

CAPTO-DATIVE SUBSTITUENT EFFECTS

XIII *. C₄-BRIDGED RADICAL DIMERISATION WITH α-PHENYLSELENOACRYLIC ACID DERIVATIVES

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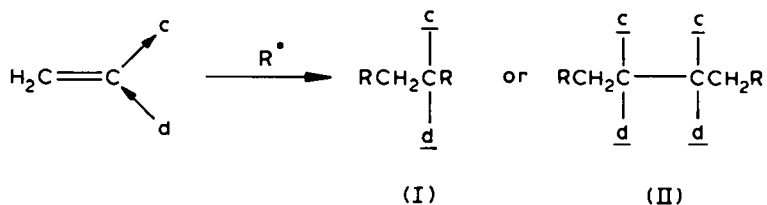
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Summary

Several capto-dative olefins containing the phenylselenenyl group have been obtained via selenenyl halide addition to acrylic derivatives followed by halide elimination. Some of the olefins efficiently trap the radicals formed from azobisisobutyronitrile (AIBN) and methyl azobisisobutyrate (MAIB) to form intermediate bridged dehydrodimers, which spontaneously lose diphenyldiselenide to produce new highly functionalised fumaronitriles and fumaric ester derivatives.

Introduction

Capto-dative (cd) olefins are efficient as traps for various radicals, giving either diadducts I or more often adduct-dimers II.



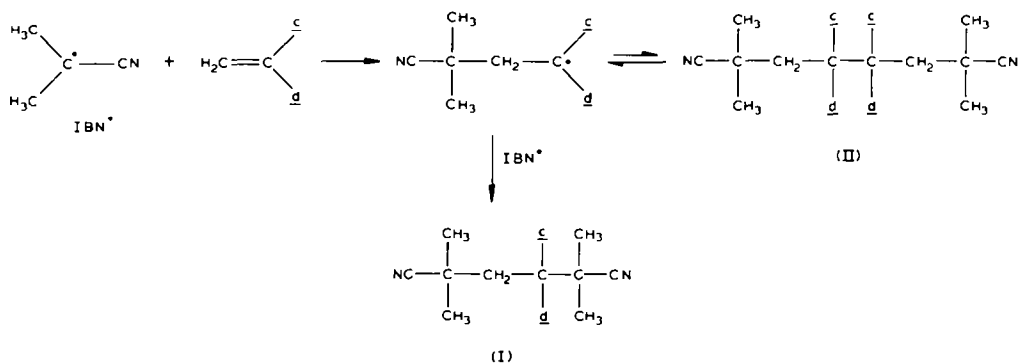
α-Alkyl- and aryl-thioacrylate and acrylonitrile are particularly useful radical scavengers [2].

Despite many similarities with sulphur compounds, selenium analogs frequently show different reactivities. Furthermore the ease of removal of selenenyl moieties has

* For part XII see ref. 1.

greatly stimulated interest in their use in synthesis. It was therefore of interest to compare the behaviour of *cd*-olefins bearing either sulphur or selenium substituents in radical additions.

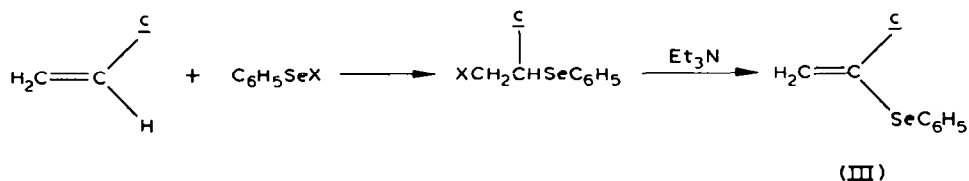
Isobutyronitrile radicals (IBN) were generated thermally (80°C, benzene) from azobisisobutyronitrile (AIBN). IBN radicals have been shown in our previous additions to *cd*-olefins [3] to form mainly diadducts I rather than adduct dimers II. This behaviour appears to result from the ease of homolysis of the expected (but not yet isolated) adducts II, which dissociate easily because of internal radical stabilisation [4].



(a) Results and discussion

Synthesis of cd seleno-substituted olefins (III)

The selenoether olefins III were prepared by benzeneselenenyl chloride or bromide addition to the respective acrylic acid derivatives followed by hydrogen halide elimination with triethylamine. IIIa is known to be formed in only 18% yield from methyl acrylate, lithium diisopropylamide and benzeneselenenyl bromide [5]. Our approach is more efficient for IIIa (57% yield), and is quite general, since even acrylonitrile reacts, to give the expected selenoether IIIb (Table 1).



The selenenyl halide adducts need not be isolated. In contrast to the reactions involving sulphenyl chlorides, only one regioisomer was formed in all the cases studied.

Olefins III having aldehyde or ketone groups as acceptor substituents are not stable at room temperature [6].

Addition of IBN and methyl isobutyrate (MIB) radicals

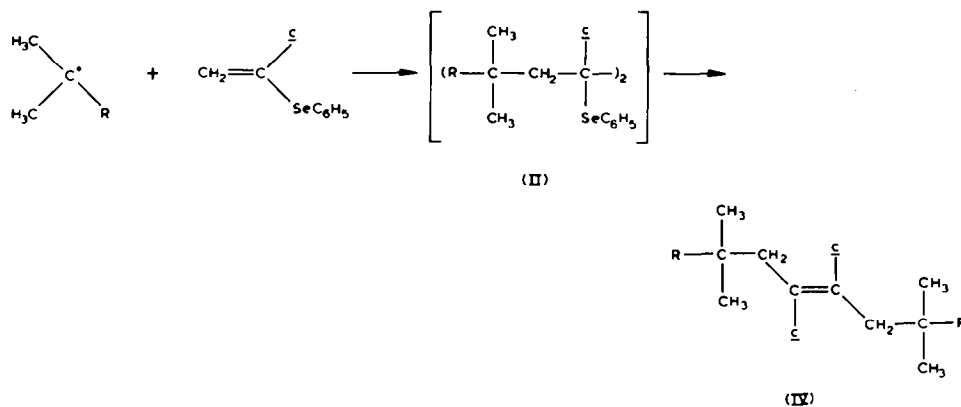
Olefins IIIa, IIIb were treated with equimolar amounts of AIBN or MAIB in degassed ampoules in benzene as solvent at 80°C. Interestingly, the diselenide

TABLE 1
SYNTHESIS OF SELENYLATED CAPTO-DATIVE OLEFINS

	ξ	X	Yield (%)	B.p. or M.p. (°C)
IIIa	COOCH ₃	Cl, Br	57	65-67/0.01
IIIb	CN	Cl, Br	32	80/0.01
IIIc	COCH ₃	Br	85	32.5
IIId	CHO	Br	68	^a
IIIe	COC ₆ H ₅	Br	50	^a

^a Isolated by column chromatography.

elimination products IV (Table 2) derived from adduct dimers II were obtained [7]. These dicyanobutene compounds (IV) are usefully functionalized bridged radical derivatives, and their reactions are under study.



The analysis of the reaction mixture has shown that in addition to diphenyldiselenide products, V and VI are also formed in variable amounts.

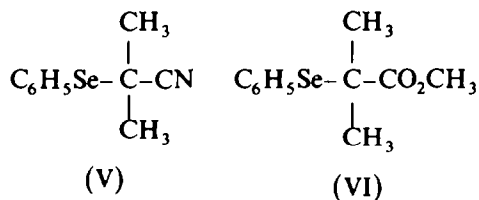
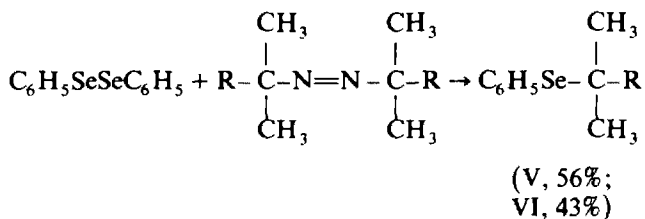


TABLE 2
DISUBSTITUTED FUMARIC ACID DERIVATIVES IV

	R	ξ	Yield (%)	M.p. (°C)
IVa	CN	CN	75	149
IVb	CN	COOCH ₃	65	131
IVc	COOCH ₃	COOCH ₃	75	81

The assumption that IBN and MIB radicals reacts with diphenyldiselenide in a S_H -type reaction was confirmed by independent experiments in the absence of olefins, which gave both substitution products in fair yields.



Experimental

All mass spectra of organoselenium compounds are given for the ^{80}Se isotope.

α-Phenylselenoacrylonitrile (IIIb) [11]

Acrylonitrile (2.15 g, 40 mmol) in 10 ml CH_2Cl_2 was slowly added to benzeneselenenyl bromide (9.44 g, 40 mmol) in 30 ml CH_2Cl_2 . The mixture was refluxed for 24 h and after cooling to room temperature triethylamine (5 g, 50 mmol) in 100 ml benzene was added. The mixture was stirred overnight at room temperature, then filtered, and the solvent evaporated. Vacuum distillation $80^\circ C/0.01$ Torr gave 2.67 g of a pale yellow oil (yield 32%). An analytical sample can be obtained by column chromatography (SiO_2/C_6H_6). 1H NMR ($CDCl_3$): δ 5.95 (1H,d), 6.35(1H,d), 7.4 ppm (5H,m). IR (film) ν 3090, 3040, 2200, 1560, 1460, 1420, 1360, 1135 cm^{-1} . Mass spectrum: 209 (M^+), 182, 157, 129, 117, 102, 82, 77.

α-Phenylselenomethylacrylate (IIIa)

Benzeneselenenyl bromide (9.44 g, 40 mmol) and methyl acrylate (3.44 g, 40 mmol) were stirred in CH_2Cl_2 (40 ml) for 0.5 h at $20^\circ C$. Triethylamine (5 g, 50 mmol) in benzene (100 ml) was then added and stirring continued for 0.5 h. The mixture was worked up as for IIIb. (5.19 g, 57%). B.p. $65-67^\circ C/0.01$ Torr). An analytical sample is obtained by chromatography (SiO_2/CH_2Cl_2). 1H NMR ($CDCl_3$): δ 3.7 (3H,s), 5.15 (1H,s), 6.45 (1H,s), 7.3 ppm (5H,m). IR (film): 2940, 1700, 1580, 1420, 1365, 1260, 1225, 1090, 1005, 900 cm^{-1} . Mass spectrum: 243 ($M + 1$) $^+$; 165, 157, 77.

α-Phenylseleno vinylphenyl ketone (IIIe) [9]

Phenyl vinyl ketone (2.64 g, 20 mmol) in 10 ml CH_2Cl_2 was added to benzeneselenenyl bromide (4.72 g, 20 mmol) in 30 ml CH_2Cl_2 at $-40^\circ C$. When the mixture became colorless triethylamine (2.5 g, 25 mmol) in 40 ml C_6H_6 was added at $-40^\circ C$ and the solution stirred at room temperature for 2 h. Filtration and evaporation of the solvents gave a crude product which was purified by column chromatography (SiO_2/C_6H_6) to yield 2.88 g of III as a yellow oil this must be stored below $-20^\circ C$. 1H NMR ($CDCl_3$): δ 5.55 (1H,d), 6.05 (1H,d), 7.4 ppm (10H,m). IR (film), ν 3070, 1640, 1590, 1570, 1470, 1440, 1260, 1020, 970, 910 cm^{-1} .

α-Phenylselenoacroleine (IIIId) [6]

The procedure was the same as for IIIe. Purification by chromatography

(SiO₂/CH₂Cl₂) gave an unstable pale yellow oil. (68%). ¹H NMR (CDCl₃): δ 5.85 (1H,d), 6.45 (1H,d), 7.4 (5H,m), 9.45 ppm (1H,s). IR (film): ν 3010, 2850, 2820, 1680, 1580, 1440, 1020, 980, 690 cm⁻¹.

3-(Phenylseleno)-3-buten-2-one (IIIc) [6]

The procedure was identical as for IIIe. The product was recrystallised from CCl₄ at -20°C (85%, m.p. 32°C, and was unstable at room temperature). ¹H NMR (CDCl₃): δ 2.4 (3H,s), 5.45 (1H,d), 6.4 (1H,d), 7.4 ppm (5H,m). IR (CH₂Cl₂): ν 3010, 1660, 1600, 1570, 1400, 1360, 1250, 1020, 910 cm⁻¹. Mass spectrum: 226 (M⁺), 183, 157, 77, 43.

AIBN addition to IIIa [11]

α-Phenylselenoacrylonitrile (1.05 g, 5 mmol), AIBN (0.82 g, 5 mmol) and 80 ml benzene were placed in an ampoule which was degassed in three freeze-thaw cycles and sealed under vacuum. Subsequent heating at 80°C during 16 h and evaporation of the solvent gave a residue, which was chromatographed on silica gel (Eluent: CH₂Cl₂/Et₂O, 9/1) to give fumaronitrile (IVa), this was recrystallised from ethyl acetate (0.45 g, 75%, m.p. 149–150°C). ¹H NMR (CDCl₃): δ 1.55 (12H,s), 2.85 ppm (4H,s). IR (CH₂Cl₂): ν 3000, 2250, 1455, 1380, 1200, 910 cm⁻¹. Mass spectrum (DCI, NH₃): 258 (M + 18)⁺.

AIBN addition to IIIb [11]

Same procedure as above; 0.46 g of colorless crystals, 65%, m.p. 131°C recrystallised from ethyl acetate. ¹H NMR (CDCl₃): δ 1.4(12H,s), 2.9 (4H,s), 3.9 ppm (6H,s). IR (CH₂Cl₂): ν 3000, 2250, 1735, 1440, 1245, 1190 cm⁻¹. Mass spectrum: 307 (M + 1)⁺, 275, 238.

Addition of MAIB to IIIb [11]

Same procedure as above using MAIB instead of AIBN; 0.7 g of colorless crystals, 75%, m.p. 81–82°C, recrystallised from ethylacetate, ¹H NMR (CDCl₃): δ 1.15 (12H,s), 2.8(4H,s), 3.6 (6H,s), 3.7 ppm (6H,s). IR (CH₂Cl₂): ν 2970, 1720, 1435, 1240, 1200, 1145 cm⁻¹. Mass spectrum: 373 (M + 1)⁺, 341, 313, 271.

2-Methyl-2-phenylselenopropionitrile V [11]

Diphenyldiselenide (0.78 g, 2.5 mmoles) and AIBN (0.41 g, 2.5 mmol) in 15 ml benzene were refluxed during 16 h under argon. Evaporation of the solvent and chromatography (SiO₂/CH₂Cl₂) gave nitrile V, which was purified by vacuum distillation (0.62 g, 56%, b.p. 65°C/0.05 Torr). ¹H NMR (CDCl₃): δ 1.6 (6H,s), 7.45 ppm (5H,m). IR (film): ν 3000, 2240, 1420, 1125, 1025, 750 cm⁻¹. Mass spectrum: 225 (M⁺), 199, 157, 77, 68.

2-Methyl-2-phenylselenomethylpropionate VI [10]

Diphenyldiselenide (0.78 g, 2.5 mmol) and MAIB (0.575 g, 2.5 mmol) were refluxed in benzene (15 ml) for 16 h. The usual work-up gives 0.55 g of VI, which was recrystallised from Et₂O/pentane (1/9) at -20°C (Yield 43%, m.p.: 44–45°C) ¹H NMR (CDCl₃): δ 1.5 (6H,s), 3.45 (3H,s), 7.2 ppm (5H,m). IR(CH₂Cl₂): ν 2960, 1725, 1440, 1280, 1160, 1120 cm⁻¹. Mass spectrum: 258 (M⁺), 225, 199, 137, 101, 77.

Acknowledgement

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- 11 Correct elemental analyses were obtained.