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Mono- *vs.* Dialkylation of Carbanions. Effects of Absolute and Relative Acidity of the Conjugate Carbon Acids in Selectivity Control[1,2]

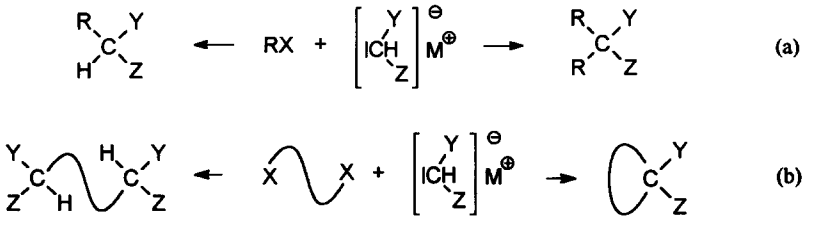
Luděk Ridvan and Jiří Závada*

Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic,
166 10 Prague 6, Czech Republic

Abstract: The title problem was investigated in the reaction of the dibromide **1** with carbanions **2a** – **2g** covering a range greater than 15 pK units in DMSO. It was found that the bis(monoalkylated) product **3** arises exclusively or predominantly from the carbanions **2d** – **2g** derived from the less acidic carbon acids **7d** – **7g** whereas the cyclic product of dialkylation **4** prevails in the reaction of the carbanions **2a** – **2c** derived from the more acidic carbon acids **7a** – **7c**. The alkylation selectivity thus depends critically on the absolute acidity of the carbon acid participating in the reaction. Rationale for this novel, and on basis of earlier studies unexpected finding is provided in terms of eqs. (1) – (4).

Mono- *vs.* dialkylation selectivity of carbanions represents a problem of considerable practical as well as theoretical importance. The role of the carbanion basicity and/or the conjugate carbon acid acidity in the selectivity control has been the subject of an intense investigation in the alkylations proceeding according to Scheme 1a. It has been shown[3] that *relative* acidity of the conjugate monoalkylated and non-alkylated carbon acids, defined as the acidity differential, ΔpK, between the two participating acids, is the key factor which steers selectivity in the reaction.

In this paper, we wish to report an unexpected case of carbanion alkylation, in which *absolute* acidity of the conjugate carbon acid, defined by the pK value, controls selectivity of the reaction. The novel observation concerns the frequently occurring situation, in which the mono- *vs.* dialkylation duality is accompanied by the duality of acyclic *vs.* cyclic product formation (Scheme 1b).



Scheme 1

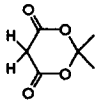
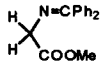
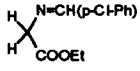
RESULTS AND DISCUSSION

Relationship between the pK Value of the Conjugate Carbon Acid and Selectivity of the Carbanion Alkylation with 1,2-bis(Bromomethyl)benzene

The absolute equilibrium acidities are available [4,5] for a broad spectrum of carbon acids in dimethyl sulfoxide (DMSO), in which, in dilute solution, ion-pairing is avoided.

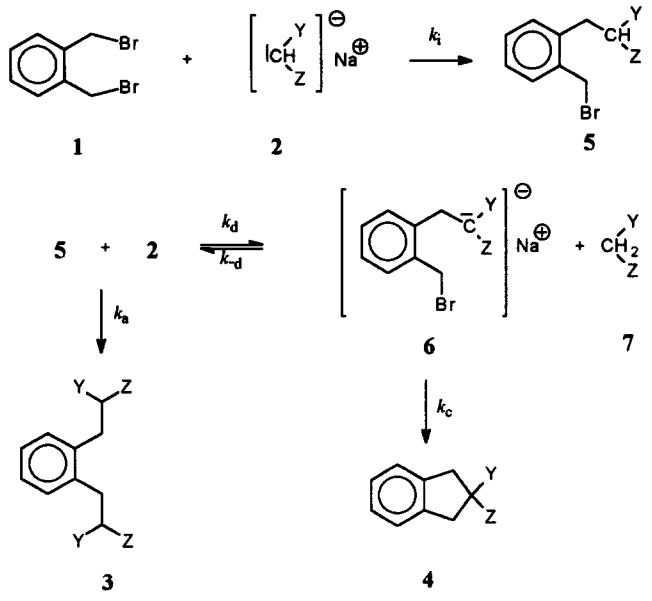
Table 1 summarizes the absolute as well as the relative acidities of 7 homologous pairs of monoalkylated and non-alkylated carbon acids covering a range greater than 15 pK units. The carbanions derived from the individual parent (non-alkylated) carbon acids have been generated upon addition of the acid to one equivalent of NaH in DMSO and subjected to alkylation with the dibromide **1** (Scheme 2) in the stoichiometric ratio 2:1.

Table 1. Effect of Absolute (pK) and Relative (ΔpK) Acidity of the Participating Carbon Acid on Selectivity (**3** : **4** Ratio) in the Carbanion Alkylation with Dibromide **1** in DMSO

Carbon Acid		pK	ΔpK[a]	**3** : **4** Ratio
7a		7.3[b]	0.1[b]	< 1 : 100
7b		11.1[c]	1.3[c]	< 1 : 100
7c		13.3[b]	1.8[b]	1 : 10
7d		15.9[b,d]	2.1[b,d]	25 : 1
7e		18.7[e]	4.5[e]	> 100 : 1
7f		18.8[e]	0.4[e]	> 100 : 1
7g		21.9[c]	1.1[c]	> 100 : 1

[a] Difference between the known pK values of the monomethylated and non-methylated carbon acid was taken as an approximation. [b] From ref. 5. [c] From ref. 4a. [d] Data for the corresponding methyl ester. [e] From ref. 3.

The composition of the resulting mixture of the bis(monoalkylated) and dialkylated products **3** and **4**, respectively, was evaluated chromatographically and compared with the pertinent acidity data in Table 1.



Scheme 2

As the Table shows, the cyclic product of dialkylation **4** is the sole product in the reaction of carbanions arising from the most acidic carbon acids **7a** and **7b**. In a contrast, the product of bis(monoalkylation) **3** is the exclusive product in the reaction with the carbanions derived from the least acidic carbon acids **7e** – **7g**. An intermediate situation is found in the reaction with the carbanions corresponding to the carbon acids of medium acidity **7c** and **7d**, yielding a mixture of the bis(monoalkylated) and dialkylated products **3** and **4** in proportions which are also strongly pK-dependent.

A striking relationship thus exists between the absolute acidity of the parent carbon acid, pK, and selectivity of the carbanion alkylation with the dibromide **1**. *On the other hand, no correlation is apparent between the relative acidity, ΔpK, of the corresponding monoalkylated and non-alkylated carbon acid pair, and selectivity in the carbanion reaction.*

Explanation of the complete disagreement between the present and the earlier[3] findings may be provided on basis of the kinetic analysis of the investigated reaction.

Kinetic Analysis of the Carbanion Alkylation with the Dibromide 1

The sequence of reaction steps anticipated in the alkylation is given in Scheme 2. In the first step, the dibromide **1** reacts with the carbanion **2** under formation of the intermediate **5**. Another molecule of the carbanion **2** then attacks the carbon terminus of the C-Br bond in the intermediate **5**, yielding the

bis(monoalkylated) product **3**. In an alternative pathway, the carbanion **2** attacks the hydrogen terminus of the acidic C-H bond in the intermediate **5** leading *via* proton transfer to the carbanion **6**, which cyclizes subsequently under formation of the dialkylated product **4**.

As we already pointed out in our earlier[2a] study of alkylation of the malonester carbanion **2d**, two limiting, kinetically distinct, situations may arise in the reaction with **1**, in dependence on the relative rates of the carbanion **6** formation, k_d, and its cyclization, k_c.

In one extreme, the rate of the proton transfer from **5** to **2** is *faster* than the subsequent cyclization, $k_d > k_c$. Under such condition, the alkylation selectivity is given by the equation

$$\frac{v_a}{v_c} = \frac{k_a \cdot [7]}{k_c \cdot K} \tag{1}$$

where [7] is the concentration of the free conjugate acid **7** of the parent carbanion **2** and K is the equilibrium constant related to the acidobasic equilibrium between the participating non-alkylated and monoalkylated species, **6** + **7** $\rightleftharpoons$ **2** + **5**.

In the other extreme, the proton transfer from **5** to **2** is *slower* than the subsequent cyclization, $k_d < k_c$, which leads to the alkylation selectivity given by the equation

$$\frac{v_a}{v_c} = \frac{k_a}{k_d} \tag{2}$$

Alkylation Selectivity as a Mechanistic Criterion

As it follows from the kinetic analysis, two different patterns of alkylation selectivity may arise in the reaction. If $k_d > k_c$, and eq. (1) accordingly holds, intrinsic propensity of the carbanion **6** to cyclization (formation of 5-membered ring!), expressed by k_c, provides a powerful driving force[6] for dialkylation. Accordingly, low values of the selectivity ratio, $v_a/v_c < 1$, are expected to result in the reaction (unless the accelerating effect of k_c is outweighed by the opposing effects of [7] and/or K; *vide infra*).

On the other hand, if $k_d < k_c$, and eq. (2) accordingly holds, the driving force for dialkylation provided by k_c is absent in the selectivity control and bis(monoalkylation) may prevail in the reaction, $v_a/v_c > 1$.

In this way, it appears justifiable to propose that magnitude of the selectivity ratio, v_a/v_c, can serve as a mechanistic criterion, distinguishing between the alternatives $k_d > k_c$ and $k_d < k_c$ in Scheme 2. A principal soundness of this hypothesis has been confirmed by investigation of the effect of concentration of the free parent carbon acid **7** on selectivity of the carbanion **2** alkylation. Table 2 summarizes the pertinent data obtained for three carbon acids **7b** – **7d** differring in absolute acidity.

As the experimental data show, a very pronounced increase of the value of the selectivity ratio v_a/v_c occurs on increasing the free carbon acid concentration [7] in the reaction of the carbanions derived from the two more acidic carbon acids **7b** and **7c** which intrinsically (in the absence of the free acid) prefer dialkylation.

It follows that the reaction proceeds in accord with eq. (1), demonstrating accordingly that preferential dialkylation takes place when $k_d > k_c$.

Table 2. Effect of Concentration of the Free Carbon Acid **7** on Selectivity (**3** : **4** Ratio) in the Carbanion Alkylation with Dibromide **1** in DMSO

Parent Acid	[7] : [2] Ratio	**3** : **4** Ratio
7b	0 : 1	-[a]
	2.5 : 1	0.01[b]
	5 : 1	0.06[b]
	10 : 1	0.21[b]
7c	0 : 1	0.10[c]
	2.5 : 1	0.41[c]
	5 : 1	0.98[c]
	10 : 1	1.78[c]
7d	0 : 1	24[d]
	2.5 : 1	49[d]
	5 : 1	49[d]
	10 : 1	49[d]

[a] The proportion of **3b** was immeasurably low. [b] **3b** : **4b** Ratio. [c] **3c** : **4c** Ratio. [d] **3d** : **4d** Ratio; data taken from ref. 2a.

On the other hand, a near-independence of the selectivity ratio v_a/v_c on [7] is found in the reaction of the carbanion derived from the less acidic carbon acid **7d** which intrinsically prefers bis(monoalkylation). It follows that the reaction obeys eq. (2), indicating that preferential bis(monoalkylation) occurs when $k_d < k_c$.

Differential Effect of pK on Relative Rates of the Cyclization (k_c) and Proton-Transfer (k_d) Pathways in the Alkylation

It has been amply demonstrated by Bordwell and his coworkers[7,8] that reactivity of carbanions in DMSO (including S_N2[7] as well as proton-transfer[8] reactions) obeys satisfactorily the Brønsted equation

$$\log k_{B^-} = pK_{HB} + C \qquad (3)$$

in which the carbanion reactivity ($\log k_{B^-}$) is correlated with the absolute acidity of the conjugate carbon acid (pK_{HB}). An inverse logarithmic relationship

$$-\log k_{HB} = pK_{HB} + C \qquad (4)$$

holds[9] for the deprotonization of the conjugate carbon acids with a common base.

Accordingly, *a steady increase of the rate of the carbanion cyclization* **6** → **4** ($\log k_c$) *with the increasing pK value of the conjugate carbon acid* (**5a** → **5g**) may be anticipated on basis of eq. (3) in Scheme 2.

On the other hand, a co-operation of eqs. (3) and (4) is envisioned in the proton-transfer pathway **5** + **2** → **6** + **7** in Scheme 2. The effect of the increasing (**2a** → **2g**) carbanion basicity, which assumedly accelerates the proton-transfer in accord with eq. (3) is counterbalanced[10,11] by the accompanying effect of the decreasing (**5a** → **5g**) carbon acid acidity, which tends to retard the reaction rate in accord with eq. (4). *A near-independence of the rate of proton-transfer* ($\log k_d$) *on the pK value* should result from a levelling-out of the two opposing effects in the reaction.

As a consequence of the different effects of pK on rates of the cyclization and the proton-transfer pathways, $\log k_c$ and $\log k_d$ may diverge dramatically in the carbanion series **2a** – **2g**, in dependence on absolute acidity (pK) of the conjugate carbon acid (Fig. 1). Conceivably, therefore, the rates of the cyclization are smaller than the corresponding rates of the proton-transfer ($k_c < k_d$) in the reaction involving the less basic carbanions, whereas the opposite ($k_c > k_d$) holds for the more basic carbanions. A simple rationale is thus provided for the key findings in Table 1.

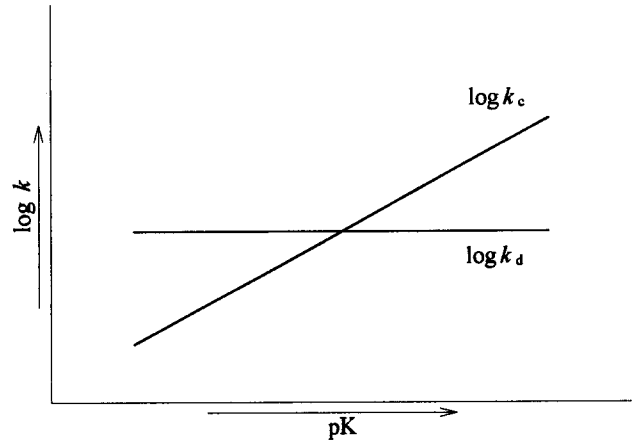
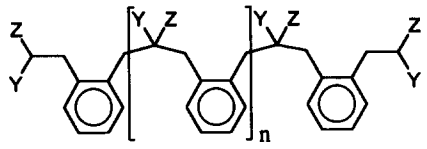


Fig. 1 Schematic representation of the Brønsted plots predicted for the cyclization ($\log k_c$) and the proton-transfer ($\log k_d$) pathways

pK-Dependent Oligomerization Accompanying the Carbanion Alkylation with the Dibromide 1

As we noted already in the preceding paper[2a], Scheme 2 represents an oversimplication of the actual situation in the carbanion alkylation with dibromide **1**. In particular, proton-transfer between the parent carbanion **2** and the bis(monoalkylated) product **3**, which has been omitted from consideration, represents a potential complication in that it may trigger a consecutive formation of the oligomeric products **8** in the alkylation reaction.



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A powerful incursion of the oligomerization has been indeed encountered in the reaction of the least acidic carbon acid **7g** with **1** under standard alkylation conditions (Table 3).

Table 3. Composition of the Product Mixture Arising in the Alkylation of the Carbon Acid **7g** with the Dibromide **1** in DMSO

Product	**3g**	**8g (n=0)**	**8g (n=1)**	**8g (n=2)**	**8g (n=3)**	**8g (n=4)**
%[a]	24.0	29.4	20.3	12.9	9.1	4.3

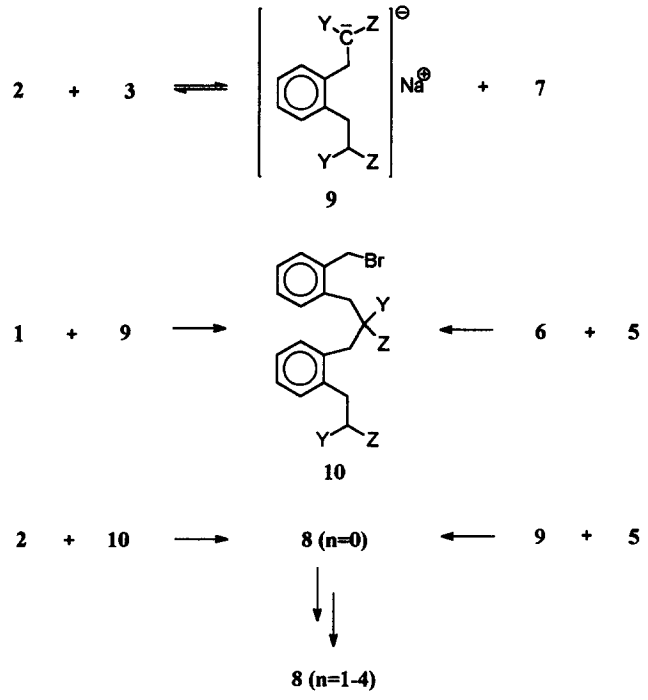
[a] Uncorrected values from HPLC analysis (UV detection, 260 nm).

A similar but less pronounced participation of the oligomerization has been found also in the corresponding alkylation of the more acidic carbon acid **7f** and **7d** (Table 4). Only minor proportion of the oligomerization product has been established in the reaction of the most acidic carbon acid **7c**. In this way, the results indicate that participation of the oligomerization in the carbanion alkylation is pK-dependent. Mechanistic scenario for the oligomerization is outlined in Scheme 3.

Table 4. FAB MS-Analysis of the Crude Product Mixture Arising in the Alkylation of the Carbon Acid **7c** – **7g** with the Dibromide **1** in DMSO

Carbon Acid	**3**	**8(n = 0)**	**8(n = 1)**	**8(n = 2)**	**8(n = 3)**
7c	100	11	-	-	-
7d	100	21	2	-	-
7f	91	100	35	10	-
7g	88	100	67	34	25

[a] Relative intensities of the individual molecular peaks.

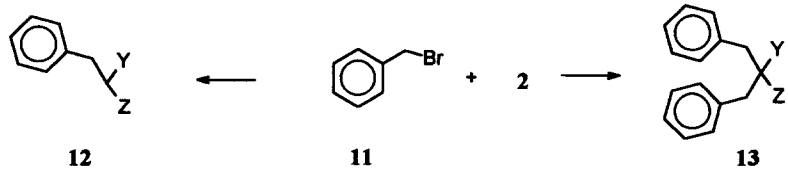


Scheme 3

A simple consideration of Scheme 3 suggests that, other things being equal, importance of the oligomerization will rise with the increasing proportion of the bis(monoalkylated) product **3** in the initial reaction (Scheme 2). Since the formation of **3** has been shown to be pK-dependent, it does not come as a surprise that it pertains, qualitatively, also for the consecutive oligomerization.

Comparison of Selectivity in Carbanion Alkylations Proceeding According to Scheme 1a and 1b

In a parallel study, we have determined selectivity in a model alkylation proceeding according to Scheme 1a. The pertinent data obtained from the reaction of the carbanions **2a** – **2g** with benzyl bromide **11** in DMSO (Scheme 4) are summarized in Table 5.



12 **11** **13**

Scheme 4

Table 5. Selectivity Ratio in the Carbanion Alkylation with Monobromide **11** in DMSO[a]

Parent Acid	**7a**	**7b**	**7c**	**7d**	**7e**	**7f**	**7g**
12 : **13** Ratio	< 0.04	0.7	2.3	5.0	> 24	2.3	2.6

[a] Carbanions 2a – 2g were generated from the parent acids upon addition of one equivalent of NaH and subjected to alkylation with **11** in the stoichiometric ratio 1:1.

In contrast to the clear-cut dependence of the alkylation selectivity on the pK value of the parent carbon acid established in the reaction of the carbanions **2a** – **2g** with the dibromide **1** (Table 1), no analogous trend is apparent in the corresponding reaction with the monobromide **11**, the values of the mono-/dialkylation ratios, **12/13**, ranging in most instances close to unity (Table 5).

As a closer inspection reveals, two marked deviations found in the reaction series concern the carbon acids **7a** and **7e**, the former preferring strongly dialkylation, whereas the latter monoalkylation. Notably, the two exceptional cases can be correlated with the ΔpK values, corresponding to the acidity differential between the monoalkylated and non-alkylated carbon acids participating in the reaction, the differential being the smallest in the former (**7a**) and the greatest in the latter (**7e**) extreme found in the reaction series (cf. Table 1).

It strongly suggests that the relative acidity (ΔpK) plays role in the selectivity control of carbanion alkylation with the monobromide **11**, in accord with the earlier investigation[3] based on Scheme 1a. Selectivity control by the absolute acidity (pK) thus appears to be a privilege of the alkylation proceeding in accord with Scheme 1b.

SUMMARY

Mono-/dialkylation selectivity has been investigated in the reaction of the carbanions **2a** – **2g** with the monobromide **11** and with dibromide **1** in DMSO. In the reaction with the monobromide **11**, the selectivity has been found to depend on the relative acidity of the participating monoalkylated and non-alkylated conjugate carbon acids, defined by the acidity differential ΔpK, in accord with earlier literature predictions[3]. In a striking contrast, the relative acidity is entirely inessential in the alkylation with dibromide **1**. Instead, absolute acidity of the parent (non-alkylated) carbon acid, defined by the pK value, has been established to be the key factor which controls selectivity in the reaction. Namely, the carbanions **2a** – **2c** derived from the carbon acids with higher absolute acidity (pK 7.3 – 13.3) lead exclusively or predominantly to the cyclic product of dialkylation **4**. Whereas, the carbanions **2d** – **2g** derived from the carbon acids with lower absolute acidity (pK 15.9 – 21.9) lead to bis(monoalkylated) product **3**, again exclusively or at least predominantly.

A clue to explanation of this novel, and entirely unexpected, finding has been obtained from the kinetic

analysis of the alkylation which showed that two distinctly different selectivity patterns may emerge in dependence on the relative rates of the proton-transfer and S_N2 (cyclization) pathways (k_d and k_c, respectively) participating in the overall reaction (Scheme 2). If $k_d > k_c$, the selectivity is governed by eq. (1) which favours di- over monoalkylation. On the other hand if $k_d < k_c$, the selectivity proceeds in accord with eq. (2) favouring the bis(monoalkylation).

An independent evidence has been provided that the relative rates of the two alternative rate-limiting pathways, k_d and k_c, depend on the absolute acidity of the participating carbon acid. A simple rationale for the established dependence has been proposed in terms of the Brønsted relationships for reactivity of carbanions and their conjugate carbon acids expressed by eqs. (3) and (4).

Assumedly, also other factors than absolute acidity of the carbon acid may participate in the selectivity control of the alkylation. Important role played by solvent and leaving group of the alkylating agent has been already demonstrated in the preceding study[2a].

EXPERIMENTAL SECTION

General

DMSO was dried by storing over molecular sieves. Melting points were determined on a Kofler block and are uncorrected. ^{1}H NMR spectra (200 MHz, FT mode) were recorded in $CDCl_3$ with TMS as internal standard. EI mass spectra were obtained at 70 eV; FAB spectra were measured in 2-hydroxyethyl sulfide matrix. GC analyses were performed on a HP-1 column (methylsilicone, 5 m × 0.53 mm × 2.65 nm; temperature gradient from 50 to 300°C, flame ionization detector). HPLC analyses were carried out on silica gel (column Partisil 10 SILICA 250 × 4.6 mm). The starting compounds were commercial products (**1**, **11**, **7a** – **7d** and **7g**; Aldrich) or were prepared by known[3] procedures (**7e** and **7f**).

General Procedure

Sodium hydride (60 % in mineral oil, 227 mg; 5.5 mmol) was washed with light petroleum and suspended in DMSO (12.5 ml). An appropriate carbon acid (**7a** – **7g**) was added to the stirred slurry, followed (after homogenization; cca 5 min. stirring at rt.) by 1,2-bis(bromomethyl)benzene **1** (0.66 g; 2.5 mmol) or benzyl bromide **11** (0.60 ml; 5 mmol). The reaction mixture was stirred at 50°C for 2h, poured into 0.04 M aqueous HCl (150 ml; 0°C) and extracted with ether or chloroform (3 × 15 ml). The combined extracts were washed with water, dried over $MgSO_4$ and evaporated. The residue was analyzed by GC or HPLC and the individual products were isolated as specified below. Purity of the isolated products was invariably better than 95% (GC). Isolation of the reaction products **3d** and **4d** has been described in the preceding paper[2a].

1,2-Benzenedi(α-cyanopropanenitrile) (3b): Obtained from **7b** and **1** (under conditions described in Table 2) by crystallization of the reaction residue. Mp 135-137 °C [ethyl acetate/petrolether]. ^{1}H NMR δ 2.47 (d,

4H), 3.97 (t, 2H), 7.40-7.50 (m, 4H). EI MS *m/z* (relative intensity) 234 (M^+, 33), 169 (100), 142 (31), 104 (68). Anal. Calcd. for $C_{14}H_{10}N_4$ (234.3) C, 71.78; H, 4.30; N 23.92; Found C, 71.53; H, 4.16; N, 23.95.

1,2-Benzenedi(2-acetyl-3-oxobutane) (3c): Obtained as the minor product from **7c** and **1** by a column chromatography (silica gel; dichloromethane-ethyl acetate 9:1). Mp 115-119 °C. ^{1}H NMR (enol form) δ 2.06 (s, 12H), 3.63 (s, 4H), 7.05-7.25 (m, 4H). EI MS *m/z* (relative intensity) 302 (M^+, 2), 259 (15), 187 (18), 159 (42), 145 (16), 43 (100). HRMS(EI) Found 259.1280 (MH^+-CH_3CO), $C_{16}H_{19}O_3$ requires 259.1334.

Dimethyl 1,2-benzenedi[α-(diphenylmethylenamino)propanoate] (3e): Obtained from **7e** and **1** by column chromatography (silica gel; light petroleum-ether 1:1). Solid oil. ^{1}H NMR δ 3.08 (m, 4H), 3.71 (d, 6H), 4.18 (m, 2H), 6.40-7.60 (m, 24H). FAB MS *m/z* (relative intensity) 601 (MH^+, 100). Anal. Calcd. for $C_{40}H_{36}N_2O_4$ (608.7) C, 78.92; H, 5.96; N 4.60; Found C, 78.64; H, 6.00; N, 4.77.

Diethyl 1,2-Benzenedi[α-(4-chlorobenzylidenamino)]propanoate (3f): Obtained from **7f** and **1**. Owing to the hydrolytic instability, the product was isolated as the free acid **3h** (*vide infra*).

1,2-Benzenedi(α-phenylpropanenitrile) (3g): The reaction of **7g** and **1** afforded, after a usual work-up, a complex mixture (Table 3) containing **3g** and oligomers **8g(n=0-4)** which was partly separated by preparative HPLC (silica gel, 250 × 50 mm column). Product **3g** was eluted with a light petroleum-ethyl acetate gradient 4:1 – 1:1. Oil. ^{1}H NMR δ 3.15-2.85 (m, 4H), 3.90-3.73 (m, 2H), 7.15-7.40 (m, 14H). FAB MS *m/z* (relative intensity) 337 (MH^+, 50). Anal. Calcd. for $C_{24}H_{20}N_2$ (336.4) C, 85.68; H, 5.99; N 8.33; Found C, 85.41; H, 6.07; N, 8.12.

1,2-Benzenedi(α-aminopropanoic acid) (3h): Crude product **3f** (*vide supra*) was dissolved in ether (100 ml) and stirred with 1M aqueous HCl (20 ml) for 2h at rt. The aqueous layer was separated and evaporated to dryness *in vacuo*. The residue was dissolved in conc. aqueous HCl (20 ml), stirred for 4h under reflux, treated with charcoal and after filtration taken to dryness *in vacuo*. The residue was dissolved in abs. ethanol (20 ml) and treated with propylene oxide (2.8 ml; 40 mmol) under stirring for 1h at rt. The precipitate was filtered off, washed with ether and dried at the oil pump at 50°C. Yield 0.80 g (60%). Solid oil (mixture of diastereoisomers). ^{1}H NMR (D_2O) δ 3.18-3.54 (m, 4H), 4.05- 4.25 (m, 2H), 7.45 (s, 4H). FAB MS *m/z* (relative intensity) 253 (MH^+, 100). HRMS(FAB) Found 253.1078 (MH^+), $C_{12}H_{17}N_2O_4$ requires 253.1188.

Indane⟨2-spiro-5⟩2,2-dimethyl-1,3-dioxane-4,6-dione (4a): Obtained from **7a** and **1** by crystallization of the reaction residue. Mp 139-142 °C [ethanol]. ^{1}H NMR δ 1.78 (s, 6H), 3.64 (s, 4H), 7.22 (s, 4H). EI MS *m/z* (relative intensity) 246 (M^+, 69), 231 (71), 189 (62), 143 (100). Anal. Calcd. for $C_{14}H_{14}O_4$ (246.3) C, 68.28; H, 5.73; Found C, 68.29; H, 5.71.

2,2-Indanedicarbonitrile (4b): Obtained from **7b** and **1** by filtration of the reaction residue in ether through a short column of silica gel. Mp 130-132 °C [ether] (lit.[12] 129-131 °C). ^{1}H NMR δ 3.74 (s, 4H), 7.31 (s, 4H). EI MS *m/z* (relative intensity) 168 (M^+, 85), 141 (100), 114 (12).

2,2-Diacetylindane (4c): Obtained from **7c** and **1** by a column chromatography (silica gel; dichloromethane - light petroleum 1:1). Mp 57-59 °C [ether] (lit.[13] 61-62 °C). ^{1}H NMR δ 2.20 (s, 6H), 3.53 (s, 4H), 7.20 (s, 4H). EI MS *m/z* (relative intensity) 202 (M^+, 2), 187 (5), 159 (100), 145 (8), 115 (20).

4,9-Dibenzo-2,7,12-triphenyl-7-cyanotridecanedinitrile [8g(n=0)]: Separated from **3g** (*vide supra*) by a preparative HPLC (silica gel, 250 × 50 mm column; light petroleum-ethyl acetate gradient 2:1 – 1:2). Solid oil. ^{1}H NMR δ 2.81-3.38 (m, 8H), 3.73- 3.90 (m, 2H), 7.20-7.40 (m, 23H). FAB MS *m/z* (relative intensity) 556 (MH^+, 100). Anal. Calcd. for $C_{40}H_{33}N_3$ (555.7) C, 86.45; H, 5.99; N, 7.56; Found C, 86.18; H, 5.94; N, 7.55.

Higher Oligomers [8g(n=1) – 8g(n=4)]: Obtained after separation of **3g** and **8g(n=0)**, *vide supra*, by elution with a 1:2 – 1:4 light petroleum-ethyl acetate gradient. The inseparable oligomeric mixture was analyzed by FAB MS (Table 6).

Table 6. Relative Intensities of the Individual Molecular Peaks in the Oligomeric Mixture **8g(n=1 – 4)** in FAB MS

Product	**8g(n=1)**	**8g(n=2)**	**8g(n=3)**	**8g(n=4)**
MH^+ (rel. int.)	775.5 (100)	994.6 (80)	1214.7 (55)	1432.9 (40)

Benzylmalononitrile (12b): Obtained from **7b** and **11** by distillation of the reaction residue *in vacuo*. Mp 88-89 °C (lit.[14] 90.5-91.5 °C). ^{1}H NMR δ 3.29 (d, 2H), 3.91 (t, 1H), 7.39 (s, 5H). EI MS *m/z* (relative intensity) 156 (M^+, 20), 91 (100), 65 (12).

3-Benzyl-2,4-pentanedione (12c): Obtained from **7c** and **11** by distillation of the reaction residue *in vacuo*. Oil[15,16]. ^{1}H NMR δ (keto form) 2.08 (s, 6H), 3.15 (d, 2H), 4.01 (t, 4H), 7.10-7.40 (m, 5H); (enol form) 2.13 (s, 6H), 3.66 (s, 2H), 7.10-7.40 (m, 5H). EI MS *m/z* (relative intensity) 190 (M^+, 9), 172 (8), 147 (100), 129 (25), 105 (15), 91 (34).

Diethyl Benzylmalonate (12d): Obtained from **7d** and **11** by distillation of the reaction residue *in vacuo*. Oil[17]. ^{1}H NMR δ 1.21 (t, 6H), 3.22 (d, 2H), 3.65 (t, 1H), 4.16 (q, 4H), 7.20-7.25 (m, 5H). EI MS *m/z* (relative intensity) 250 (M^+, 65), 205 (12), 176 (95), 159 (42), 131 (100), 91 (76).

Methyl 2-Diphenylmethylenamino-3-phenylpropanoate (12e): Obtained as the sole product from **7e** and **11** by crystallization of the reaction residue. Mp 116-118 °C [ether/light petroleum]. ^{1}H NMR[18] δ 3.22 (m, 2H), 3.74 (s, 3H), 4.26 (dd, 1H), 6.55-7.60 (m, 15H). FAB MS *m/z* (relative intensity) 344 (M^+, 100). Anal. Calcd. for $C_{23}H_{21}NO_2$ (343.4) C, 80.44; H, 6.16; N, 4.08; Found C, 80.42; H, 6.22; N, 4.33.

Ethyl 2-(4-Chlorobenzylidenamino)-3-phenylpropanoate (12f): Obtained from **7f** and **11** by preparative HPLC chromatography (SPX-RPS column; 10 mm; 300 × 40 mm; methanol-0.01% aq. $NaHCO_3$). Oil[3]. ^{1}H NMR δ 1.25 (t, 3H), 2.80-4.28 (m, 5H), 7.10-7.70 (m, 9H), 7.85 (s, 1H). FAB MS *m/z* (relative intensity) 316 (M^+, 47). HRMS(FAB) Found 316.1086 (MH^+), $C_{18}H_{19}ClNO_2$ requires 316.1104.

2,3-Diphenylpropanenitrile (12g): Obtained from **7g** and **11** by distillation of the reaction residue *in vacuo*. Mp 55-56 °C (lit.[19] 58 °C). ^{1}H NMR δ 3.12+3.21 (dd+dd, 2H), 4.00 (dd, 1H), 7.10-7.40 (m, 10H). EI MS *m/z* (relative intensity) 207 (M^+, 12), 91 (100).

5,5-Dibenzyl-2,2-dimethyl-1,3-dioxane-4,6-dione (13a): Obtained from **7a** and **11** by crystallization of the reaction residue. Mp 230-232 °C [acetone] (lit.[20] 232-233 °C). ^{1}H NMR δ 0.64 (s, 6H), 3.46 (s, 4H), 7.15-7.35 (m, 10H). EI MS *m/z* (relative intensity) 324 (M^+, 10), 238 (52), 175 (38), 91 (100).

Dibenzylmalononitrile (13b): Obtained from **7b** and **11** by column chromatography (silica gel; light petroleum-ether 4:1) of the distillation residue (after separation of **12b**; *vide supra*). Mp 128-130°C [ether] (lit.[13] 131-132°C). ^{1}H NMR δ 3.25 (s, 2H), 7.40 (s, 10H). EI MS *m/z* (relative intensity) 246 (M^+, 18), 91 (100), 65 (10).

3,3-Dibenzyl-2,4-pentanedione (13c): Obtained from **7c** and **11** by crystallization of the distillation residue (after separation of **12c**; *vide supra*). Mp 110-112 °C [ether] (lit.[13] 112-114 °C). ^{1}H NMR δ 2.12 (s, 6H), 3.28 (s, 4H), 7.00-7.30 (m, 10H). EI MS *m/z* (rel. int.) 280 (M^+, 5), 237 (87), 189 (93), 159 (24), 147(100),91(90).

Diethyl Dibenzylmalonate (13d): Obtained from **7d** and **11** by column chromatography (silica gel; light petroleum - ether 1:1) of the distillation residue (after separation of **12d**; *vide supra*). Oil[17]. ^{1}H NMR δ 1.17 (t, 6H), 3.24 (s, 2H), 4.12 (q, 4H), 7.20-7.24 (m, 10H). EI MS *m/z* (relative intensity) 340 (M^+, 5), 295 (5), 249 (52), 203 (100), 91 (84).

Ethyl 2-Benzyl-2-(4-chlorobenzylidenamino)-3-phenylpropanoate (13f): Separated from **12f** by preparative HPLC (*vide supra*). Oil. ^{1}H NMR δ 1.22 (t, 3H), 3.22 (d, 2H, J = 13.4 Hz), 3.47 (d, 2H, J = 13.4 Hz), 4.12 (q, 4H), 7.10-7.58 (m, 14H). FAB MS *m/z* (relative intensity) 406 (MH^+, 10). HRMS(FAB) Found 406.1612 (MH^+), $C_{25}H_{25}ClNO_2$ requires 406.1574.

2-Benzyl-2,3-diphenylpropanenitrile (13g): Obtained from **7g** and **11** by crystallization of the distillation residue (after separation of **12g**; *vide supra*). Mp 82-83 °C [toluene/light petroleum] (lit.[19] 83 °C). ^{1}H NMR δ 3.12 (s, 4H), 7.00-7.40 (m, 15H). EI MS *m/z* (relative intensity) 297 (M^+, 20), 91 (100).

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