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Synthesis of 2-Bromo-2-methyl-1-(*o*-bromomethylphenyl)-propylidene-malononitrile and its Reactions with Selected Nucleophiles

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The title compound was synthezised and reacted with selected nucleophiles: alkoxide, cyanide or hydride (from $NaBH_4$) ion. Methoxide ion (1 mol equivalent) gave a mixture of a substituted cyclopropane and a benzazepine derivative, the latter being formed through attack of methoxide on the cyano carbon to form an imidate anion and subsequent nucleophilic attack of the imidate anion on the benzyl bromide part. Further attack of methoxide ion resulted in a tricyclic compound where both a cyclopropane and an azepine ring is incorporated. Hydride ion attack yielded a substituted cyclopropane. Cyanide and *tert*-butoxide ion gave isopropylidene-2,2-indandicarbonitrile, probably through base-promoted debromination to form the five-membered ring. Isopropoxide ion gave mixtures of cyclopropane, azepine and indan derivatives.

It has been reported that 2-bromoalkylidene malonates (*1*, X=CO_2Me, R=H) and malononitriles (*1*, X=CN, R=H or Ar) normally yield cyclopropane *2* when reacted with nucleophiles like methoxide, cyanide or hydride ion.[1-3] Exceptions have been observed with *1* (X=CN, R=H) using either methoxide ion where Δ^2-pyrrolines were formed,[4] or hydride ion (from $NaBH_4$) where open-chain substituted malononitriles were formed.[2] However, in both cases cyclopropanes were postulated as intermediates which then were cleaved by the nucleophiles.

When *3* (X=CO_2Me) reacted with methoxide or cyanide ion indan *4* was formed,[5] while hydride ion replaced the bromo group.[6] Malononitrile *3* (X=CN) gave indan *4* with methoxide ion, while with potassium cyanide the results were more complex. Thus indan *4* was formed when aqueous acetonitrile was used as solvent while a dimer most likely was formed in aqueous acetone.

It was then decided to design a molecule combining the allylic halide and the benzylic halide functions (the latter may be regarded as a vinylogue of the former), and to study the competition between cyclopropane and indan formation in the reaction of nucleophiles with such systems (*5b* or *5d*).

Synthesis of the alkylidene malonate *5a* could not be achieved. Thus *o*-tolyl isopropyl ketone (*6a*) evaded condensation with dimethyl malonate using the common Knoevenagel conditions or the Lehnert modification (titanium tetrachloride – THF – pyridine).[7] Since phenyl isopropyl ketone can be condensed with dimethyl malonate (although in only 15 % yield) using the Lehnert modification,[7] steric factors are evidently quite important. Condensation of *6a* with malononitrile (Knoevenagel conditions) was also unsuccessful. However, in the Grignard reaction of isobutyronitrile with *o*-tolylmagnesium bromide the imine salt *6b* is an intermediate. By adding malononitrile to the Grignard reaction solution (instead of hydrolysis),[8] we obtained malononitrile *5c* in 58 % yield. When anhydrous ammonia was added to the Grignard reaction solution,[9] a product was obtained consisting of approximately 65 % *6c* and 35 % of its tautomer, enamine *7* (^1H NMR). Essentially quantitative yields of *5c* were obtained in the reaction of malononitrile with this ketimine-enamine mixture. All attempts to react dimethyl malonate with the ketimine-enamine mixture were in vain, even using base (sodium methoxide) or Lewis acid (BF_3-etherate) catalyst.

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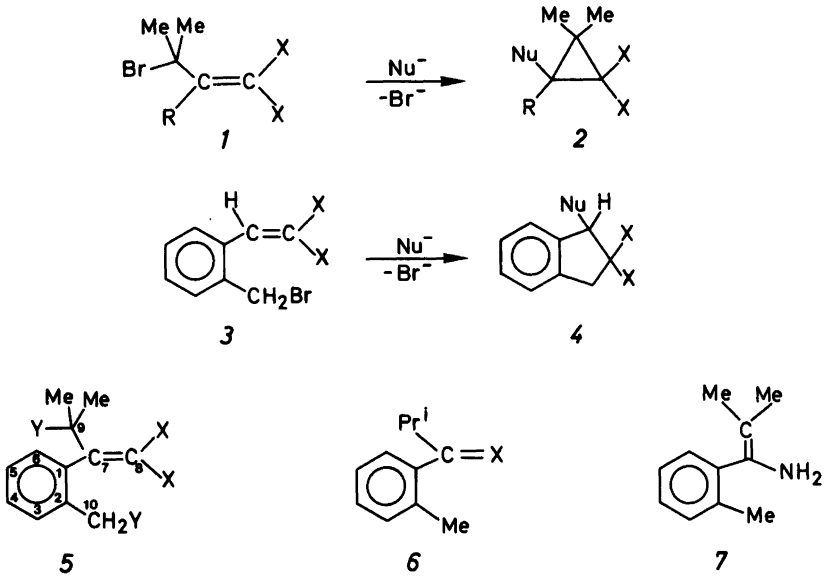


Scheme 1. *5a*, X = CO_2Me, Y = H; *5b*, X = CO_2Me, Y = Br; *5c*, X = CN, Y = H; *5d*, X = CN, Y = Br; *6a*, X = O; *6b*, X = NMgX; *6c*, X = NH.

Attempts to alcohollyze *5c* to *5a* led to formation of γ,γ-dimethyl-β-(2-methylphenyl)-γ-butyrolactone.[10]

The ^{1}H NMR spectrum of *5c* in deuteriochloroform showed four resonance lines for the isopropyl methyl groups. As asymmetric carbon atoms are lacking, this nonequivalence indicates restricted rotation around the C1 – C7 bond (rapid rotation of the isopropyl group around the C7 – C9 bond is of course assumed); the steric requirements of the isopropyl group and the asymmetrical substitution of the aromatic ring make the whole molecule nonplanar and chiral. Within each enantiomer thus present the isopropyl methyl groups are diastereotopic each giving a doublet due to coupling with the methine proton at C9. The absence of asymmetric carbon was also demonstrated by the coalescence occurring at aroung 116 °C in *p*-dichlorobenzene.*

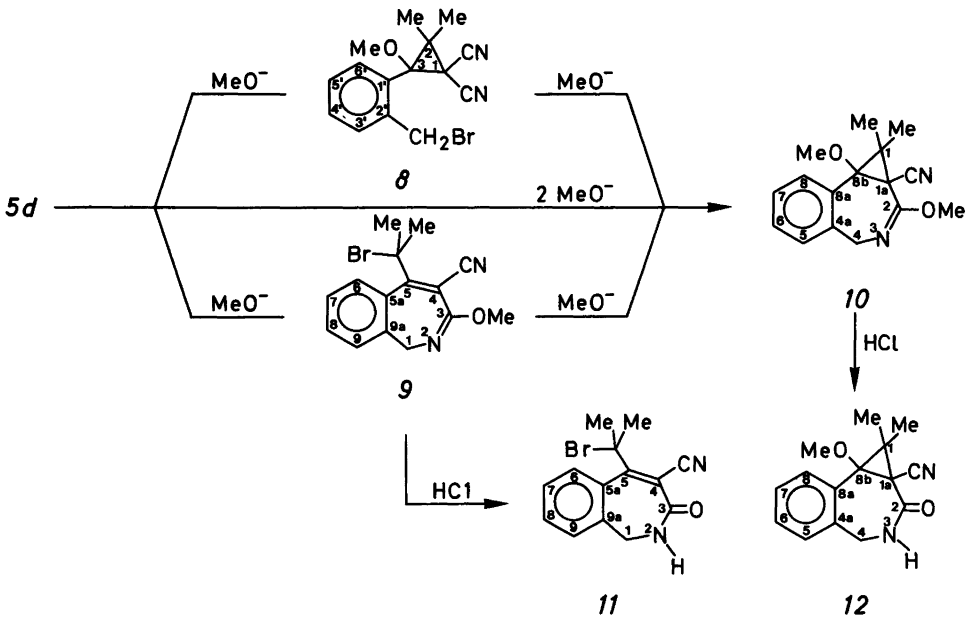
Bromination of *5c* to *5d* using *N*-bromosuccinimide was achieved only with great difficulty due to benzylic dibromination competing with allylic bromination. As expected, the ^{1}H NMR spectrum of *5d* also indicated restricted rotation around the C1 – C7 bond. Introduction of bromine at C9 and C10 raises the barrier to rotation as shown by the abscence of coalescence below 170 °C.

Malononitrile *5d* was then reacted with methoxide, isopropoxide, *tert*-butoxide, cyanide and hydride ion. With one mol equivalent of sodium methoxide two products were formed in approximately equal proportions (^{1}H NMR), *viz.* *8* and *9*. (Scheme 2). The spectroscopic properties of *8* (^{1}H NMR, ^{13}C NMR and IR) were very similar to those of 2-methoxy-3,3-dimethyl-2-phenylcyclopropane-1,1-dicarbonitrile.[3] In contrast to *8*, *9* exhibits only one nitrile carbon resonance line. Other spectroscopic properties summarized in Experimental together with the fact that nitriles (especially with electronegative α substituents) give imidates with alcohol-alkoxide,[12] make the cyclic imidate *9* a plausible product of the reaction of *5d* with methoxide ion.

When *5d* was reacted with two mol equivalents of methoxide ion, or cyclopropane *8* or benzazepine *9* with one mol equivalent of methoxide ion the tricyclic compound *10* was formed as the sole product.

Salts of imidates are formed in the Pinner reaction,[13] and if the temperature is allowed to rise above 5 °C they may decompose to amides in a thermal first-order process.[14] In order to get chemical confirmation of *9* and *10* being cyclic imidates

* Atropisomerism in highly substituted styrenes has been studied.[11]

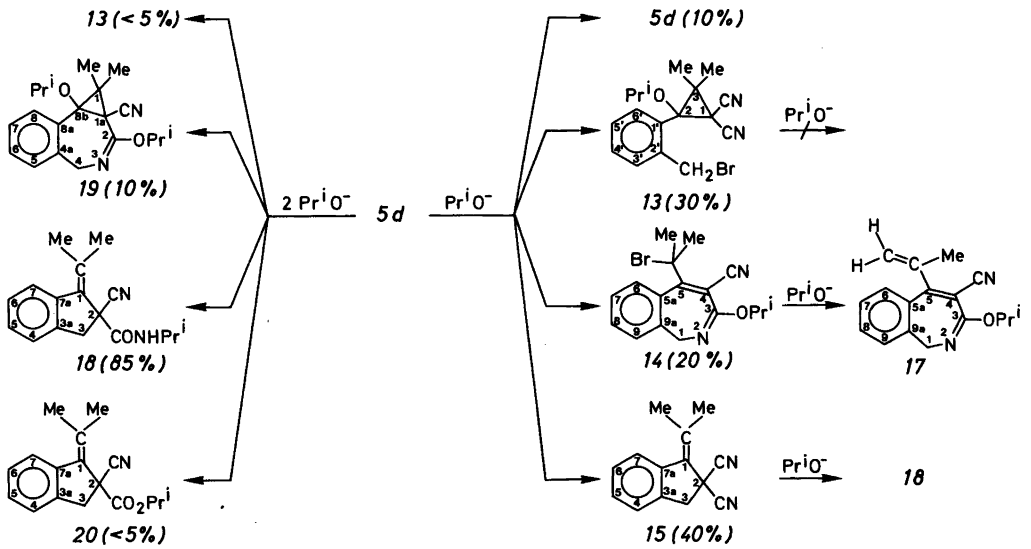


Scheme 2. Reaction of *5d* with methoxide ion.

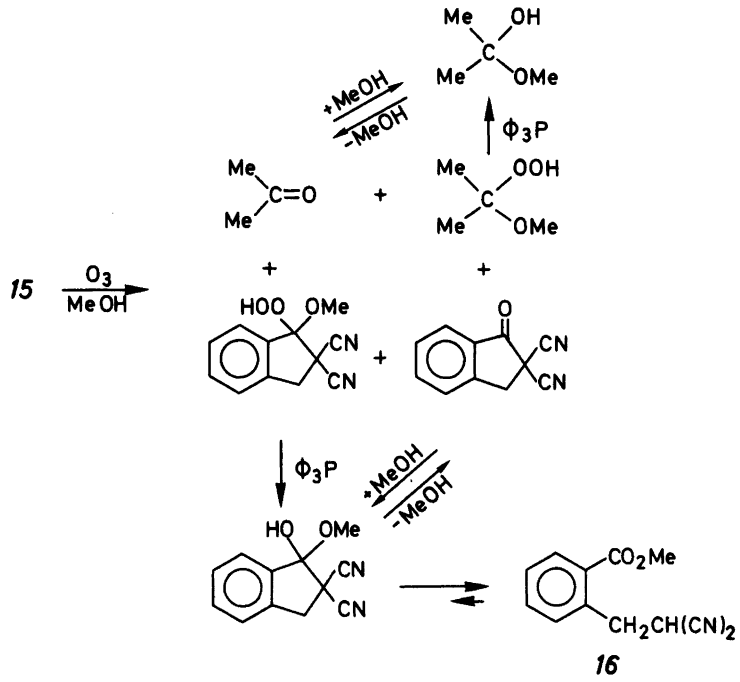
we therefore prepared their hydrochloride salt and, indeed, under our reaction conditions they decomposed to the lactames *11* and *12*, respectively.

Closure of rings of this size and fashion may be named as 7-Exo-Tet and is considered as favoured.[15]

The reaction of *5d* with sodium isopropoxide was somewhat more complicated. In the equimolar reaction three products were formed (Scheme 3). Two of these had their parallels in the methoxide reactions, *viz.* cyclopropane 13 and benzazepine



Scheme 3. Reaction of *5d* with isopropoxide ion.



Scheme 4. Ozonolysis of *15*.

(imidate) *14*. In ^{1}H NMR two doublets were observed for the isopropyl methyl groups of *14* which at first sight points to an *N*-isopropyl lactam structure (with an inversion barrier). However, the carbon resonance for C3 occurs at 156.5 ppm, close to what is observed for C3 in *9* (157.3 ppm), while C3 in lactam *11* absorbs at 164.8 ppm. Thus C3 in *14* is most likely double-bonded to nitrogen and single-bonded to oxygen and not *vice versa*. Lack of planarity of the ring system makes the molecule chiral and the isopropyl methyl groups are therefore nonequivalent.

The third product (*15*) from the isopropoxide reaction was unexpected. Its structure was chemically confirmed by its reaction with ozone (Scheme 4).

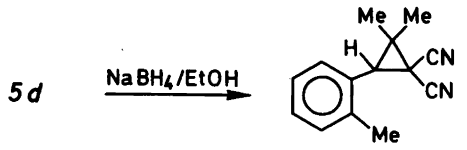
The formation of the *o*-substituted benzoic ester *16* is at first sight somewhat unexpected. However, current ideas on ozonolyses in protic solvents include formation of hydroperoxides (*e.g.*, α-methoxyhydroperoxides when methanol is used as solvent).[16] Triphenylphosphine is an excellent reducing agent for most peroxides,[17] and would lead to hemiketals (or -acetals) which normally can be identified as the parent carbonyl compound. However, the hemiketal of 1-oxo-indan-2,2-dicarbonitrile would most certainly rearrange to the thermodynamically more stable *16* (Scheme 4).

Additionally, the structure of *15* was confirmed by X-ray structural determination.[18] Its formation is rather strange and will be discussed later on.

Contrary to the methoxide reaction, further attack of isopropoxide on *13*, *14* and *15* led to results diverging from those obtained when the starting material *5d* was subjected to reaction with two mol equivalent of isopropoxide (Scheme 3). *13* did not react at all, while *14* suffered dehydrobromination to *17* instead of ring closure to *19*. *15* gave *18* in good yields, probably through a Chapman-like rearrangement of an initially formed imidate.[19]

Treatment of *5d* with two mol equivalents of isopropoxide gave only 10 % of *19* while *18* was the main product (85 %). Minor amounts of *13* (<5 %) and cyano ester *20* were formed, the latter probably through alcoholysis of *15* or *18*.

It is hard to explain the diverging results of the isopropoxide reactions. The dehydrobromination of *14* to *17* is most likely due to the size of the nucleophile. But why the tricyclic compound *19* was formed in the two-mol reaction, while its supposed pre-



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Scheme 5. Reaction of *5d* with hydride ion (from $NaBH_4$).

cursors *13* and *14* either evade reaction or react in a different way, cannot be answered at this stage.

In the reaction of *5d* with two mol equivalents of potassium *tert*-butoxide *15* was the sole product, while in the equimolar reaction approximately half of the starting material was unchanged.

Cyanide ion gave *15* as product, together with small amounts of an unidentified product (probably a dimer[6]). These results were obtained both in aqueous acetonitrile (potassium cyanide) and in nonprotic solvents (tetrabutylammonium cyanide).

Hydride ion (from sodium borohydride) reacted according to expectation giving cyclopropane *21* in which the benzylic bromide ion is replaced with hydride ion (Scheme 5).[2,6] Opening of the cyclopropane ring is not observed.

The surprising formation of isopropyliden-2,2-indandicarbonitrile *15* deserves further comment. The experimental facts are as follows:

(i) Cyanide, isopropoxide and *tert*-butoxide ion, but not hydride or methoxide ion gave *15*.

(ii) Two equivalents of nucleophile are necessary to complete the reaction.

(iii) Both protic and aprotic solvents can be used.

These facts are rather confusing. Cyanide ion, being a good nucleophile and a weak base, gives essentially the same result as *tert*-butoxide, a rather strong base, which hardly can be classified as a nucleophile due to its steric requirements. Using the soft and hard base principle,[20] hydride ion is classified as a soft base, while methoxide ion is considered as hard. Nevertheless, the outcome is essentially the same in that attack at the β carbon of the allylic double bond to yield cyclopropanes is predominant. Isopropoxide ion, a hard base, gives reults in between those of cyanide and methoxide ion.

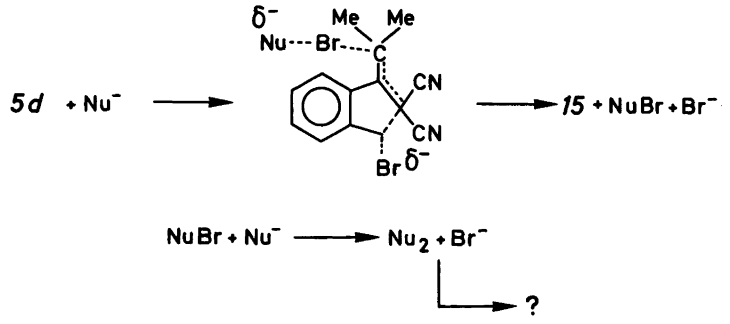
In the formation of *15* the gross reaction is a debromination with indan ring closure. Since two mol equivalents of base (nucleophile) are required, it might well be that the second mol is necessary to reduce bromine (Scheme 6).

The reaction course outlined in Scheme 6 bears some resemblance to the formation of 1,2-dibromobenzocyclobutene from bis-(*o*-dibromomethyl)benzene and iodide ion.[21] However, we have not been able to establish the presence of Nu_2 (cyanogen or dialkyl peroxides).

EXPERIMENTAL

General. Melting points (uncorrected) were determined on a micro hot-stage. IR spectra were recorded on a Jasco-IRA-1 spectrophotometer, ^1H NMR spectra on a Varian A60A spectrometer or a Varian HA 100-15D spectrometer operating at 98 MHz, ^{13}C NMR spectra on a Jeol FX60 spectrometer, mass spectra on an AEI/MS/902 instrument. Element analyses were performed by Ilse Beetz, West Germany.

2-Methyl-1-(o-tolyl)-propylidenemalononitrile (5c).[8,9] The Grignard reagent was made from 2-chloropropane (47 g, 0.6 mol) and magnesium (14.6 g, 0.6 mol) in ether (200 ml). Ether (100 ml) was distilled off and toluene (100 ml) added. The mixture



Scheme 6. Tentative formation of *15* from *5d*.

was then distilled until the distillate temperature reached 100 °C and the distillate was replaced by an equal amount of toluene. *o*-Tolunitrile (50 g, 0.4 mol) dissolved in toluene (50 ml) was then added dropwise and the mixture refluxed for 16 h. Malononitrile (52.8 g, 0.8 mol) dissolved in ether (250 ml) was added dropwise with vigorous stirring. The reaction mixture was then washed with dilute hydrochloric acid, several times with water, dried ($MgSO_4$) and distilled, b.p. 97–100 °C/0.05 mmHg, yield 48.8 g (58 %), m.p. 47–48 °C. Anal. $C_{14}H_{14}N_2$: C, H. ^{1}H NMR ($CDCl_3$): δ 6.8–7.4 (4H, m), 3.43 (1H, septet, $J=7$ Hz), 2.25 (3H, s), 1.29 (3H, d, $J=7$ Hz), 1.04 (3H, d, $J=7$ Hz). ^{13}C NMR ($CDCl_3$): δ 187.3 (C7), 134.4–133.5 (C1+C2), 131.1–129.8–126.1–125.9 (C3–C6), 111.8+111.5 (2C≡N), 88.0 (C8), 36.8 (C9), 21.1 (C10), 19.6 (2×Me).

Isopropyl o-tolyl ketimine (6c).[9] The above procedure was repeated, except that instead of adding malononitrile, anhydrous ammonia was passed into the reaction mixture for 1 h. After centrifugation the clear liquid was distilled, yield 26 g, b.p. 92–94 °C/8 mm Hg. Anal. $C_{11}H_{15}N$: C, H. ^{1}H NMR (CCl_4): Ketimine *6c* (65 %): δ 6.9–7.3 (4H, m), 2.75 (1H, m), 2.22 (3H, s), 1.12 (6H, d, $J=6$ Hz), enamine *7* (*1-amino-2-methyl-1-(o-tolyl)-propene*, 35 %): 6.9–7.3 (4H, m), 2.22 (3H, s), 1.57 (3H, s), 1.32 (3H, s).

Isopropyl o-tolyl ketimine and malononitrile. Ketimine-enamine mixture (0.5 g, 3 mmol) was mixed with malononitrile (0.2 g, 3 mmol) and stirred at room temperature for 15 h. *5c* crystallized. Yield 0.6 g (95 %), m.p. 47–48 °C.

2-Bromo-2-methyl-1-(o-bromomethylphenyl)-propylidenemalononitrile (5d). *5c* (10.5 g, 0.05 mol), *N*-bromosuccinimide (26.7 g, 0.15 mol) bis-(1-cyano-1-methylethyl)diazene (50 mg) in tetrachloromethane (50 ml) was refluxed for 15 h in UV light. The ^{1}H NMR spectrum showed the presence of unreacted starting material and that some benzylic dibromination had taken place. Usual work-up gave a crude product which was crystallized from methanol to give 2.5 g (13 %), *5d*. M.p. 137–138 °C. Anal. $C_{14}H_{12}Br_2N_2$: C, H. IR (KBr): 2215(s), 1570(m) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.0–7.8 (4H, m), 4.75 and 4.12 (2H, 2d, AB-quartet, $J=11$ Hz), 2.15 (3H, s), 2.00 (3H, s). ^{13}C NMR ($CDCl_3$): δ 180.8 (C7), 134.4–133.7 (C1+C2), 131.9–131.1–129.2–126.9 (C3–C6), 111.7–111.2 (2C≡N), 92.8 (C8), 55.9 (C9), 34.3–33.7 (2×Me), 29.8 (C10).

Reactions of 5d with nucleophiles

A. One mol equivalent methoxide. 5d (2 g, 5 mmol) was dissolved in methanol (10 ml). Sodium methoxide (0.27 g, 5 mmol) was added. After stirring for 1 h, methanol was evaporated, water added and the solution extracted with chloroform. The extract was dried ($MgSO_4$) and the solvent evaporated. ^{1}H NMR spectrum of the clear yellow oil showed the presence of two products in approx. equal proportions. Column chromatography (SiO_2, dichloromethane as eluent) was used to separate the compounds. *2-(o-Bromomethylphenyl)-2-*methoxy-*3,3-dimethyl-1,1-cyclopropanedicarbonitrile.* (8) Yield 0.3 g (38 %). M.P. 112–114 °C (MeOH). Anal. $C_{15}H_{15}BrN_2O$: C, H. IR (KBr): 2240(s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.2–7.8 (4H, m), 4.41 (2H, s), 3.28 (3H, s), 1.72 (3H, s), 1.20 (3H, s). ^{13}C NMR ($CDCl_3$): δ 138.3–127.5 (C1′+C2′), 132.7–131.0–131.0–128.7 (C3′–C6′), 113.8–112.9 (2 C≡N), 80.6 (C2), 55.6 (MeO), 40.7 (C3), 28.4 (CH_2Br), 20.7–16.8 (2Me), 18.9 (C1). MS: *m/e* 240 (M+1–Br), 239 (M–Br). *5-(1-Bromo-1-methylethyl)-4-cyano-3-methoxy-*1H-*benz*[*c*]*azepine* (9). Yield 0.25 g (25 %). M.p. 140–142 °C (MeOH). Anal. $C_{15}H_{15}BrN_2O$: C, H. IR (KBr): 2210 (s), 1640 (s). ^{1}H NMR ($CDCl_3$): δ 7.3–8.0 (4H, m), 4.47 and 3.80 (2H, 2d, AB-quartet, $J=12$ Hz), 3.67 (3H, s), 2.42 (3H, s), 2.07 (3H, s). ^{13}C NMR ($CDCl_3$): δ 167.7 (C5), 157.3 (C3), 141.8–133.2 (C5a+C9a), 130.2–128.3–127.0–126.3 (C6–C9), 115.3 (C≡N), 107.0 (C4), 57.4 (Me_2CBr), 55.1 (MeO), 51.5 (C1), 36.5–36.1 (2Me). MS: *m/e* 240 (M+1–Br), 239 (M–Br).

B. Two mol equivalents methoxide. 5d (2 g, 5 mmol) was dissolved in methanol (30 ml). Sodium methoxide (0.55 g, 10 mmol) was added. After stirring for 15 h, methanol was evaporated, water added, and the solution extracted with chloroform. After drying ($MgSO_4$) the solvent was evaporated. The crude product was crystallized from methanol to give *1a-cyano-2,8b-dimethoxy-1,1-dimethyl-1a,8b-dihydro-4*H-*cyclopropano*[e]*benz*[c]*azepine* (10) (62 %). M.p. 121–123 °C. Anal. $C_{16}H_{18}N_2O_2$: C, H. IR (KBr): 2220 (s), 1680 (s) cm^{-1}, ^{1}H NMR ($CDCl_3$): δ 7.5–7.2 (4H, m), 4.92 and 4.34 (2H, 2d, AB-quartet, $J=13$ Hz), 3.66 (3H, s), 3.33 (3H, s), 1.63 (3H, s), 0.74 (3H, s). ^{13}C NMR ($CDCl_3$): δ 158.1 (C2), 138.9–132.0 (C4a+C8a), 131.1–129.0–129.0–128.6 (C5–C8), 116.1 (C≡N), 72.0 (C8b), 53.9 (2×MeO), 50.6 (C4), 33.6–30.1 (C1+C1a), 21.4–17.3 (2×Me). MS: *m/e* 270 (M^+), 255 (M–Me, 100 %).

When either *8* or *9* was treated with one additional mol equivalent sodium methoxide and stirred for 20 h, work-up as in above experiment gave *10* in 71 and 62 % yields, respectively.

C. With one mol equivalent sodium isopropoxide. To *5d* (2.5 g, 6.8 mmol) dissolved in isopropyl alcohol (200 ml) was added (dropwise) an equivalent amount of sodium isoproxide dissolved in isopropyl alcohol (27 ml, 0.25 M). After stirring at room temperature for 0.5 h, work-up as above gave a mixture of products which was separated by column chromatography (SiO_2). The components below are listed in the sequence they were eluted, eluting sol-

vents and relative concentration (obtained by ^1H NMR on the crude product) are given. *Starting material*, benzene, 10 %. *Isopropylidene-2,2-indandicarbonitrile* (15), benzene, 40 %. M.p. 103–105 °C (MeOH). Anal. $C_{14}H_{12}N_2$: C, H, N. IR (KBr): 2220 (s), 1650 (s) cm-^{1}. ^1H NMR ($CDCl_3$): δ 7.8–7.1 (4H, m), 3.88 (2H, s), 2.32 (3H, s), 2.22 (3H, s). ^{13}H NMR ($CDCl_3$): δ 138.4–137.4(2)–128.4 (C1, C3a, C7a, $=C(Me)_2$), 129.7–128.4–125.1–124.9 (C4–C7), 115.8 (2×(C≡N), 44.6 (C3), 35.7 (C2), 25.0–23.0 (2×Me). MS: *m/e* 208 (M^+, 100 %). *2-(o-Bromomethylphenyl)-2-isopropoxy-3,3-dimethyl-1,1-cyclopropanedicarbonitrile* (*13*), benzene, 30 %. M.p. 108–110 °C (MeOH). Anal. $C_{17}H_{19}BrN_2O$: C, H. IR (CCl_4): 2220 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.9–7.3 (4H, m), 4.45 (2H, s) 3.77 (1H, m), 1.68 (3H, s), 1.33 (3H, d, J=6 Hz), 1.15 (3H, s), 0.87 (3H, d, J=6 Hz). *5-(1-Bromo-1-methylethyl)-4-cyano-3-isopropoxy-1H-benz*[c]*-azepine* (*14*), dichloromethane, 20 %. M.p. 125–127 °C (MeOH). Anal. $C_{17}H_{19}BrN_2O$: C, H. IR (KBr): 2210 (s), 1640 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.8–7.1 (4H, m), 4.93 (1H, m), 4.49 and 3,86 (2H, 2d, AB-quartet, J= 12 Hz), 2.47 (3H, s), 2.12 (3H, s), 1.34 (3H, d, J=6 Hz), 1.17 (3H, d, J=6 Hz). ^{13}C NMR ($CDCl_3$): δ 167.0 (C5), 156.5 (C3), 142.0–133.3 (C5a+C9a), 130.1–128.4–127.0–126.3 (C6–C9), 115.5 (C≡N), 107.9 (C4), 69.9 (O-*C*H(Me)$_2$), 57.7 (Br-*C*(Me)$_2$), 51.6 (C1), 36.5 (Br–C(*Me*)$_2$), 21.6–21.1 (O-CH(*Me*)$_2$).

D. Two mol equivalents isopropoxide. To *5d* (1.5 g, 4 mmol) dissolved in isopropyl alcohol (100 ml) was added dropwise sodium isopropoxide in isopropyl alcohol (35 ml, 0.25 M). After stirring at room temperature for 15 h, work-up as before gave a mixture mixture with four components which were isolated by column chromatography (SiO_2). The components are listed in the sequence they were eluted, eluting solvents and relative concentrations (^1H NMR) are given. *Compound* 13, benzene, <5 %. *Isopropyl isopropylidene-2-cyanoindancarboxylate* (*20*), benzene, <5 %. M.p. 79–81 °C (MeOH). Anal. $C_{17}H_{19}NO_2$: C, H. IR (KBr) 2230 (s), 1740 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.8–7.2 (4H, m), 5.13 (1H, m), 3.68 (2H, s), 2.18 (3H, s), 2.08 (3H, s), 1.27 (3H, d, J=6 Hz). MS: m/e 269 (M^+), 182 ($M-CO_2Pr^i$, 100 %). *1a-Cyano-2,8b-diisopropoxy-1,1-dimethyl-1a, 8b-dihydro-4H-cyclopropano*[e]*benz*[c]*acepine* (*19*), benzene-dichloromethane (1:1), 10 %. M.p. 112–115 °C (MeOH). Anal. $C_{20}H_{26}N_2O_2$: C, H. IR (CCl_4): 2220 (s), 1680 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.4–7.2 (4H, m), 5.30 (1H, d, J=13 Hz), 4.95 (1H, m), 4.05 (1H, m), 4.00 (1H, d, J=13 Hz), 1.62 (3H, s), 1.35 (3H, d, J=2Hz), 1.28 (3H, d, J=2 Hz), 1.12 (3H, d, J=6 Hz), 0.73 (3H, s), 0.72 (3H, d, J=6 Hz). MS: *m/e* 326 (M^+). *Isopropylidene-2-cyano-N-isopropyl-2-indancarboxamide* (*18*), benzene–dichloromethane (1:1), 85 %. M.p. 98–100 °C (MeOH). Anal. $C_{17}H_{20}N_2O$: C, H, N. IR (KBr): 3280 (s), 2220 (s), 1650 (s), 1640 (s) cm^{-1}. When *18* (30 mg) was refluxed in CD_3OD (1 ml) for 3 h, the residue after evaporation exhibited an IR absorption at 2460 cm^{-1} (N-D). ^1H NMR ($CDCl_3$): δ 7.8–7.2 (4H, m), 5.13 (1H, m), 3.78 and 3.52 (2H, 2d, AB-quartet, J=17 Hz), 2.23 (3H, s), 2.04 (3H, s), 1.35 (3H, d, J=2 Hz), 1.25 (3H, d, J=2 Hz), NH-proton hidden in noise. ^{13}C NMR ($CDCl_3$): δ 166.9 (C=O), 140.5–139.0–136.1–132.9 (C1, C3a, C7a, $=C(Me)_2$), 127.7(2)–124.9(2) (C4–C7), 120.2 (C≡N), 70.2 (*C*H(Me)$_2$), 50.6 (C2), 45.0 (C3), 25.1–23.1 (=C(*Me*)$_2$), 21.4(2) (HC(*Me*)$_2$). MS: *m/e* 268 (M^+), 182 ($M-CONHPr^i$, 100 %).

E. Potassium tert*-butoxide.* To *5d* (250 mg, 0.68 mmol) *tert*-butyl alcohol was added potassium *tert*-butoxide (150 mg, 1.3 mmol). After stirring for 4 h, usual work-up followed by column chromatography ($SiO_2-CH_2Cl_2$) gave a 51 % yield of *15*. No other products were observed in ^1H NMR of the crude product. When only one mol equivalent of *tert*-butoxide was used, approximately half of the starting material could be recovered (column chromatography).

F. Cyanide ion. (i) *5d* (1.7 g, 4.6 mmol) was dissolved in acetonitrile (15 ml). Potassium cyanide (0.6 g, 9.2 mmol) dissolved in water (5 ml) was added dropwise at toom temperature. After stirring for 20 h at this temperature, usual work-up gave a dark oil which after column chromatography (SiO_2) gave two products: *15*, dichloromethane, *35 %*. *Unknown*, chloroform, <5 %. M.p. 230–235 °C (acetone). MW ~ 817. ^1H NMR ($CDCl_3$): Only broad signals at 7.8–7.0, 4.7–4.4, 2.0–1.3 ppm.

(ii) *5d* (200 mg, 0.54 mmol) was dissolved in dichloromethane (5 ml). Tetrabutylammonium cyanide (300 mg, 1.1 mmol) dissolved in dichloromethane (10 ml) was added dropwise. After stirring for 2 h, the reaction mixture was washed repeatedly with water, the organic phase dried ($MgSO_4$) and the solvent evaporated to give a dark oil. Column chromatography (SiO_2–dichloromethane) gave a 55 % yield of *15* with only traces of the unknown compound.

G. Hydride ion. Sodium borohydride (260 mg, 6.7 mmol) was dissolved in ethanol (5 ml). While the temperature was kept at 10–15 °C, solid *5d* (1.0 g, 2.7 mmol) was added during 30 min. The reaction solution was stirred at room temperature for 20 h. Excess $NaBH_4$ was destroyed by adding acetic acid to pH 6. Ethanol was evaporated, water added and the solution extracted with chloroform. Drying ($MgSO_4$) and evaporation of chloroform gave a yellow oil. Column chromatography (Al_2O_3, neutral, act I-dichloromethane) gave *3,3-dimethyl-2-o-tolyl-1,1-cyclopropandicarbonitrile* (21) in 35 % yield. M.p. 93–94 °C (MeOH). Found: C 79.4, H 6.9. Calc. for $C_{14}H_{14}N_2$: C 79.9, H 6.7. IR (KBr): 2220 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.33 (4H, s),

2.87 (1H, s), 2.35 (3H, s), 1.68 (3H, s), 1.35 (3H, s). ^{13}C NMR ($CDCl_3$) [only the non-aromatic carbon resonance positions given, the analogous signals for *3,3-dimethyl-2-phenyl-1,1-cyclopropanedicarbonitrile* in brackets[3]]: δ 114.9 – 113.1[114.9 – 112.9] (2 × C≡N), 44.8 [44.8] (C2), 36.1[36.0] (C3), 24.0 (Arom. Me), 19.7 – 18.7[24.2 – 18.8] (2 × Me), 16.0 [16.1] (C1). MS: *m/e* 210 (M^+), 195 (M – Me, 100 %).

Reactions of products 13, 14 *and* 15 *with sodium isopropoxide.* (i) To *15* (60 mg, 0.29 mmol) dissolved in isopropyl alcohol (5 ml) was added sodium isopropoxide solution (1.5 ml, 0.25 M) at room temperature. After stirring for 15 h, usual work-up gave after recrystallization 45 mg (58 %) of *18*.

(ii) *13* was recovered unchanged after a similar treatment.

(iii) *14* (50 mg, 0.14 mmol) dissolved in isopropyl alcohol was treated with one mol equivalent of sodium isopropoxide as in (i) to give *4-cyano-3-isopropenyl-5-isopropoxy-benz*[c]*azepine* (17). M.p. 127 – 130 °C (MeOH). Anal. $C_{17}H_{18}N_2O$: C, H. IR (KBr): 2220 (s), 1660 (m), 1650 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.6 – 7.4 (4H, m), 5.60 (1H, d, J = 1 Hz), 5.50 (1H, d, J = 1 Hz), 4.93 (1H, m), 4.25 (2H, s), 1.95 (3H, d, J = 1 Hz), 1.32 (3H, s), 1.20 (3H, s). MS: *m/e* 266 (M^+), 251 (M – Me), 225 (M – isopropenyl).

Rearrangements of cyclic imidates 9 *and* 10. (i) *9* (100 mg, 0.3 mmol) was dissolved in diethyl ether (8 ml). Dry hydrogen chloride was passed through the solution for 20 min. A white precipitate was formed, collected and recrystallized from acetone to give *5-(1-bromo-1-methylethyl)-4-cyano-3-methoxy-3-oxo-2,3-dihydro-1H-benz*[c]*azepine* (*11*), m.p. 223 – 30 °C. Anal. $C_{14}H_{13}BrN_2O$: C, H. IR (KBr): 3320 (s), 2220 (s), 1660 (s), 1640 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.0 – 7.6 (1H, m), 7.5 – 7.2 (4H, m), 4.1 (2H, m), 2.38 (3H, s), 2.08 (3H, s). Irradiation of the multiplet at 8.0 – 7.6 gave an AB-quartet (δ_A 4.05, δ_B 4.30, J = 14 Hz). ^{13}C NMR ($CDCl_3$): δ 164.8 (C3 + C5), 139.6 + 133.3 (C5 + C9a) 130.5 – 128.9 – 127.2 (2) ($C_6 - C_9$), 115.4 (C≡N), 57.7 (2) (C4 + Br – *C*(Me_2)), 45.0 (C1), 36.1 (2 × Me). MS: *m/e* 306/304 (M^+), 195 (M – $C(Me)_2Br$, 100 %).

(ii) *10* (150 mg, 0.55 mmol) was treated likewise. A white precipitate formed, but dissolved shortly afterwards. After evaporation of the solvent, the white residue was recrystallized from methanol to give *1a-cyano-8b-methoxy-1,1dimethyl-2-oxo-1a,2,3,8b-tetrahydro-4H-cyclopropano*[e]*benz*[c]*azepine* (*12*), m.p. 166 – 167 °C. Anal. $C_{15}H_{16}N_2O_2$: C,H,N. IR (KBr): 3400 (s), 2230 (s), 1680 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.0 – 7.7 (1H, m), 7.5 – 7.1 (4H, m), 5.1 – 4.8 (1H, 2d) and 4.1 – 3.7 (1H, 2d), 3.32 (3H, s), 1.67 (3H, s), 0.83 (3H, s). The signals around 5 and 4 ppm are both well resolved doublets of doublets constituting the A and M parts of an AMX spectrum were the broadening of the X part is caused by quadrupole effects from nitrogen. However, all parameters (except δ_X) are easily derived by first order treatment of the A and M-part: J_{AM} = 14 Hz, J_{AX} = 7 Hz, J_{MX} = 5 Hz, δ_A = 3.96, δ_M = 4.85. The former coupling constant is also confirmed by irradiation of the NH-multiplet at 8.0 – 7.7 ppm. ^{13}C NMR ($CDCl_3$): δ 166.0 (C2), 137.9 – 131.9 (C4a + C8a), 131.8 – 129.6 (2) – 128.5 (C5 – C8), 116.6 (C≡N), 72.5 (C8b), 54.0 (MeO), 44.7 (C4), 34.1 – 32.4 (C1 + C1a), 21.3 – 17.6 (2 × Me). MS: *m/e* 257 (M + 1), 256 (M^+).

Ozonolysis of isopropylidene-2,2-indancarbodinitrile (*15*). *15* (175 mg, 0.8 mmol) was dissolved in methanol (10 ml). At −78 °C ozone (0.8 mmol) was passed through the solution. Triphenylphosphine (262 mg, 1 mmol) was then added and, while stirring, the reaction solution was slowly warmed up to toom temperature. Gas liquid chromatography was used to estimate the acetone being formed. Found: 93.5 % of theoretical amount. The rest of the reaction solution was concentrated and the residue subjected to column chromatography (SiO_2-benzene). Three products were obtained, the first and third eluted were triphenylphosphine and triphenylphosphine oxide, respectively, and the second product was *methyl* [o-*(2,2-dicyano)-ethyl*] *benzoate* (*16*). M.p. 86 – 88 °C (MeOH). Anal. $C_{12}H_{10}N_2O_2$: C,H. IR (KBr): 2260 (s), 1740 (s). ^1H NMR ($CDCl_3$): δ 8.3 – 8.0 (1H, m), 7.7 – 7.3 (3H, m), 4.55 (1H, t, J = 7 Hz), 3.95 (3H, s), 3.63 (2H, d, J = 7 Hz). MS: *m/e* 214 (M^+), 183 (M – MeO, 55 %), 182 (M – MeOH, 97 %), 91 (tropylium, 100 %).

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