Tetrahedron, Vol 37, Supplment No 1, pp 111 to 115, 1981
Printed in Great Britain

0040-4020/81/Suppl 1/0111-05 $02.00/0

CAPTO-DATIVE SUBSTITUENT EFFECTS—VIII[1]

BRIDGED DEHYDRODIMERISATION AS A GENERAL METHOD OF SYNTHESIS: C_4-BRIDGING WITH α-TERT-BUTYLMERCAPTOACRYLONITRILE

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(*Received in U.K. 11 July* 1980)

Abstract- Dehydrodimerization is suppressed completely in the presence of radicophiles such as cd-substituted olefins. Particularly α-t-butylmercaptoacrylonitrile (TBMA) has been examined as a trapping agent for carbon centered radicals. The adducts dimerize thus building C_4-bridges between the original radicals. This general principle is synthetically useful as demonstrated by C_4-bridging of alkanes, ethers, amines, amides, aldehydes and ketones.

Apart from concerted reactions C C bond formation is most frequently achieved through the interaction of electron deficient (electrophilic) centers with electron-rich (nucleophilic) ones, i.e. by polar reaction pathways. Radical reactions represent the alternative fundamental approach to achieve this goal. Radical additions to olefins followed by polymerization or hydrogen abstraction as well as dehydrodimerisation[1] are well-established applications.[2,3,4]

Recently we introduced the term of radicophilicity to describe the propensity of olefins bearing simultaneously electron-withdrawing and donating groups to undergo *twofold* carbon radical addition leading to diadducts **2** or adduct-dimers **1**.[3,6] Following this principle many new examples of C-C bond formation become possible. Whereas generally C H oxidations in the pure phase lead to dehydrodimerization, in the presence of radicophiles C_4-bridged dehydrodimerization becomes the exclusive reaction path.

From the many radicophilic olefins available, TBMA has proven to be a powerful radical scavenger in a wide temperature range[7] and it represents a valuable complement to the known reagents. Besides giving easily detectable radical adducts,[7] TBMA adds preparatively both electrophilic and nucleophilic radicals leading in the majority of cases to high yields of C_4-bridged dehydrodimers **4** as a mixture of *d, l* and *meso* forms.

Upon heating, **4** dissociate reversibly back to **3** as shown by ESR measurements and interconversion of pure isomers to give the equilibrium mixture.[7,8]

From the point of view of synthesis both the thioether and cyano groups are useful functions which can be modified selectively and **4** are moreover masked α-diketones.[9]

In all reactions t-butyloxy radicals served as the oxidizing agent, and mostly di-t-butylperoxide (DTBP) at 130 was used as their precursor but di-t-butylperoxalate can be used at 60 if milder conditions are required. The initially formed electrophilic t-BuO radicals may further decompose to acetone and nucleophilic Me radicals. The latter can abstract H atoms from electron-poor substrates (e.g. nitriles, ketones and esters) whereas t-BuO radicals fail. Thus a great number of C–H bonds can be oxidized to radicals which are then "C_4-bridged" via addition to TMBA followed by dimerisation. The addition of methyl radicals to TBMA however, leading to **4a**, may become a competitive reaction in the case of acceptor substituted substrates. Table 1 summarises the Bridged Dehydrodimerisation of alkanes, ethers, amines, amides and ketones. Analogous reactions with cd-substituted dienes and styrenes are being investigated.

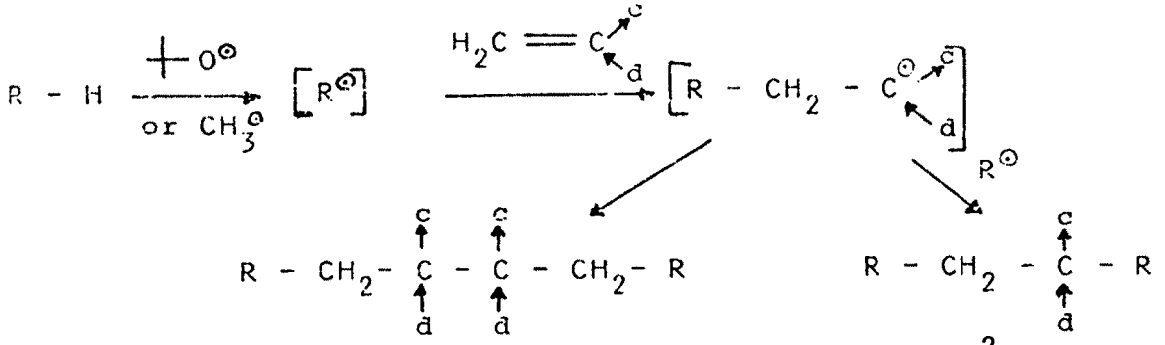
EXPERIMENTAL

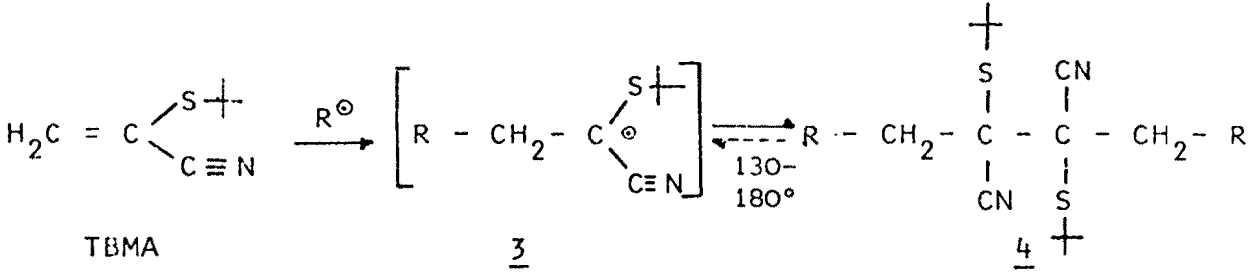
1 H NMR: Measured in $CDCl_3$ soln at 60 or 200 MHz on Varian EM-360 and XL-200 spectrometers. 13C NMR: measured at 20 MHz on Varian CFT-20 spectrometer (Multiplicity due to one-bond couplings: S = singlet, D = doublet, T = triplet, Q = quadruplet, M = multiplet; multiplicity due to long range coupling: s, d, t, q, ... sept. and m) IR: Perkin Elmer 297 infrared spectrometer, measured in $CHCl_3$. Mass: Varian MAT-44S spectrometer.

General procedure using di-t-butylperoxalate[10]: 0.01 M (1.41 g) TBMA,[11] 0.005 M (1.17 g) peroxalate and 0.1 M of the substrate R–H are placed in an ampoule which is then degassed in three freeze-thaw cycles and sealed. After heating for 6 hr to 60, the ampoule is cooled in liquid N_2 and opened. The excess of substrate is recovered by distillation and the residue is crystallised or chromatographed. The procedure with DTBP is the same except that the ampoule is heated for 12 hr to 130. Caution: the reactions are done behind safety shields and all organic peroxides must be handled with due care.

The adduct dimers **4** are obtained as a mixture of 2, or 6 stereomers depending on the number of chiral sites, e.g. 2 or 4. The total yield on isolated product is indicated in Table 1. Full product analysis including separation of the stereomers and their characterisation shall be published independently. Here only the crystallised fractions are described.

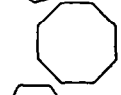
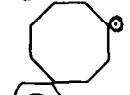
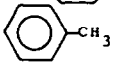
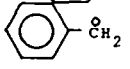
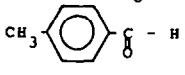
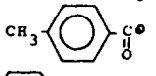
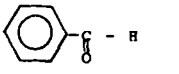
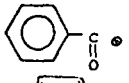
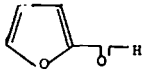
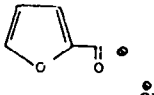
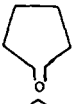
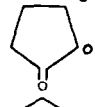
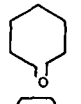
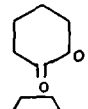
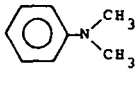
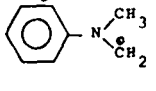
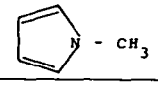
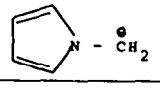
Compound **4b**, recrystallisation from ether/hexane gives the *meso* stereomer,[12] m.p.: 162–163. 1 H NMR: δ = 1.58 (s, 9 H), 1.3–2.5 (m, 9 H), 1.96 (dd, 1 H, J_{gem} = 13.5 Hz, J_{vic} = 2.8 Hz) 2.60 (dd, 1 H, J_{gem} = 13.5 H, J_{vic} = 8.5 Hz).





α-t-butylmercaptoacrylonitrile

Table 1. Adduct dimers *4* from TBMA and various radicals

	RH	$R^{\odot}$	*Yield of 4 (%)*	
			DTBP	*Di-tert-butyl-peroxalate*
a			32[6]	48
b				77
c			52	79
d				68
e				66
f				51
g	CH_3-O-CH_3	$CH_3-O-\overset{\odot}{C}H_2$	51	
h			52	72
i	$CH_3-CH_2-O-CH_2-CH_3$	$CH_3-CH_2-O-\overset{\odot}{C}H-CH_3$	55	61
j			59	63
k			41	58
l				54
m	$CH_3-\overset{O}{\overset{\|}{C}}-H$	$CH_3-\overset{O}{\overset{\|}{C}}\cdot$		67
n	$CH_3-(CH_2)_4-\overset{O}{\overset{\|}{C}}-H$	$CH_3-(CH_2)_4-\overset{O}{\overset{\|}{C}}\cdot$		68
o				70
p				63
q				54
r	$CH_3-\overset{O}{\overset{\|}{C}}-N(CH_3)_2$	$CH_3-\overset{O}{\overset{\|}{C}}-N(\overset{\odot}{C}H_2)CH_3$		74
s	$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$	$CH_3-\overset{O}{\overset{\|}{C}}-\overset{\odot}{C}H_2$		38
t				46
u				47
v			50	
w			70	

13C NMR: δ = 24.7, 25.6, 35.2 and 36.7 (T, m) 4 ring CH_2, 32.7 (D.m) ring CH; 31.8 (Q.sept) and 50.2 (S, m) t-butyl; 45.0 (T, m) and 55.9 (S, m) CH_2-C(CH); 117.8 (S.d; ^3J = 10.3 Hz) C≡N. IR: 2240 cm^{-1} (ν C≡N, w); MS: M$^+$ 420; 275, 243, 211, 155, 41. (Found: C, 68.48; H, 9.59; N, 6.38; S, 14.88. $C_{24}H_{40}N_2S_2$ requires: C, 68.52; H, 9.58; N, 6.65; S, 15.24%.)

Compound **4c**, recrystallisation from ether/hexane gives the *meso* stereomer. M.p. 143–144 . 1 H NMR: δ = 1.58 (s, 9 H), 1.1–1.9 (m, 12 H), 2.45 (dd, 1 H, J_{gem} = 14 Hz, J_{vic} = 6 Hz). IR = 2230 cm^{-1} (ν C≡N, w). MS = M$^+$ 448, 225, 169. (Found: C, 69.59; H, 9.96; N, 6.14; S, 14.16. $C_{26}H_{44}N_2S_2$ requires: C, 69.58; H, 9.88; N, 6.24; S, 14.28%.)

Compound **4d**, purified by column-chrom. on silicagel (CH_2Cl_2), recrystallisation from ether/hexane, gives the *meso* stereomer. M.p. 142–143 . 1 H NMR: δ = 1.58 (s, 9 H), 1.5–2.1 (m, 14 H), 2.54 (dd, 1 H, J_{gem} = 13.6, J_{vic} = 6.4 Hz. IR: 2240 cm^{-1} (ν C≡N, w). M$^+$: 476, 239; 183, 138, 41. (Found: C, 70.55; H, 10.13; N, 5.92; S, 13.40. $C_{28}H_{48}N_2S_2$ requires: C, 70.53; H, 10.15; N, 5.87; S, 13.45%.)

Compound **4e**, purified by column chrom. on silicagel (CH_2Cl_2), recrystallisation from ether gives the meso isomer. M.p.: 155–156 . 1 H NMR: δ = 1.59 (s, 9 H), 1.4–1.8 (m, 14 H), 2.0–2.1 (m, 2 H), 2.54 (dd, 1 H, J_{gem} = 14 Hz, J_{vic} = 7 Hz); 13C NMR: δ = 24.6, 25.9, 26.3, 26.8, 27.4, 34.4 and 35.9 (T.m) 7 ring CH_2; 32.3 (D.m) ring CH; 32.0 (Q.sept) and 50.4 (S.m) t-butyl; 46.5 (T.m) and 56.2 (S.m) CH_2-C(CH); 117.4 (S.dd), ^3J = 10.5 and 1.5 Hz) C≡N. IR: 2230 cm^{-1} (ν C≡N, w). M$^+$: 504, 253, 195, 138. (Found: C, 71.46; H, 10.41; N, 5.59; S, 12.60. $C_{30}H_{52}N_2S_2$ requires: C, 71.37; H, 10.38; N, 5.55; S, 12.70%.)

Compound **4f**, purified by chromatography on silicagel (CH_2Cl_2), recryst. from benzene. Mixture of stereomers M.p.: 164–166 1 H NMR: δ = 1.60 (s, 9 H) 2.1–3.3 (m, 4 H) 7.0–7.6 (m, 5 H). IR: 2240 cm^{-1} (ν C≡N, w). MS: M$^+$: 465; 290, 234, 207, 176, 57, 43. (Found: C, 71.61; H, 7.71; N, 6.11; S, 13.49. $C_{28}H_{36}N_2S_2$ requires: C, 72.36; H, 7.81; N, 6.03; S, 13.80%.)

Compound **4g**, recrystallisation from hexane gives the *meso* isomer, m.p.: 150–151 1 H NMR: δ = 1.59 (s, 9 H), 2.13 (d.t, 1 H, J_{gem} = 13.6, J_{vic} = 6.5 Hz), 3.02 (d.t, 1 H, J_{gem} = 13.6, J_{vic} = 7.6 Hz), 3.40 (s, 3 H), 3.87 (d.d, 2 H). 13 C NMR: δ = 31.6 (Q) and 50.7 (S) t-butyl; 37.8 (T) and 52.9 (S) CH_2-C(CH); 58.7 (Q) and 69.4 (T) H_3C-O-CH_2-) IR: 2230 cm^{-1} (ν C≡N, w). MS: M$^+$ = 372; 315, 243, 227, 186, 163. (Found: C, 58.30; H, 8.56; N, 7.51; O, 8.79; S, 17.19. $C_{18}H_{32}N_2O_2S_2$ requires: C, 58.03; H, 8.66; N, 7.52; O, 8.59; S, 17.21%.)

Compound **4h** *with DTBP*. Chromatography on silicagel ($CHCl_3$), recryst. from ether/hexane. M.p.: 151–153 ; with Ditert-butylperoxalate: recryst. from ether/hexane: mixture of the stereomers. M.p.: 151–153, 1 H NMR: δ = 1.61 (s, 9 H), 1.75–3.0 (m, 2 H), 3.4–5.25 (m, 7 H). IR: 220 cm^{-1} (ν C≡N, w), 1100 cm^{-1} (ν C-O, s). MS: DCI NH_3, (M + NH_4): 474; 296, 247, 52. (Found: C, 57.60; H, 7.98; N, 5.83; O, 13.6; S, 13.90. $C_{22}H_{36}O_4S_2N_2$ requires: C, 57.86; H, 7.94; N, 6.13; O, 14.013; S, 14.042%).

Compound **4i** *with DTBP*. Chromatography on silicagel ($CHCl_3$). With ditert-butylperoxalate: recryst. from hexane. M.p.: 136–138 1 H NMR: δ = 1.2–1.4 (m, 6 H), 1.56 (s, 9 H), 2.3–3.0 (m, 2 H), 3.2–4.2 (m, 3 H). IR: 2240 cm^{-1} (ν C≡N, w), 1090 cm^{-1} (ν C-O, s). MS: DCI CH_4(M + H)$^+$: 429, 271, 216, 57. (Found: C, 61.73; H, 9.25; O, 7.57; N, 6.21; S, 14.81; $C_{22}H_{40}N_2O_2S_2$ requires: C, 61.63; H, 9.40; O, 7.46; N, 6.534; S, 14.95%.)

Compound **4j**, chromatography on silicagel (ethylacetate/-CH_2Cl_2, 4/3) and crystallisation in hexane gives a mixture of the 3 stereomers having the meso configuration on the central carbon. M.p.: 170–171 . ^{1}H NMR: δ = 1.57, 1.58 and 1.59 (s, 9 H) 1.5–2.3 (m, 5 H), 2.60, 2.75 and 2.98 (dd, 1 H, $J_{gem} \approx$ 14 Hz, $J_{vic} \approx$ 7.5 Hz), 3.71 (m, 1 H), 3.8–4.0 (m, 1 H), 4.35–4.5 (m, 1 H). IR: 2250 cm^{-1} (ν C≡N, w). MS: M$^+$ 424; 247, 213, 157, 123, 71, 68, 57, 43. (Found: C, 61.92; 4, 8.42; S, 15.18. $C_{22}H_{36}N_2O_2S_2$ requires: C, 62.22; H, 8.54; S, 15.10%.)

Compound **4k** *with DTBP*. Chromatography on silicagel (ethyl acetate CH_2Cl_2, 4/3) recryst. from hexane, M.p.: 143–145 . 1 H NMR: δ = 1.56 (s, 9 H), 2.2–3.3 (m, 8 H), 3.4–4.3 (m, 3 H). IR: 2240 cm^{-1} (ν C≡N, w). MS: M$^+$ 452, 275, 227, 171, 138, 85. (Found: C, 63.40; H, 9.16; S, 14.71. $C_{24}H_{40}N_2O_2S_2$ requires: C, 63.67; H, 8.90; S, 14.16%.)

Compound **4l** *with DTBP*, purified by chromatography on silicagel (CH_2Cl_2) recryst. from pet. ether 40–60 . Ditert-butylperoxalate: recryst. from hexane. M.p.: 135–136 , mixture of isomers. 1 H NMR: δ = 1.56 (s, 9 H), 1.6–3.0 (m, 10 H), 3.4–4.3 (m, 3 H). IR: 2230 cm^{-1} (ν C≡N, w). MS: M$^+$: 481, 425, 298, 242, 184, 99, 57. (Found: C, 65.01; H, 9.20; N, 5.81; O, 6.64; S, 13.32. $C_{26}H_{44}O_2N_2S_2$ requires: C, 64.95; H, 9.23; N, 5.83; O, 6.66; S, 13.34%.)

Compound **4m**, chromatography on silicagel ($CHCl_3$), recrystallisation from $CHCl_3$–ether gives one of the isomers m.p.: 210–211 . 1 H NMR: δ = 1.57 (s, 9 H); 2.30 (s, 3 H); 3.31 (d, 1 H); 3.79 (d, 1 H), J_{gem} = 15.7 Hz. IR: KBr, 2220 cm^{-1} (ν C≡N, w), 1700 (ν CO, s). MS: M$^+$ 368; 127, 56, 43. (Found: C, 58.41; H, 7.61; N, 7.35; O, 8.28; S, 16.53. $C_{18}H_{28}N_2O_2S_2$ requires: C, 58.66; H, 7.65; S, 17.39; O, 8.68%.)

Compound **4n**, recrystallisation from ether; one of the stereomers is isolated. M.p.: 161 . 1 H NMR: δ = 1.53 (s, 9 H), 0.92 (m, 9 H), 1.20–1.60 (m, 6 H), 3.21 (d, 1 H) 3.70 (d, 1 H) J_{gem} = 16.0 Hz. 13 C NMR: δ = 14.2 (Q.m), 22.7, 31.5, 23.3 and 45.2 (T.m) CH_3-CH_2-CH_2-CH_2-CH_2 , 31.5 (Q. sept) and 52.1 (S.m) t-butyl; 48.9 (DD.s, ^1J = 127.5 and 132.8) and 51.0 (S.m) CH_2-C(CH); 116.0 (S.dd, ^3J = 9.7 and 2.4 Hz) C≡N; 201.7 (S.m) C=O. IR: 2250 cm^{-1} (ν C≡N, w), 1710 (ν CO, s); MS: DCI (CH_4), (M + H)$^+$: 481, 296, 240. (Found: C, 64.93; H, 9.21; N, 5.81; O, 6.69; S, 13.39. $C_{26}H_{44}N_2O_2S_2$ requires: C, 64.95; H, 9.23; N, 5.83; O, 6.66; S, 13.34%.)

Compound **4o**, recrystallisation from benzene: mixture of stereomers. M.p.: 194–195 . **Meso**: 1 H NMR: = 1.63 (s, 9 H), 2.44 (s, 3 H), 3.86 (d, 1 H), 4.35 (d, 1 H) J_{gem} = 15.6 Hz, 7.4 (m, 2 H), 7.8 (m, 2 H) **d, l**: 1 H NMR: = 1.60 (s, 9 H), 2.44 (s, 3 H), 4.15 (d, 1 H), 4.28 (d, 1 H), J_{gem} = 15.8 Hz, 7.4 (m, 2 H), 7.8 (m, 2 H). IR: 2230 cm^{-1} (ν C≡N, w), 1690 (ν CO, s). MS: M$^+$ -$(CH_3)_3$CSH: 430, 259, 190, 119, 91, 57. (Found: C, 69.16; H, 6.85; N, 5.11; O, 6.46; S, 12.25. $C_{30}H_{36}N_2O_2S_2$ requires: C, 69.19; H, 6.97; N, 5.38; O, 6.14; S, 12.31%.)

Compound **4p**, recrystallisation from benzene, m.p.: 196–197 1 H NMR: = 1.56 (s, 9 H), 3.60 (d, 1 H), 4.16 (d, 1 H) J_{gem} = 15.9 Hz; 6.56 (q, 1 H), 7.25 (d, 1 H), 7.60 (s, 1 H). IR: 2240 cm^{-1} (ν C≡N, w); MS: M$^+$ 472, 295, 181, 95, 41: (Found: C, 68.21; H, 6.62; N, 5.66; O, 6.31; S, 13.25. $C_{28}H_{32}N_2O_2S_2$, requires: C, 68.25; H, 6.60; N, 5.68; O, 6.49; S, 13.01%.)

Compound **4q**, recrystallisation from benzene, m.p.: 183 . 1 H NMR: δ = 1.59 (s, 9 H), 3.90 (d, 1 H), 4.39 (d, 1 H) J_{gem}: 15.7 Hz; 6.55 (dd, 1 H), 7.25 (dd, 1 H), 7.60 (dd, 1 H); IR: 2230 cm^{-1} (ν C≡N, w); MS: M$^+$ 368; 185, 127, 112, 56, 43. (Found: C, 60.99; H, 5.95; N, 5.90; O, 13.39; S, 13.22. $C_{24}H_{28}N_2O_4S_2$ requires: C, 60.99; H, 6.00; N, 5.93; O, 13.54; S, 13.57%.)

Compound **4r** recrystallised from $CHCl_3$–ether, m.p.: 160–163 , mixture of stereomers. 1 H NMR: δ = 1.59, 1.60 and 1.68 (s, 9 H); 2.10, 2.12, 2.19 and 2.21 (s, 3 H); 2.0–2.4 (m, 2 H); 2.98, 3.00, 3.07 and 3.09 (s, 3 H), 3.3–4.0 (m, 2 H); IR: 2240 cm^{-1} (ν C≡N, w), 1610 cm^{-1} (ν CO, s). MS: M$^+$ 455; 277, 229, 171, 128, 83, 28. (Found: C, 57.72; H, 8.26; N, 12.09; O, 6.65; S, 13.97; $C_{22}H_{38}N_4O_2S_2$ requires: C, 58.12, H, 8.42; N, 12.32; O, 7.03; S, 14.10%.)

Compound **4s**, chromatography on silicagel ($CHCl_3$), recryst. from $CHCl_3$-ether: mixture of the stereomers. M.p.: 154–155° 1 H NMR: δ = 1.59 (s, 9 H), 2.26 (s, 3 H), 1.8–3.1 (m, 4 H). IR: 2230 cm^{-1} (ν C≡N, w), 1705 (ν CO, s). MS: DCI NH_3 (M + NH_4)$^+$: 414; 372, 236, 194, 136, 74, 52. (Found: N, 6.74; O, 8.08; S, 15.97, $C_{20}H_{32}N_2O_2$ requires: N, 7.09; O, 8.07; S, 16.16%.)

Compound **4t**, chromatography on silicagel ($CHCl_3$), recryst. from $CHCl_3$-ether, m.p. 218–219°, mixture of

stereomers. 1 H NMR: δ = 1.56 (s, 9 H), 1.2–2.8 (m, 9 H). IR: 2240 cm^{-1} (ν C≡N, w), 1740 (ν CO, s). MS: DCI NH_3, $(M + NH_4)^+$: 466; 257, 134, 74, 52.

Compound **4u**, chromatography on silicagel (CH_2Cl_2–ether; 4/1), recryst. from $CHCl_3$ ether, m.p.: 225°, mixture of stereomers. 1 H NMR: δ = 1.56 (s, 9 H), 1.2–2.8 (m, 11 H); IR: 2240 cm^{-1} (ν C≡N, w); 1730 (ν CO, s). MS: DCI NH_3, $(M + NH_4)^+$ 494; 238, 128, 74, 52. (Found: H, 8.21; N, 5.81; O, 6.68; S, 13.77. $C_{26}H_{40}N_2O_2S_2$ requires: H, 8.45; N, 5.87; O, 6.71; S, 13.45%.)

Compound **4v**, chromatography on silicagel (benzene), recryst. from $CHCl_3$–ether; one of the stereomers, m.p. 162° 1 H NMR: δ = 1.57 (s, 9 H), 2.05 (m, 1 H), 2.79 (m, 1 H), 2.93 (s, 3 H), 3.81 (m, 2 H), 6.65–6.76 (m, 3 H), 7.21 (m, 2 H). IR: 2230 cm^{-1} (ν C≡N, w); MS: M^+ $(CH_3)_3CSH$: 433, M^+ HCN = 406, significant fragments: 344, 300, 262, 121. (Found: C, 68.69; H, 8.03; N, 10.51; S, 12.54. $C_{30}H_{42}N_4S_2$ requires: C, 68.66; H, 8.45; N, 10.68; S, 12.22%.)

Compound **4w** chromatography on silicagel (benzene), recryst. from $CHCl_3$-ether, one of stereomers m.p.: 204° 1 H NMR: δ = 1.59 (s, 9 H), 2.3 (m, 1 H), 2.95 (m, 1 H) 4.28 (m, 1 H), 4.58 (m, 1 H), 6.20 (m, 2 H), 6.73 (m, 2 H). IR: 2240 cm^{-1} (ν C≡N, w). MS: M^+: 442; 264, 221, 200, 165, 138, 131, 105.

Acknowledgements – One of us (S.M.) is greatly indebted to the Rhône-Poulenc Industries for a grant. Further, we gratefully acknowledge generous support from the Ministère de la Politique Scientifique.

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