603-80-2; chloroform, 67-66-3; sodium ethoxide, 141-52-6; diethyl cyanomalonate, 4513-67-1.

References and Notes

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