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CAPTODATIVE SUBSTITUENT EFFECTS—XV[1]

GENERALISATION OF BRIDGED DEHYDRODIMERISATION[2] BY VARYING RADICOPHILES AND POLARITY OF ATTACKING RADICALS

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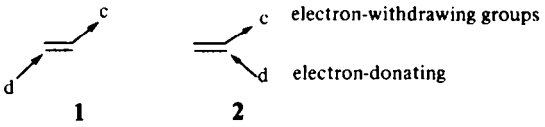
Abstract—Captodative olefins efficiently trap both electrophilic or nucleophilic radicals, i.e. various thiyl, acetyl, acetamidomethyl and *N*-methylanilinomethyl radicals. In the first three cases, good yields of adduct-dimers **4** are formed and these reactions are preparatively useful. In the last case when anilinomethyl radicals are formed at 140°, also dismutation or double adduct **5** formation may occur depending on the choice of c and d groups in **2**.

INTRODUCTION

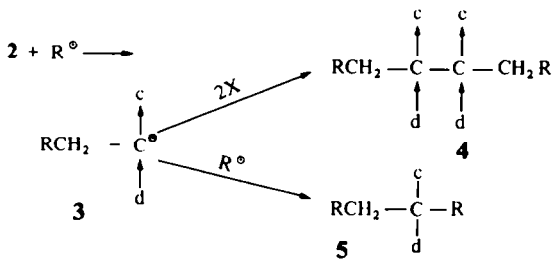
Compared with fully conjugated push-pull olefins **1**, the corresponding cross-conjugated captodative counterparts **2** are even more versatile reagents in organic synthesis. Thus, the use of **2** as Michael acceptors in reactions with carbanions is widely documented.[3] Of more recent note is their increasing application as π_2-components in Diels–Alder reactions,[4] in (2 + 2) cycloadditions,[5] as dipolarophiles in (3 + 2) cycloadditions[6] and as enophiles in Lewis acid catalyzed ene reactions.[7]



1 **2**

We have demonstrated, that cd olefins (**2**) constitute efficient radicophiles for the preparative trapping of various radicals,[8] and also the use of α-t-butylmercaptoacrylonitrile (**2a**; c = CN, d = S-t-C_4H_9) as a new spin-trap for ESR detection of transient radicals.[9]

The propensity of **2** to add radicals is due to the synergic captodative effect[10] in radical adducts **3**, where a donor and an acceptor substituent are linked to the same radical center. The resulting thermodynamic, although not kinetic,[11] stabilisation of **3** causes them to dimerize to adduct-dimers **4** or to trap eventually another radical R° leading to diadducts **5**. Typical reactions of vinylic monomers, i.e. polymerisation, copolymerisation and oligomerisation, are in general absent with **2**, although they can be induced under special circumstances.[12]

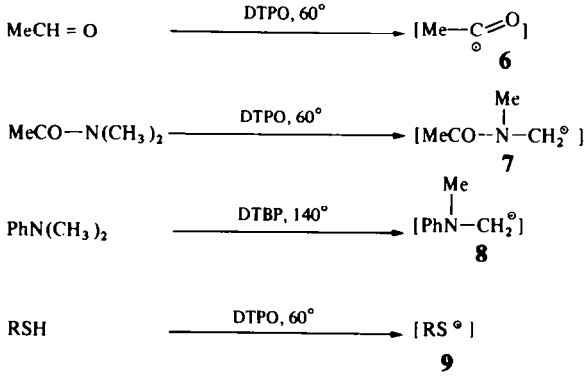


In the preceding paper,[2] we described a number of examples of preparative additions of radicals derived from alkanes, ethers, aldehydes, amides, amines and ketones to **2a**.

In order to generalize the bridged dehydrodimerisation, the present paper describes the additions of three nucleophilic radicals, namely acetyl (**6**), acetamidomethyl (**7**), *N*-methylanilinomethyl (**8**), and of electrophilic species, i.e. phenylthiyl and alkylthiyl radicals (**9**), to a number of cd-olefins.

RESULTS AND DISCUSSION

Radical **8** was produced by hydrogen abstraction from *N,N*-dimethylaniline using di-t-butylperoxide (DTBP) at 140°, as the use of di-t-butylperoxalate (DTPO) is incompatible with relatively basic alkyl and aralkyl amines, on account of the uncontrollable induced decomposition. Species **6**, **8** and **9** were generated in the usual way from acetaldehyde and thiols using DTPO at 60°.



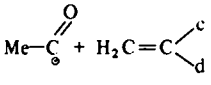
Trapping of acetyl radicals (**6**)

As the Table 1 shows, the nucleophilic[13] acetyl radical adds smoothly to various cd acrylic compounds to form exclusively adduct-dimers **10** in good yields. The efficiency of trapping varies little with the substituents c and d present in **2a–g**. Compounds **10**

Table 1. Formation of adduct-dimers **10** from cd-olefins **2** and acetaldehyde

2	d	c	10	Yield (%)
a	t-C_4H_9S	CN	a	67[a]
b	EtS	CN	b	63
c	MeS	CN	c	67
d	t-C_4H_9S	CO_2Me	d	64
e	MeO	CN	e	71
f	MeO	CO_2Me	f	61
g	PhS	CN	g	71

[a]See Ref. 2.



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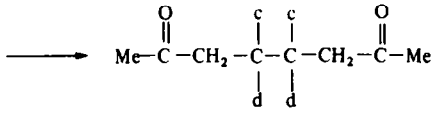
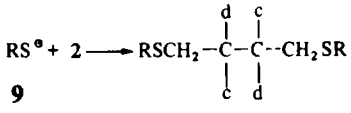


10

are 1,6-diketones, and moreover the two central cd-substituted carbon atoms are masked carbonyl groups. Owing to their basic nature, cd enamines like α-dimethylaminoacrylonitrile afford only ill-defined mixtures in the presence of DTPO at 60°.

Trapping of thiyl radicals (**9**)

There are countless reports of the very smooth free-radical chain addition of thiols to olefins and acetylenes.[14] The primary radical adducts almost invariably abstract hydrogen from the thiol present in a chain process. In striking contrast, cd olefins form adduct-dimers **11** when exposed to excess of thiol in the presence of an equimolar amount of hydrogen-abstracting-butyloxy radicals.



9 **11**

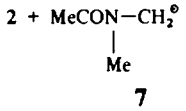
Table 2. Formation of adduct-dimers **11** and **2** and thiyl radicals

2	d	c	R in RS⊙	11	Yield (%)
a	t-C_4H_9S	CN	Ph	a	71
a	t-C_4H_9S	CN	Et	b	61
a	t-C_4H_9S	CN	Me	c	66
a	t-C_4H_9S	CN	t-C_4H_9	d	61
b	EtS	CN	Ph	e	55
b	EtS	CN	t-C_4H_9	f	53
c	MeS	CN	Ph	g	69
d	t-C_4H_9S	CO_2Me	t-C_4H_9	h	64
f	MeO	CO_2Me	t-C_4H_9	i	71

Blank experiments in the absence of peroxide have established that Michael addition of thiols does not occur under conditions employed.

Trapping of acetamidomethyl radicals (**7**)

N,N-dimethylacetamide is oxidised exclusively at the position α to the nitrogen by t-butoxy radicals.[15] Thus, radical **7** is trapped in good yield to give the bridged dehydrodimers **13** with various cd olefins.



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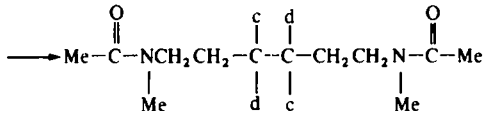
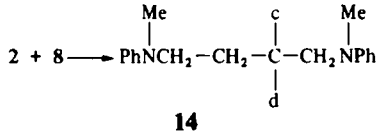


13

Addition of anilinomethyl radicals **8**

Finally, the oxidation of dimethylaniline in the presence of various olefins **2** was examined. As discussed above, because of its basic nature, di-t-butylperoxide had to be used as the abstracting species instead of DTPO. This entails working at much higher temperature (140°) than in the preceding examples and the product composition depends strongly on the nature of c and d groups in **2**. Thus, besides the expected adduct-dimers and/or diadducts, dismutation products **16** are encountered with cd olefins **2h–g**.



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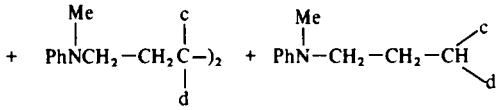
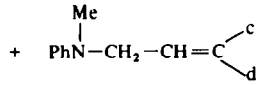


15 **16a**



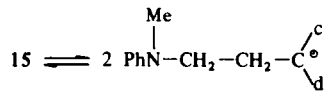
16b

Table 3. Bridged dehydrodimerisation of *N,N*-dimethylacetamide

2	d	c	13(%)
a	t-C_4H_9S	CN	74[a]
e	MeO	CN	51.5
g	t-C_4H_9S	CO_2Et	47

[a]See Ref. 2.

This behaviour is rationalised by consideration of the equilibrium between **15** and radical adducts **17**. The latter can readily be observed by ESR.[16]



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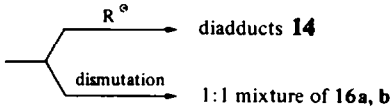
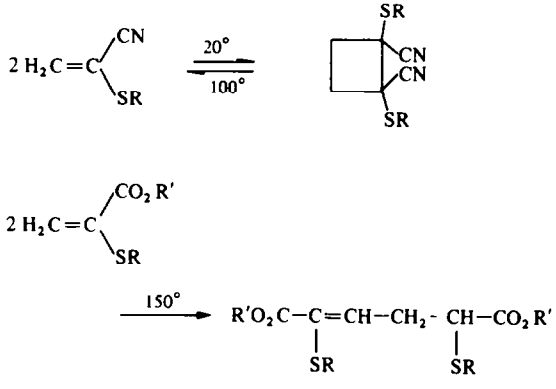


The equilibrium constant depends upon how much the central C–C bond in **15** is weakened by the cd substituent effect combined with steric strain[17] around this bond. Thermolabile C–C bonds obviously favor the formation of double adduct and of dismutation products.

Inspection of Table 4 shows that adduct-dimers **15** are still the exclusive products with α-alkylthioacrylonitriles **2a–c**. In contrast, the corresponding ester leads only to the diadduct **14**. Thus both the radicophiles **2a** and **2d** lead to the corresponding radical adducts, which evolve in a rather different fashion. It should be recalled that the thermal dimerisation of both classes of compounds also follows two distinct paths: nitriles **2a–c** form cyclobutanes in head-to-head cycloadditions, whereas α-alkylthioacrylates form α,α-bis-(alkylthio)-α,β-dihydromuconic esters.[5]



Enaminonitriles **2i, j**, on the other hand, afford dismutation products **16a,b** and the same is true for diphenylethylene which was used for comparison. This suggests a low dissociation energy in the presumed intermediates **15i, j** which have not been isolated as yet.

One can conclude that bridged dehydrodimerisation using cd olefins is a general principle which can be used for constructing highly functionalized and previously inaccessible classes of compound.

Table 4. Addition of *N,N*-dimethylaniline to **2** at 140°

2	d	c	Yield of 14(%)	Yield of 15(%)	Yield of 16a,b(%)
a	t-C_4H_9S	CN	—	50	—
b	EtS	CN	—	46	—
c	MeS	CN	—	47	—
d	t-C_4H_9S	CO_2Me	33	—	—
f	MeO	CO_2Me	12	18	—
h	Ph	Ph	—	—	51
i	ON	CN	—	—	45
j	Me_2N	CN	—	—	35

EXPERIMENTAL

^{1}H-NMR: Measured in $CDCl_3$ solutions at 60 or 200 MHz on Varian EM-360 and XL-200 Spectrometers. IR: Perkin–Elmer 297 spectrometer, in $CHCl_3$ solution. Mass: Varian MAT–44S spectrometer. Identification of *meso* and *d,l* isomers (generally formed in nearly 1:1 ratio) was done by X-ray diffraction for **10a** *meso*, **10c**, *d,l*.[18] In other cases, the NMR technique using the chiral shift reagent Eu(hfc)$_3$ was applied. Unless indicated otherwise, only one form, probably the *meso*, was characterised.

Additions of acetaldehyde: general procedure. 0.01 M of the captodative olefin **2**, 0.005 M (1.2g) DTPO and 0.2 M (8.4g) of acetaldehyde were placed in an ampoule and degassed in 3 freeze-thaw cycles, sealed, and heated to 60° for 8 hr. The crude product was directly recrystallized or chromatographed.

Compound **10a**. See Ref. 2. *Meso* **10b** was obtained by recrystallization from ether, m.p. 205–207°. ^{1}H-NMR: δ = 1.32 (t, 6H), 2.27 (s, 6H), 3.1–3.2 (m, 4H), 3.25 (d, 2H) (J_{gem} = 17.1 Hz), 3.69 (d, 2H); MS: M^+ = 312; 291, 252, 229, 199, 152, 61, 43. (Found: C, 53.8; H, 6.4; S, 20.3; N, 9.1; O, 10.6. $C_{14}H_{20}S_2O_2$ requires C, 53.8; H, 6.4; S, 20.5; N, 9.0; O, 10.2%.)

Compound d,l-**10c** was obtained by recryst. from $CHCl_3$:ether; m.p. 202°. ^{1}H-NMR: δ = 2.19 (s, 6H), 2.53 (s, 6h), 3.17 (d, 2H) (J_{gem} = 17.3 Hz), 3.61 (d, 2H); MS: DCI (isobutane) $(M + 1)^+$ = 285, 247, 191, 143, 95, 73. (Found: C, 50.9; H, 5.8; N, 9.9; S, 22.7; O, 11.7. $C_{12}H_{16}N_2O_2$ requires C, 50.7; H, 5.6; N, 9.8; S, 22.5; O, 11.2%.)

Compound **10d** (one diastereomer) was obtained by chromatography on SiO_2, benzene: $CHCl_3$ = 4:3; recryst. ether:pet. ether = 2:3; m.p. 182–183°. ^{1}H NMR: δ = 1.46 (s, 18H), 2.06 (s, 6H), 3.56 (s, 3H), 3.63 (d, 2H) (J_{gem} = 17 Hz), 3.91 (d, 2H); IR: 1720, 1750 cm^{-1}; MS: M^+–C_4H_8 = 378, 304, 271, 227, 195, 162, 130, 87, 57, 43.

Compound **10e**, *meso and d,l*, recryst. from ether, m.p. 175–177°. ^{1}H NMR of *meso*-form: δ = 2.21 (s, 6H), 3.03 (d, 2H), 3.23 (d, 2H), 3.53 (s, 3H); *d,l* form: 2.21 (s, 6H), 2.96 (s, 4H), 3.63 (s, 6H); IR: 2240, 1720, 1200, 1100 cm^{-1}; MS: DCI (isobutane), $(M + 1)^+$ = 253, 234, 169, 127, 84, 57, 44.

Compound **10f**, obtained as one diastereomer, recryst. from ether:pet. ether = 2:3; m.p. 178°. ^{1}H NMR: δ = 2.16 (s, 3H), 2.93 (d, 2H) (J_{gem} = 18 Hz), 3.30 (s, 6H), 3.47 (d, 2H), 3.66 (s, 6H); IR: 3010, 1720–1760, 1420, 1500 cm^{-1}; MS: M^+ –CO_2Me = 259, 227, 160, 117, 85, 57, 43.

Compound **10g** (mixture of meso and *d–l*), recryst. from benzene, m.p. 198–201°. *Meso*-form: ^{1}H NMR: δ = 2.02 (s, 6H), 3.17 (d, 2H) (J_{gem} = 17.7 Hz), 3.69 (d, 2H), 7.4–7.5 (m, 6H), 7.8 (m, 4H): *d,l*-form: δ = 2.07 (s, 6H), 3.23 (d, 2H) (J_{gem} = 18.0 Hz), 3.50 (d, 2H), 7.4–7.5 (m, 6H), 7.85 (m, 4H); IR: 2230, 1710 cm^{-1}; MS: M^+ = 408, 279, 247, 205, 162, 109, 43.

Addition of thiyl radicals. The procedure was the same as for acetyl radicals.

Compound **11a**, recryst. from benzene afforded one diastereomer, m.p. 163–164°; ^{1}H NMR: δ = 1.58 (s, 18H), 3.60 (d, 2H) (J_{gem} = 13 Hz), 4.13 (d, 2H), 7.06–7.66 (m, 10H); IR: 2240 cm^{-1}; MS: M^+ = 500, 444, 411, 355, 218, 109, 57.

Compound **11b**, recryst. from benzene yielded one diastereomer, m.p. 92–93°; ^{1}H NMR: δ = 1.26 (t, 6H) (J = 7Hz), 1.60 (s, 18H), 2.78 (q, 4H), 3.06 (d, 2H) (J_{gem} = 14Hz), 3.70 (d, 2H). IR: 2230 cm^{-1}: M^+ = 404, 375, 348, 292, 259, 225, 197, 141, 93, 75, 57, 41.

Compound **11c**, recryst. from ether:pet. ether = 2:3 gives one diastereomer, m.p. 108°; ^{1}H NMR: δ = 1.60 (s, 18H), 2.33

(s, 6H), 3.06 (d, 2H) (J_{gem} = 14Hz), 3.66 (d, 2H); IR: 2240 cm^{-1}; MS: DCI/isobutane, $(M + 1)^+$ = 217, 189, 169, 141, 104, 85.

Compound **11d**, work-up as for **11c**, one diastereomer, m.p. 183°; ^1H NMR: δ = 1.40 (s, 18H), 1.60 (s, 18H), 3.10 (d, 2H) (J_{gem} = 12.6Hz), 3.63 (d, 2H); IR: 2230 cm^{-1}; MS: M^+ = 460, 403, 347, 291, 235, 203, 174, 141, 103, 57, 41.

Compound **11e**, recryst. from benzene, one diastereomer, m.p. 132°; ^1H NMR: δ = 1.30 (t, 6H) (J = 7Hz), 3.03 (q, 4H), 3.50 (d, 2H) and 3.80 (d, 2H) (J_{gem} = 14Hz), 6.96–7.60 (m, 10H); IR: 2220, 1590 cm^{-1}; MS: M^+ = 444, 397, 362, 331, 267, 218, 160, 65.

Compound **11f**, work-up as for **11c**, one diastereomer, m.p. 154–155°; ^1H NMR: δ = 1.33 (t, 6H) (J = 7Hz), 1.40 (s, 18H), 3.08 (q, 4H), 3.16 (d, 2H) and 3.45 (d, 2H) (J_{gem} = 12Hz); IR: 2240 cm^{-1}; MS: M^+ = 404, 347, 321, 291, 264, 229, 202, 146, 103, 75, 57, 41.

Compound **11g**, recryst. from benzene:ether afforded a mixture of diastereomers, m.p. 131°; ^1H NMR: (1) δ = 2.56 (s, 6H), 3.33 (d, 2H) and 3.76 (d, 2H) (J_{gem} = 13Hz), 7.13–7.73 (m, 10H); (2) δ = 2.56 (s, 6H), 3.56 (d, 2H) and 3.83 (d, 2H) (J_{gem} = 14Hz), 7.13–7.73 (m, 10H); IR: 2220 cm^{-1}; M.S.: M^+–CH_3S = 369, 317, 260, 218, 160, 123, 65, 45.

Compound **11h**, chromatography on SiO_2, CH_2Cl_2 afforded a mixture of diastereomers, recryst. from ether:pet. ether = 2:3; m.p. 107–108°; ^1H NMR: δ = 1.33–1.46 (36H), 3.16–3.96 (m, 4H), 3.66 (s, 6H); IR: 1720, 1430, 1360 cm^{-1}; MS: M^+ = 526, 469, 413, 357, 301, 267, 207, 151, 118, 86, 57, 41.

Compound **11i**, chromatography on SiO_2, CH_2Cl_2 and subsequent recrystallisation from ether gave one diastereomer, of m.p. 80–81°; ^1H NMR: δ = 1.26 (s, 18H), 2.96 (d, 2H) and 3.26 (d, 2H) (J_{gem} = 13Hz), 3.43 (s, 6H), 3.63 (s, 6H); IR: 1730, 1450 cm^{-1}; MS: (DCI/NH_3) $(M + 1)^+$ = 411; $(M + NH_4)^+$ = 428, 319, 224, 134, 35; $(2M + NH_4)^+$ = 838. The chromatography furnished also the minor diastereomer (19%).

Addition of dimethylaniline: General procedure using di-t-butylperoxide.

0.01 M Captodative olefin **2**, 0.005 m (0.7g) DTBP and 0.1 M of the substrate RH in an ampoule were degassed in three freeze-thaw cycles and then sealed. After heating 12hr at 130° the excess of substrate was removed by distillation and the residue was chromatographed.

Compound **15a**—see ref. 2. *Compound* **15b**, chromatography on SiO_2, benzene, recryst. from $CHCl_3$, m.p. 158–160°; ^1H NMR: δ = 1.37 (t, 6H), 1.98 (m, 2H), 2.34 (m, 2H), 2.93 (s, 6H), 3.03 (q, 4H), 3.72 (m, 2H), 3.83 (m, 2H), 6.65–6.8 (m, 6H), 7.2 (m, 4H); IR: 2230 cm^{-1}; MS: M^+ = 446, 405, 377, 344, 300, 372, 333, 121, 105, 91, 77.

Compound **15c**, chromatography on SiO_2, $CHCl_3$, recryst. from benzene, m.p. 146°; ^1H NMR: δ = 2.0–2.4 (m, 4H), 2.53 (s, 6H), 2.95 (s, 6H), 3.6–3.8 (m, 4H), 6.5–6.8 (m, 6H), 7.15 (m, 4H); IR: 2220 cm^{-1}; MS: M^+ = 438, 391, 364, 344, 258, 219, 169, 120, 105, 77.

Compound **14d**, work-up as for **15c**, m.p. 153°, ^1H NMR: δ = 1.33 (s, 9H), 1.66–2.33 (m, 2H), 2.83 (s, 3H), 2.88 (s, 3H), 3.13–3.60 (m, 4H), 3.66 (s, 3H), 6.3–7.3 (m, 10H); IR: 1600 cm^{-1}; MS: $M^+ - C_6H_5$ = 336, 295, 276, 264, 223, 174, 134, 120.

1:1 *Mixture of Compounds* **16h(a,b)**, chromatography on SiO_2, CCl_4, oil. ^1H NMR of 1,1-diphenyl-3-methylanilinopropene: δ = 2.78 (s, 3H), 3.90 (d, 2H), 6.00 (t, 1H), 6.53–7.23 (m, 15H); 1,1-diphenyl-3-methylanilinopropane: δ = 2.78 (s, 3H), 2.26 (m, 2H), 3.24 (t, 2H), 6.00 (t, 1H), 6.53–7.23 (m, 15H); IR: 1620 cm^{-1}; MS: M^+ = 299, 195, 106, 77.

1:1 *Mixture of Compounds* **16i(a, b)**, chromatography on SiO_2, $CHCl_3$, oil. ^1H NMR of 2-morpholino-4-methylanilinocrotonitrile in the 1:1 mixture: δ = 2.66–3.06 (m, 4H), 2.8 (s, 3H), 3.6–3.9 (m, 4H), 4.16 (d, 2H) (J = 7Hz), 5.16 (t, 1H), 6.33–6.83, 6.90–7.36 (m, 5H); 2-morpholino-4-methylanilinobutyronitrile: δ = 1.8–2.40 (m, 2H), 2.8 (s, 3H) 2.66–3.06 (m, 4H), 3.16–3.60 (m, 3H), 3.56–3.90 (m, 4H), 6.33–6.83, 6.90–7.36 (m, 5H); IR: 2240, 1600 cm^{-1}; MS: M^+ = 259 and 257, 172, 230, 153, 106, 77.

Compounds **16j(a,b)**, chromatography on SiO_2, benzene: $CHCl_3$ = 4:3, oil. ^1H NMR of 2-dimethylamino-4-methylanilinocrotonitrile: δ = 2.26 (s, 3H), 2.90 (s, 6H), 4.13 (d, 2H) and 4.9 (t, 1H), 6.43–6.90 (m, 2H), 7.0–7.46 (m, 3H); 2-dimethylamino-4-methylanilinobutyronitrile: δ = 1.66–2.13 (m, 2H), 2.26 (s, 3H), 2.66 (s, 6H), 3.2–3.76 (m, 3H), 6.43–6.90 (m, 2H), 7.0–7.46 (m, 3H); IR = 2230 cm^{-1}; MS: M^+ = 217 and M^+ = 215, 196, 120, 106, 83, 77, 47.

Reaction with methyl 2-methoxyacrylate **2f** (chromatography on SiO_2, $CHCl_3$) affords two fractions:

Compound **14f**, oil. ^1H NMR: δ = 2.11 (t, 2H) (J = 7.9Hz), 2.80–2.90 (6H), 3.20–3.60 (m, 7H), 3.63 (s, 3H), 6.33–6.76 (m, 4H), 6.83–7.50 (m, 6H); IR = 1610 cm^{-1}; MS: M^+ = 356, 240, 116, 77, 51, 43, 38.

Compound **15f**, recryst. from ether:pet. ether = 3:2, m.p. 161°; ^1H NMR: 2.0–2.5 (m, 2H), 2.91 (s, 3H), 3.50 (s, 3H), 3.23–3.45 (m, 2H), 3.74 (s, 3H), 6.40–6.80 (m, 2H), 6.86–7.39 (m, 3H); IR = 1610 cm^{-1}; MS: $(M^+/2)$-CH_3OH = 204, 169, 155, 105, 77, 51.

Addition of N,N-*dimethylacetamide*: the same procedure as for acetyl and thiyl radicals.

Compound **13a**—see ref. 2; *compound* **13e**, recryst. from $CHCl_3$, m.p. 184–5°; ^1H NMR: δ = 2.06 (s, 6H), 2.2–2.3 (m, 4H), 3.03 (s, 6H), 3.5–3.7 (m, 4H), 3.66 (s, 6H); IR: 2250, 1630 cm^{-1}; MS: DCI/isobutane (M + 1) = 339, 268, 195, 122, 58.

Compound **13g**, recryst. from $CHCl_3$, m.p. 179–182°; ^1H NMR: δ = 1.35 (m, 6H), 1.43 (s, 18H), 2.16 (s, 6H), 2.6–2.8 (m, 4H), 2.93 (s, 6H), 3.5–3.8 (m, 4H), 4.15 (m, 4H); IR: 1720, 1620 cm^{-1}; MS: $(M^+-C_4H_9)$ 491, 435, 371, 304, 274 $(M^+/2)$, 304, 218, 174, 131, 86, 44.

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