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MONOSODIUM ACETONITRILES, THEIR PREPARATION, PROPERTIES AND REACTIONS

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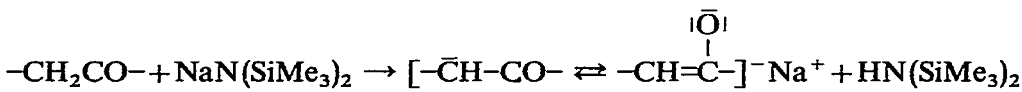
Sodium acetonitrile, $NaCH_2CN$, and related compounds have been postulated as intermediates in various condensation reactions of nitriles containing α-hydrogen atoms[1], or as intermediates in alkylation reactions of those nitriles[2]. No compounds of this type have been isolated or characterised with the exception of the stable sodium salt of diphenylacetonitrile. We have shown in a preceding paper[3] that sodium bis(trimethylsilyl)amide, (I), $NaN(SiMe_3)_2$, is a very suitable reagent for the preparation of sodium enolates (eqn. 1).



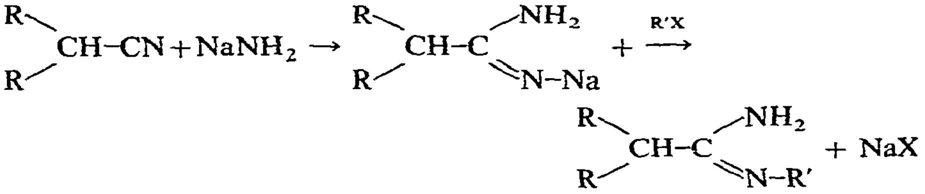
$$-CH_2CO- + NaN(SiMe_3)_2 \rightarrow [-\bar{C}H-CO- \rightleftarrows -CH{=}\overset{|\bar{O}|}{C}-]^-Na^+ + HN(SiMe_3)_2 \quad (1)$$

The reaction of (I) with various nitriles containing α-hydrogen atoms has now been investigated.

In a series of exchange reactions between hydrocarbons of different acidity and sodium bis(trimethylsilyl)amide (I) in ether solution, the approximate pK_a value of hexamethyldisilazane, the corresponding acid to (I), has been estimated. Whereas fluorene as well as xanthene readily and completely exchange one hydrogen atom against metal, the reaction between triphenylmethane and (I) leads to an equilibrium, as does the corresponding reaction between sodium·triphenylmethide and hexamethyldisilazane. Sodium bis(trimethylsilyl)amide therefore appears to be a metalating agent as powerful as sodium triphenylmethide (pK_a of triphenylmethane[4] ~ 33) over which it possesses certain preparative advantages, *e.g.*, easy accessibility of the starting materials, stability towards oxygen, and solubility in non-polar solvents; its specific reactions and the remarkable simplicity of the separation of the reaction products are further points in its favor. Cleavage of C–O–C bonds of the solvents used was never observed.

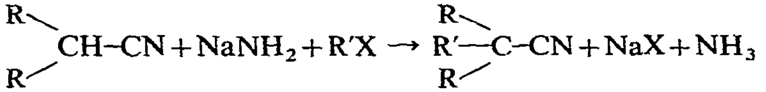
SODIUM ACETONITRILES, THEIR PREPARATION AND STRUCTURE

Holtzwart claimed in a paper on the dimerisation of acetonitrile by sodium to "diacetonitrile" that sodium acetonitrile, $NaCH_2CN$, should be the reacting intermediate[5]. He saw proof for this contention in the formation of monoalkylated acetonitriles on the addition of alkyl halides to the reaction mixtures. Ziegler and coworkers investigated the reactions of aliphatic nitriles with sodamide as well as with N-metal-substituted aliphatic amines[2a]; sodamide adds to the cyano group to give the corresponding amidines in high yield, the subsequent alkylation of which yields alkylated amidines (eqn. 2).



$$\mathrm{R_2CH{-}CN + NaNH_2 \rightarrow R_2CH{-}C(NH_2){=}N{-}Na} + \xrightarrow{\mathrm{R'X}} \mathrm{R_2CH{-}C(NH_2){=}N{-}R' + NaX} \quad (2)$$

Surprisingly, in presence of alkyl halides, the aliphatic nitrile is converted to alkyl-substituted nitriles, according to eqn. (3):



$$\mathrm{R_2CH{-}CN + NaNH_2 + R'X \rightarrow R'{-}CR_2{-}CN + NaX + NH_3} \quad (3)$$

In contrast, addition of aliphatic nitriles to an ethereal solution of lithium diethylamide gives rise to the formation of lithium-substituted nitriles rather than amidines. These may then be alkylated to compounds analogous with the reaction products of nitriles with sodamide and alkyl halides (eqn. 3). Obviously, lithium diethylamide in no case adds to the cyano group, but rather forms lithium acetonitrile by an exchange reaction. The lithium derivatives of aliphatic nitriles so prepared are stated to be soluble in ether; they have not been isolated. In due course, sodium acetonitrile was prepared as intermediate in alkylation reactions by treating sodium naphthalene with acetonitrile in tetrahydrofuran solution by Horner *et al.*[2b]; again it was not isolated.

We used sodium bis(trimethylsilyl)amide as the metalating agent of acetonitriles since we presumed that addition to the cyano group would not take place for steric reasons. Self-condensation of the nitriles was avoided by addition of the nitriles, having α-hydrogen atoms, to an ether solution of (I) at temperatures between $-40°$ and $-60°$. Sodium acetonitrile (II), which precipitated as a white, microcrystalline solid, is sensitive towards oxygen and humidity. The compound, when isolated and dried, is stable at room temperature, darkens on exposure to air and decomposes under an atmosphere of dry argon at about 85° without melting. It is insoluble in non-polar organic solvents, but dissolves readily in pyridine at 40°. At lower temperature an addition product crystallizes in long, colorless needles. We were unable to obtain this addition product in analytically pure form, as the addend is lost even by washing with pentane at low temperatures, as well as by drying in high vacuum at low temperature, yielding purified sodium acetonitrile. The solution of (II) in pyridine is not stable at room temperature since it turns brown after a few hours. On exposure to air the surface of the liquid turns blue.

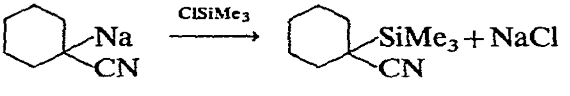
Careful hydrolysis of sodium acetonitrile by treatment with an excess of ice-water forms acetonitrile in quantitative yield. At higher concentrations sodium acetonitrile reacts with already formed acetonitrile to give the dimer, 2-aminocrotononitrile. The structures of sodium acetonitrile and its analogs prepared in the same fashion were proved by means of their NMR and IR spectra, as well as by their chemical behavior.

IR spectra were taken in KBr pellets, or of solutions in pyridine or pyridine-d_5 in an inert atmosphere. In the region of the nitrile, acetylenic, and allenic group vibrations, intense absorptions were observed at 2050, 2240, 2160, and 2115 cm^{-1}. The last absorption band was shown to be due to the presence of small amounts of the sodium derivative of the dimer of acetonitrile, the formation of which cannot be prevented completely in the course of the synthesis of (II). A relatively intense and sharp absorption at 3260 cm^{-1} indicates the presence of acetylenic hydrogen; the possibility of this being due to an overtone or a combination vibration can be excluded. A broad NH vibration is located at 3130 cm^{-1}. Combination of these results leads to the conclusion that all possible tautomeric forms are present in the solid mixture.

This result was confirmed by the NMR spectra, which were taken in pyridine or pyridine-d_5 solution. Subtracting the spectrum of the condensation product, present as a 5–10% impurity, we interpreted an intense, broad peak at τ 9.07, corresponding to 75% of the protons present, as due to the protons in the form $NaCH_2CN$. The electron withdrawal of the nitrile group is counterbalanced by the electropositive metal, thus causing absorption at high field.

In addition, olefinic protons at τ 5.88 (6%) and acetylenic protons at τ 8.8, together with the corresponding NH protons at τ 4.4 (together 19%), confirm the predicted composition.

According to the NMR spectra, taken at −30° and +70°, the ratio of tautomers is not temperature-sensitive in this range. On the other hand, the sodium derivative of phenylacetonitrile, prepared in a similar fashion and readily soluble in benzene as well as in ether (where it forms a mono-etherate), seems to exist only in the organometallic form, PhCH(Na)CN. The compound exhibits only one CN vibration at 2080 cm^{-1}, and the NMR spectrum of a solution in benzene-d_6, indicates the presence of the organometallic species, with CH at τ 7.32 and phenyl protons at τ 3.09. Similarly, cyclohexanecarbonitrile forms only the organometallic species, as shown by the exclusive transformation of the latter into the trimethylsilyl derivative:



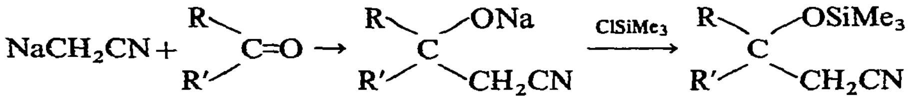
(4)

REACTIONS OF SODIUM ACETONITRILES

In their chemical reactions sodium acetonitrile and its homologs behave as the organometallic species only; their reactions are similar to those of Grignard reagents. They add readily to polar double bonds, *e.g.* carbonyl or cyano groups of compounds whose pK_a value is not significantly lower than that of the metalated nitrile[6]. These reactions are known in principle but have never been performed with the isolated, metalated nitrile.

Thus, the reaction of sodium acetonitrile (II) with benzophenone gives the sodium derivative of 2-hydroxy-2,2-diphenylpropionitrile, which has been converted by reaction with trimethylchlorosilane[3], to its O-trimethylsilyl derivative.

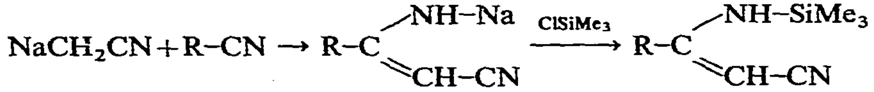
Acetone and benzaldehyde (eqn. 5) give the corresponding products (see *experimental part*).



$$\mathrm{NaCH_2CN} + \begin{matrix}\mathrm{R}\\ \mathrm{R'}\end{matrix}\!\!>\!\mathrm{C{=}O} \rightarrow \begin{matrix}\mathrm{R}\\ \mathrm{R'}\end{matrix}\!\!>\!\mathrm{C}\!<\!\!\begin{matrix}\mathrm{ONa}\\ \mathrm{CH_2CN}\end{matrix} \xrightarrow{\mathrm{ClSiMe_3}} \begin{matrix}\mathrm{R}\\ \mathrm{R'}\end{matrix}\!\!>\!\mathrm{C}\!<\!\!\begin{matrix}\mathrm{OSiMe_3}\\ \mathrm{CH_2CN}\end{matrix} \quad (5)$$

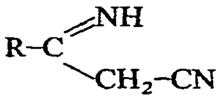
$R = R' = Ph$; $R = R' = CH_3$; $R = Ph$, $R' = H$

The addition to cyano groups proceeds similarly (eqn. 6).



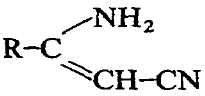
$$\mathrm{NaCH_2CN + R{-}CN} \rightarrow \mathrm{R{-}C}\!\begin{matrix}\diagup\mathrm{NH{-}Na}\\ \diagdown\mathrm{CH{-}CN}\end{matrix} \xrightarrow{\mathrm{ClSiMe_3}} \mathrm{R{-}C}\!\begin{matrix}\diagup\mathrm{NH{-}SiMe_3}\\ \diagdown\mathrm{CH{-}CN}\end{matrix} \quad (6)$$

We can therefore confirm the proposed mechanism of the condensation reactions of nitriles in presence of alkali metal[5]. When R is methyl, the sodium derivative of "diacetonitrile" was obtained as a white salt, stable towards oxygen. We were able to prove by means of IR and NMR spectra (details are given in the *experimental part*) that this type of salt and the corresponding parent substances do not exist in the ketimine form A as postulated in earlier papers[7], but rather in the two (*cis* and *trans*) enamine forms B, as already suggested by the UV and IR spectra of the dimeric nitriles[8].



$$\mathrm{R{-}C}\!\begin{matrix}\diagup\!\!\diagup\mathrm{NH}\\ \diagdown\mathrm{CH_2{-}CN}\end{matrix}$$

A



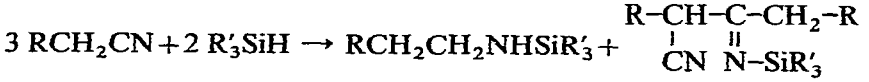
$$\mathrm{R{-}C}\!\begin{matrix}\diagup\mathrm{NH_2}\\ \diagdown\!\!\diagdown\mathrm{CH{-}CN}\end{matrix}$$

B

R = alkyl or aryl

Reaction of B with trimethylchlorosilane gave the corresponding N-trimethylsilyl compounds in good yields. For $R = Ph$ we were able to isolate a pure (probably *trans*) compound by fractional crystallisation of the *cis/trans* mixture.

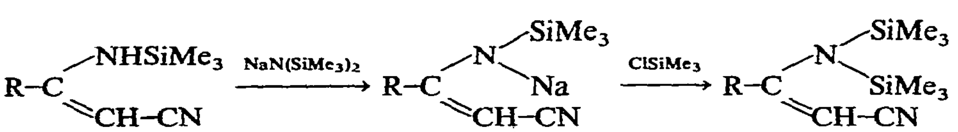
Calas had obtained silyl-substituted compounds of this type by addition of silanes to nitriles[9] according to eqn. (7).



$$3\,\mathrm{RCH_2CN} + 2\,\mathrm{R'_3SiH} \rightarrow \mathrm{RCH_2CH_2NHSiR'_3} + \mathrm{R{-}\underset{\displaystyle CN}{\underset{|}{C}H}{-}\underset{\displaystyle N{-}SiR'_3}{\underset{\|}{C}}{-}CH_2{-}R} \quad (7)$$

Apparently the assumed ketimine structure may not be correct.

The NH group in these silylated enamines may be fully silylated after metalation with (I) and subsequent reaction with trimethylchlorosilane

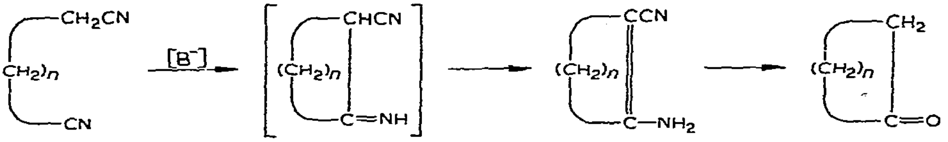


$$\mathrm{R{-}C}\!\begin{matrix}\diagup\mathrm{NHSiMe_3}\\ \diagdown\!\!\diagdown\mathrm{CH{-}CN}\end{matrix} \xrightarrow{\mathrm{NaN(SiMe_3)_2}} \mathrm{R{-}C}\!\begin{matrix}\diagup\mathrm{N}\!<\!\begin{matrix}\mathrm{SiMe_3}\\ \mathrm{Na}\end{matrix}\\ \diagdown\!\!\diagdown\mathrm{CH{-}CN}\end{matrix} \xrightarrow{\mathrm{ClSiMe_3}} \mathrm{R{-}C}\!\begin{matrix}\diagup\mathrm{N}\!<\!\begin{matrix}\mathrm{SiMe_3}\\ \mathrm{SiMe_3}\end{matrix}\\ \diagdown\!\!\diagdown\mathrm{CH{-}CN}\end{matrix} \quad (8)$$

Thus the enamine structure is proven by chemical means. On hydrolysis all the silyl-substituted compounds revert to the corresponding enamines in good yields.

Intermediates of the enamine type are involved in the synthesis of cyclic ketones from aliphatic dinitriles, by the procedures of Thorpe[10] and Ziegler[11] (eqn. 9).

In this reaction, the air-sensitive N-lithio-N-ethylaniline, or preferably sodium methylaniline is commonly used as the condensing agent, giving primarily the mono-



(9)

alkali dinitrile, which adds to the terminal cyano group as described above. Sodium bis(trimethylsilyl)amide should therefore be a useful condensing base in this reaction; indeed, without the need for an inert atmosphere the yield of 1-amino-2-cyano-1-cycloheptene, starting from suberonitrile, was 96%. The enamine structure of this compound as well as of the other enamines described so far was proven by its IR and NMR spectra. Wave numbers of $\nu(NH)_2$, $\nu(CN)$ and $\nu(C{=}C)$ vibrations and chemical shifts of the NH_2– and =CH– groups and other substituents are given in detail in the *experimental part*.

Addition of sodium acetonitrile to less active multiple bonds (olefins or acetylenes) was not observed. However, in the course of these investigations we found that sodium acetonitrile may act as a carbene generator.

If one refluxes sodium acetonitrile suspended in cyclohexene for a short period, norcarane can be detected in the distillate by gas chromatography in about 2% yield, whereas the solid residue contains the equivalent amount of NaCN, indicating a reaction eqn. (10)

(10)

Addition of various cyanide acceptors [*e.g.* anhydrous $ZnCl_2$, $HgCl_2$ or $Ni(CN)_2$] to the heterogeneous reaction mixture slightly improved the yield of norcarane to maximally 3.4%. Reaction of a homogeneous solution of sodium acetonitrile in pyridine with cyclohexene raised the yield to 4.1%, whereas a mixture of $ZnCl_2$ and pyridine gave 4.3% of norcarane.

Carbene reactions of this type were described in 1928 by Rising and Zee[13]. Hydrolysis of a sodium derivative of phenylacetonitrile, the properties of which are not in accordance with those of the compound prepared by us, gave HCN and benzyl alcohol in 52% yield. The corresponding sodium derivative of phenylbutyronitrile, however, was said to give HCN and diethylstilbene in 69% yield (under the same conditions). In accordance with our observations, the authors were unable to repeat the synthesis of the metalated nitriles by their method of treating sodium with the nitrile in ether solution[14].

While we do not wish, at this stage, to propose a mechanism for this reaction—whether via a carbene complex or an organometallic, two-step mechanism—we do wish to emphasize the close relationship of the chemical behavior to certain analogous compounds. In 1962, Runge[15] noted that methoxymethylmagnesium chloride, CH_3OCH_2MgCl, gave addition reactions of this type with about 1% yield. Dichloromethyllithium is known to undergo similar reactions; it also is capable of addition to benzophenone[16]. Finally, our compounds show close similarity to (halomethyl)-aluminum compounds, R_2AlCH_2X, prepared by Hoberg[17].

EXPERIMENTAL PART

Starting materials

Sodium bis(trimethylsilyl)amide was prepared from sodamide and hexamethyldisilazane, following a procedure given by Wannagat and Niederprüm[18]. All nitriles used were distilled under argon after being dried over with P_2O_5. Further reagents were of commercial-grade purity, and distilled prior to use. Solvents were dried and purified by distillation over sodium tetraethylaluminium or sodium–potassium alloy. All reactions were carried out in an atmosphere of dry argon with strict exclusion of moisture.

Sodium acetonitrile (I)

To a solution of 189 g sodium bis(trimethylsilyl)amide in 3 l of dry ether, a solution of 41 g acetonitrile in 250 ml ether was added within 3 h, the stirred reaction mixture was kept at −60°. The turbid suspension of sodium acetonitrile was stirred for another 3 h, filtered through a precooled glass frit (G 3), and the white residue thus obtained was washed twice with 100 ml of precooled ether, and dried at room temperature on a high-vacuum line. The yield in (I) was 57 g (90.5%). (Found: C, 38.48; H, 3.75; Na, 36.89, 36.29. C_2H_2NNa calcd.: C, 38.10; H, 3.20; Na, 36.48%.) For IR and NMR data see page 127.

Sodium acetonitrile forms small, white needles, which on exposure to air darken immediately. In precipitated form it is insoluble in organic solvents with the exception of pyridine. It reacts violently with water, and dissolves slowly in alcohol under solvolysis. Thermal decomposition in the solid state starts at 80° in an inert atmosphere.

Sodium phenylacetonitrile (II)

To 36.6 g sodium bis(trimethylsilyl)amide in 300 ml ether, a solution of 23.5 g phenylacetonitrile in 100 ml ether was added within 3 h; the stirred mixture was kept at −60°. The slightly yellow solution was stirred for another 5 h and filtered through a glass frit (G4); treatment with 100 ml pentane and drying in high vacuum. temperature in vacuum, and the residue, after being dried in high vacuum, suspended in 300 ml pentane. Sodium phenylacetonitrile (27.2 g, 98%) was isolated by filtration through a glass frit (G4); treatment with 100 ml pentane and drying in high vacuum. The slightly yellow, voluminous powder thus obtained is extremely sensitive towards air. (Found: Na, 16.33, 16.53. C_6H_8NNa calcd.: Na, 16.53%.) For IR and NMR data see page 127.

The compound is readily soluble in benzene or ether. Out of the ether solution, an etherate crystallized at −50°. It was purified by recrystallization from ether at −50°, and dried at −30° in high vacuum. The monoetherate thus obtained is liquid at room temperature and thermally very unstable. The addend could be removed in vacuum at room temperature. The NMR spectrum is in accordance with that of a monoadduct. (Found: Na, 11.13, 11.24. $C_{12}H_{16}NNaO$ calcd.: Na, 10.79%.)

The benzene-soluble sodium cyclohexanecarbonitrile (III) was prepared analogously.

(Trimethylsilyl)cyclohexanecarbonitrile (IV)

To a solution of 6.55 g (0.05 mole) sodium cyclohexanecarbonitrile (III) in

150 ml benzene, 10.8 g of trimethylchlorosilane were added, the stirred suspension was refluxed for 2 h. After filtration, the solvent and excess of trimethylchlorosilane were removed *in vacuo*, the remaining residue was twice sublimed in high vacuum at about 60°, yielding 7.1 g (79 %) of colorless crystals of (IV), m.p. 79°. (Found: C, 65.82; H, 10.07; N, 7.92. $C_{10}H_{19}NSi$ calcd.: C, 66.23; H, 10.56; N, 7.72 %.) IR: ν(CN) 2210 cm^{-1}. NMR: τ($SiMe_3$) 9.86; ring protons τ 8.30.

3-(*Trimethylsiloxy*)-3,3-*diphenylpropionitrile* (*V*)

To a stirred suspension of 12.6 g (0.2 mole) of sodium acetonitrile (I) in 250 ml ether, a solution of 36.4 g benzophenone in 150 ml ether was added at 20° within 3 h. The resulting voluminous suspension was refluxed for another 3 h, when 25 g of trimethylchlorosilane were slowly added. After the suspension had been stirred for 2 h at room temperature, sodium chloride was removed by filtration through a glass frit. Following evaporation of the solvent, the residue was distilled twice through a 15 cm column filled with glass helices; 52.5 g (89 %) of (V), b.p. 139–40° (0.2 mm) was obtained as a colorless oil, which crystallized after a few hours at room temperature. Colorless leaflets from methanol/water, m.p. 72–3°. (Found: C, 73.28; H, 7.09; N, 4.64. $C_{18}H_{21}NOSi$ calcd.: C, 73.18; H, 7.16; N, 4.74 %.) NMR (τ): 2.66, 6.76, 9.96 (ratio 10:2:9).

3-(*Trimethylsiloxy*)-3-*phenylpropionitrile* (*VI*)

This compound was similarly prepared from benzaldehyde and (I) in 57 % yield. Colorless oil, b.p. 131–2° (8 mm), n_D^{20} 1.4829 (Found: C, 65.71; H, 7.68; N, 6.55. $C_{12}H_{17}NOSi$ calcd.: C, 65.72; H, 7.82; N, 6.39 %.) NMR (τ): 2.74, 5.07 (tripl.), 7.49 (doubl.), 9.93 (ratio 5:1:2:9).

3-(*Trimethylsiloxy*)-3,3-*dimethylpropionitrile* (*VII*)

Sodium acetonitrile (12.6 g) and acetone (11.6 g, 0.2 mole) gave, as described under (V), 14.2 g of a fraction boiling between 180–194°, containing 90 % (by VPC) of (VII) (38.7 %). Part of this fraction was further purified by preparative gas chromatography (Wilkens Autoprep, SE 30). Colorless oil, b.p. 187–8°, n_D^{20} 1.4182. (Found: C, 56.18; H, 10.22; N, 8.65. $C_8H_{17}NOSi$ calcd.: C, 56.08; H, 10.00; N, 8.18 %.) NMR (τ): 7.85, 8.64, 9.87 (ratio 2:6:9). IR: ν(CN) 2240 cm^{-1}; ν(SiOC) 1050 cm^{-1}; $\nu[C(CH_3)_2]$ 1370, 1385 cm^{-1}. Mass spectrum: 171 (molpeak), 156 ($-CH_3$), 131, 98, 73.

Hydrolysis gives 3-hydroxy-3,3-dimethylpropionitrile, n_D^{20} 1.4263, in quantitative yield.

3-[(*Trimethylsilyl*)*amino*]*cinnamonitrile* (*VIII*)

To a suspension of 25.2 g (0.4 mole) sodium acetonitrile in 500 ml benzene, a solution of 41.2 g benzonitrile in 50 ml benzene was added within 10 min., causing a slight increase of the temperature of the reaction mixture. After 2 h stirring at 70°, 43.5 g of trimethylchlorosilane were added within 15 min; the mixture was refluxed for additional 6 h, sodium chloride removed by filtration through a glass frit, the solvent evaporated *in vacuo*, and the remaining residue distilled under reduced pressure; 69.2 g of a raw material, b.p. 108–16° (0.1 mm) were obtained, which on repeated distillation through a spinning band column (40 cm) gave 57.6 g of a solidifying fraction, b.p. 136–8° (2 mm), m.p. 59°. (Found: C, 66.75; H, 7.40; N, 13.18.

$C_{12}H_{16}N_2Si$ calcd.: C, 66.62; H, 7.45; N, 12.95%.) NMR of the *cis-trans* mixture (τ): 9.96/9.98, 6.01/5.74 (CH), 5.16/5.43 (NH), 2.67 (C_6H_5).

The ratio between both isomers differs slightly in different experiments. One of the isomers was isolated by repeated fractional crystallisation from hexane, m.p. 113°. The IR-spectra of the isolated compound and of the mixture are almost identical: conj. nitrile 2190 cm^{-1}; ν(NH) 3320 cm^{-1}; ν(SiN) 906 cm^{-1}.

For hydrolysis 0.814 g of the isomer mixture was dissolved in 4 ml methanol/water 3:1, and kept at 50° for 8 h. After recrystallisation from aqueous methanol, the yield in aminocinnamonitrile was 0.3 g (71%), m.p. 89.5°. (Found: C, 74.68; H, 5.77; N, 19.35. $C_9H_8N_2$ calcd.: C, 74.97; H, 5.59; N, 19.43%.) The mixture shows an analogous NMR (τ) pattern as the silylated starting materials: 6.11/5.81, 5.43/4.96, 2.57/2.98. IR: conj. nitrile 2170 cm^{-1}; ν(NH) 3350 cm^{-1}; δ(NH_2) 1635 cm^{-1}.

3-[*Bis(trimethylsilyl)amino*]*cinnamonitrile* (*IX*)

Sodium bis(trimethylsilyl)amide (18.3 g) was dissolved in 200 ml abs. ether, and a solution of 21.6 g (VIII) in 100 ml ether added at room temperature. The solution was stirred for 8 h; then 12.9 g trimethylchlorosilane (20% excess) was added and the reaction mixture was stirred for another 6 h. After filtration, the solvent and the hexamethyldisilazane formed were removed in vacuum, and the remaining residue was repeatedly distilled to give 20.5 g (IX), b.p. 110–1° (0.1 mm), as an oily, colorless liquid. (Found: C, 62.68; H, 8.21; N, 9.79. $C_{15}H_{24}N_2Si_2$ calcd.: C, 62.44; H, 8.38; N, 9.71%.) The NMR spectrum indicates a *cis-trans* mixture (τ): 9.79/9.87, 4.46/5.05 (CH), 2.60 (C_6H_5). IR: ν(CN) 2200 cm^{-1}; ν(Si–N–Si) 930 cm^{-1}; no NH vibration. The correct molar weight was found by mass spectrometry (mol. wt. minus 15 at 273).

Hydrolysis of (IX) gives results identical to (VIII).

3-(*Sodioamino*)*crotononitrile* (*X*)

To a suspension of 6.3 g (0.1 mole) of sodium acetonitrile in 300 ml ether, 4.1 g acetonitrile in 100 ml ether was added at room temperature within 3 h. The suspension was stirred for another 12 h; the white precipitate was isolated by filtration through a glass frit. After washing with ether and drying in vacuum, 10.3 g (99%) of (X) was obtained as a white powder which was stable towards dry air. (Found: Na, 21.85. $C_4H_5N_2Na$ calcd.: Na, 22.09%.) NMR (in pyridine-d_5) (τ): 7.77/8.07 (CH_3), 6.06/6.68 (CH), 3.62 (NH). Ratio of *cis-trans* isomers 3:4.

Hydrolysis of (X) gives in quantitative yield 3-aminocrotononitrile.

3-[(*Trimethylsilyl*)*amino*]-*2-methyl-2-pentenenitrile* (*XI*)

To 36.6 g of sodium bis(trimethylsilyl)amide in 200 ml ether, 22 g of propionitrile in 150 ml ether were added within 2 h at room temperature. After addition of about half of the reactant, the sodium salt of (XI) started to separate. The suspension was stirred for 6 h; 22 g of trimethylchlorosilane was added and the mixture refluxed for 2 further hours. After removal of NaCl, hexamethyldisilazane and the solvent, the residue was distilled under reduced pressure, to give 20.7 g (XI), b.p. 135–7° (12 mm), n_D^{20} 1.4990. (Found: C, 58.86; H, 9.85; N, 16.23. $C_9H_{18}N_2Si$ calcd.: C, 59.28; H, 9.95; N, 15.36%.)

For hydrolysis, 4.55 g of (XI) was digested with 20 ml of methanol and kept at 50° for 6 h. After removal of the solvent, 1.7 g of 3-amino-2-methyl-2-pentenenitrile, b.p. 128–30° (3 mm), m.p. 45°, was obtained. NMR (in benzene-d_6) (τ): 7.73 (quart., CH_2), 8.99 (tripl. CH_3–CH_2), 8.52 (CH_3–C=C), 5.88 (NH_2), indicating only one form of the possible *cis-trans* isomers.

3-[(*Trimethylsilyl*)*amino*]*crotononitrile* (*XII*)

This compound was prepared analogously to (XI); b.p. 118–20° (15 mm), n_D^{20} 1.5040. (Found: C, 54.60; H, 9.11. $C_7H_{14}N_2Si$ calcd.: C, 54.49; H, 9.14%.)

The same compound may be obtained by the reaction of (X) in ether suspension with trimethylchlorosilane. IR: ν(NH) 3280 cm^{-1}; ν(CN) 2195 cm^{-1}; ν(C=C) 1597 cm^{-1}.

Hydrolysis, as described, gave in quantitative yield *cis-trans*-3-aminocrotononitrile in *cis-trans* ratios depending on conditions of hydrolysis and recrystallization. (Found: C, 58.70; H, 7.50; N, 33.97. $C_4H_6N_2$ calcd.: C, 58.51; H, 7.37; N, 34.12%.) NMR (in benzene-d_6) (τ): 8.33/8.75 (CH_3), 6.16/6.57 (CH), 5.90 (NH_2).

Cyclisation of suberonitrile

To a solution of 38.8 g sodium bis(trimethylsilyl)amide in 600 ml ether, 27.2 g (0.2 mole) of suberonitrile in 100 ml ether was added within 3 h at room temperature. The resulting white suspension [N-sodium salt of (XIII)] was stirred for another 16 h. After addition of 300 ml 1 *N* HCl, the ether layer was washed twice and dried. 1-Amino-2-cyano-1-cycloheptene (XIII) was recrystallized from isopropyl ether. Yield 26.5 g (97.5%); m.p. 97.5°. (Found: C, 70.57; H, 8.97. $C_8H_{12}N_2$ calcd.: C, 70.54; H, 8.82%.) IR: ν(CN) 2167 cm^{-1}; ν(NH_2) 3230, 3335 cm^{-1}; ν(C=C) 1647 cm^{-1}; δ(NH_2) 1597 cm^{-1}.

1-[(*Trimethylsilyl*)*amino*]-*2-cyano-1-cycloheptene* (*XIV*)

This compound was prepared by the addition of 25 g of trimethylchlorosilane to the suspension of the sodium salt of (XIII) and reflux of the mixture for 2 h. (XIV) was obtained in 72% yield, b.p. 111–2° (2 mm); n_D^{20} 1.4938. (Found: C, 63.32; H, 9.82; N, 12.93. $C_{11}H_{20}N_2Si$ calcd.: C, 63.40; H, 9.67; N, 13.44%.) Molecular weight (cryoscopic in benzene): calcd./found 208.39/196.

Reaction with aqueous methanol gave (XIII) in 89% yield.

Addition of sodium acetonitrile to olefins

Sodium acetonitrile (0.1 mole) was suspended in an excess (30–50 ml) of cyclohexene by means of a magnetic stirrer, and refluxed for 6 h. After vacuum distillation, norcarane was identified and determined gas-chromatographically. The cyanide content of the solid distillation residue was determined after hydrolysis. In experiments with cyanide acceptors [$ZnCl_2$, $HgCl_2$, $Ni(CN)_2$], these were mixed prior to reaction with sodium acetonitrile in a 1 : 1 molar ratio. In cases where dry pyridine was used as solvent for sodium acetonitrile, the solvent was removed from the distillate by extraction with water. The results of the experiments are given on page 129.

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SUMMARY

Monosodium acetonitrile and homologous compounds are prepared by the reaction of sodium bis(trimethylsilyl)amide with acetonitrile or the corresponding nitriles in ether solution at low temperature. The IR and NMR spectra of these compounds are discussed. Sodium acetonitrile adds to polar double bonds (carbonyl and cyano groups) only. It is shown that sodium acetonitrile and analogous compounds are the intermediates in the condensation reactions of nitriles to enamines. Sodium acetonitrile acts as carbene generator, preferably in the presence of cyanide acceptors.

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