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Reaction between 2-Phenyl-1,1-dicyanoallyl Anion and *N*-Methyl-2,2-dimethylpropionitrilium and N^1,N^2,N^2-Trimethyl-2,2-dimethylpropionylamidinium Trifluoromethanesulfonates

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The reaction of 2-phenyl-1,1-dicyanoallyl anion with *N*-methyl-2,2-dimethylpropionitrilium ion (**2**) in acetonitrile solution resulted in formation of [3-(*N*-methylamino)-4,4-dimethyl-1-phenyl-2-pentenylidene]propanedinitrile (**6**), which at elevated temperature (25–50 °C, depending on the solvent) undergoes a ring closure to 2-(*N*-methylamino)-3-cyano-4-phenyl-6-*tert*-butylpyridine (**7**) or in the presence of aqueous acid to 3-cyano-4-phenyl-6-*tert*-butyl-2-pyrone (**8**). Using *N*,*N*-dimethylformamide as solvent, in addition to **7**, two other compounds are formed, viz. (3-(*N*,*N*-dimethylamino)-1-phenyl-2-propenylidene)propanedinitrile (**9**) and *N*-(4,4-dicyano-3-phenyl-1, 3-butadienyl)-*N*,2,2-trimethylpropanamide (**10**). The latter two compounds are results of a primary reaction of the title nitrilium ion with the solvent to give N^1,N^2,N^2-trimethyl-N^1-2,2-dimethylpropionylamidinium trifluoromethanesulfonate (**11**) which in turn reacted with the title allyl anion **2** to give **9** and **10**, for which X-ray crystal structures were determined. Strong indications of a tetrahedral mechanism in the reaction of **2** with **11** are presented.

In connection with our recent studies on alkylation and acylation of the ambident nucleophiles 1,1-dicyanoallyl anions[1] we also looked into the possibility of expanding the arsenal of alkylation reagents. There are overwhelming indications of nucleophilic attack at the nitrile carbon in *N*-alkylnitrilium ions **1**[reaction (i)].[2]

$$\underset{\textbf{1a}}{R\text{-}\overset{+}{C}\text{=}N\text{-}CH_3} \longleftrightarrow \underset{\textbf{1b}}{R\text{-}C\text{≡}\overset{+}{N}\text{-}CH_3} \qquad \text{(i)}$$

If, however, resonance form **1b** contributes to some extent to the structure of nitrilium ions **1**, there should in principle be possible for our allyl anions to demethylate such nitrilium ions, especially since the neutral nitrile should be a very good leaving group in this nucleophilic reaction. Meerwein[3] has given one example of cleavage of the *N*-alkyl bond [reaction (ii)]:

$$(Ph\text{-}CN\text{-}CH_2OMe)^+SbCl_6^- \longrightarrow Ph\text{-}CN + (Pyr^+\text{-}CH_2OMe)SbCl_6^- \qquad \text{(ii)}$$

Acid hydrolysis of the salt gave benzonitrile. It has also been reported that *N*-isopropylnitrilium salts are dealkylated by primary carboxamides, probably through nucleophilic attack of the amide nitrogen on the central alkyl carbon.[4] It is also reported that *N*-tert-butylnitrilium salts easily were dealkylated,[5] results in line with the above observation by Meerwein[3] where the methoxymethyl cation also should be fairly stable due to resonance, thus rendering the *N*-alkyl bond somewhat weakened. The potassium salt of (1-phenylethylidene)propanedinitrile (**2**)[1] was allowed to react with *N*-methylacetonitrilium triflate (**3**) (prepared from acetonitrile and methyl trifluoromethanesulfonate)[6] in acetonitrile solution, resulting only in protonation of the salt (Scheme 1).

The proposed ketenimine product is more tentative and no effort has been made to isolate and identify any further secondary product from this reactive species, since it was beyond the scope of this investigation. To circumvent this acid–base reaction the *N*-methylnitrilium salt of 2,2-dimethylpropanenitrile (**5**) was prepared. It was also a possibility that introduction of the bulky *tert*-butyl group would increase the free activation energy for attack at the nitrilium carbon atom, thus allowing for nucleophilic attack at the *N*-methyl group. However, when subjected to reaction with **2** in acetonitrile solution the result was quite different, as only attack at the nitrilium carbon atom took place (Scheme 2).

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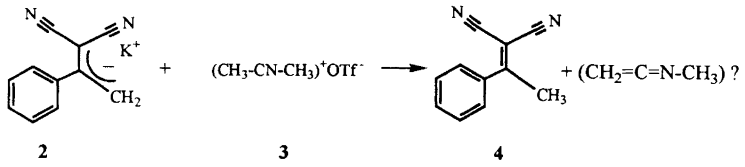
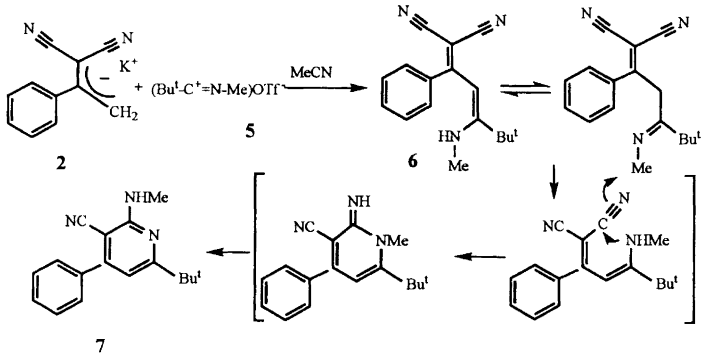


2 3 4

Scheme 1.

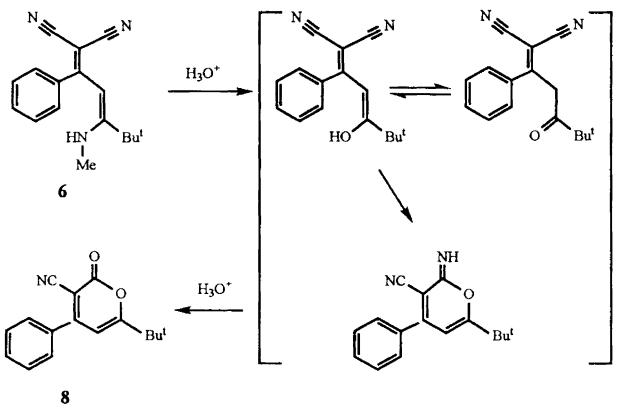


2 5 6 7

Scheme 2.

IR, ^1H and ^{13}C NMR spectroscopy indicated that **6** was in the enamine form, most likely for conjugative reasons. It is reported that even a primary enamine (ethyl 2-amino-3-methyl-2-butenoate) does not tautomerize to the imine analogue, even when distilled;[7] the reason for this is probably that the conjugation of an ester group with a carbon–carbon double bond is more effective than with a carbon–nitrogen double bond. The ring closure of **6** to the substituted pyridine compound **7** took place within 1 h at 50 °C in acetonitrile-d_3 and at room temperature within 3 h in *N*,*N*-dimethyl formamide-d_6. The rather unusual 1,3-methyl shift is probably due to lowering the energy in the aromatization process. When the enamine **6** was treated with dilute HCl, the substituted 2-pyrone **8** was obtained in acceptable yields (Scheme 3).

The ring closure most likely takes place involving the enol form which, analogously to the enamine **6**, is thermodynamically stabilized by conjugation. When the reaction between the potassium salt **2** and the nitrilium salt **5** (Scheme 2) was run in *N*,*N*-dimethylformamide (DMF) the outcome was quite different (Scheme 4).



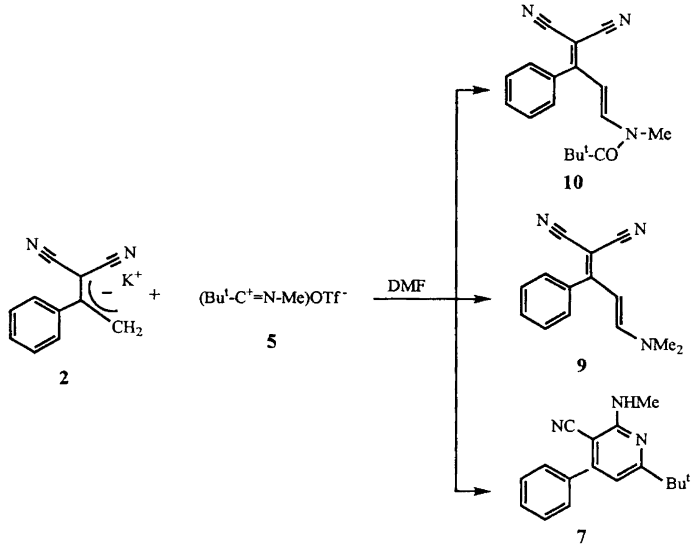
6 8

Scheme 3.

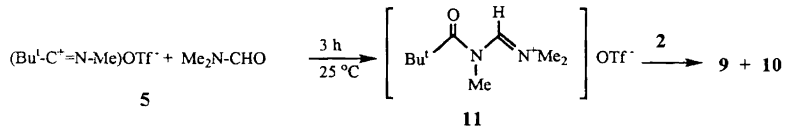
The product ratio **7**/**9**/**10** was approx. 2:1:1. While product **7** is the final result of nucleophilic attack on the nitrilium salt (Scheme 2), the structures of **9**[8] and **10** indicate that a solvent molecule may have been incorporated. It is reported that nitrilium ions react with *N*,*N*-disubstituted amides to form stable N^1,N^2,N^2-trisubstituted N^1-acylamidinium salts, which could be reacted with suitable nucleophiles.[9] Thus the reaction outlined in Scheme 4 may represent a competitive reaction of our nitrilium salt with the nucleophile **2** to form product **7** (via **6**) and with DMF to form the acylamidinium salt **11** which in turn reacts with the nucleophile **2** to give **9** and **10** in approximately equal amounts (Scheme 5). Indeed, when the nitrilium salt **5** was dissolved in DMF and left for 3 h and then equimolar amounts of **2** were added, only products **9** (60%) and **10** (40%) were formed. This reaction could be formulated as an attack of the ambident nucleophile **2** by its softest atom (HSAB-terminology) at the iminium carbon of **11**, possibly in a S_N2-manner, but most likely in an addition–elimination way (the tetrahedral mechanism)[10] due to low nucleofugal capacities of the leaving groups (Scheme 6).

The addition step in Scheme 6 complies well with recent observations that of the two electrophilic centres in the amidinium ion, viz. the carbonyl carbon and the iminium carbon, the latter one is the preferred point of attack when it carries a hydroden.[11] Regarding the elimination step, it has been claimed that if N^1 (in amidinium ion **11**) is unsubstituted, the dialkylamino group is always the leaving group;* and when N^1 carries an alkyl group, the amido group is expelled.[9]

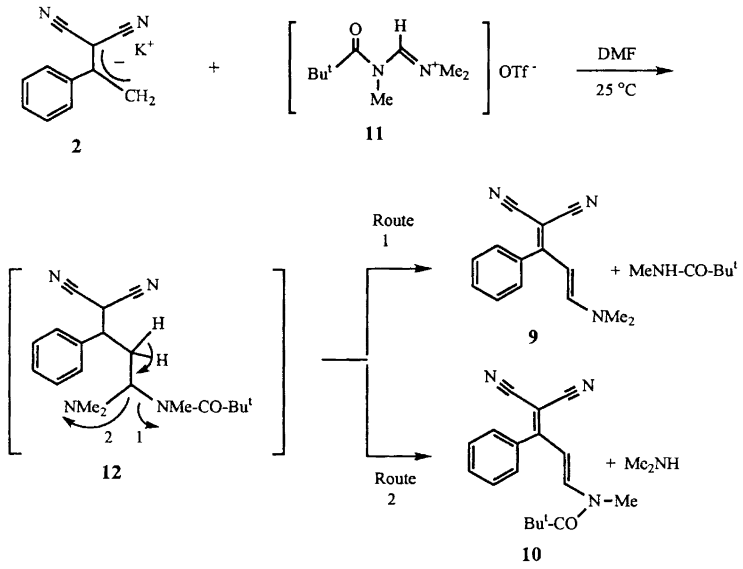
* We have confirmed that our amidinium salt is hydrolyzed to give *N*-formyl-*N*,2,2-trimethylpropanamide in practically quantitative yields, see Experimental.



Scheme 4.



Scheme 5.



Scheme 6.

The latter conclusion (with alkylated N^1) is somewhat moderated[11] using different heteronucleophiles (H_2O, ROH, ArSH, RNH_2), but the reported results always indicate that only one of the cleavage modes (analogous to Route 1 or 2 in Scheme 6) is followed, while we observe a competitive expulsion of the two leaving groups. A possible reason for this could be that we are using a charged nucleophile leading to a neutral addition intermediate (**12**) with a longer lifetime allowing for a more complex product control. We have found that the addition step is rather fast, as expected when the addition partners both are ionic. Thus, shortly after the reactants, the potassium salt **2** and the amidinium salt **11**, are mixed in DMF, hydrolysis shows the presence of amine **9** and amide **10**, and none of the hydrolysis products from the reactants [(1-phenylethylidene)propanedinitrile from **2** and *N*-formyl-*N*,2,2-trimethylpropanamide from **11**] was observed. Further, we have found that the elimination step is solvent-dependent, being rather slow in polar aprotic solvent like DMF and very fast in protic

solvents (water or ROH), and also pH-dependent. We intend to investigate these processes more closely and report the results in a separate forthcoming paper. An IR absorption band with medium intensity at 1701 cm^{-1} is assigned to the amide carbonyl group in **10** based on the effect of the conjugated system on the amino side, which tends to increase the frequency of the C=O group by reducing the contribution of the ionized form of the amide.[12] In this connection it is interesting to note that when such conjugative influence is removed as in *N,N*,2,2-tetramethylpropanamide, this absorption occurs at 1625 cm^{-1}.[13] The high degree of conjugation is also reflected in the UV spectrum, and will be further discussed in connection with the X-ray crystallographic structure determination (see below). The rather small $^3J_{CH}$ *trans* coupling constant in both **9** ($J = 12.4$ Hz) and **10** ($J = 13.2$ Hz) is probably also a consequence of the enhanced conjugation; if the contribution of the ionic resonance form is important in the description of the structure of both **9** and **10**, then the positive nitrogen atom with its assumed high electronegativity should explain the rather small coupling constant (cf. the modified Karplus equation $J_{trans} = 19.0 - 3.2\,(E_X - E_H)$,[14] where E_X and E_H represent the electronegativity of the nitrogen and the hydrogen atom, respectively).

Description of the crystal structures

N-*(4,4-Dicyano-3-phenyl-1,3-butadienyl)*-N,*2,2-trimethylpropanamide* (**10**). The structure was determined by single-crystal X-ray diffraction methods; the coordinates of the non-hydrogen atoms are listed in Table 1. The asymmetric unit contains four molecules, one of which is illustrated in Fig. 1. The four molecules have, within the accuracy of the determination, the same bond lengths and angles but differ slightly in torsion angles and have different intermolecular contacts. The variation of torsion angles along the main chain of carbon and nitrogen atoms is less than 9° from a planar arrangement in all molecules, but the torsion angle about the C4–phenyl bond varies from 75 to 89°. In all four molecules one of the methyl carbon atoms of the *tert*-butyl group is situated *ap* to the amide nitrogen atom whereas one of the *sc* methyl groups is within the van der Waals' distance from the phenyl ring plane (H–C separations in the interval 3.0–3.2 Å). This is also reflected in the solid-state ^{13}C NMR spectra, where separated resonance positions for the three methyl groups in the *tert*-butyl group are observed. Selected bond lengths and angles are listed in Table 2; one may observe a moderate degree of conjugation along the main chain. The structure of the amide group is influenced by this conjugation. The C–O bond length is 1.222(3) Å in comparison with 1.24 in a oligopeptide chain; N3–C14 is 1.403(3) Å in comparison with 1.32 Å in such chains. This is in accordance with the IR data discussed above.

*3-*N,N*-dimethylamino-1-phenyl-2-propenylidene) propanedinitrile (***9***)* was also subjected to X-ray single-crystal analysis. A PLUTO plot of the structure is presented in Fig. 2; the coordinates for non-hydrogen atoms are listed in Table 1. The main chain of carbon and nitrogen atoms is close to coplanar, the torsion angles deviating less than 9° from 0 or 180°. The phenyl ring is rotated by 56° about C4–C5 bond relative to the plane of the main chain. In this molecule there is a high degree of conjugation along the main chain (cf. Table 2), with bond lengths corresponding to a nearly aromatic situation. In both molecules the conjugation between the phenyl ring and the main chain is destroyed by the large dihedral angle; this results in a C4–C5 bond length (1.49 Å in both molecules) as expected for a similar unconjugated system (1.49 Å).[15] For comparison the selected bond lengths and bond angles of methyl 2-(2,2-dicyano-1-methylethenyl)benzoate[16] are entered in Table 2. In this compound there is also no conjugation between the aromatic moiety

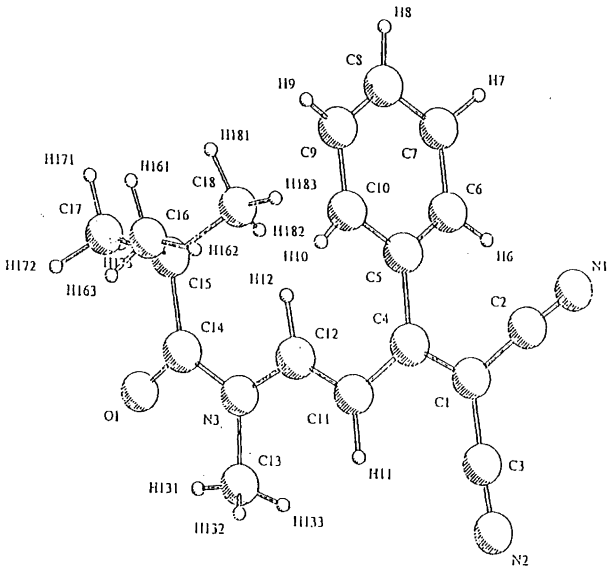


Fig. 1. PLUTO plot of **10**.

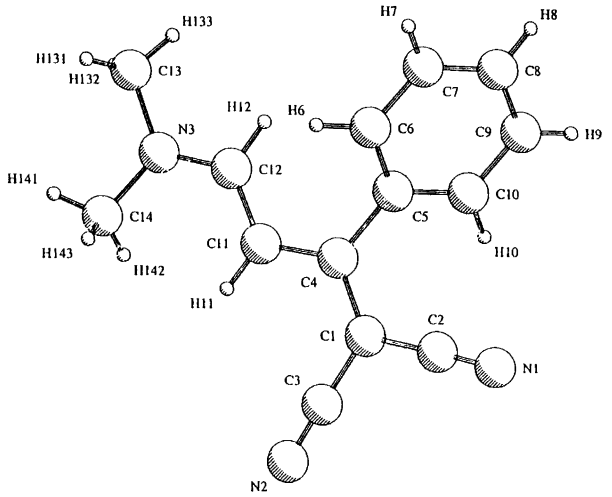


Fig. 2. PLUTO plot of **9**.

Table 1. Final fractional coordinates and equivalent temperature factors.

Atom	*x*	*y*	*z*	U_{eq}[a]
N-(4,4-Dicyano-3-phenyl-1,3-butadienyl)-*N*,2,2-trimethylpropanamide (**10**)				
O1	0.454 29(18)	0.441 85	0.440 15(12)	0.056
O21	0.512 76(18)	0.170 06(36)	0.033 84(13)	0.065
O41	1.093 95(17)	0.418 41(37)	0.499 05(11)	0.054
O61	−0.097 79(16)	0.239 95(35)	−0.000 71(11)	0.049
N1	0.487 4(2)	−0.512 2(4)	0.302 9(1)	0.047
N2	0.242 1(2)	−0.315 9(4)	0.318 3(1)	0.054
N3	0.432 95(18)	0.211 45(35)	0.409 88(12)	0.031
N21	0.534 3(2)	1.113 1(4)	0.187 2(2)	0.058
N22	0.768 5(2)	0.879 0(5)	0.165 7(2)	0.057
N23	0.550 44(17)	0.379 93(36)	0.082 09(12)	0.031
N41	0.837 1(2)	0.524 9(4)	0.101 3((1)	0.050
N42	1.101 7(2)	0.683 8(4)	0.186 2(1)	0.054
N43	1.054 89(17)	0.486 80(36)	0.405 92(12)	0.031
N61	−0.100 9(2)	−0.093 9(4)	0.301 1(1)	0.054
N62	0.178 6(2)	−0.022 9(5)	0.385 0(1)	0.064
N63	−0.056 32(17)	0.165 97(36)	0.091 93(12)	0.03
C1	0.412 6(2)	−0.287 3(4)	0.335 1(1)	0.030
C2	0.455 4(2)	−0.411 2(4)	0.318 7(2)	0.034
C3	0.318 3(2)	−0.301 5(5)	0.326 6(2)	0.037
C4	0.458 0(2)	−0.164 4(4)	0.358 4(1)	0.027
C5	0.556 5(2)	−0.160 0(4)	0.365 6(1)	0.026
C6	0.591 4(2)	−0.138 3(4)	0.318 7(2)	0.035
C7	0.683 1(2)	−0.127 3(5)	0.325 8(2)	0.041
C8	0.739 9(2)	−0.140 4(4)	0.380 3(2)	0.039
C9	0.704 8(2)	−0.162 8(4)	0.427 8(2)	0.034
C10	0.614 0(2)	−0.171 8(4)	0.420 7(2)	0.031
C11	0.414 6(2)	−0.039 5(4)	0.374 3(1)	0.030
C12	0.463 3(2)	0.080 7(4)	0.394 7(1)	0.028
C13	0.336 6(2)	0.230 5(5)	0.400 5(2)	0.045
C14	0.489 6(2)	0.326 8(4)	0.432 0(2)	0.034
C15	0.591 4(2)	0.314 0(4)	0.448 8(2)	0.032
C16	0.619 3(3)	0.206 0(5)	0.500 1(2)	0.039
C17	0.628 0(3)	0.463 0(5)	0.470 8(2)	0.049
C18	0.632 4(3)	0.270 8(5)	0.398 9(2)	0.041
C21	0.599 9(2)	0.874 6(5)	0.158 6(2)	0.036
C22	0.562 8(3)	1.005 9(5)	0.173 4(2)	0.042
C23	0.693 7(2)	0.876 5(5)	0.162 3(2)	0.041
C24	0.548 7(2)	0.753 1(4)	0.141 4(1)	0.030
C25	0.450 3(2)	0.764 4(4)	0.134 0(2)	0.029
C26	0.397 5(2)	0.838 1(5)	0.087 2(2)	0.037
C27	0.305 4(2)	0.839 2(5)	0.077 9(2)	0.040
C28	0.266 2(2)	0.769 0(4)	0.115 6(2)	0.036
C29	0.318 6(2)	0.696 9(5)	0.163 4(2)	0.039
C30	0.410 6(2)	0.691 4(5)	0.172 3(2)	0.037
C31	0.585 3(2)	0.618 0(5)	0.128 2(2)	0.032
C32	0.529 1(2)	0.510 8(4)	0.102 2(1)	0.030
C33	0.645 1(2)	0.340 6(5)	0.092 2(2)	0.043
C34	0.485 6(2)	0.282 1(4)	0.051 5(2)	0.035
C35	0.386 4(2)	0.312 8(4)	0.040 1(1)	0.027
C36	0.355 6(2)	0.454 0(5)	0.007 1(2)	0.043
C37	0.358 9(3)	0.306 6(5)	0.097 9(2)	0.043
C38	0.338 0(3)	0.189 3(5)	0.001 1(2)	0.041
C41	0.954 8(2)	0.569 4(4)	0.197 2(2)	0.031
C42	0.887 8(2)	0.546 3(5)	0.144 4(2)	0.035
C43	1.036 4(2)	0.633 3(5)	0.191 4(2)	0.036
C44	0.942 5(2)	0.528 1(4)	0.249 8(1)	0.028
C45	0.854 3(2)	0.467 0(4)	0.252 0(1)	0.028
C46	0.788 6(2)	0.556 8(4)	0.262 2(2)	0.036
C47	0.707 9(2)	0.498 0(5)	0.266 6(2)	0.040
C48	0.692 8(2)	0.350 5(5)	0.260 9(2)	0.038
C49	0.758 5(3)	0.260 4(5)	0.251 0(2)	0.045
C50	0.839 6(2)	0.316 8(5)	0.247 2(2)	0.037
C51	1.011 6(2)	0.540 0(4)	0.302 8(2)	0.030
C52	0.996 1(2)	0.490 9(4)	0.352 3(2)	0.030

(*cont.*)

Table 1. (continued)

Atom	x	y	z	U_{eq}[a]
C53	1.147 1(2)	0.533 7(5)	0.410 7(2)	0.042
C54	1.033 0(2)	0.431 1(5)	0.455 5(2)	0.036
C55	0.937 2(2)	0.390 5(5)	0.455 0(2)	0.037
C56	0.872 6(2)	0.519 4(5)	0.437 1(2)	0.047
C57	0.907 4(3)	0.251 1(5)	0.419 1(2)	0.053
C58	0.938 4(3)	0.352 1(5)	0.518 2(2)	0.051
C61	0.051 8(2)	0.000 5(4)	0.291 4(2)	0.032
C62	−0.032 7(2)	−0.053 0(5)	0.296 1(2)	0.037
C63	0.123 0(2)	−0.011 3(5)	0.343 4(2)	0.045
C64	0.063 8(2)	0.062 6(4)	0.242 0(2)	0.029
C65	0.153 7(2)	0.117 8(4)	0.241 1(1)	0.026
C66	0.173 8(2)	0.264 9(4)	0.249 0(2)	0.038
C67	0.257 5(2)	0.314 4(5)	0.247 1(2)	0.041
C68	0.320 4(2)	0.221 9(5)	0.237 2(2)	0.038
C69	0.300 7(2)	0.073 7(5)	0.229 0(2)	0.039
C70	0.218 0(2)	0.023 1(4)	0.231 2(2)	0.036
C71	−0.007 9(2)	0.076 9(4)	0.190 6(2)	0.030
C72	0.005 6(2)	0.140 2(4)	0.143 1(2)	0.029
C73	−0.150 1(2)	0.131 8(5)	0.089 2(2)	0.041
C74	−0.036 3(2)	0.220 8(4)	0.041 8(2)	0.031
C75	0.059 8(2)	0.254 9(4)	0.040 2(2)	0.032
C76	0.121 6(2)	0.122 4(5)	0.056 3(2)	0.041
C77	0.057 0(3)	0.298 3(5)	−0.022 3(2)	0.044
C78	0.094 6(3)	0.387 5(5)	0.079 2(2)	0.043
(3-(*N*,*N*-Dimethylamino)-1-phenyl-2-propenylidene)propanedinitrile (**9**)				
N1	0.311 8(3)	−0.054 06(12)	0.543 19(16)	0.044
N2	0.305 1(2)	0.337 50(12)	0.547 30	0.033
N3	0.550 1(2)	0.355 50(11)	0.906 70(14)	0.039
C1	0.379 0(2)	0.140 79(13)	0.632 45(14)	0.023
C2	0.343 7(2)	0.031 83(14)	0.584 25(15)	0.028
C3	0.336 4(2)	0.249 71(13)	0.585 77(14)	0.039
C4	0.451 1(2)	0.141 64(12)	0.719 99(14)	0.019
C5	0.514 1(2)	0.023 89(12)	0.756 63(14)	0.020
C6	0.451 3(2)	−0.022 05(14)	0.839 08(15)	0.024
C7	0.509 3(2)	−0.133 34(14)	0.871 07(16)	0.029
C8	0.629 5(2)	−0.198 20(14)	0.821 56(17)	0.031
C9	0.694 2(3)	−0.153 88(13)	0.739 64(16)	0.030
C10	0.637 0(2)	−0.042 83(13)	0.707 19(16)	0.025
C11	0.463 8(2)	0.249 61(13)	0.770 65(14)	0.022
C12	0.540 7(2)	0.256 64(13)	0.856 02(14)	0.021
C13	0.622 8(3)	0.352 42(16)	0.999 20(15)	0.030
C14	0.479 5(3)	0.470 34(13)	0.874 69(16)	0.026

[a] $U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$.

and the 1,1-dicyanoethenyl group. The bond lengths in the chain indicate alternative single/double bond character, as the chain is shorter and, in contrast to **9** and **10**, it lacks a nitrogen atom in the chain.

Experimental

General. Melting points are uncorrected. Infrared spectra were recorded on a Nicolet Magna 550 FTIR spectrometer using an attenuated total reflectance (ATR) ZnSe plate for solid samples, high resolution NMR spectra (^{1}H and ^{13}C) on Varian Gemini 200 and Bruker Spectrospin Avance DPX 300 spectrometers using $SiMe_4$ as internal standard, solid state ^{13}C NMR spectra on a Bruker Spectrospin Avance DMX 200 spectrometer, ultraviolet spectra on a Shimadzu UV-260 spectophotometer and mass spectra were obtained using a Fison Instruments VG ProSpec Q.

Solvents. All solvents used were dried according to literature recommendations.[17]

*Potassium salt of (1-phenylethylidene)propanedinitrile (**2**).* Potassium *tert*-butoxide (0.7 g, 6.5 mmol) was suspended in diethylether (25 ml), and *tert*-butanol was added dropwise to obtain an almost homogeneous solution. (1-Phenylethylidene)propanedinitrile[18] (1.0 g, 6.0 mmol) in diethylether (25 ml) was added dropwise

Table 2. Comparison of selected bond lengths (in Å) and bond angles (in °) in compounds **10** and **9** and the ester 1b of Ref. 16, together with corresponding unconjugated bond lengths (Ref. 15).

Bond	**10**	**9**	Ester	Unconjugated
N1–C2	1.151(3)	1.152(2)	1.146(3)	
N2–C3	1.152(3)	1.150(2)	1.144(3)	
C1–C2	1.428(3)	1.425(2)	1.437(3)	1.428
C1–C3	1.435(3)	1.425(2)	1.443(3)	1.428
C1–C4	1.369(3)	1.394(3)	1.346(3)	1.336
C4–C11	1.435(3)	1.411(2)		1.478
C11–C12	1.348(3)	1.383(3)		1.336
C12–N3	1.369(3)	1.326(2)		
N3–C13	1.471(3)	1.463(3)		
N3–C14	1.403(3)	1.460(3)		
C14–O1	1.222(3)			
C4–C5	1.494(3)	1.491(2)	1.496(3)	
C2–C1–C3	115.5(2)	116.0(2)	116.5	
C2–C1–C4	122.1(2)	122.4(2)	121.2	
C3–C1–C4	122.2(2)	121.7(2)	122.3	

while stirring (room temperature). The precipitated white salt was filtered in a stream of dry N_2 and washed with some diethylether. 1.2 g (97%). IR: ν_{max} 2196 and 2171 (s, CN) cm^{-1}. ^1H NMR (200 MHz, acetone-d_6): δ 7.4–7.3 (2 H, m), 7.3–7.2 (3H, m), 4.35 (1 H, d, *J* 1.8 Hz), 4.08 (1 H, d, *J* 1.8 Hz) ppm. ^{13}C NMR (50 MHz, acetone-d_6): δ 148.7 (quart. C), 143.5 (quart. C), 128.5 (quart. C), 128.4 (tert. C), 128.0 (tert. C), 127.3 (tert. C), 93.4 (sec. C) ppm. UV [CH_3CN (log ε)]: λ_{max} 226.8 (4.12) nm.

Potassium salt **2** *and* N-*methylacetonitrilium triflate* **1**, R=Me).[6] Potassium salt **2** (50 mg, 0.24 mmol) was dissolved in acetonitrile (1.8 ml), and **1** (0.54 g, 0.26 mmol) dissolved in acetonitrile (0.7 ml) was added. After stirring for 3 h (N_2) at room temperature, H_2O was added and the mixture extracted with diethylether. The product (50 mg) was identified as (1-phenylethylidene)propanedinitrile.[18]

N-*Methyl-2,2-dimethylpropionitrilium trifluoromethanesulfonate* (**3**). 2,2-Dimethylpropionitrile (Fluka) (1.0 g, 12 mmol) and methyl trifluoromethanesulfonate (Fluka) (2.0 g, 12 mmol) were mixed and stirred for 24 h. White crystals: 2.5 g (84%). M.p. 90–95 °C (2,2-dimethylpropionitrile/pentane). ^1H and ^{13}C NMR spectra data (see below) fitted very well with those observed for the analogous hexachloroantimonate salts,[5] except that the central carbon of the *tert*-butyl group is shifted upfield about 24 ppm. FTIR: ν_{max} 3020 (s), 2405 (m, CN[6]) cm^{-1}. ^1H NMR (CD_3CN): δ 3.72 (3 H, t, $^2J_{NH}$ 3.0 Hz), 1.55 (9 H, s) ppm. ^{13}C NMR (CD_3CN): δ 120.7 (q, *J* 137 Hz, CF_3SO_3). 112.0 (CN, t, $^1J_{CN}$ 42.7 Hz), 31.5 (CH_3, d, $^1J_{CN}$ 6.9 Hz), 30.6 (CMe_3), 26.0 ($C(CH_3)_3$) ppm.

Reaction between potassium salt **2** *and* N-*methyl-2,2-dimethylpropionitrilium salt* **3** *in acetonitrile.* Potassium salt **2** (100 mg, 0.48 mmol) was dissolved in acetonitrile (5 ml) and cooled in ice-water, and **3** (130 mg, 0.53 mmol) was added. After stirring for 3 h at room temperature, diethylether (25 ml) was added and after washing with water, the organic phase was dried ($MgSO_4$) and evaporated. After a dichloromethane solution of the crude product had been filtered through a short column (SiO_2), (3-(*N*-methylamino)-4,4-dimethyl-1-phenyl-2-pentenylidene)propanedinitrile (**6**) (light yellow crystals) was obtained in 55% yield. M.p. 107–108 °C (decomp.) (ether/pentane). Owing to thermal instability (cf. discussion above) neither elemental analysis nor high resolution mass spectroscopy could not be obtained. IR: ν_{max} 3260 (broad, NH), 2150 (s, CN) cm^{-1}. ^1H NMR (CD_3CN): δ 7.5–7.4 (5 H, m), 7.1 (1 H, broad, N*H*), 5.25 (1 H, s), 2.33 (3 H, s), 1.24 (9 H, s) ppm. ^{13}C NMR ($CDCl_3$): δ 176.7, 169.0, 138.0, 131.0, 129.5, 120.5, 118.2, 116.9, 93.2, 61.1, 38.9, 35.6, 29.2 ppm. UV [CH_2Cl_2, (log ε)]: λ 422 (4.30), 293 (3.90), 228 (3.80) nm.

*Ring closure of (3-(*N*-methylamino)-4,4-dimethyl-1-phenyl-2-pentenylidene)propanedinitrile* (**6**) *to 2-methylamino-3-cyano-4-phenyl-6-*tert*-butylpyridine* (**7**). When a solution of **6** in acetonitrile was kept at 50 °C for 1 h, ring closure to **7** took place. M.p. 147–148 °C (ether/pentane). Anal. $C_{17}H_{19}N_2$: C, H, N. IR: ν_{max} 3323 (broad, NH), 2215 (m, CN), 1618 and 1569 (s, pyridine quadrant stretch)[19] cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.5–7.4 (5H, m), 5.98 (1 H, s), 3.68 (3 H, s), 1.47 (9 H, s) ppm. ^{13}C NMR ($CDCl_3$): δ 161.4, 159.7, 154.8, 136.8, 130.1, 128.8, 127.7, 116.9, 102.8, 97.4, 37.6, 36.6, 30.2 ppm. MS [EI, 70 eV: *m/z* (% rel. int.)]: 265 (18, $M^{+\cdot}$), 250 (100, *M*-Me), 208 (20, *M*-C_4H_9). UV[CH_2Cl_2 (log ε)]: λ 407.6 (3.78), 263.1 (4.32) nm; [MeOH (log ε)]: λ 393.4 (3.53), 342.6 (3.59), 285.2 (3.88) nm.

*Ring closure of (3-(*N*-methylamino)-4,4-dimethyl-1-phenyl-2-pentenylidene)propanedinitrile* (**6**) *to 3-cyano-4-phenyl-6-*tert*-butyl-2-pyrone* (**8**). To the potassium salt **2**

(1.00 g, 4.85 mmol) dissolved in acetonitrile (50 ml) was added *N*-methyl-2,2-dimethylpropionitrilium salt **3** (1.32 mg, 5.34 mmol). After stirring for 1 h at room temperature dilute hydrochloric acid (50 ml, 0.1 N) was added, and after further stirring for 9 h the solution was extracted with diethylether (3 × 50 ml). After drying ($MgSO_4$) and evaporation of diethylether, the crude product (0.92 g) was dissolved in CH_2Cl_2 and filtered through a short SiO_2 column, giving light-yellow crystals (0.58 g), m.p. 155–156 °C ($CHCl_3$/pentane). Anal. $C_{16}H_{15}NO_2$: C, H, N. IR: ν_{max} 2224 (w, CN), 1735 (s, C=O), 1619 (m, C=C) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.7–7.6 (2H, m), 7.6–7.5 (3 H, m), 6.32 (1 H, s), 1.30 (9 H, s) ppm. ^{13}C NMR ($CDCl_3$): δ 176.6, 164.0, 159.5, 134.2, 131.9, 129.1, 127.9, 114.4, 102.0, 95.2, 37.0, 27.7 ppm. MS [EI 70 eV: *m/z* (% rel. int.)]; 253 (51, $M^{+\cdot}$), 211 (47, *M*-CH_2CO), 196 (100, *M*-C_4H_9), 57 (57, $C_4H_9^+$). UV [MeOH (log ε)]: λ 335.5 (3.97), 294.1 (4.10), 227.1 (4.10), 207.1 (4.25) nm.

Reaction of potassium salt **2** *with* N-*methyl-2,2-dimethylpropionitrilium trifluoromethanesulfonate* **3** *in DMF.* Potassium salt **2** (1.00 g, 4.9 mmol) was dissolved in DMF (50 ml) and **3** (2.21 g, 5.3 mmol) was added. After stirring for 3 h, diethyl ether (100 ml) was added, and after washing with water, the organic phase was dried ($MgSO_4$) and evaporated. The crude product (brown oil: 0.97 g) was flash-chromatographed on silica gel (Merck Kieselgel 60, 40–63 μm) using (1) dichloromethane and (2) acetonitrile as solvents to obtain the following compounds in order of elution:

*N-(4,4-Dicyano-3-phenyl-1,3-butadienyl) -N,2,2-trimethylpropanamide (**10**).* Isolated yield: 0.16 g, light yellow crystals. M.p. 136–136.5 °C (chloroform/pentane) (X-ray crystal structure determined, see below). IR: ν_{max} 2224 (m, CN), 1701 (m, C=O) 1593 (s, conj. C=C) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.6–7.5 (3 H, m), 7.50 (1 H, d, *J* 13.2 Hz), 7.4–7.3 (2 H, m), 6.35 (1 H, d, *J* 13.2 Hz), 3.28 (3 H, s), 1.04 (9 H, s) ppm. ^{13}C NMR ($CDCl_3$): δ 175.9, 170.9, 147.4, 132.6, 129.8, 128.2, 127.3, 113.2, 112.7, 105.2, 76.5, 39.8, 32.3, 28.5 ppm. MS [EI 70 eV; *m/z* (% rel. int.)]: 293 (9, $M^{+\cdot}$), 236 (3, *M*-C_4H_9), 57 (100, $C_4H_9^+$). UV [(MeOH (log ε)]: λ 363 (4.22), 284 (3.38), 207 (3.85) nm.

*(3-(N,N-Dimethylamino)-1-phenyl-2-propenylidene)-propanedinitrile (**9**).*[8] Isolated yield: 0.20 g, lilac crystals. M.p. 142–143 °C (acetone/pentane) (X-ray crystal structure determined, see below). IR: ν_{max} 2207 (m. CN), 1618 (s, conj. C=C) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.5–7.4 (3 H, m), 7.4–7.3 (2 H. m), 6.63 (1 H, d, *J* 12.4 Hz), 5.82 (1 H, d, *J* 12.4 Hz), 3.04 (3 H, s), 3.02 (3 H, s) ppm. ^{13}C NMR ($CDCl_3$): δ 170.6, 155.1, 134.1, 129.3, 128.0, 116.1, 115.7, 97.8, 64.7, 46.2, 38.1 ppm. MS [EI 70 eV; *m/z* (% rel. int.)]: 223 (100, $M^{+\cdot}$), 208 (11, *M*-Me), 179 (16, *M*-NMe_2). UV (MeOH (log ε)]: λ 388 (4.75), 268 (3.64), 207 (4.16) nm.

*2-(*N-*Methylamino)-3-cyano-4-phenyl-6-*tert-*butylpyridine* (**7**). Isolated yield: 0.42 g.

N^1,N^2,N^2-*Trimethyl-*N^1*-2,2-dimethylpropionylamidinium trifluoromethanesulfonate* (**11**). A solution of nitrilium salt **3** (0.8 g, 3.24 mmol) in dichloromethane (5 ml) was

Table 3. Crystal and experimental data.

	10	**9**
Compound	$C_{18}H_{19}N_3O$	$C_{14}H_{13}N_3$
M.p./°C	136–136.5	142–143
Crystal dimensions/mm	0.6 × 0.6 × 0.7	0.25 × 0.4 × 0.4
Crystal system	Monoclinic	Orthorhombic
a/Å	15.523(2)	7.641(2)
b/Å	9.179(2)	11.088(2)
c/Å	23.876(4)	14.632(3)
β/°	104.74(1)	
V/Å^3	3290.0(1.1)	1239.7(4)
T/K	138	138
Space group	$P\,2_1$	$P\,na2_1$
Formula weight	293.37	223.28
Z	8	4
D_x/g cm^{-3}	1.184	1.196
Scan mode	ω/2θ	ω/2θ
Scan speed/° min^{-1}	10.0	4.0
Scan range/°	1.7	2.0
Maximum (sin θ/λ)/Å^{-1}	0.60	0.85
No. of independent measurements	6396	3720
No. with $I > 3.0\,\sigma(I)$	4962	2725
No. of parameters	1084	205
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.043	0.045
$R_w = [\Sigma w(F_o - F_c)^2/\Sigma w F_o^2]^{1/2}$	0.043	0.050
$S = [\Sigma w(F_o - F_c)^2/(n-m)]^{1/2}$	2.06	2.60
Max. Δρ/e Å^{-3}	0.26	0.28
Min. Δρ/e Å^{-3}	−0.20	−0.25

cooled to −78 °C, and DMF (0.26 g, 3.56 mmol) in dichloromethane (5 ml) was added dropwise. After warming to room temperature and further stirring for 1 h, the solution was cooled to −50 °C and diethyl ether (25 ml) was added slowly. A clear oil was precipitated. After decantation of the mother liquor, dichloromethane (2.5 ml) was added, and the oil was reprecipitated slowly with diethyl ether (50 ml). After decantation the oil was washed with diethyl ether, and excess solvents were removed in a stream of dry N_2. The spectroscopic parameters (IR and NMR, see below) compared very well with those reported for the analogous hexachloroantimonate salts.[5] IR: ν_{max} 2940 (m), 1700 (m), 1640 (s) cm^{-1}. ^1H NMR (CD_3CN): δ 8.36 (1 H, s), 3.49 (3 H, s), 3.45 (3 H, s), 3.34 (3 H, s), 1.34 (9 H, s) ppm. ^{13}C NMR (CD_3CN): δ 178.1 (*C*=O), 159.2 (*C*=N), 120.7(q, *J* 137 Hz, $CF_3SO_3^-$), 47.6, 42.4, 41.8, 37.3, 27.8 ppm.

Reaction of amidinium salt **11** *with water.* Nitrilium salt **3** (0.50 g, 2.0 mmol) was dissolved in DMF (5 ml) at −30 °C. After 15 min water (5 ml) was added, and the solution was stirred for 1 h. The solution was allowed to warm to room temperature and was extracted with diethyl ether. After drying ($MgSO_4$), evaporation and filtering through a layer of SiO_2 (CH_2Cl_2) a clear oil was obtained (0.29 g ≈ 100% yield), identified as *N*-formyl-*N*,*N*,2-trimethylpropanamide. B.p. 203 °C. Anal. $C_7H_{13}NO_2$: C, H, N. IR (film): ν_{max} 3414 (w), 3365 (w), 2978 (m), 1716 (m, CHO), 1663 (s, C=O, amide) cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.31 (1 H, s), 3.03 (3 H, s), 1.27 (9 H, s) ppm. ^{13}C NMR ($CDCl_3$): δ 179.4 (*C*HO), 163.3 (amide *C*=O), 40.3 (N-CH_3), 28.2 (3 CH_3) 27.7 (CMe_3) ppm. MS [EI 70 eV: *m/z* (% rel. int.)]: 144 (0.8, $M+H^+$, found 144.102871. $C_7H_{14}NO_2$ requires 144.102454), 143 (0.1, $M^{+\cdot}$), 142 (0.4, $M-H^+$, found 142.087746. $C_7H_{12}NO_2$ requires 142.086804), 128 (1.0, *M*-Me, found 128.070707. $C_6H_{10}NO_2$ requires 128.071154), 115 (20, *M*-CO), 57 (100, $C_4H_9^+$), 41 (79), 29 (75). UV [MeOH (log ε)]: λ_{max} 216.9 (3.86) nm.

Reaction between potassium salt **2** *and* N^1,N^2,N^2-*trimethyl*-N^1-*2,2-dimethylpropionylamidinium trifluoromethane sulfonate* (**11**). Nitrilium salt **5** (65 mg, 0.26 mmol) was dissolved in DMF (3 ml) and stirred at room temperature for 1 h to form the amidinium salt **11**. Potassium salt **2** (50 mg, 0.24 mmol) was added and stirring continued for 3 h. Diethylether (25 ml) was added, and the reaction mixture was washed with water. After drying ($MgSO_4$) and evaporation, a brown oil (40 mg) was obtained, which was shown (^1H NMR) to consist of only **9** (ca. 40%) and **10** (ca. 60%).

X-Ray crystal structure determination. The experiments were carried out using a Nicolet *P3/F* four-circle diffractometer. The radiation was Mo *Kα* (λ = 0.71069 Å), and the crystals were cooled by a cold nitrogen stream to 138 K. Unit cell parameters were determined from the settings of 25 carefully centered general reflections by a least-squares procedure. Crystal data and the conditions for the data collection are given in Table 3. The intensity data were corrected for Lorentz and polarization effects but not for absorption and extinction. Standard deviations for the intensities were based on intensity statistics with an addition of 2% of the net intensity. Atomic coordinates of all non-hydrogen atoms were determined by direct methods (MITHRIL).[20] Refinements were performed by least-squares calculations.[21] Hydrogen positions were all found from difference syntheses and included in the refinements with isotropic thermal parameters. Final figures of merit are included in Table 3. Positional parameters of the non-hydrogen atoms are listed in Table 1, together with their equivalent isotropic thermal parameters.

Lists of structure factors, anisotropic thermal parameters and hydrogen parameters, and a complete list of bond lengths, bond angles and torsion angles may be obtained from C. R. upon request.

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