Regiochemistry in alkylation, acylation and methoxycarbonylation of alkali salts from 2-substituted alkenylpropanedinitriles

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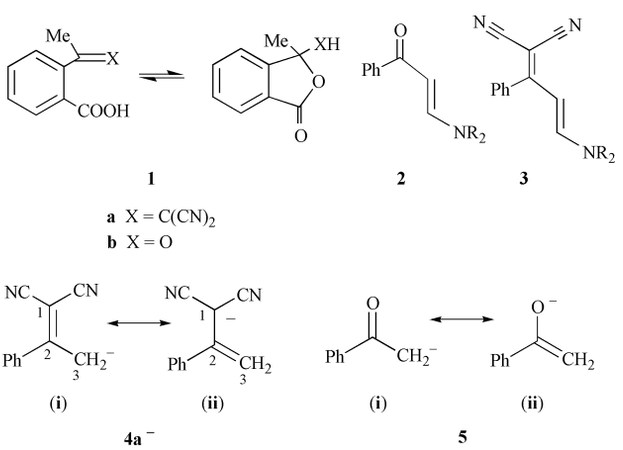
Alkali salts ($\mathbf{4}^-$) of several 2-substituted alkenylpropanedinitriles are prepared, isolated and characterised by ^{1}H and ^{13}C NMR spectroscopy. By treating the salt $\mathbf{4a}^-$ with **4a** a dimer, 2-dicyanomethylene-6-methyl-4,6-diphenyl-1,2,5,6-tetrahydronicotinonitrile **6**, is formed, for which a single-crystal X-ray structure is presented. Alkylation of the ambident salts $\mathbf{4}^-$ with MeX (X = I, Tf, or Br) leads to regioisomers, 1- and 3-alkylation, and comparison with O *vs.* C-alkylation of ketones is made. Double alkylation is also observed, 3-alkylation followed by 1-alkylation. Thus from $\mathbf{4a}^-$ a mixture of (*E*)- and (*Z*)-2-methyl-2-(1-phenylprop-1-enyl)propanedinitrile **9b** is formed, and the X-ray structure of the former is presented. Acylation of $\mathbf{4a}^-$ with benzoyl chloride gives only the 3-regioisomer; using equimolar amounts of reactants gives a ring-closure product, 2-oxo-4,6-diphenyl-2*H*-pyran-3-carbonitrile **12**, while excess of benzoyl chloride gives the double-acylation product, (*Z*)-4,4-dicyano-1,3-diphenylbuta-1,3-dienyl benzoate (*Z*)-**13**, for which the X-ray structure is presented. Acylation of $\mathbf{4a}^-$ with acetyl chloride gives both regioisomers; the 1-acylated product evaded isolation, and the 3-acylation product reacted further to give the (*E*)- and (*Z*)-form of 4,4-dicyano-1-methyl-3-phenylbuta-1,3-dienyl acetate **15**. The X-ray structure of the latter isomer, (*Z*)-**15**, is presented. Methoxycarbonylation of salts $\mathbf{4}^-$ with methyl chloroformate gives both regioisomers, while use of methyl cyanoformate gives only the 3-regioisomer, in addition to a Michael adduct from reaction of the CN^- group with protonated salt $\mathbf{4}^-$.

Introduction

Our observation of ring–chain tautomerism in 2-(2,2-dicyano-1-methylethyl)benzoic acid[1] **1a**, similar to the behavior of 2-acetylbenzoic acid **1b** in solution,[2] supports the qualitative similarity between an oxygen atom and the $C(CN)_2$ group expressed by K. Wallenfels *et al.* in their review article on 'Die O–$C(CN)_2$-analogie'.[3] Structural comparisons between 3-(*N*,*N*-dialkylamino)propenones **2** and the analogously substituted 1,1-dicyanobuta-1,3-dienes **3** were made using dynamic ^{1}H NMR, X-ray crystallography and quantum chemical calculations.[4] The latter compounds were synthesised in reactions between the potassium salt of (1-phenylethylidene)propanedinitrile **4a** and appropriate amidinium salts,[5] and the kinetics of this reaction, involving a tetrahedral intermediate, were studied.[6]

The above potassium salt $\mathbf{4a}^-$, which could be isolated and characterised,[5] bears obvious resemblance to the enolate salt of acetophenone (**5**). The ambident nature of such salts should in principle lead to different products when they react with electrophiles. In base-promoted reactions of ketones where metal enolates are considered to be intermediates, they are defined as O- or C-products. In our system such terminology is meaningless, thus we prefer to call the analogous products 1- or 3-products, respectively.† The different reaction parameters which influence the O/C-alkylation or -acylation ratio for ketones are discussed in extensive reviews.[7] As we in the present study on reactions of the salts $\mathbf{4}^-$ with electrophiles also experienced a competition between 1- and 3-products, it was of interest to see how some of these parameters influenced the competition.



Results and discussion

Preparation of potassium salts

The general procedure for salt preparations has been described,[5] using solvents with the lowest polarity possible in order to precipitate out the salt. Furthermore, to avoid dimerisation, which occurs when the salt *and* the carbon acid are both present at the same time (see below), the carbon acid was added to the base, potassium *tert*-butoxide. This procedure gave us in hand very pure salts (>95%, ^{1}H NMR) in excellent yields (>90%), which were used in the alkylation studies (Scheme 1).

Unfortunately, it has not been possible, so far, to obtain crystals suitable for single-crystal X-ray crystallography.

† The terms '1- or 3-products' will only be used to indicate competition in regiochemistry. In naming compounds IUPAC recommendations will be used.

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Table 1 Methylation of salts of **4** (**4**$^-$) with MeX[a]

Expt	Compd	Solvent	X	Cation	**4**	**7**	**8**	**9**(*E*)	**9**(*Z*)	**10**	1-Me/3-Me	Remarks
1	**4a**$^-$	CH_3CN	I	K	26	35	6	30	2	2	0.88	Same results with 18-crown-6
2	**4a**$^-$	DMSO	I	K	25	28	5	35	2	1	0.65	
3	**4a**$^-$	CH_3CN	Br	K	22	50	2	23	2		1.85	
4	**4a**$^-$	CH_3CN	Tf	K		75	21				3.57	Same results with 18-crown-6
5	**4b**$^-$	CH_3CN	Tf	K				91	9		∞	
6	**4c**$^-$	CH_3CN	Tf	K	6	93					∞	
7	**4d**$^-$	CH_3CN	Tf	K	4	73	17	3	2		3.32	Same results with 18-crown-6
8	**4d**$^-$	CH_3CN	I	Li	8	59	10	10	4		2.46	
9	**4d**$^-$	CH_3CN	Tf	Li	1	73	16	1			4.29	
10	**4e**$^-$	CH_3CN	Tf	K	4			73	17		∞	Starting material: (*E*)/(*Z*) ≈ 75/25
11	**4f**$^-$	CH_3CN	Tf	K	4	81	14				5.79	
12	**4g**$^-$	CH_3CN	Tf	K	4	70	21				3.33	

[a] Yields in percent.

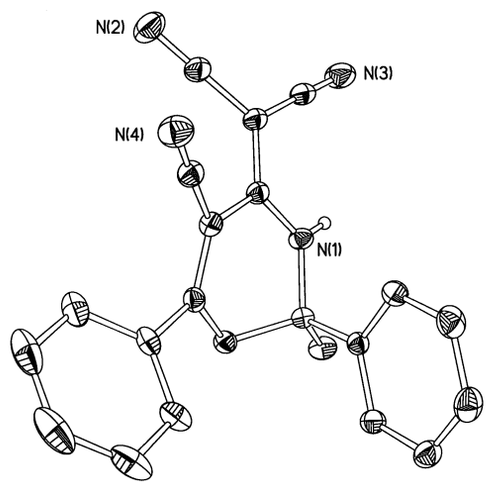
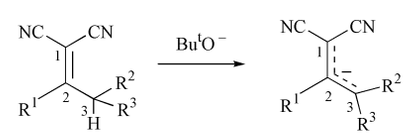


Fig. 1 ORTEP plot of 2-dicyanomethylene-6-methyl-4,6-diphenyl-1,2,5,6-tetrahydronicotinonitrile **6**. (For clarity, a molecule of acetone present in the unit cell has been removed.)



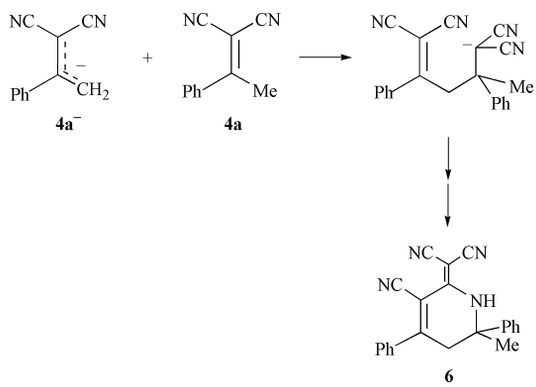
4 **4**$^-$

a R^1 = Ph, R^2 = R^3 = H
b R^1 = Ph, R^2 = Me, R^3 = H
c R^1 = Ph, R^2 = R^3 = Me
d R^1 = Cyclopropyl, R^2 = R^3 = H
e R^1 = Cyclopropyl, R^2 = Me, R^3 = H
f R^1 = *i*-Propyl, R^2 = R^3 = H
g R^1 = Ph, R^2 = R^3 = $(CH_2)_2$

Scheme 1

However, ^{1}H NMR spectra of all salts (Experimental section) indicate non-equivalence of the methylene protons making resonance structure **4a**$^-$ (**ii**) the more dominant one for describing the structure of the salts. A slight shift to higher field of the methylene protons points to a somewhat increased electron density at this site as compared with protons at standard sp^2 carbons.

As mentioned above, to avoid dimerisation of **4**, an excess of base had to be used in salt preparations. When, intentionally, equivalent amounts of **4a** and its potassium salt were mixed in acetonitrile, a dimer, 2-dicyanomethylene-6-methyl-4,6-diphenyl-1,2,5,6-tetrahydronicotinonitrile **6**, could be isolated. The formation of dimer **6** (Scheme 2) is initiated by Michael addition of **4a**$^-$ to the neutral carbon acid followed by a multistep ring closure as suggested.[8] Since the spectroscopic parameters of this compound were not completely in line with those reported, a single-crystal X-ray structure analysis was carried out (Fig. 1), showing that their postulated structure was correct.



4a$^-$ **4a** **6**

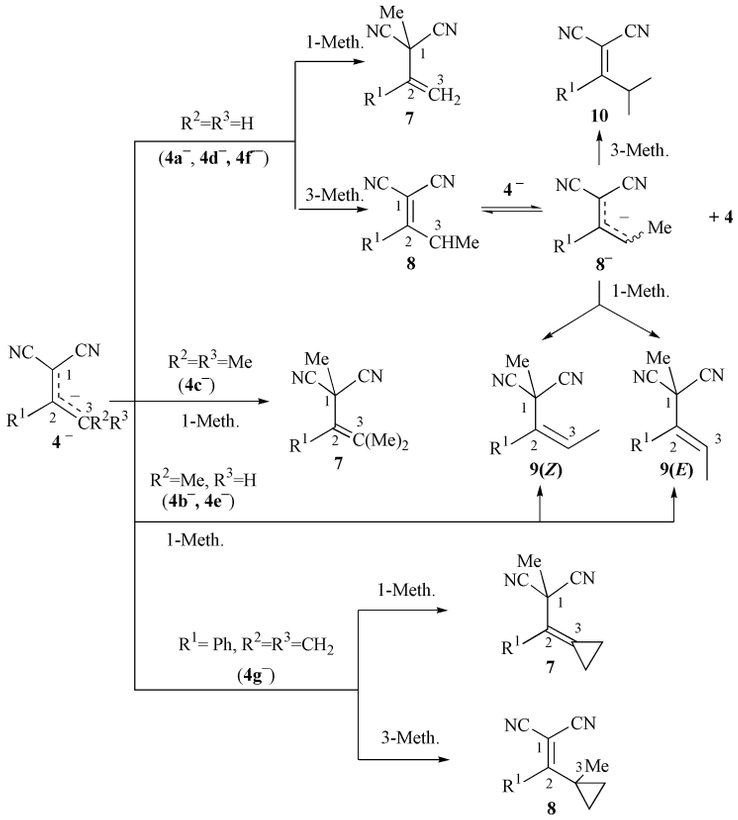
Scheme 2

Alkylation of the salts

The alkylation of the different 2-substituted alkylidenepropanedinitriles **4** was done by first preparing the pure salts **4**$^-$; followed by reaction in selected solvents with electrophiles of the type MeX. As can be seen from Scheme 3 and Table 1, double alkylation is quite common, thus excess of MeX had to be used.

The doubly alkylated products and concurrently the reformation of **4** is a consequence of an acid–base equilibrium involving **4**$^-$ and the 3-alkylation product **8**. The existence of such an equilibrium was confirmed by mixing equimolar amounts of **4a**$^-$ and presynthesised **8a** (= **4b**), giving equal proportions of (*E*)- and (*Z*)- salt **8a**$^-$, reflecting thermodynamic equality. The alkylation of the salts **8a**$^-$ is not an equilibrium reaction, giving **9a** with a ratio (*E*) : (*Z*) ≈ 15 : 1, perhaps due to different reactivity of the two salts **8a**$^-$. When the reaction between **4a**$^-$ and **8a** was repeated in the presence of excess of MeI, the (*E*) : (*Z*) ratio of product **9a** was 19 : 1. When salt **4b**$^-$ was made directly from **4b** using potassium *tert*-butoxide, the (*E*) : (*Z*) ratio of salts **4b**$^-$ was 91 : 9, and methylation with MeTf gave **9b** with (*E*) : (*Z*) ≈ 91 : 9. The stereochemistry of **9b**(*E*) was established using single-crystal X-ray diffraction (Fig. 2).

One of the objectives of this study was to get some information about the competition between 1- and 3-alkylation, and, in principle, the product ratio **7** : **8** should be used as a measure. However, the secondary reactions **8**→**9** and **8**→**10** are very fast and, in fact, when only 0.5 equivalent of MeI was used as electrophile in the reaction with **4a**$^-$, 21% of the total products was **9a**(*E*). The reason for this is probably (1) that the acid–base equilibrium **4**$^-$ + **8** ⟾ **4** + **8**$^-$ is very quickly established, and (2) that carbanion **8a**$^-$ is more reactive than **4a**$^-$ due to its higher alkylation. Consequently, one must therefore classify the secondary products **9** and **10** as '3-methylation' products. However, in the alkylation of **4b**$^-$ and **4e**$^-$ where the starting materials already have a methyl group in the 3-position (Scheme 3), products **9** must be considered as 1-methylation products.



Scheme 3

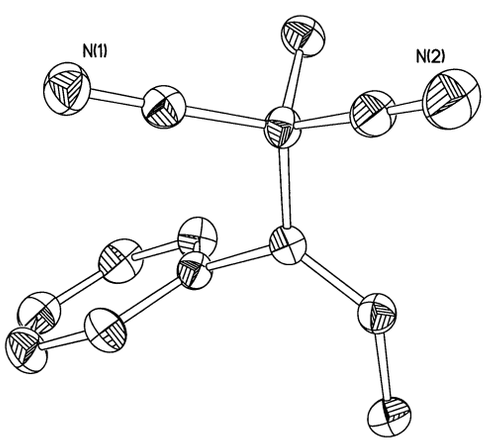


Fig. 2 ORTEP plot of (*E*)-2-methyl-2-(1-phenylprop-1-enyl)propanedinitrile (*E*)-**9b**.

As mentioned in the Introduction section, one of the aims of this study was to see whether and how the different reaction parameters influencing the O : C alkylation of ketones also play a similar role in determining the regiochemistry in our system. In general the alkylation of ambident nucleophiles is controlled according to the principle of 'hard' and 'soft' acids and bases (HSAB); 'hard' alkylation reagents attack the 'hard' site of the nucleophile and *vice versa*.[9,10] In alkylation of the enolates from ketones the O : C ratio seems to be controlled by several reaction parameters.[11] An important factor is the solvent's capacity to assist the dissociation of the salt. The dipolar aprotic solvent DMSO is considered to be a good cation solvator by its capacity as an electron-pair donator (EPD).[12] This is demonstrated in the alkylation of the enolate of cyclohexanone where the O : C ratio changes from 24 : 44 in 1,2-dimethoxyethane (DME) to 71 : 18 in DMSO.[13] In this study we do not find a similar solvent effect, the 1-methylation : 3-methylation ratio (1-Me : 3-Me) being 88 : 100 in acetonitrile and in DMSO 65 : 100. Moreover, the use of 18-crown-6, considered to be a specific K-complexing agent,[14] does not have any effect on the 1-Me : 3-Me ratio. Changing the cation to Li^+ does not have a significant effect on the 1-Me : 3-Me ratio (Expt. 7 *vs.* 9). All these findings point to a looser Coulombic attraction between the ions in our system. As most of the negative charge of the anion is located on the carbon atom in the $C(CN)_2$ group, *cf.* the ^1H NMR spectra of $\mathbf{4}^-$, a steric effect exerted by the cyano groups could result in a larger distance between the ions. Another, and perhaps better, explanation could be that the charge of the anion may be intrinsically stabilised by the inductive effect of the cyano groups. Similar arguments were used to explain the more efficient contribution of the $C(CN)_2$ compared with the C=O group in stabilising conjugated systems.[4]

Increasing alkylation at the α-position in ketones leads to higher O : C ratios,[15,16] results also obtained with our system where only 1-alkylation was observed (Expts. 5 and 6 *vs.* 4 and 10 *vs.* 7). The high preference for O- or 1-alkylation in these reactions may be a result of increased steric hindrance; however, another explanation could be of electronic nature. The left-hand resonance structures of both $\mathbf{4}^-$ and enolate **5**, see above, should be energetically destabilised, while the right-hand structures should be stabilised upon increased α-alkylation, increasing the 'hardness' of the oxygen atom or the 1-position of the anions in question.

In terms of the HSAB principle, in ambident nucleophiles like enolates **5** the oxygen atom represents the 'hard' and the carbon atom the 'soft' site, and consequently in $\mathbf{4}^-$ the $C(CN)_2$ group should be the 'hard' site. We have never observed any attack at the nitrogen atom of the cyano group, which should be the consequence of increased electron density on the nitrogen if the cyano group is part of a conjugated system. We have previously suggested that the cyano group stabilises a negative charge on the carbon atom by its −I effect, based on the bond lengths in the $C(CN)_2$ group in some highly conjugated 4-amino-1,1-dicyanobuta-1,3-dienes.[4] The absence of any *N*-alkylated compounds in our study does not weaken this proposal. The 'hardness' of the electrophile MeX is a function of the 'hardness' of the leaving group X. In the alkylation

Table 2 Acylation of potassium salts 4^- with RCOCl[a]

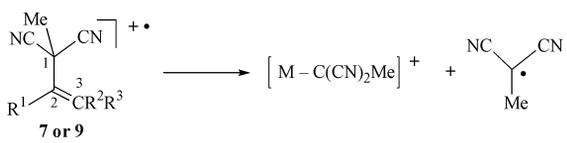
Compd	R	Molar ratio **4**:RCOCl (A:B)	Order of mixing	**12**	**13**	**14**	**15**(*E*)	**15**(*Z*)	**4**	Remarks
$\mathbf{4a}^-$	Ph	1:1	B to A	80	0					
$\mathbf{4a}^-$	Ph	1:5	A to B	0	>80					
$\mathbf{4a}^-$	Me	1:1				49	6	19	26	NMR-expt.
$\mathbf{4a}^-$	Me	1:1	B to A			0	6	17	77	**14** dec. to **4** on chrom. column
$\mathbf{4c}^-$	Me	1:5	A to B		>80					

[a] Yields in percent.

of the enolate of propiophenone with *n*-pentyl halides the O/C-quotient is 1.2, 0.64 and 0.23, respectively, on going from Cl to Br to I.[16] We observed a similar trend in 1-Me/3-Me: Tf 3.57, Br 1.85, I 0.88 (expts. 4, 3, 1).

1-Methylation products

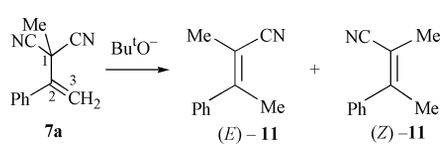
The base peak in the MS spectra of all 1-methylated products **7** and **9** (except **7g**) is obviously an example of a fragmentation route which is more governed by the stability of the radical and not as usual by the fragment stability (Scheme 4).



7 or 9

Scheme 4

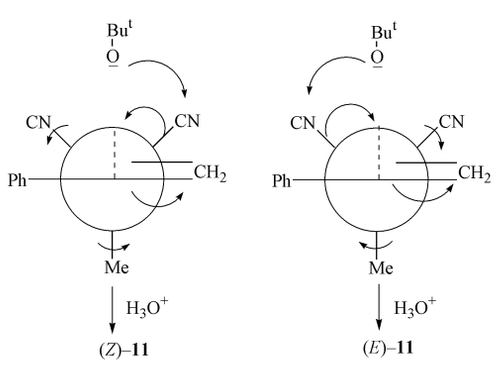
As discussed in the Experimental section, problems in obtaining pure samples of the 1-methylated compounds were encountered. As the 3-methylated compounds **8** or **10** contain an acidic proton, Expt. 4 (Table 1) was repeated on a larger scale and a diethyl ether solution of the products **7a** and **8a** was extracted with dil. sodium hydroxide, resulting in a rapid decomposition of the 1-methylated product **7a**. A chromatographically pure sample of **7a** was therefore treated with potassium *tert*-butoxide, for details see Experimental section, leading to a mixture of (*E*)- and (*Z*)-methyl-3-phenylbut-2-ene nitrile **11** (Scheme 5). The reaction may be depicted as a nucleophilic



7a (*E*) – **11** (*Z*) –**11**

Scheme 5

attack of the alkoxide ion on one of the nitrile carbon atoms with the rest of the molecule as the leaving group in a stereoelectronic manner as shown in Scheme 6.



Scheme 6

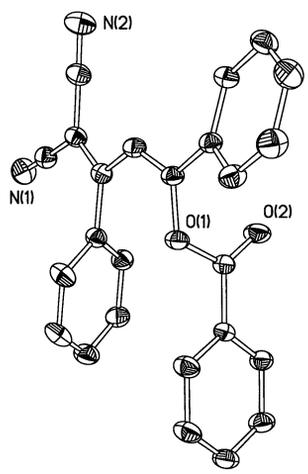


Fig. 3 ORTEP plot of (*Z*)-4,4-dicyano-1,3-diphenylbuta-1,3-dienyl benzoate (*Z*)-**13**.

Acylation and methoxycarbonylation

It should be expected that acylation with acid chlorides and methoxycarbonylation with α-substituted formates, in principle, should follow similar reaction pathways as in alkylation and that the regiochemical outcome should be governed by the principles of the HSAB theory. However, this theory is based on reactivity, a kinetic parameter, which implies that precise application of this theory requires that the products formed are stable under the reaction conditions. For the alkylation reactions discussed above, this condition is considered to be fulfilled.[17] In contrast, in acylation and, probably to a lesser degree, also methoxycarbonylation reactions it appears to be difficult to achieve kinetic conditions. This is mainly due to the observed fact that unless the applied electrophile is used in very large excess, the O-acylation-product (1-acylation-product in our system) itself can compete with the applied electrophile to give the thermodynamically more stable C-acylation products (3-acylation-product here).[18] We will therefore not try to apply the HSAB theory in this part of the presentation, but merely present the preparation of some new acylation and methoxycarbonylation products in the reactions of our salts 4^- with selected electrophiles.

The outcome of acylations of 4^- with acetyl and benzoyl chloride is sketched out in Scheme 7 and Table 2.

Only 3-acylation products (or secondary products **12** from them) were isolated with benzoyl chloride, even when using excess of electrophile to avoid thermodynamic reaction conditions, which only led to the double acylation product **13**(*Z*) instead of the cyclic product **12**. A single-crystal X-ray structure of **13**(*Z*) is presented in Fig. 3.

On the other hand, use of acetyl chloride led to substantial yields of the 1-acylation product **14**, which unfortunately evades isolation since it decomposes on chromatographic columns (SiO_2) or in contact with aqueous solutions. The

3-acylation product could not be isolated as it reacts further with acetyl chloride, and when using excess of reagent followed by aqueous work-up, these double-acylation products, **15**(*E*) and (*Z*), were the only products, together with substantial amounts of starting material, partially formed according to the lower equilibrium in Scheme 7 and mostly from the hydrolysis of the 1-acylation product **14**. The stereochemistry of **15**(*Z*) was established by single-crystal X-ray structure determination (Fig. 4).

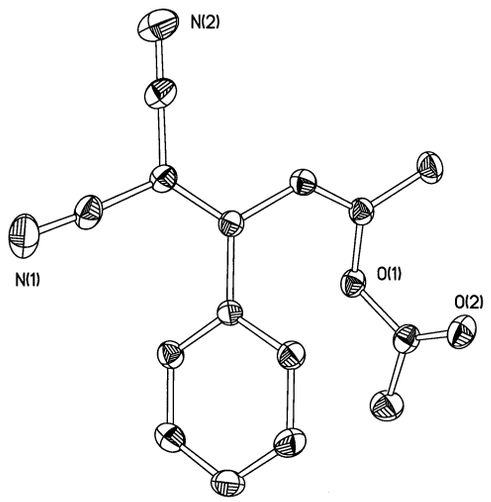


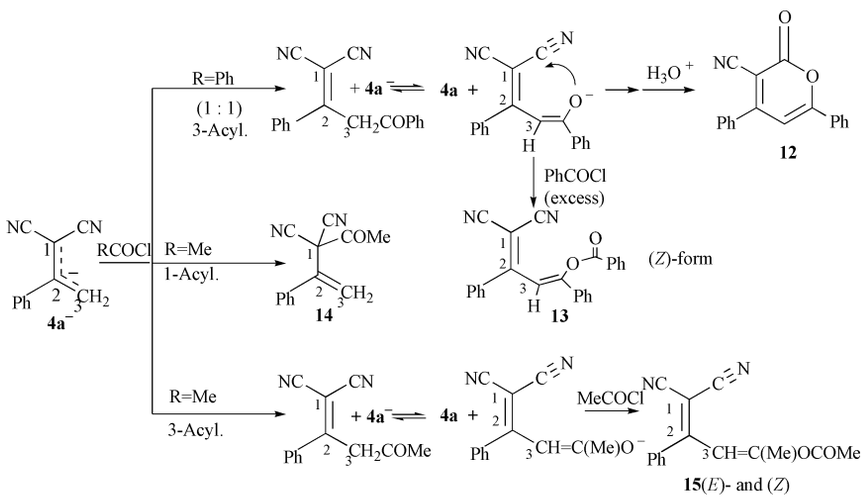
Fig. 4 ORTEP plot of (*Z*)-4,4-dicyano-1-methyl-3-phenylbuta-1,3-dienyl acetate (*Z*)-**15**.

Increased alkylation at the 3-position of the reacting salt (**4c**$^-$) led to exclusive acylation in the 1-position to give **14c**, a result in line with alkylation reactions, see above.

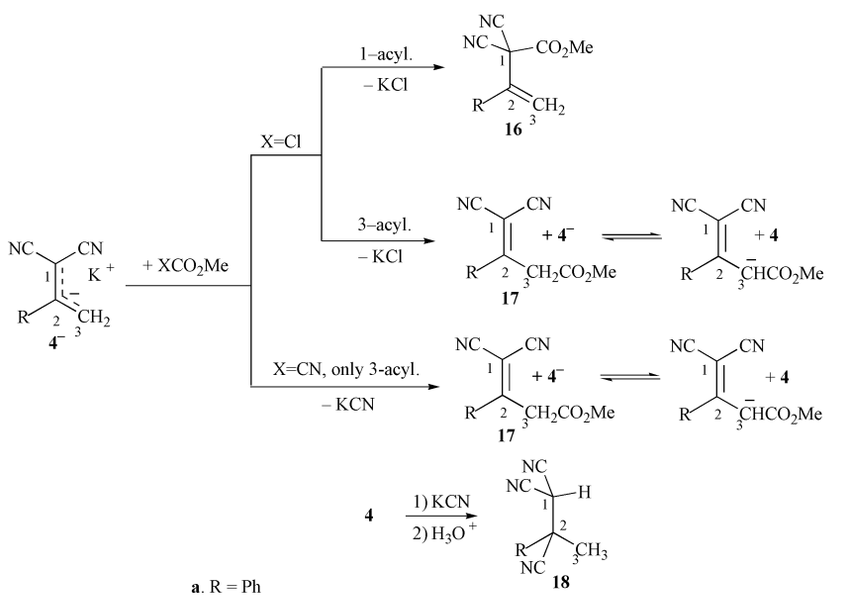
The methoxycarbonylation reagents, methyl chloro- and cyanoformate, also react differently with the salts **4**$^-$, reflecting their different 'hardness' as electrophiles. The chloride ion is the much better leaving group, making the chloroformate the 'harder' acid in the HSAB sense and the outcome of these reactions is summarised in Scheme 8 and Table 3.

Double methoxycarbonylation products are not observed with these reagents, and as the acidity of 3-product **17** probably will be higher than that of starting material **4**,‡ the equilibria involving **17** and **4**$^-$ will be shifted to the right. This property has been utilised to separate the two methoxycarbonylation products **16** and **17** (Experimental section).

‡ Estimated to have a pK_a-value ≈11.5.[19]



Scheme 7

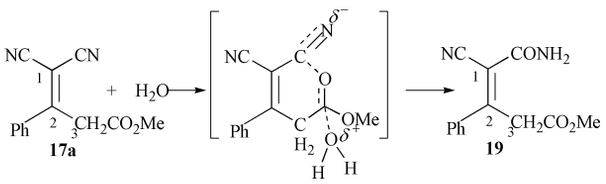


Scheme 8

Table 3 Methoxycarbonylation of potassium salts 4^- with methyl chloro- and cyanoformate[a]

Compd	X	Molar ratio 4^- : XCO_2Me	**16**	**17**	**4**	**18**
4a$^-$	Cl	1 : 5	40	26	36	
4c$^-$	Cl	1 : 5	>90	0	Traces	
4d$^-$	Cl	1 : 5	22	32	42	
4a$^-$	CN	1 : 5	0	51		49
4d$^-$	CN	1 : 5	0	65		31

[a] Yields in percent.



Scheme 9

In the methoxycarbonylation reactions chloride or cyanide ion are the leaving groups which in turn might react as nucleophiles in Michael reactions with the protonated salts formed in the equilibria sketched out in Scheme 8 for 3-attacks. Only cyanide ions react in this fashion as these ions are better nucleophiles, but also because the reversibility of the analogous chloride reaction should be more pronounced, due to the much better leaving-group capacity of the latter ion. That this Michael reaction is a secondary reaction was confirmed in the following way: shortly after the reaction with methyl cyanoformate was finished, a sample was withdrawn and analysed by GLC, showing only small amounts of the Michael product and substantial amounts of protonated salts, a situation which changed rapidly to give the product composition given in Table 3.

Other electrophiles

Bromine, considered to be a 'soft' acid,[10] reacts accordingly with **4a**$^-$, **4b**$^-$ and **4c**$^-$ to give exclusive attack at the 3-position. On the other hand, a proton is a very 'hard' acid[10] which preferentially should give 1-attack, and, indeed, when an ethereal solution of **4c**$^-$ was stirred with aq. HCl, ^{1}H NMR spectroscopy showed the presence of both 1- and 3-protonated products (≈70% of 1-protonation) in the organic phase. Attempts to purify the products led to tautomeric rearrangement of the 1-isomer to the more stable product 3-isomer, **4c**. On the other hand, **4a**$^-$, unsubstituted at the 3-position, gave only 3-protonation upon the same treatment.

Experimental

General

Mps were measured on a Reichert Thermopan (Wien) apparatus and are uncorrected. IR spectra were recorded on a Nicolet Magna 550 FTIR spectrometer using an attenuated total reflectance (ATR) ZnSe plate for solid samples (unless otherwise noted); GLC-FTIR experiments were accomplished using a Varian 3300 gas chromatograph in front of the FTIR instrument. High-resolution NMR spectra (^{1}H and ^{13}C) were obtained using Bruker Spectrospin Avance DMX 200 and DMX 300 spectrometers where the reference compound $SiMe_4$ is software controlled; *J*-values are given in Hz. UV spectra are recorded using a Shimadzu UV-260 spectrophotometer, and mass spectra were obtained using a Fison Instrument VG ProSpec Q. NMR peak assignments were done using 2D spectroscopy or other suitable pulse programs.

Solvents used for salt preparations and the alkylation studies were commercial (FLUKA's brand, dried to a water content <0.01%, stored under nitrogen over molecular sieves). All experiments involving the salts were carried out in an inert atmosphere (argon or nitrogen).

Materials

The 2-substituted ethylidenepropanedinitriles **4** were synthesised in good yields from the corresponding ketones and malononitrile using the Cope method:[20] **4a**, mp 94–95 °C (from aq. EtOH) (lit.,[21] 95 °C); **4b**, mp 67–68 °C (from aq. EtOH) (lit.,[22] 69–70 °C); **4c**, mp 56–58 °C (from aq. EtOH) (lit.,[22] 60–62 °C); **4d** mp 69–70 °C (from aq. EtOH) (lit.,[23] 64–65 °C); **4e**, mp 36–38 °C (from CH_2Cl_2–pentane) (lit.,[24] 36–38 °C); **4f**, bp 103–104 °C/14 mmHg (lit.,[25] 104 °C/11 mmHg). *2-[Cyclopropyl-(phenyl)methylene]propanedinitrile* **4g** was synthesised with reasonable yields (53%) from cyclopropyl phenyl ketone and malononitrile using the Cope method.[20] Mp 118–119 °C (from aq. EtOH); ν_{max}/cm^{-1} 3022w, 2920m, 2223s, 1559s; δ_H($CDCl_3$) 0.8–0.9 (2 H, m), 1.3–1.4 (2 H, m), 2.4–2.5 (1 H, m), 7.2–7.3 (2 H, m), 7.5–7.6 (3 H, m); δ_C($CDCl_3$) 10.4, (C-4, C-5), 19.5 (C-3), 85.0 (C-2), 112.1–112.5 (2 × CN), 127.2, 128.7, 130.4, 131.8 (Ar-C), 183.7 (C-1); MS (EI, 70 eV) *m/z* 194 (71%, $[M]^{+\bullet}$), 193 (100, $[M - H]^+$), 179 (74), 167 (74), 77 (23); HRMS: Found: M^+, 194.08504. $C_{13}H_{10}N_2$ requires *M*, 194.08440 (−3.3 ppm).

Preparations of potassium salts of 4

To stirred, powdered potassium *tert*-butoxide suspended in diethyl ether was added dropwise *tert*-butyl alcohol until a homogenous solution was obtained. A compound **4**, dissolved in diethyl ether, was added dropwise while vigorous stirring was maintained. In order to avoid reaction between salts and starting material, see below, a small excess of potassium *tert*-butoxide was always used. The corresponding white precipitate (**4**$^-$) was filtered off under nitrogen and stored at −10 to −15 °C (argon). Yields >90%. Purity >95% by ^{1}H NMR. Spectroscopic parameters are entered in Table 4.

Lithium salt of 4d

To *tert*-BuLi (1.5 M; 7.3 ml, 11 mmol) dissolved in pentane was added diethyl ether (15 ml); 2-(1-cyclopropylidene)propanedinitrile **4d** (1.3 g, 10 mmol) was dissolved in diethyl ether (25 ml) and added dropwise at −15 °C. The precipitate formed was collected (under nitrogen) after 5 min, washed with diethyl ether and dried (SiO_2) for 30 min in a desiccator (yield 1.1 g, 78%); δ_H(DMSO-d_6) 0.3–0.4 (2 H, m), 0.5–0.6 (2 H, m), 1.1–1.3 (1 H, m), 3.6 (1 H, m), 3.8 (1 H, m).

Reaction between potassium salt 4a$^-$ and 2-(1-phenylethylidene)-propanedinitrile 4a in acetonitrile

Salt **4a**$^-$ (0.500 g, 2.45 mmol) and **4a** (0.410 g, 2.45 mmol) were dissolved in acetonitrile (25 ml) and the solution was stirred overnight under argon. 1 M HCl saturated with NaCl was added and the mixture extracted with dichloromethane (DCM). The organic layer was dried ($MgSO_4$), and evaporated under reduced pressure. The crude product (0.87 g, yellow–

Table 4 NMR data for the potassium salts of compounds **4**[a]

Compd	^{1}H			^{13}C[b]
	R^1	R^2	R^3	
4a$^-$	7.2–7.3 (3 H, m), 7.3–7.4 (2 H, m)	4.36 (1 H, d, *J* 1.8)	4.08 (1 H, d, *J* 1,8)	93.4, 128.0, 128.4, 128.5, 143.5, 148.7
4b(*E*)$^-$	7.1–7.4 (5 H, m)	1.45 (3 H, d, *J* 7.0)	4.91 (1 H, q, *J* 7.0)	14.7, 101.6, 126.3, 127.6, 129.2, 129.7, 139.4, 140.7
4b(*Z*)$^-$	7.1–7.4 (5 H, m)	1.84 (3 H, d, *J* 7.0)	4.83 (1 H, q, *J* 7.0)	14.7, 101.6, 126.3, 127.6, 129.2, 129.7, 139.4, 140.7
4c$^-$	7.1–7.2 (5 H, m)	1.53 (3 H, s)	1.87 (3 H, s)	24.3, 24.6, 115.7, 126.5, 128.1, 131.1, 131.2, 144.6
4d$^-$	0.3–0.4 (2 H, m), 0.4–0.6 (2 H, m), 1.3–1.4 (1 H, m)	3.90 (1 H, s)	3.60 (1 H, s)	9.6 (2 C), 15.0, 85.2, 127.5, 133.6, 147.2
4e(*E*)$^-$	0.2–0.3 (2 H, m), 0.3–0.4 (2 H, m), 1.2–1.3 (1 H, m)	1.62 (3 H, d, *J* 7.0)	4.28 (1 H, dq, *J* 0.9, 7.0)	N. S.
4e(*Z*)$^-$	0.2–0.3 (2 H, m), 0.3–0.4 (2 H, m), 1.2–1.3 (1 H, m)	1.66 (3 H, d, *J* 7.0)	4.69 (1 H, dq, *J* 0.9, 7.0)	N. S.
4f$^-$	1.03 (6 H, d, *J* 6.8), 2.3–2.4 (1 H, m, *J* 6.7)	4.02 (1 H, s)	3.83 (1 H, s)	Dec.
4g$^-$	6.9–7.8 (5 H, m)	0.3–0.5 (2 H, m)	0.5–0.7 (2 H, m)	Dec.

[a] Spectra recorded in acetone-d_6. [b] N. S.: too many overlapping signals from the other isomer for assignment. Dec.: compound decomposes too quickly in the available solvents.

brown solid) was washed with a small quantity of diethyl ether to give a yellow solid (0.53 g, 70%). After recrystallisation, 0.47 g of yellow crystals of 2-dicyanomethylene-6-methyl-4,6-diphenyl-1,2,5,6-tetrahydronicotinonitrile **6** were obtained, mp 206–208 °C (from acetone–pentane) (lit.,[8] 208–210 °C); ν_{max}/cm^{-1} 3265w (NH), 2216m (CN), 2198m (CN), 1594s, 1573m, 1545m; δ_H($CDCl_3$) 1.84 (3 H, s), 3.20 (1 H, d, *J* 18.1), 3.53 (1 H, dd, *J* 18.1, 0.7), 6.63 (1 H, br s), 7.3–7.4 (2 H, m), 7.4–7.6 (8 H, m); δ_H(acetone-d_6) 1.91 (3 H, s), 3.46 (1 H, d, *J* 18.2), 3.82 (1 H, d, *J* 18.2), 7.3–7.6 (10 H, m); δ_C($CDCl_3$) 29.3, 45.7, 54.2, 56.8, 102.0, 112.6, 112.7, 114.6, 124.4, 125.9, 127.9, 128.3, 128.7, 129.2, 129.5, 132.2, 135.5, 141.3, 157.2, 166.5; δ_C(acetone-d_6) 45.8, 52.6, 58.0, 58.2, 102.9, 114.0, 114.6, 115.5, 125.9, 128.7, 129.1, 129.7, 129.8, 132.7, 137.1, 143.7, 158.7, 168.7; MS (EI, 70 eV) *m*/*z* 336 ([M]$^{+\bullet}$, 58%), 321 ([M − CH_3]$^+$, 100); HRMS: Found: M^+, 336.136 173. Calc. for $C_{22}H_{16}N_4$: *M*, 336.137 497 (−3.1 ppm); Found: M^+, 337.139 208. Calc. for $^{12}C_{21}{}^{13}CH_{16}N_4$: *M*, 337.140 852 (4.9 ppm); Found: *m*/*z*, 206.071 997. Calc. for $C_{13}H_8N_3$: *m*/*z* 206.071 822 (−0.8 ppm); Found: *m*/*z*, 130.065 610. Calc. for C_9H_8N: *m*/*z*, 130.065 674 (0.5 ppm); λ_{max}[MeOH (log ε)] 206 (4.29), 249 (3.99), 325 (4.03) nm. Single-crystal X-ray analysis, see below.

Alkylation of the salts 4$^-$

General. *MeI*. After purging of the selected solvent (5 ml) with argon, a salt **4**$^-$ (0.485 mmol) was added, and argon purging was continued for 5 min. Iodomethane (1.45 mmol) was added and the reaction mixture was stirred overnight at room temperature in the dark. Diethyl ether (15 ml) was added and the solution was washed three times with 1 M HCl saturated with NaCl (5 ml). After drying of the organic phase ($MgSO_4$), evaporation left a yellow–brown oil. The oil was analysed by ^{1}H and ^{13}C NMR, GLC-MS and GLC-FTIR to establish the identity of the components, and GLC and ^{1}H NMR were used to establish the relative amounts of the individual components, which are listed in Table 1.

MeTf. Similar procedure as above was carried out, but as initial experiments with this electrophile revealed that only tiny amounts of doubly alkylated products were formed, a much smaller excess (≈10%) of electrophile was used. Moreover, as the reaction with this electrophile was considerably faster, work-up as above was started after 1 h of reaction time. Analytical procedures as above. The results are given in Table 1.

Identification of the products. The reaction products were subjected to column chromatography (SiO_2). The 3-methylated products, **8** and **10**, except **8g** (see below), are equivalent to some of the starting materials; *e.g.* **8a** = **4b**, **8d** = **4e** and **10a** = **4c**.

Unfortunately, we were not able to obtain all new products, *i.e.* the 1-methylated compounds, in a state pure enough for elemental analysis or single-crystal X-ray analysis. However, using GLC-FTIR the IR spectra of most components were recorded. Mass spectra, including HRMS, could be obtained for all compounds using GLC-MS. NMR assignments, both for ^{1}H and ^{13}C, could be made using spectra of chromatographic fractions with different product compositions, coupled with software-controlled difference spectra if one or more of the components could be isolated in a pure state.

The following compounds have been isolated: 2-Methyl-2-(1-phenylvinyl)propanedinitrile **7a**, chromatographically pure, colorless oil (mp < −15 °C); (*E*)-2-methyl-2-(1-phenylprop-1-enyl)propanedinitrile (*E*)-**9b**, mp 32–33 °C (from acetone–pentane), X-ray analysis: see below; 2-methyl-2-(2-methyl-1-phenylprop-1-enyl)propanedinitrile **7c**, chromatographically pure, colorless oil; 2-(1-cyclopropylvinyl)-2-methylpropanedinitrile **7d**, bp 219 °C (Found: C, 73.6; H, 7.2; N, 19.0. $C_9H_{10}N_2$ requires C, 73.9; H, 7.0; N, 19.2%); 2-[cyclopropylidene(phenyl)-methyl]-2-methylpropanedinitrile **7g**, chromatographically pure, colorless oil. Their spectroscopic parameters, obtained on pure compounds, are entered in Tables 5 and 6.

The rest of the 1-methylated compounds; *viz*. (*Z*)-2-methyl-2-(1-phenylprop-1-enyl)propanedinitrile (*Z*)-**9b**; (*E*)-2-(1-cyclopropylprop-1-enyl)-2-methylpropanedinitrile (*E*)-**9e**; (*Z*)-2-(1-cyclopropylprop-1-enyl)-2-methylpropanedinitrile (*Z*)-**9e**; 2-(1-isopropylvinyl)-2-methylpropanedinitrile **7f** were not obtained in a pure state; their spectroscopic parameters were recorded according to the principles described above and the results are entered in Tables 5 and 6.

2-[1-Methylcyclopropyl(phenyl)methylene]propanedinitrile **8g** was not obtained pure and its spectroscopic parameters were obtained in the same way as described for the 1-methylated compounds above: GLC-FTIR: ν_{max}/cm^{-1} 3088s, 2974s, 2230m (CN), 1671s, 1561m; δ_H($CDCl_3$) 0.9–1.0 (4 H, m, 2 × CH_2), 1.53 (3 H, s), 7.3–7.6 (5 H, m, Ph); δ_C($CDCl_3$) 16.8, 23.4, 24.8, 86.3 (C-1), 112.5–113.3 (2 × CN), 128.2, 128.8, 132.0, 135.4 (Ph), 182.6 (C-2); MS (EI, 70 eV) *m*/*z* 208 ([M]$^{+\bullet}$, 15%), 207 ([M − H]$^+$, 40), 193 ([M − Me]$^+$, 100), 166 (61); HRMS (GLC-MS) Found: M^+, 208.10005. $C_{14}H_{12}N_2$ requires *M*, 208.09905 (4.8 ppm).

Table 5 HRMS of molecular ions of 1-methylated compounds **7** and **9**

Compd	Mol. formula	Mass found	Mass calc.	Dev. (ppm)	Remarks
7a	$^{12}C_{12}H_{10}N_2$	182.084 637	182.084 398	−1.3	
	$^{12}C_{11}{}^{13}CH_{10}N_2$	183.087 609	193.087 753	+0.3	
9b(*E*)	$^{12}C_{13}H_{12}N_2$	196.100 116	196.100 048	−0.3	
	$^{12}C_{12}{}^{13}CH_{12}N_2$	197.103 756	197.103 403	−1.8	
9b(*Z*)	$^{12}C_{13}H_{12}N_2$	196.100 936	196.100 048	−4.5	
	$^{12}C_{12}{}^{13}CH_{12}N_2$	197.102 045	197.103 403	+6.9	
7c	$^{12}C_{14}H_{14}N_2$	210.115 209	210.115 699	+2.3	
	$^{12}C_{13}{}^{13}CH_{14}N_2$	211.118 387	211.119 053	+3.2	
7d	$^{12}C_9H_{10}N_2$	146.084 382	146.084 398	+0.1	
9e(*E*)	$^{12}C_{10}H_{12}N_2$	160.100 820	160.100 048	−4.8	
7g	$^{12}C_{13}H_{11}N$ ([M − HCN]$^+$)	181.088 83	181.089 15	+1.8	([M]$^+$ too small to measure)

Table 6 Spectroscopic parameters of 1-methylated products **7** and **9**[a]

	^{1}H NMR	^{13}C NMR	FTIR[b]	MS
7a	1.86 (3 H, s), 5.50 (1 H, s), 5.91 (1 H, s), 7.4 (5 H, m)	25.2 (1-Me), 36.7 (C-1), 115.1 (2 × CN), 120.1 (C-3), 128.3, 128.5, 129.0, 135.4 (Ar C), 140.9 (C-2)	2250w, 1495m, 1451m, 1444m	182 ([M]$^{+\bullet}$, 30%), 103 ([M − C(C-N)$_2$Me]$^+$, 100)
9b(*E*)	1.54 (3 H, d, *J* 6.8), 1.77 (3 H, s), 6.42 (1 H, q, *J* 6.8), 7.1–7.2 (2 H, m), 7.4–7.5 (3 H, m)	14.9 (3-Me), 25.4 (1-Me), 37.9 (C-1), 115.4 (2 × CN), 128.8 (C-3), 129.7, 129.9, 132.9 (Ar C), 133.2 (C-2)	2243w, 1494m, 1451m, 1443m	196 ([M]$^{+\bullet}$, 39%), 181 ([M − Me]$^+$, 4), 117 ([M − C(CN)$_2$Me]$^+$, 100)
9b(*Z*)	1.78 (3 H, s), 2.13 (3 H, d, *J* 7.5), 5.95 (1 H, q, *J* 7.5), 7.1–7.2 (2 H, m), 7.3–7.4 (3 H, m)	15.0 (3-Me), 25.8 (1-Me), 31.3 (C-1), 115.5 (2 × CN), 128.3 (C-3), 128.6, 128.8, 133.0 (Ar C), 133.9 (C-2)	N. S.	196 ([M]$^{+\bullet}$, 36%), 117 ([M − C(CN)$_2$-Me]$^+$, 100)
7c	1.55 (3 H, s), 1.57 (3 H, s), 2.21 (3 H, s), 7.0–7.1 (2 H, m), 7.3–7.4 (3 H, m)	22.5–24.9 (2 × 3-Me), 26.9 (1-Me), 32.1 (C-1), 115.8 (2 × CN), 125.8, 127.5, 129.1, 136.1 (Ar C), 128.1 (C-3), 140.5 (C-2)	2243m, 1649m, 1491s, 1451s, 1444s	210 ([M]$^{+\bullet}$, 61%), 195 ([M − Me]$^+$, 6), 131 ([M − C(CN)$_2$Me]$^+$, 100)
7d	0.6–0.7 (2 H, m), 0.8–0.9 (2 H, m), 1.4–1.5 (1 H, m), 1.96 (3 H, s), 5.02 (1 H, d, *J* 1.1), 5.38 (1 H, d, *J* 1.1)	7.3–12.4 (3 × Cyclopropyl C), 25.4 (1-Me), 37.6 (C-1), 112.3 (C-3), 115.2 (2 × CN), 142.3 (C-2)	3098m, 3016s, 2955w, 1645m	146 ([M]$^{+\bullet}$, 7%), 131 ([M − Me]$^+$, 9), 67 ([M − C(CN)$_2$Me]$^+$, 100)
9e(*E*)	0.7–0.9 (2 H, m), 0.8–0.9 (2 H, m), 1.3–1.4, (1 H, m), 1.83 (3 H, dd, *J* 1.9, 7.2), 1.96 (3 H, s), 6.11 (1 H, dq, *J* 1.9, 7.29)	5.9, 9.3, 13.8 (3 × Cyclopropyl C), 24.8 (1-Me), 36.9 (C-1), 115.9 (2 × CN), 129.9 (C-3), 130.6 (C-2)		160 ([M]$^{+\bullet}$, 12%), 145 ([M − Me]$^+$, 13), 118 (86), 81 ([M − C(CN)$_2$Me]$^+$, 100)
9e(*Z*)	0.4–0.5 (2 H, m), 0.7–0.8 (2 H, m), 1.4–1.5, (1 H, m), 1.89 (3 H, dd, *J* 1.9, 7.5), 2.01 (3 H, s), 5.70 (1 H, *J* 1.9, 7.5)	5.5, 13.8, 15.8 (3 × Cyclopropyl C), 24.1 (1-Me), 32.4 (C-1), 115.3 (2 × CN), 127.6 (C-3), 131.8 (C-2)	N. S.	160 ([M]$^{+\bullet}$, 23%), 159 ([M − H]$^+$, 11), 145 ([M − Me]$^+$, 26), 81 ([MC(CN)$_2$-Me]$^+$, 99), 66 (100)
7f	1.19 (6 H, d, *J* 6.8), 1.90 (3 H, s), 2.4–2.5 (1 H, m, *J* 6.8), 5.32 (1 H, d, *J* 1.4), 5.55 (1 H, d, *J* 1.4)	24.2 (2 × Me), 25.8 (1-Me), 30.6 (2-*C*Me$_2$), 37.5 (C-1), 113.9 (C-3), 115.2 (2 × CN), 147.9 (C-2)	N. S.	148 ([M]$^{+\bullet}$, 1%), 133 ([M − Me]$^+$, 9), 106 ([M − C(Me)$_2$]$^+$, 28), 69 ([M − C(CN)$_2$Me]$^+$, 100)
7g	1.25 (2 H, dd, *J* 10.5, 9.0), 1.70 (2 H, *J* 10.5, 9.0), 1.96 (3 H, s), 7.3–7.4 (5 H, m)	2.9–6.3 (2 × Cyclopropyl C), 36.2 (C-1), 115.6 (2 × CN), 120.9 (C-3), 128.3, 128.4, 128.5, 130.7 (Ar C), 135.9 (C-2)	3059s, 2984s, 2247s, 1445s	207 ([M − H]$^+$, 3%), 181 (81), 166 (100), 128 ([M − C(CN)$_2$Me]$^+$, 61)

[a] Numbering of the carbon atoms refers to Scheme 3, compound **7**, *cf.* footnote †. [b] N. S. Not sufficient separation from other products to give individual IR spectra.

Reaction between 2-methyl-2-(1-phenylvinyl)propanedinitrile 7a and potassium *tert*-butoxide

Potassium *tert*-butoxide (68 mg, 0.60 mmol) was suspended in diethyl ether (5 ml) and *tert*-butyl alcohol was added dropwise to obtain an almost homogeneous solution. A solution of compound **7a** (0.10 g, 0.55 mmol) in diethyl ether (5 ml) was added dropwise to the stirred mixture (room temperature). After 5 min diethyl ether (5 ml) was added, the reaction mixture was washed three times with HCl saturated with NaCl (5 ml), dried with $MgSO_4$, and evaporated under reduced pressure to give a yellow oil (96 mg). The crude product was purified through a silica gel column with ethyl acetate–hexane (1 : 9). Fraction 1: Clear oil, 23 mg [(*E*)-2-methyl-3-phenylbut-2-enenitrile (*E*)-**11**, major isomer]; $\delta_H(CDCl_3)$ 1.82 (3 H, d, *J* 1.6), 2.34 (3 H, d, *J* 1.6), 7.1 (2 H, m), 7.3–7.5 (3 H, m); $\delta_C(CDCl_3)$ 117.6, 24.7, 105.7, 119.8, 127.1, 128.3, 128.5, 139.2, 154.2; MS (EI, 70 eV) *m/z* 157 (100%, [M]$^{+\bullet}$), 156 (63, [M − H]$^+$), 142 (32, [M − Me]$^+$); HRMS: Found: M$^+$, 157.088 886. Calc. for $C_{11}H_{11}N$: *M*, 157.089 149 (1.7 ppm); Found: M$^+$, 158.091 880. Calc. for $^{12}C_{10}{}^{13}CH_{11}N$: *M*, 158.092 504 (3.9 ppm).

Fraction 2: 0.44 g, mixture of starting material and (*Z*)-2-methyl-3-phenylbut-2-enenitrile (*Z*)-**11** (minor isomer). Spectroscopic data for (*Z*)-**11**: GLC-FTIR: ν_{max}/cm^{-1} 2212s (CN), 1493m, 1442m; NMR (difference spectra) $\delta_H(CDCl_3)$ 2.05 (3 H, d, *J* 1.0), 2.15 (3 H, d, *J* 1.0), 7.2–7.4 (5 H, m); $\delta_C(CDCl_3)$ 17.5, 20.6, 105.2, 127.2, 128.4, 140.9, 154.3.

Acylation

Potassium salt 4a$^-$ and benzoyl chloride. Two modes of reaction were run: One (1 : 1) where salt **4a**$^-$ was kept in excess throughout the reaction and one (1 : 5) where a large excess of benzoyl chloride was used.

Table 7 Spectroscopic parameters for products from acylation and methoxycarbonylation of salts **4**$^-$ [a]

	^{1}H NMR	^{13}C NMR	FTIR	MS
12[b]	6.98 (1 H, s), 7.5–7.6 (6 H, m), 7.7–7.8 (2 H, m), 7.9–8.0 (2 H, m)	95.9, 103.7, 105.0, 126.9, 128.3, 129.6, 129.7, 130.4, 132.3, 133.0, 134.8, 159.4, 163.6, 164.4	2226w, 1726s, 1610m, 1513s, 1495m	273 ([M]$^{+\bullet}$, 96%), 245 (100)
13[c]	7.1–7.2 (1 H, m), 7.2–7.3 (2 H, m), 7.32 (1 H, s), 7.4–7.5 (2 H, m), 7.5–7.6 (5 H, m), 7.6–7.7 (3 H, m), 7.7–7.8 (2 H, m)	85.2, 113.7, 113.8, 114.1, 127.2, 128.3, 129.0, 129.2, 129.5, 130.1, 130.7, 131.6, 132.4, 134.6, 135.0, 135.3, 158.7, 163.5, 168.9	2224s, 1742s, 1608s, 1575m, 1523m, 1449m	376 ([M]$^{+\bullet}$, 4%), 105 (100)
14a	2.35 (3 H, s), 5.82 (1 H, d, *J* 1.3), 6.04 (1 H, d, *J* 1.3), 7.3–7.5 (5 H, m)	24.9, 55.1, 111.2, 123.4, 127.7, 128.9, 129.8, 134.3, 136.9, 188.4	2163w, 2127w, 1767s	210 ([M]$^{+\bullet}$, 0.2%), 168 (4), 140 (8)
15a(*E*)	1.49 (3 H, d, *J* 0.8), 2.18 (3 H, s), 6.53 (1 H, q, *J* 0.8), 7.4–7.5 (5 H, m)	19.5, 21.0, 83.5, 112.6, 113.1, 116.9, 128.7, 129.4, 132.1, 134.1, 162.6, 168.1, 169.0	2227w, 1782m, 1640m, 1200s, 1154s	252 ([M]$^{+\bullet}$, 1.0%), 237 (16), 183 (12), 140 (6), 43 (100)
15a(*Z*)	1.32 (3 H, s), 2.15 (3 H, d, *J* 0.9), 6.36 (1 H, q, *J* 0.9), 7.3–7.4 (2 H, m), 7.4–7.5 (3 H, m)	19.7, 22.2, 83.6, 112.5, 112.9, 113.2, 127.9, 128.9, 130.9, 134.5, 160.8, 166.8, 168.1	2227w, 1783m, 1646m, 1194s, 1165s	252 ([M]$^{+\bullet}$, 2.0%), 237 (17), 183 (14), 140 (6), 43 (100)
16a	3.82 (3 H, s), 5.74 (1 H, d, *J* 1.0), 6.05 (1 H, d, *J* 1.0), 7.3–7.4 (5 H, m)	48.6, 55.7, 110.6, 122.9, 127.9, 128.7, 129.6, 134.5, 137.1, 175.5	1782s, 1228s	226 ([M]$^{+\bullet}$, 7%), 195 (1), 167 (12), 140 (35), 59 (100)
16c	1.69 (3 H, s), 2.11 (3 H, s), 3.61 (3 H, s), 7.1–7.2 (2 H, m), 7.3–7.4 (3 H, m)	21.5, 24.2, 46.0, 55.2, 111.2, 123.4, 128.5, 128.6, 129.8, 136.8, 142.5, 160.9		254 ([M]$^{+\bullet}$, 27%), 209 (100), 195 (84), 59 (84)
16d	0.6–0.7 (2 H, m), 0.8–0.9 (2 H, m), 1.4–1.5 (1 H, m), 4.00 (3 H, s), 5.2 (1 H, m), 5.6 (1 H, m)	7.4, 11.0, 13.1, 55.7, 110.7, 116.1, 138.7, 160.6	2256vw, 1781s, 1237s	190 ([M]$^{+\bullet}$, 0.5%), 150 (22), 105 (27), 59 (100)
17a	3.68 (3 H, s), 3.95 (2 H, s), 7.4–7.5 (5 H, m)	42.1, 52.9, 87.9, 112.1, 112.2, 127.6, 129.2, 132.4, 134.4, 166.8, 169.8	2231m, 1741s, 1587m, 1566m	226 ([M]$^{+\bullet}$, 100%), 195 (25), 140 (69), 59 (76)
17d	1.0–1.1 (2 H, m), 1.3–1.4 (2 H, m), 2.3–2.4 (1 H, m), 3.10 (2 H, s), 3.70 (3 H, s)	10.8, 19.2, 35.3, 53.1, 87.2, 111.8, 111.9, 166.7, 176.6	3017w, 2956w, 2230m, 1739s	190 ([M]$^{+\bullet}$, 35%), 175 (10), 130 (91), 59 (100)
18a	2.15 (3 H, s), 5.47 (1 H, s), 7.5–7.6 (3 H, m), 7.7–7.8 (2 H, m)	24.5, 35.8, 45.7, 111.7, 119.6, 127.0, 130.4, 130.9, 134.9	2253w, 1493m, 1449s	195 ([M]$^{+\bullet}$, 6%), 168 (14), 130 (100), 103 (29)
18d	0.6–0.9 (4 H, m), 1.1–1.2 (1 H, m), 1.71 (3 H, s), 4.09 (1 H, s)	3.2, 4.0, 17.1, 23.2, 33.0, 43.5, 110.0, 110.1, 116.7	3016m, 2909s, 2259w, 2247w, 1463s	159 ([M]$^{+\bullet}$, 0.8%), 132 (25), 131 (19), 94 (100)

[a] Solvent (NMR): $CDCl_3$, unless otherwise noted. [b] CD_2Cl_2. [c] Acetone-d_6.

Molar ratio 1 : 1. Salt **4a**$^-$ (0.50 g, 2.42 mmol) was dissolved in acetonitrile (12.5 ml) and a solution of benzoyl chloride (0.34 g, 2.42 mmol) in acetonitrile (12.5 ml) was added dropwise. 1 M HCl saturated with NaCl (25 ml) was added after a few minutes. The mixture was extracted with diethyl ether (25 ml), and the organic phase was washed with saturated aq. NaCl (25 ml), dried ($MgSO_4$), and evaporated to give a brown oil/solid (0.62 g). Washing of the residue with diethyl ether gave a solid compound (0.1 g), which was purified by passage through a short SiO_2 column using DCM as eluent to give bright yellow crystals (80 mg) of 2-oxo-4,6-diphenyl-2*H*-pyran-3-carbonitrile **12**, mp 210–212 °C (from DCM–pentane). Spectroscopic parameters, see Tables 7 and 8.

Molar ratio 1 : 5. To benzoyl chloride (1.70 g, 12.1 mmol) dissolved in acetonitrile (12.5 ml) was added dropwise a solution of salt **4a**$^-$ (0.50 g, 2.42 mmol) in acetonitrile (12.5 ml). Work-up was as described above, except that excess of benzoyl chloride was removed from the residue by passage through a SiO_2 column using hexane as first eluent. Subsequent elution with DCM gave a yellow oil (0.60 g) which after crystallisation gave light yellow crystals (0.20 g) of (*Z*)-4,4-dicyano-1,3-diphenylbuta-1,3-dienyl benzoate (*Z*)-**13**, mp 60–62 °C (decomp.) (from DCM–pentane). Spectroscopic parameters, Table 7 and 8. Single-crystal X-ray structure determination (Fig. 3), see below.

Potassium salt 4a$^-$ and acetyl chloride. *NMR experiment.* Equimolar amounts of salt **4a**$^-$ and acetyl chloride were dissolved in CD_3CN and analysed by ^{1}H NMR spectroscopy, and the following compounds were observed: 2-Acetyl-2-(1-phenylvinyl)propanedinitrile **14a** (1-acylation product, 49%), 4,4-dicyano-1-methyl-3-phenylbuta-1,3-dienyl acetate **15a** (3-acylation products, 19% (*Z*)- and 6% (*E*)-form) and 2-(1-phenylethylidene)propanedinitrile **4a** (starting material, 26%).

Since compound **14a** decomposes (deacetylation) upon chromatography and in aqueous solution, its NMR spectroscopic parameters were obtained directly from the above spectra, and using GLC-FTIR, GLC-MS and HRMS, the other parameters were obtained (see Tables 7 and 8).

Preparative experiment. Salt **4a**$^-$ (0.30 g, 1.45 mmol) was dissolved in acetonitrile (7.5 ml) and a solution of acetyl chloride (0.114 g, 1.45 mmol) in acetonitrile (7.5 ml) was added dropwise. 1 M HCl saturated with NaCl (25 ml) was added after a few minutes. The mixture was extracted with diethyl ether (50 ml), and the organic phase was washed with saturated aq. NaCl (25 ml), dried ($MgSO_4$), and evaporated to give a brown oil (0.28 g). Column chromatography (SiO_2), using first DCM to elute (1-phenylethylidene)propanedinitrile **4a** [formed by deacetylation of 2-acetyl-2-(1-phenylvinyl)-propanedinitrile **14a**, and as reaction product, see above] and then hexane–ethyl acetate (4 : 1) as eluent gave two main fractions of the (*Z*)- and (*E*)-form of 4,4-dicyano-1-methyl-3-phenylbuta-1,3-dienyl acetate **15**. Fraction 1 (37 mg) was the pure (*Z*)-form, while fraction 2 (33 mg) contained a 1 : 1 mixture of both isomers. (*Z*)-4,4-Dicyano-1-methyl-3-phenylbuta-1,3-dienyl acetate (*Z*)-**15** had mp 102–103 °C. Spectroscopic parameters, Tables 7 and 8. Single-crystal X-ray structure determination of (*Z*)-**15** (Fig. 4), see below.

The spectroscopic parameters for (*E*)-4,4-dicyano-1-methyl-3-phenylbuta-1,3-dienyl acetate (*E*)-**15** were obtained using

Table 8 HRMS of molecular ions of acylated and methoxycarbonylated compounds **12**–**18**

Compd	Mol. formula	Mass found	Mass calc.	Dev. (ppm)
12	$C_{18}H_{11}NO_2$	273.079 219	273.078 979	−0.9
	$^{12}C_{17}{}^{13}CH_{11}NO_2$	274.082 544	274.082 334	−0.8
13(*Z*)	$C_{25}H_{16}N_2O_2$	376.119 527	376.121 178	+4.4
	$^{12}C_{24}{}^{13}CH_{16}N_2O_2$	377.123 576	377.124 533	+2.5
15a(*Z*)	$C_{15}H_{12}N_2O_2$	252.087 998	252.089 878	+7.5
16c	$C_{15}H_{14}N_2O_2$	254.106 709	254.105 528	−4.6
	$^{12}C_{14}{}^{13}CH_{14}N_2PO_2$	255.110 251	255.108 883	−5.4
16d	$C_{10}H_{10}N_2O_2$	190.074 235	190.074 228	0
	$^{12}C_9{}^{13}CH_{10}N_2O_2$	191.077 262	191.077 583	+1.7
17a	$C_{13}H_{10}N_2O_2$	226.073 758	226.074 228	+2.1
	$^{12}C_{12}{}^{13}CH_{10}N_2O_2$	227.076 347	227.077 583	+5.4
17d	$C_{10}H_{10}N_2O_2$	190.074 598	190.074 228	−1.9
18a	$C_{12}H_9N_3$	195.080 565	195.097 647	−4.7
	$^{12}C_{11}{}^{13}CH_9N_3$	196.083 176	196.083 002	−0.9
18d	$C_9H_9N_3$	159.079 896	159.079 647	−1.6

GLC-FTIR, GLC-MS, and software-controlled difference ^1H and ^{13}C NMR spectra, see Tables 7 and 8.

Potassium salt 4c$^-$ and acetyl chloride. Acetyl chloride (0.837 g, 0.758 ml, 10.7 mmol) was dissolved in acetonitrile (11 ml) and a solution of potassium 1,1-dicyano-3-methyl-2-phenylbutenide (0.500 g, 2.13 mmol) in acetonitrile (11 ml) was added dropwise under rigorous stirring. 30 min after addition the reaction mixture was evaporated under reduced pressure. The crude product (0.71 g) was dissolved in diethyl ether and washed successively with 1 M HCl and water, dried ($MgSO_4$), and evaporated under reduced pressure to give an orange oil (0.43 g). Pentane was added and, after stirring, the pentane layer was removed. This procedure was repeated and the combined pentane fractions were evaporated under reduced pressure to give a yellow oil (0.3 g) which was 2-acetyl-2-(2-methyl-1-phenylprop-1-enyl)propanedinitrile **14c**.

Methoxycarbonylation

Standard procedure. Methyl chloro- or cyanoformate (10 mmol) was dissolved in acetonitrile (11 ml) and the appropriate potassium salt **4**$^-$ (2 mmol) as a solution in acetonitrile (11 ml) was added dropwise under vigorous stirring. After 30 min the solution was evaporated at reduced pressure to leave an oil, which was dissolved in diethyl ether and washed successively with 1 M HCl (saturated with NaCl), and water, dried ($MgSO_4$), and evaporated to give a yellow oil. Product distribution (Scheme 8) was estimated using ^1H NMR and/or GLC and entered in Table 3. Details of the separation procedures given below. All spectroscopic parameters are entered in Tables 7 and 8.

Isolation of the products. *Salt **4a**$^-$ and methyl cyanoformate.* To the above yellow oil was added diethyl ether (150 ml) and the mixture was extracted with saturated aq. $NaHCO_3$ (100 + 50 ml). The combined aqueous solution was acidified (HCl) and extracted with diethyl ether. After drying of the organic phase ($MgSO_4$), evaporation gave 0.88 g of a brownish oil, which was eluted with DCM through a short SiO_2 column to give 0.72 g of a chromatographically pure light yellow oil, methyl 4,4-dicyano-3-phenylbut-3-enoate **17a**. Spectroscopic parameters, Tables 7 and 8.

The organic phase after extraction was dried ($MgSO_4$) and evaporated to give 1.2 g of a brown oil, which after elution (DCM) through a short SiO_2 column and crystallisation gave 0.68 g of white crystals of 3-cyano-2-methyl-2-phenylsuccinonitrile **18a**, mp 122–123 °C (from $CHCl_3$–pentane), identical to the Michael product synthesised from **4a** and tetrabutylammonium cyanide.

*Salt **4d**$^-$ and methyl cyanoformate.* The oil (0.32 g) was shown by ^1H NMR analysis to consist of 65% methyl 4,4-dicyano-3-cyclopropylbut-3-enoate **17d** and 31% 3-cyano-2-cyclopropyl-2-methylsuccinonitrile **18d**. The latter compound decomposed to **4d** when submitted to GLC. However, preparative GLC could be used to obtain product **17d** in a pure state, as crystals, mp 39–40 °C. Authentic samples of **18d** were obtained by reaction of **4d** with tetrabutylammonium cyanide in a standard way; purification by elution (DCM) through a short acid Al_2O_3 column gave white crystals, mp 53–55 °C.

*Salt **4a**$^-$ and methyl chloroformate.* To the reaction solution (before work-up as described in the standard procedure above) was added diethyl ether (25 ml), causing precipitation of KCl and salt **17a**$^-$. After filtration, the ethereal solution was washed successively with 1 M HCl saturated with NaCl (25 ml) and saturated aq. NaCl (25 ml) and dried ($MgSO_4$) to give a blue-green oil (0.30 g) which was shown (^1H NMR) to consist of a mixture of **4a** (40%) and methyl 2,2-dicyano-3-phenylbut-3-enoate **16a** (60%). Compound **16a** decomposes on SiO_2 gel and its spectral parameters were therefore obtained using GLC-FTIR, GLC-MS and computer-controlled difference NMR spectra.

The above mixture of salts was treated with diethyl ether–1 M HCl, and the organic phase was washed with water, dried ($MgSO_4$), and evaporated to give 0.12 g of chromatographically pure methyl 4,4-dicyano-3-phenylbut-3-enoate **17a**.

*Salt **4c**$^-$ and methyl chloroformate.* The above yellow oil (0.70 g) was dissolved in diethyl ether (25 ml) and washed successively with 1 M HCl (saturated with NaCl), and water, dried ($MgSO_4$), and evaporated to give an orange oil (0.45 g). Pentane (20 ml) was added and after being stirred for some minutes, the pentane layer was removed. After repetition of this operation, the combined pentane layer was evaporated to give a light yellow oil (0.30 g), namely methyl 2,2-dicyano-4-methyl-3-phenylpent-3-enoate **16c**.

*Salt **4d**$^-$ and methyl chloroformate.* The above oil (0.32 g) was shown by NMR (^1H and ^{13}C) analyses to consist of **4d** (42%), **17d** (32%) and 22% methyl 2,2-dicyano-3-cyclopropylbut-3-enoate **16d**, which could be separated by preparative GLC.

Hydrolysis of 17a

Compound **17a** was dissolved in aq. acetonitrile and after stirring overnight the solution was evaporated to dryness to leave a solid, which after crystallisation gave yellow needles of methyl 4-carbamoyl-4-cyano-3-phenylbut-3-enoate **19**, mp 124–125.5 °C (from $CHCl_3$–pentane); ν_{max}/cm^{-1} (FTIR) 3425m (NH), 3331m (NH), 3191m, 2218w (CN), 1736s (CO), 1685s (CO); $\delta_H(CDCl_3)$ 3.66 (3 H, s), 4.17 (2 H, s), 5.89 (1 H, br), 6.46 (1 H, br), 7.4–7.5 (5 H, m); $\delta_C(CDCl_3)$ 40.8, 52.4, 108.5, 117.1, 127.4, 128.9, 130.6, 139.2, 162.6, 164.4, 169.1; MS (EI 70 eV) *m/z* 244 ([M]$^{+\bullet}$, 15%), 227 (42), 199 (51), 184 (100); HRMS Found: M^+, 244.085 756. $C_{13}H_{12}N_2O_3$ requires *M*, 244.084 792

(−3.9 ppm); Found: M^+, 245.088 165. $^{12}C_{12}{}^{13}CH_{12}N_2O_3$ requires M, 245.088 147 (−0.1 ppm).

Reaction with other electrophiles

Reaction of salts $4a^-$, $4b^-$ and $4c^-$ with Br_2. In separate experiments the salts were suspended in CCl_4 and equivalent amounts of Br_2 added. After being stirred for 3 h in the dark, the organic phases were washed with water, dried ($MgSO_4$), and evaporated to give high yields (>90%) of the following bromo compounds: (2-bromo-1-phenylethylidene)propanedinitrile, mp 120–121 °C (from EtOH) (lit.,[26] 122 °C); (2-bromo-1-phenylpropylidene)propanedinitrile, mp 103–105 °C (from MeOH) (lit.,[26] 104.5–105.5 °C) and (2-bromo-2-methyl-1-phenylpropylidene)propanedinitrile, mp 89–91 °C (from benzene) (lit.,[26] 91–92 °C).

Reaction between salt $4c^-$ and aq. HCl. To a suspension of salt **4c**$^-$ (0.88 g, 3.76 mmol) in diethyl ether (50 ml) was added HCl (50 ml; 1 M) under vigorous stirring. After separation of the two layers, the aqueous layer was extracted with diethyl ether (50 ml). The combined organic layers were dried ($MgSO_4$) and evaporated, to leave 0.70 g of a yellow oil. ^{1}H NMR analysis of this oil showed that the major product (≈70%) was 2-(2-methyl-1-phenylprop-1-enyl)propanedinitrile; $\delta_H(CDCl_3)$ 1.65 (3 H, s), 2.01 (3 H, s), 4.91 (1 H, s), 7.2 (2 H, m), 7.3–7.4 (3 H, m). Efforts to purify this 3-protonated product led to tautomerisation to the more stable isomer, *viz.* 2-(2-methyl-1-phenylpropylidene)propanedinitrile **4c** which also constituted the minor constituent of the yellow oil.

X-Ray crystallographic analysis data for compounds 6, (*E*)-9b, (*Z*)-13 and (*Z*)-15§

X-Ray data were collected on a Siemens SMART CCD diffractometer[27] using graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Data-collection method: ω-scan, range 0.6°, crystal-to-detector distance 5 cm. Data reduction and cell determination were carried out with the SAINT and XPREP programs.[27] Absorption corrections were applied by the use of the SADABS program.[28] The structure was determined and refined using the SHELXTL program package.[29] The non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were located from difference Fourier maps and refined with isotropic thermal parameters.

Crystal data for compound 6. $C_{22}H_{16}N_4{\cdot}C_3H_6O$, M = 394.47, monoclinic, $P2_1/c$, a = 7.099(1), b = 18.261(1), c = 16.496(1) Å, β = 100.47(1)°, V = 2102.92(1) Å^3, Z = 4, D_x = 1.246 Mg m^{-3}, μ = 0.078 mm^{-1}, T = 150(2) K, measured 30 823 reflections in 2θ-range 5.1–64.1°, R_{int} = 0.044. 359 Parameters refined against 7288 F^2, R = 0.056 for $I_o > 2\sigma(I_o)$ and 0.076 for all data.

Crystal data for compound (*E*)-9b. $C_{13}H_{12}N_2$, M = 196.25, monoclinic, $P2_1/n$, a = 10.414(1), b = 7.626(1), c = 14.178(1) Å, β = 96.33(1)° V = 1119.1(1) Å^3, Z = 4, D_x = 1.165 Mg m^{-3}, μ = 0.070 mm^{-1}, T = 150(2) K, measured 16 549 reflections in 2θ-range 6.8–66.2°, R_{int} = 0.026. 184 Parameters refined against 4145 F^2, R = 0.049 for $I_o > 2\sigma(I_o)$ and 0.059 for all data.

Crystal data for compound (*Z*)-13. $C_{25}H_{16}N_2O_2$, M = 376.40, triclinic, P-1, a = 8.157(1), b = 10.846(1), c = 12.121(1) Å, α = 68.57(1)°, β = 76.12(1)°, γ = 80.52(1)°, V = 965.6(1) Å^3, Z = 2, D_x = 1.295 Mg m^{-3}, μ = 0.083 mm^{-1}, T = 150(2) K, measured 12 776 reflections in 2θ-range 15.8–66.3°, R_{int} = 0.021. 326 Parameters refined against 5897 F^2, R = 0.049 for $I_o > 2\sigma(I_o)$ and 0.062 for all data.

Crystal data for compound (*Z*)-15. $C_{15}H_{12}N_2O_2$, M = 252.27, orthorhombic, $P2_12_12_1$, a = 7.325(1), b = 9.440(1), c = 19.246(1) Å, V = 1330.8(2) Å^3, Z = 4, D_x = 1.259 Mg m^{-3}, μ = 0.085 mm^{-1}, T = 150(2) K, measured 24 377 reflections in 2θ-range 10.3–66.3°, R_{int} = 0.026. 220 Parameters refined against 4872 F^2, R = 0.038 for $I_o > 2\sigma(I_o)$ and 0.043 for all data.

§ CCDC reference number 207/504. See http://www.rsc.org/suppdata/p1/b0/b009175h/ for crystallographic files in .cif format.

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