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Electrochemical Acylation and Carboxylation of Some Activated Olefins

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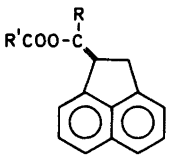
The electrochemical acylation and carboxylation of some activated olefins have been investigated. Acenaphthylene yields thus on reductive electrochemical acetylation mainly the *Z* and *E* enol acetates of 1-(1,2-dihydro-1-acenaphthylidene) ethanone, whereas carboxylation followed by methylation gives *trans*-1,2-dimethoxycarbonyl-1,2-dihydroacenaphthene. Ethyl cinnamate can be acylated and carboxylated in the 3-position, whereas benzoylacetone could be carboxylated but not acetylated. Neither carboxylation nor acylation were able to compete with the dimerization of benzylidenemalonitrile. Cyclic voltammetry showed that carboxylation generally was faster than acetylation.

The electrochemical acylation of activated olefins [1–6] has been shown to be a useful and rather general reaction. In some cases, however, *e.g.* during the reductive acylation of anthracene,[1] acenaphthylene [2] and cinnamonitrile,[2] it has been briefly reported that the enol acetate of the expected ketone was the isolated product rather than the ketone. A more detailed study of this reaction is reported below, and it is compared with the carboxylation reactions.

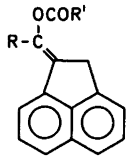
Acenaphthylene (*1*), cinnamonitrile (*2*), benzalacetone (*3*) and benzylidenemalonitrile (*4*) have been reduced in *N,N*-dimethylformamide (DMF) in the presence of acetic anhydride (*5*), 4-chlorobutyric anhydride (*6*) and carbon dioxide. The olefins were chosen as examples of a symmetrical (*1*), a mono-activated olefin (*2* and *3*) and a doubly activated olefin (*4*); *6* was included to investigate the possibility of a simultaneous acylation and ring closure.[7,8]

RESULTS

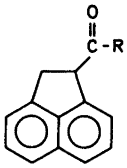
Acenaphthylene. On cyclic voltammetry *1* shows a reversible reduction at −1.65 V (aq.SCE) and an irreversible peak at $E_p = -2.45$; on addition of a tenfold excess of *5* the peak height of the first peak grows to about 1.6 times the original height and the anodic peak disappears; the second peak, if present, is hidden by the reduction of *5*. On increasing the sweep rate



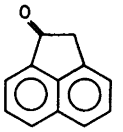
7a R = R' = CH_3
b R = R' = $(CH_2)_2CH_2Cl$
c R = $(CH_2)_2CH_2Cl$, R' = cyclopropyl



8a R = R' = CH_3
b R = R' = $(CH_2)_2CH_2Cl$
c R = $(CH_2)_2CH_2Cl$, R' = cyclopropyl



9a R = CH_3
b R = $(CH_2)_2CH_2Cl$



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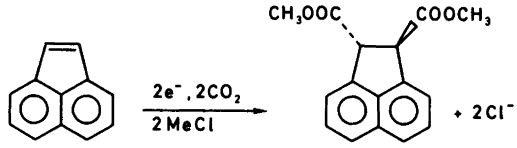


Scheme 1.

the reduction of *1* in the presence of *5* becomes reversible; the pseudo first-order rate constant of the reaction between $1^{\cdot-}$ and *5* was about 50 s^{-1}.[9]

Preparative electrochemical reduction of *1* at a mercury cathode in DMF in the presence of an excess of *5* gave predominantly the *Z* (*7a*) and *E* (*8a*) enol acetate of 1-(1,2-dihydro-1-acenaphthylidene)ethanone (*9a*) together with a little acenaphthene (*10*); minor amounts of *9a* and acenaphthylenone (*11*) were sometimes isolated, possibly formed during the work-up. No *C*-diacetylated derivatives were isolated (Table 1).

The choice between the *Z* and *E* forms was made from ^{1}H NMR Difference Nuclear Overhauser Effects and the assignment is consistent with expected chemical shifts and coupling constants (see Experimental).

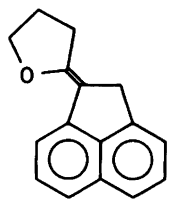
Reduction of *1* in DMF in the presence of carbon dioxide and methyl chloride yields mainly *trans* 1,2-dimethoxycarbonyl-1,2-dihydroacenaphthene (Scheme 1).

Cyclic voltammetry of *1* after addition of *6* resembles that in the presence of *5*. *6* gives an irreversible peak at −2.35 V.

Preparative reduction of *1* in the presence of an excess of *6* gave *9b* as the major product (Table 1) together with minor amounts of *7b* and *8b*. The *Z*–*E* assignment of *7b* and *8b* was done on the basis of the ^{1}H NMR spectra (see Experimental). In this case too the *Z*-isomer was formed in higher yield than the *E*-isomer. Besides these compounds, some acenaphthylenone (~8 %) was also isolated.

Reduction of a solution containing equivalent concentrations of *1* and *6* yielded no *9b*, but *7b* and *8b* together with the cyclopropane derivatives *7c* and *8c* besides some *10* and *11*. *7b* and *8b* can be transformed into *7c* and *8c* in the presence of a strong base; during the reduction, bases are generated and, in the absence of an excess of *6*, the electrogenerated base, *e.g.* $1^{\cdot-}$, may induce the ring closure. Thus if $1^{\cdot-}$ was generated in a mixture (7:3) of *7b* and *8b*, *7c* and *8c* were formed (3:2) with some *7b* still unchanged; the transformation *8b* → *8c* is thus slightly faster than the ring closure of *7b* to *7c*.

In the presence of a strong base, *e.g.* an electrogenerated base, *9b* may be cyclized to the *Z* (*12*) and *E* (*13*) isomers of 1-(2-tetrahydrofuranylidene)-1,2-dihydroacenaphthene. The *Z*/*E* assignment was made on the basis of the chemical



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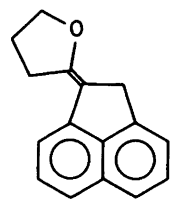

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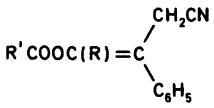
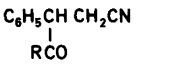
Table 1. Product distribution (isolated yield (%)) in the reductive acylation of the activated olefines *1* and *2* in the presence of *5* or *6*.

RCH=CHY	Anhydride (equiv.)	RCH_2CH_2Y and/or dimers	Ketone	Acylated enol *Z*	Acylated enol *E*	Furan derivative	Other compounds
1	*5* (10)	*10* (9)		*7a* (43)	*8a* (18)		*11* (traces)
	6 (4)	*10* (6)	*9b* (46.5)	*7b* (8.5)	*8b* (3.5)		*11* (8.5)
	6 (1)	*10* (9)		*7b* (11)	*8b* (5)		*11* (8)
				7c (3)	*8c* (4)		
2	*6* (1)	Dihydrocinnamonitrile (2)	*15b* (14)	*14b* (9)		*16* (5)	*18* (14)
		17a (6)	*15c* (7)				
		17b (10)					



14a R=R'=CH_3

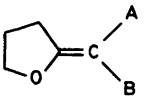
b R=$(CH_2)_2CH_2Cl$, R'=cyclopropyl



15a R=CH_3

b R=$(CH_2)_2CH_2Cl$

c R=cyclopropyl



A C_6H_5 or CH_2CN

B CH_2CN or C_6H_5

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shifts and coupling constants in the ^1H NMR spectrum (see Experimental). The transformation *9b*→*12*+*13* may be effected by electrogenerated dioxygen anion radical $O_2^{\cdot-}$ or $1^{\cdot-}$. The compounds *12* and *13* are very sensitive towards oxygen and are rapidly decomposed to *11*.

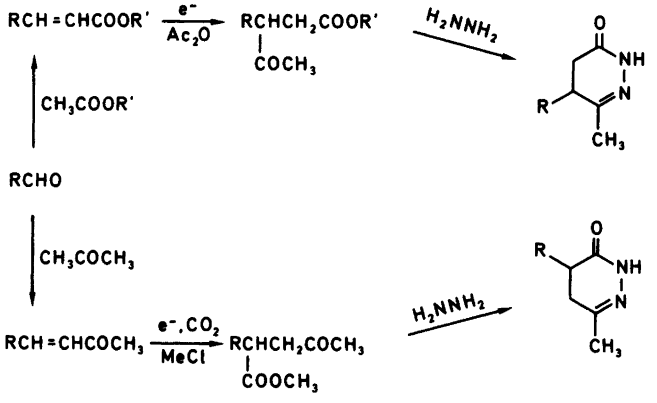
Cinnamonitrile. *2* dimerizes faster than *1* (k_{Dim}=800 M^{-1} l s^{-1});[10] CV of *2* in DMF at sweep rate v=~10 V s^{-1} gave a reversible reduction which on addition of an excess of *5* changed to an irreversible peak with increased peak height. The pseudo first-order rate constant of the reaction of $2^{\cdot-}$ with *5* was estimated from cyclic voltammetric data to be $\geq 5 \cdot 10^2$ s^{-1};[9] CV thus indicates the possibility of acetylation of $2^{\cdot-}$.

Reduction of *2* in DMF in the presence of *5* gave the enol acetate (*14a*) of 3-phenyl-4-oxovaleronitrile (*15a*) and *15a*. Similar types of products were obtained from the reduction of *2* in the presence of *6* (Table 1), but the product mixture is more complicated due to the possibility of ring closure to tetrahydrofuranylidene derivatives.

Electrochemical carboxylation of *2* followed by methylation gave methyl 3-cyano-2-phenylpropionate.

Benzalacetone. (*3*) dimerizes fast (k_{Dim}=1.35×10^5 M^{-1} l s^{-1}) [11] and reduction of *3* in the presence of *5* does not give C-acetylation in an appreciable yield, as this reaction apparently is too slow compared with the dimerization reaction. Reductive carboxylation is fast enough to compete with the dimerization, and on reductive carboxylation of *3* followed by methylation a good yield of methyl 2-phenyl-4-oxovaleriate was isolated. The acetylation of methyl cinnamate [2] gives the isomeric methyl 3-phenyl-4-oxovalerate so the two methods together give starting materials for the preparation of a number of heterocyclic compounds (Scheme 2).

Benzylidenemalonitrile (*4*) dimerizes very fast on electrochemical reduction in DMF; neither the acetylation nor the carboxylation reaction can compete with the dimerization. Reductive carboxylation followed by methylation was attempted at −35 °C, but only the ring closed dimer, *cis*-2-amino-4,5-diphenyl-1,3,3-tricyanocyclopent-1-ene,[12] plus some of the *trans* isomer were isolated.



Scheme 2.

DISCUSSION

The reduction potentials of the activated olefins *1–4* are less negative than that of the anhydride *5* and *6*; it is therefore assumed that primarily formed species is the anion radical of the activated olefin. This anion radical may react in a number of ways; it may be protonated or abstract a hydrogen atom, it may form a dimer in some way or initiate a polymerization reaction, and it may react with the anhydride.

The protonation is not a serious competing process under proper conditions, although it is difficult completely to avoid it. The rate of the dimerization reaction is dependent on the structure of the alkene; generally the rate increases with the polarization of the alkene by the activating group(s). Thus, whereas $1^{\cdot-}$ and $2^{\cdot-}$ couple with *5*, *6*, and carbon dioxide in preference to dimerization, $3^{\cdot-}$ can be carboxylated, but the dimerization is faster than the acylation; $4^{\cdot-}$ dimerizes faster than it reacts with *5* or even CO_2.

The product from the reaction between the anion radical and the anhydride is in most cases mono-C-acylated, although diacetylation has been reported at high concentrations of the anhydride.[5,6] The C-acylated product may react further with the anhydride to the O-acylated enol of the primarily formed ketone.

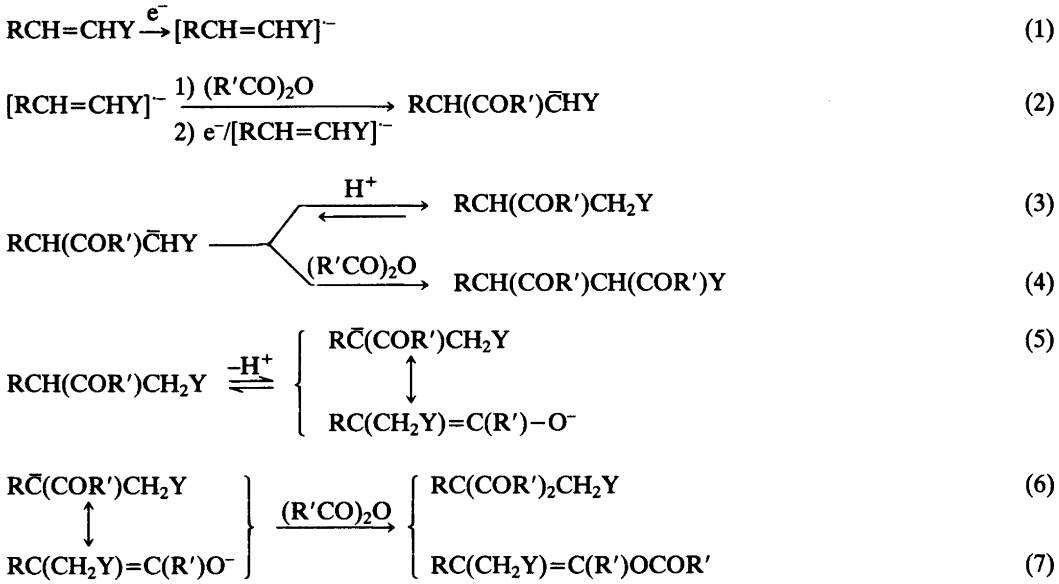
The acylation reaction is assumed to proceed as given by eqns. (1)–(7).

Reaction (4) may be important in the presence of a large excess of the anhydride; the relative importance of reactions (3) and (5) would be expected to be dependent on the relative acidity of the hydrogens at the two central carbon atoms, *i.e.* on the relative activation by Y and by R'CO (+R). Any acid-base system with a suitable pK_A, including the acylated product, may catalyze the tautomerization.

The scheme explains readily that *1* and similar symmetrically (or nearly so) activated olefins form the enol acetate on reductive acetylation. However, the product distribution must rest on a rather delicate balance involving the degree of activation and probably also experimental conditions; *2* produces comparable amounts of the enol derivatives and the ketone on reaction with *6*, whereas ethyl cinnamate gives on reaction with *5* a high yield of the ketone and no isolated yield of the enol acetate; methyl 3-phenylpropynoate yielded,[5] besides the ketone, some of the enol acetate.

The derivatives of *6* have the possibility of making a ring closure either to a cyclopropane derivative or a tetrahydrofuran derivative. Both types of ring closure require the presence of a base, which could be electrogenerated.

The tetrahydrofuran derivatives *12* and *13* are very sensitive to oxygen and are cleaved to *11*; attempts to recrystallize *12* and *13* lead to



oxidative degradation. Also hydrolysis of the enol acetate *7a* must be done in the absence of oxygen otherwise no *9a* is isolated.

EXPERIMENTAL

Reduction of 1 *in the presence of* 5. *1* (0.50 g) was reduced in DMF/0.1 M TBAI (+3.0 ml *5* at −1.7 V *vs.* SCE, n=1.8−1.9. The crude product (0.55 g) was purified on a column of silica using benzene as eluent; the following compounds were isolated (in order of elution): Acenaphthene (9 %), *7a*+*8a* (61 %) and in some experiments traces of acenaphthylenone *11* and *9a*. *7a* (43 %) and *8a* (18 %) were separated on a column of silica using acetone–hexane 1:4 as eluent.

7a (*Z*-isomer). M.p. 113−114 °C, ^{1}H NMR ($CDCl_3$): δ 2.25 (3H,s), 2.35 (3H, relatively broad s), 3.90 (2H, relatively broad s), 7.15−7.85 (6H,m). IR (KBr, cm^{-1}): 1745(s), 1680(w), 1425(m), 1365(m), 1225(s), 1185(s), 815(s), 781(s).

8a (*E*-isomer), ^{1}H NMR ($CDCl_3$): δ 2.18 (3H, relatively broad s), 2.33 (3H,s), 3.92 (2H, relatively broad s), 7.15−7.9 (6H,m). IR (film, cm^{-1}): 1740(s), 1700(w), 1370(s), 1230(s), 1177(s), 812(m), 780(s).

The *Z*/*E*-assignment was made from the following considerations: Irradiation of CH_3−C= of *7a* gave a positive NOE at C-2, whereas irradiation of CH_3CO gave a positive NOE at C-8. δ of CH_3C= in *7a* at 2.18, in *8a* at 2.35 (greater influence of the ring current in *8a*); δ of CH_3CO in *7a* 2.33, in *8a* at 2.25. J (CH_3C=/CH_2) greater in *7a* (*trans* coupling) than in *8a*.

9a. ^{1}H NMR ($CDCl_3$): δ 2.10 (3H,s), 3.4−3.7 (2H,m), 4.47 (1H,dd, J_1 7.5 Hz, J_2 4.7 Hz), 7.1−7.8 (6H,m).

Reduction of 1 *in the presence of* 6 *(1)*. *1* (0.50 g) was reduced as described above in the presence of *6* (2.5 ml), n=1.9. The crude product (0.87 g) was purified as described above. The following compounds were isolated (in order of elution): Acenaphthene (6 %), *7b* and *8b* (12 %), *9b* (46 %) and *11* (8.5 %). The isomers *7b* and *8b* were separated as described for *7a* and *8a*.

7b (*Z*-isomer). ^{1}H NMR ($CDCl_3$): δ 1.9−2.45 (4H,m), 2.65−3.00 (4H,2t), 3.62 (2H,t), 3.67 (2H,t), 4.08 (2H, rel.br.s), 7.2−7.8 (6H,m). IR (film, cm^{-1}): 3100−2800(w), 1750(s), 1675(w), 1130(s), 815(m), 778(s). MS (*m/s* (%)): 366(1), 364(4), 362(6), 258(100).

8b (*E*-isomer). ^{1}H NMR ($CDCl_3$): δ 1.9−2.5 (4H,m), 2.6−3.1 (4H,m), 3.7 (4H,2t, J 6 Hz), 3.9 (2H, rel.br.s), 7.2−7.8 (6H,m). IR (film, cm^{-1}): 3160−2850(m), 1745(s), 1675(w), 1130(s), 813(m), 775(s), MS (*m/e* (%)): 366(1), 364(4), 362(6), 258(100).

9b. ^{1}H NMR ($CDCl_3$): δ 1.9−2.3 (2H,m), 2.6−3.0 (2H, m, AB of ABM-spectrum), 3.50 (2H, t, 6 Hz), 3.62 (2H,t,6 Hz), 4.62 (1H,dd, J_1 7 Hz, J_2 5 Hz), 7.2−7.9 (6H,m). IR (film, cm^{-1}): 3100−2850(w), 1705(s), 1365(w) 778(s). MS (*m/e* (%)): 260(3), 258(9), 153(100).

In the presence of only one equivalent of *6* the reduction of *1* also forms *7c* and *8c*. They were separated on a column of silica using acetone–hexane 1:4 as eluent.

7c (*Z*-isomer). ^{1}H NMR ($CDCl_3$): δ 0.95−1.3 (5H,m), 1.8−2.3 (2H,m), 2.75 (2H,t, 6 Hz), 3.65 (2H,t, 6 Hz), 4.05 (2H,s), 7.2−7.7 (6 H,m). IR (film, cm^{-1}): 3100−2850(w), 1735(s), 1380(m), 1135(s), 812(m), 775(s).

8c (*E*-isomer). ^{1}H NMR ($CDCl_3$): δ 0.8−1.3 (5H,m), 1.5−2.3 (2H,m), 2.95 (2H,t, 6 Hz), 3.65 (2H,t, 6 Hz), 3.9 (2H,s), 7.2−7.7 (6H,m). IR (film, cm^{-1}): 3100−2850(w), 1740(s), 1380(m), 1135(s), 812(m), 775(s). MS (*m/e* (%)): 328(10), 326(29), 258(100), 152(98).

The *Z*/*E* assignment of *7c* and *8c* was based on the δ-values of CH_3−C= (*7c* 2.75, *8c* 3.95) in analogy to *7a*/*8a*; the *Z*/*E* assignment of *7b*/*8b* was made from the transformations *7b*→*7c* and *8b*→*8c* described below.

One equivalent of $1^{\cdot-}$ was generated and used as base in the presence of a 7:3 mixture of *7b* and *8b*. The reaction mixture was separated on a column of silica using diethyl ether−hexane 1:5 as eluent. Isolated were *7c*+*8c* (33 %), *7b* (13 %), *11* (7 %); *7c*:*8c* 57:43 was estimated from the integration of the ^{1}H NMR spectrum.

Cyclization of 9b. *9b* (0.30 g) was treated with $O_2^{\cdot-}$, generated by reducing air bubbling through the DMF-solution, acting as a base. The crude product (0.274 g) was separated by preparative TLC on silica with benzene as eluent. Isolated were *11*, *9b*, *12* and *13* (*Z*- and *E*-isomers of 1-(2-tetrahydrofuranylidene)-1,2-dihydroacenaphthene. *12* and *13* are slowly decomposed to *11* in the presence of O_2; they are solid compounds, but decomposed on recrystallization, so no m.p. is given.

12 (*Z*-isomer). ^{1}H NMR ($CDCl_3$): δ 1.9−2.4 (2H,m), 2.70 (2H,t, 7 Hz), 3.85 (2H,s), 4.35 (2H,t, 6 Hz), 7.1−7.8 (6H,m). IR (KBr, cm^{-1}): 3150−2900(w), 1690(m), 1610(m), 1590(m), 1190(m), 1090(s), 810(m), 775(s). MS (*m/e* (%)): 222(100), 165(87), 152(100).

13 (*E*-isomer). ^{1}H NMR ($CDCl_3$): δ 2.0−2.5 (2H,m), 2.83 (2H,t, 7 Hz), 3.98 (2H,s), 4.20 (2H,t, 6 Hz), 7.0−7.8 (6H,m). IR-spectrum (KBr, cm^{-1}): 3050−2800(w), 1680(m), 1600(w),

1175(m), 810(m), 775(s). MS (*m/e* (%)): 222(96), 165(90), 152(100).

The *Z/E* assignment of *12/13* was based on the δ-values of (CH_2–C=) signal in the hetero ring (12/13 2.70/2.83) and larger homoallylic coupling in *13* compared to *12*.

Reduction of 1 *in the presence of carbon dioxide. 1* (2 g) was reduced in DMF/TBAI at −1.7 V (SCE) at −35 °C with carbon dioxide bubbling through the catholyte. When the reduction was finished, methyl iodide (5 ml) was added. After standing overnight the solvent was removed *in vacuo*, water added and the product extracted with diethyl ether, which was dried and evaporated leaving 2.11 g. Recrystallization from methanol, gave *trans*-1,2-dicarbomethoxy-1,2-dihydroacenaphthylene m.p. 84 °C. ^{1}N NMR spectrum ($CDCl_3$): δ 3.77 (6H,s), 5.12 (2H,s), 7.2–7.8 (6H,m). The *trans* assignment was substantiated from the coupling constants of the methine protons (4.2 Hz) obtained from the satellites in the coupled ^{13}C NMR spectrum.

Reduction of 2 *in the presence of* 5. *2* (2 ml) was reduced in DMF/TBAI at −1.9 V (SCE) in the presence of *4* (10 ml). After completion of the reduction the DMF was evaporated, water and diethyl ether added, the ether layer dried and evaporated leaving a residue which mainly consisted of 3-phenyl-4-ketovaleronitrile and/or its enol ether;[2] the relative amounts differed even under apparently identical conditions. 3-Phenyl-4-ketovaleronitrile (from ethanol), m.p. 92–94 °C (94.5–95.5 °C),[13] ^{1}H NRM ($CDCl_3$): δ 2.06 (3H,s), 2.72 (1H, *J* 16.2, 7.0 Hz), 2.88 (1H, *J* 16.2, 6.8 Hz), 3.98 (1H, *J* 7.0, 6.8 Hz), 7.1–7.5 (5H,m).

Reduction of 2 *in the presence of* 6. *2* (0.5 ml, 4 mM) was reduced in DMF/TBAI in the presence of *6* (0.76 ml, 4 mM) at −1.5 to −1.8 V. After the usual work-up 0.66 g of crude product was isolated. The products were separated on a column of silica using diethyl ether–hexane 7:3 as eluent. Isolated were: 3-Phenylpropionitrile (2 %), *14b* (9 %), *15b* (14 %), *15c* (7 %), *16* (5 %), *17a* (*meso*, 6 %), *17b* (*d,l*, 10 %) and a mixture (14 %) of isomers of 1-cyano-2-amino-3-*Z/E*-tetrahydrofurfuralydene-4,5-*cis/trans*-diphenylcyclopent-1-ene (*18*).

14b. ^{1}H NMR ($CDCl_3$): δ 0.5–1.2 (5H,m), 1.95–2.4 (2H, def.q), 2.55–2.9 (2H,def.q), 3.38 (2H,s), 3.60 (2H,t, *J* 6 Hz), 7.1–7.5 (5H,m). IR (film, cm^{-1}): 3140–2850(w), 2220(w), 1755(s), 1630(m), 1110(vs), 700(s). MS (*m/e* (%)): 305(2), 303(6), 105(100).

15b. ^{1}H NMR ($CDCl_3$): δ 1.8–2.15 (2H,def.q), 2.40–2.88 (4H,m), 3.40 (2H,t, 6 Hz), 3.98 (1H,t, 7 Hz), 7.0–7.5 (5H,m). IR (film, cm^{-1}): 3100–2850(w), 2266(w), 1720(s), 702(s). MS (*m/e* (%)): 237(1), 235(4), 105(100).

15c. ^{1}H NMR ($CDCl_3$): δ 0.7–1.3 (5H,m), 2.7–3.2 (2H,m), 4.15 (1H,dd, 7 Hz, 6.5 Hz), 7.05–7.55 (5H,m). IR (film, cm^{-1}): 3100–2850(w), 2250(w), 1700(s), 1380(m), 700(s). MS (*m/e* (%)): 199(40), 77(100).

16. ^{1}H NMR ($CDCl_3$): 1.8–2.4 (2H,m), 2.6–3.1 (2H,m), .3.48 (2H,s), 4.35 (2H,t, 7 Hz), 7.1–7.5 (5H,m). IR (film, cm^{-1}): 3120–2850(w), 2200(m), 1645(m), 1175(m), 700(s). MS (*m/e* (%)): 199(90), 105(100).

17a. (*meso*-3,4-Diphenyladiponitrile), m.p. 214–216 °C (diethyl ether–hexane), ^{1}H NMR ($CDCl_3$): δ 2.3–2.5 (4H,m), 3.2–3.4 (2H,m), 7.40 (10H,s). IR (KBr, cm^{-1}): 2250(w), 1480(w), 1445(w), 1410(w), 770(m), 700(s), 625(w). MS (*m/e* (%)): 260(33), 130(100).

17b. (*d,l*-3,4-Diphenyldiponitrile), m.p. 114°C (chloroform–hexane), ^{1}H NMR ($CDCl_3$): δ 2.55–2.8 (4H,m), 3.35–3.75 (2H,m), 6.75–7.05 (4H,m), 7.15–7.40 (6H,m). IR (KBr, cm^{-1}): 2250(w), 1480(m), 1450(m), 1410(w), 780(s), 703(s), 625(m). MS (*m/e* (%)): 260(9), 130(100).

Reduction of 2 *in the presence of carbon dioxide. 2* (1 ml) was reduced in DMF/TBAI at −1.9 V (SCE) with CO_2-bubbling. After the reduction was completed, the product was methylated with methyl chloride. The solvent was evaporated, water and diethyl ether added, and the ether dried and evaporated leaving 1.33 g (A); the aqueous phase was acidified and extracted yielding 80 mg (B). The product A was nearly pure methyl 3-cyano-2-phenylpropionate, ^{1}H NMR ($CDCl_3$): δ 3.64 (3H,s), 3.6–3.9 (2H,m), 4.1–4.45 (1H,m), 7.2–7.4 (5H,br.s). MS (*m/e*): 189.

Reduction of 3 *in the presence of carbon dioxide. 3* (1 g) was reduced in DMF/TBAI at −35 °C at −1.9 V (SCE) with CO_2-bubbling, *n*=2.0. After completion of the reduction methyl iodide (5 ml) was added. The usual work-up gave 0.96 g of product, methyl 4-keto-2-phenylpentanoate, m.p. 60–65 °C; ^{1}H NMR ($CDCl_3$): δ 2.12 (3H,s), 2.65 (1H,dd, *J* 17 Hz, 5 Hz), 3.34 (1H,dd, *J* 17 Hz, 9 Hz), 4.04 (1H,dd, *J* 9 Hz, 5 Hz), 3.60 (3H,s), 7.20 (5H,s).

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