Tetrahedron Vol 47, No. 27, pp 5001-5018, 1991
Printed in Great Britain

0040-4020/91 $3.00+00

VICARIOUS NUCLEOPHILIC SUBSTITUTION OF HYDROGEN IN ELECTROPHILIC ALKENES[1]

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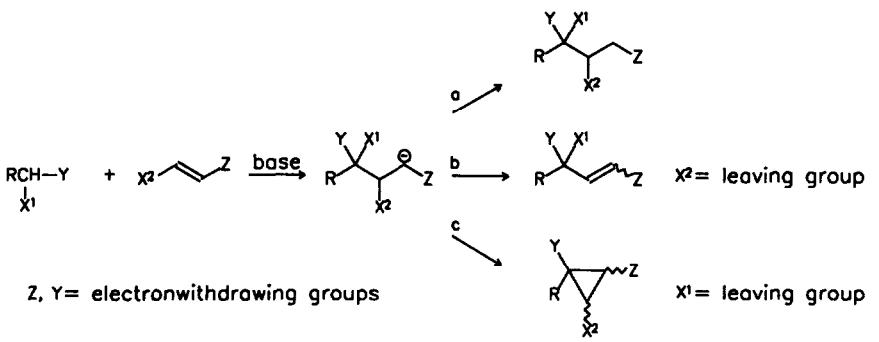
(*Received in UK* 1 *March* 1991)

Abstract: Carbanions containing leaving groups react in the presence of base with electrophilic alkenes giving products in which vinylic hydrogen is replaced with the carbanion moiety. They are formed via addition - β-elimination pathway analogous to the vicarious nucleophilic substitution in nitroarenes. In some cases, however, the cyclization - ring opening process takes place instead.

Nucleophilic addition of carbanions to electrophilic alkenes activated by one or two electron withdrawing groups (the Michael reaction) is one of the most important tools in organic synthesis for formation of a new carbon-carbon bond.[2] The new carbanion - an initial product of the addition - can be stabilized by a few pathways, the major of them are shown on scheme 1.



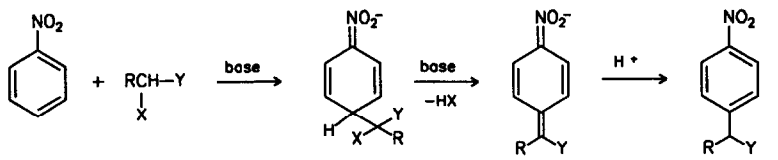
SCHEME 1

The original Michael reaction is terminated by protonation of the adduct (path a).[2] When a leaving group X^1 is present at the β-carbon atom of the alkene, elimination of X^{1-} anion with recovery of the double bond occurs so overall vinylic nucleophilic substitution takes place (path b).[3] On the other hand, when the leaving group is attached to the carbon atom of the nucleophilic reagent, intramolecular S_N2 substitution furnishing a

cyclopropane ring is the most favorable subsequent process (path c)[4].

Reactivity of electrophilic alkenes and arenes shows both similarities and differences. Nucleophilic substitution of halogens or other leaving groups in nitroarenes via addition-elimination mechanism analogous to nucleophilic substitution in electrophilic alkenes (scheme 1 path *b*) is a common process of great practical importance and was subject of thorough mechanistic ivestigations.[5] On the other hand, although the carbanions add undoubtedly to electrophilic aromatic rings also at positions connected with hydrogen and even with a higher rate, due to tendency of arenes to retain energetically favorable aromatic character, nucleophilic addition leads to reasonably stable adducts (known as the Meisenheimer complexes) only when there are two or three nitro groups in the aromatic ring.[5] Such addition to mononitroarenes usually pass unnoticed.[6] For the same reason intramolecular nucleophilic substitution leading to cyclopropane derivatives (scheme 1 path *c*) is very rarely observed in reactions of α-halocarbanions with aromatic electrophiles.[7]

Some years ago we found that nitroarenes react with carbanions containing α-leaving groups **X** in entirely different way. The intermediate σ-adducts formed by attachment of the carbanions to position bearing hydrogen undergo β-elimination of HX leading to nitrobenzylic carbanions, which upon protonation give products of the nucleophilic substitution of hydrogen by the carbanion moiety (scheme 2).[8] This new reaction named Vicarious Nucleophilic Substitution (VNS) is of general character concerning nitroarenes[9] and carbanions in which not only halogens but also PhS, PhO, -NC etc. can serve as the leaving groups eliminated in the second step of the reaction.

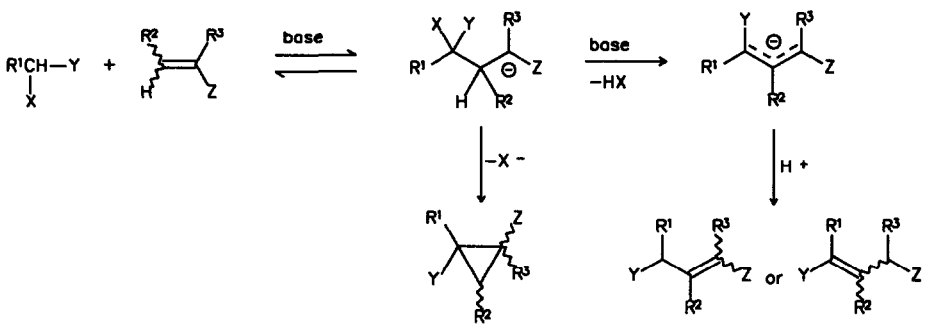


SCHEME 2

The question was then whether it is possible to afford such elimination of HX from the Michael adducts of α-halocarbanions to electrophilic alkenes avoiding formation of the cyclopropanes and to have forth so far unreported reaction pathway (scheme 3).[10]

In our preliminary communication[11] we have shown that such transformation is indeed possible and we have formulated some general requirements concerning starting materials and conditions which favor the elimination

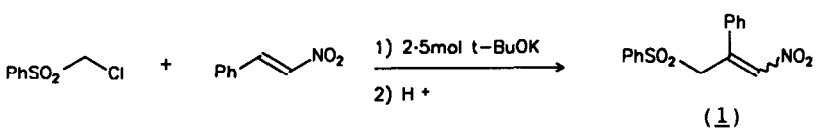
over intramolecular substitution. According to them the VNS will be preferred when: *i*) substituents Z and R^1 provide high stabilization, hence low nucleophilicity, of the intermediate carbanion; *ii*) substituent X can be eliminated as HX *via* an E2 or E1cb process but is rather reluctant toward S_N2 substitution; *iii*) substituent R^2 facilitates abstraction of a geminal proton; *iv*) the reaction is carried out in rather concentrated solutions and the system contains an excess of base.



SCHEME 3

VNS of hydrogen in nitroalkenes.

Nitroalkenes (Z = NO_2 on scheme 3) are known as very active Michael acceptors.[12] Efficient delocalization of the negative charge in the addition product - nitronate anion results in its low nucleophilicity therefore the base promoted elimination of HX should be, and indeed is favored over an intramolecular S_N2 reaction. For instance, chloromethyl phenyl sulphone reacts with β-nitrostyrene in THF, in the presence of an excess of potassium tert-butoxide at -70°C to produce after quenching of the reaction mixture with acid, the product of the vicarious substitution of the vinylic hydrogen atom:



(1)

Many other carbanions containing leaving groups were found to replace the hydrogen in β-nitrostyrene according to the VNS scheme (table 1).

TABLE 1. Reactions of carbanions with nitroalkenes.[a)]

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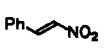
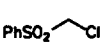
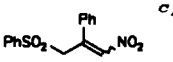
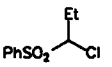
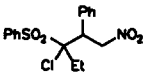
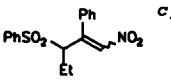
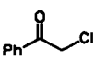
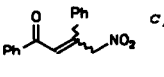
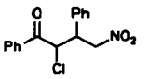
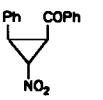
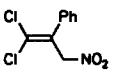
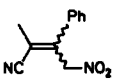
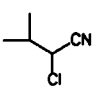
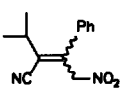
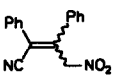
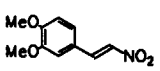
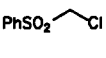
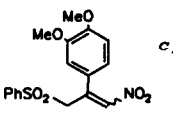
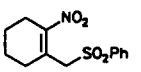
1			-15	1	 [c)]	55
2	"		-50	2		50
3	"	"	+20	3	 [c)]	35
4	"		+10	4	 [c)]	50
5 [b)]	"	"	-70	5		40
6 [b)]	"	"	+20	6		27 [e)]
7	"	$CHCl_3$	+20	7		64
8	"		0	8	 [d)]	62
9	"		0	9	 [d)]	61
10	"		0	10	 [d)]	40
11			-20	11	 [c)]	62
12		"	0	12		46

a) except entry 5 and 6 1:1:2.5 alkene/C-H acid/t-BuOK molar ratio was used
b) 1 equiv. of t-BuOK was used
c) one stereoisomer[13]
d) 1:1 *E* and *Z* isomers
e) 13% of 5 was also isolated

Protonation of the allylic anions, which are initial products of the aliphatic VNS, can produce two regioisomers of the alkenes, nevertheless in all cases only one of them (presumably the thermodynamically most stable) was formed. When unsymmetrically substituted olefin was produced, two geometrical *E* and *Z* isomers could be formed. The α,β-unsaturated nitriles (8,9 and 10) were obtained as 1:1 mixtures of the geometrical isomers, which were separated and individually characterized. The reactions of α-chlorosulphones and phenacyl chloride with β-nitrostyrene were highly stereoselective and led to only one isomer of the product.[13]

The initial temperature at which all the reactions listed in table 1 were carried out was below - 70°C, but only in the case of the reaction of chloromethyl phenyl sulphone with β-nitrostyrene the elimination process occured at that temperature furnishing the final product 1, although the better yield was achieved at higher temperature (entry 1). The reactions of the other carbanions carried out at -70° to -78°C did not go beyond formation of the Michael addition products which seem to be stable and do not react further under such conditions. In a few cases (entry 2,5) they were isolated after quenching with acid and characterized. The final aliphatic VNS products were obtained by warming up the reaction mixture, containing an excess of the base up to 0°C or higher, at which temperature the elimination process was completed. In no case the respective cyclopropane derivative was obtained. It was found that the isolated Michael adduct 2 treated with an equimolar amount of potassium *tert*-butoxide in THF did not cyclize even at room temperature over a few hours. Thus not only methoxy group but also chlorine atom α to the sulphonyl function does not undergo the intramolecular substitution with the nitronate anion and in such cases competition of the cyclisation does not take place at all. On the other hand chlorine atom α to the carbonyl or cyano group can be substituted much more easily and observations made for the reaction of phenacyl chloride show the real competition between the cyclisation and the elimination reaction (entry 4,5,6). The product of the addition of the phenacyl chloride anion to β-nitrostyrene (an anion of 5) obtained at -78°C, when warmed in the reaction mixture without excess of base up to room temperature underwent transformation to the cyclopropane 6 (entry 6), whereas when the second equivalent of the base was present the allylic nitro compound 4 was the only isolated product (entry 4).[14]

Other nitroalkenes (entry 11 and 12) react with chloromethyl phenyl sulphone anion in the same way as β-nitrostyrene. Since 1-nitrocyclohexene is relatively strong CH-acid the reaction was carried out in such a way that the lithium salt of chloromethyl phenyl sulphone was first generated and reacted with the nitroalkene at low temperature. The resulting mixture

was subsequently treated with potassium *tert*-butoxide and warmed up to 0°C.

Replacement of hydrogen in substituted methylenemalonic acid derivatives

Efficient stabilization of the carbanion produced in the addition step of the α-halocarbanions to electrophilic alkenes seems to be the crucial requirement for the subsequent elimination reaction. The nitro group is one of the best in this respect and no other group has been found to be strong enough to enable the VNS process in electrophilic alkenes by itself. On the other hand, when both substituents at C-1 (Z and R^3 on scheme 3) are electron withdrawing groups other then the nitro group, stabilization of the negative charge in the Michael adduct can be sufficient for the elimination to occur. Particularly, arylidenemalonic acid derivatives such as dinitriles, cyanoesters and cyclic diester (the Meldrum acid derivatives) react with chloromethyl phenyl sulphone in the presence of an excess of a base according to scheme 3 giving products of replacement of β-vinylic hydrogen atom with the carbanion moiety (table 2). Corresponding cyclopropanes are not formed under the reaction conditions, and independent experiments have shown that intramolecular substitution of chlorine in the intermediate is much slower than the base-induced elimination of HCl. For example, addition of chloromethyl phenyl sulphone carbanion to benzylidenemalononitrile (entry 2) gave anionic adduct (1:1 mixture of diastereomers) which did not cyclize for many hours at -20°C while an excess of the base caused rapid β-elimination even at -60°C giving the expected VNS product (entry 1).

The rate of the elimination process is very sensitive to the structure of the starting alkene. The reaction is quite fast in the case of the malononitrile and the Meldrum's acid derivative, much slower for the cyanoacetate derivative (the adduct 16 could be isolated when the reaction was arrested at -20°C), whereas the adduct to diethyl benzylidenemalonate is stable toward an excess of base for many hours even at +25°C. The apparent reason for these phenomena is of steric nature. It was expected that *p*-nitrophenyl substituent at the β-carbon atom of the olefin would facilitate abstraction of the vicinal proton from the Michael adduct and consequently also the elimination reaction. Nevertheless, also in this case the elimination process does not occur under the reaction conditions (entry 7). On the other hand, the nitrophenyl ring is an electrophilic entity by itself able to enter the aromatic VNS process (substitution of hydrogen *ortho* to the nitro group), which could compete with the addition of the carbanion to the activated double bond. The Michael addition, however, seems

TABLE 2. Reactions of carbanions with methylenemalonic acid derivatives[a)]

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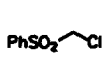
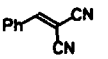
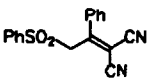
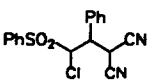
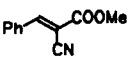
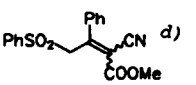
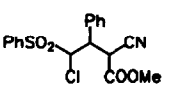
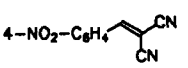
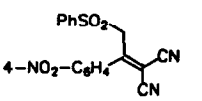
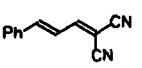
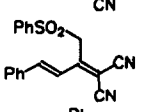
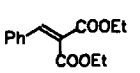
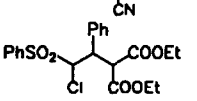
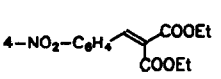
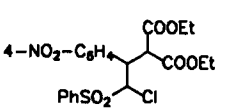
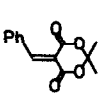
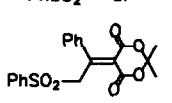
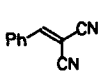
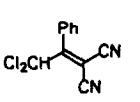
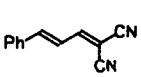
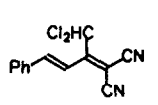
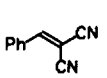
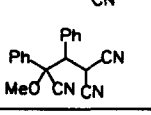
1			-60	13		40
2 [b)]	"	"	-20	14		56
3	"		-20	15	 [d)]	65
				16		12
4	"		-75	17		57
5	"		0	18		36
6	"		0	19		73
7	"		+20	20		63
8	"		0	21		40
9 [c)]	$CHCl_3$		+20	22		34
10 [c)]	"		+10	23		60
11			+20	24		56

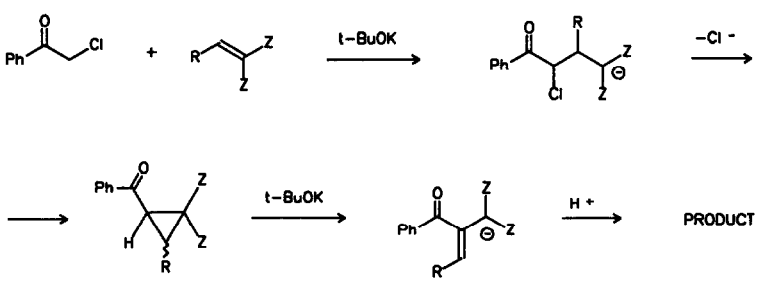
a) except entry 2,9 and 10 1:1:2.5 alkene/C-H acid/t-BuOK molar ratio was used
b) 1 equiv. of t-BuOK was used
c) 1.2 fold excess of $CHCl_3$ over the alkene was taken
d) one stereoisomer[13]

to be faster and practically irreversible reaction, giving a high concentration of the intermediate adduct (contrary to the aromatic σ-adduct formation where the equilibrium is strongly shifted to the left), and the VNS replacement of the hydrogens *ortho* to the aromatic nitro group was not observed, even when the subsequent elimination from the Michael adduct does not occur at all (entry 4 and 7).

Addition of the carbanion to the dienic dinitrile (entry 5 and 10), hence substitution according to the VNS scheme, can occur at β or δ carbon atoms, thus mimics to some extend *ortho*- and *para*- orientation in aromatic systems. The reactions with chloromethyl phenyl sulphone and chloroform were however regioselective and products of the β-substitution 18 and 23 were formed respectively.[16]

The reaction of benzylidenemalononitrile with α-methoxyphenylacetonitrile carbanion gave only the Michael adduct. Even in the reaction carried out in the presence of a great excess of base at room temperature the elimination of MeOH and formation of the VNS product was not detected. This is in contrast with the analogous reaction of β-nitrostyrene (table 1, entry 10).

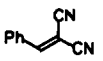
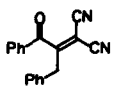
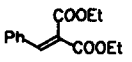
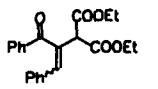
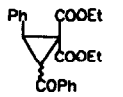
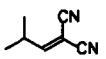
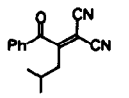
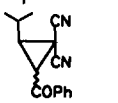
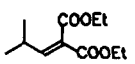
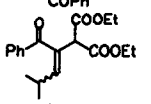
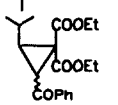
Although phenacyl chloride carbanion reacted with β-nitrostyrene according to the VNS scheme, its reactions with benzylidenemalonic acid derivatives proceed along different pathway. Products of the reactions carried out in the presence of an excess of base were isomeric to those expected from the VNS process (table 3). Structure of these products and also facile formation of the corresponding cyclopropanes (27, 29 and 31) when one equivalent of the base was used suggest, that fast cyclization is the initial reaction course, and the alkenes are produced as a result of subsequent base induced cyclopropane ring opening reaction[17] (scheme 4).



SCHEME 4

To confirm this reaction scheme isolated cyclopropane derivatives 27, 29 and 31 were treated with an excess of potassium *tert*-butoxide in THF.

TABLE 3. Reactions of phenacyl chloride with electrophilic alkenes.

ENTRY	ALKENE	*t*-BuOK EQUIV.	FINAL TEMP. °C	PRODUCT No.	PRODUCT STRUCTURE		PRODUCT YIELD %
1		2.5	0	25			50
2		2.5	-10	26		*a)*	41
3	"	1	+10	27		*b)*	58
4		2.5	+20	28			42
5	"	1	+20	29		*c)*	54
6		2.5	+20	30		*a)*	50
7	"	1	+15	31		*d)*	82

a) one stereoisomer[13]
b) *cis* : *trans* 1.2 : 1 (isolated)[32]
c) *trans* isomer[33]
d) *cis* : *trans* 2 : 1 (isolated)[32]

According to our expectations, they underwent fast ring opening process leading to products identical with those obtained in the direct reactions (entry 2,4 and 6).

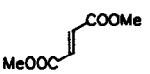
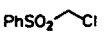
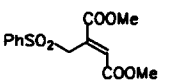
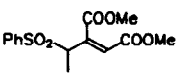
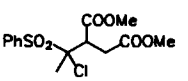
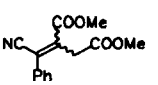
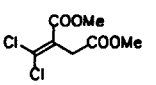
All above observations show, that VNS of the *β*-hydrogen in unsaturated malonic acid derivatives is much more difficult than in the nitroalkenes, not only for steric hindrances which can make the anionic adducts unreactive in the elimination process as in the case of the addition to diesters. It appears that an important role plays also a serious competition of the cyclization reaction (case of phenacyl chloride) and/or lower tendency to the base promoted elimination of the HX molecule from the anionic intermediates (case of the methoxy nitrile). Both of these phenomena prove the difference between ability to delocalize of negative charge by one nitro and even two weaker electronwithdrawing substituents

such as cyano groups, which was observed also in vinylic substitution reactions in related nitroalkenes and methylenemalonic acid derivative.[18]

Replacement of hydrogen in esters of maleic and fumaric acid.

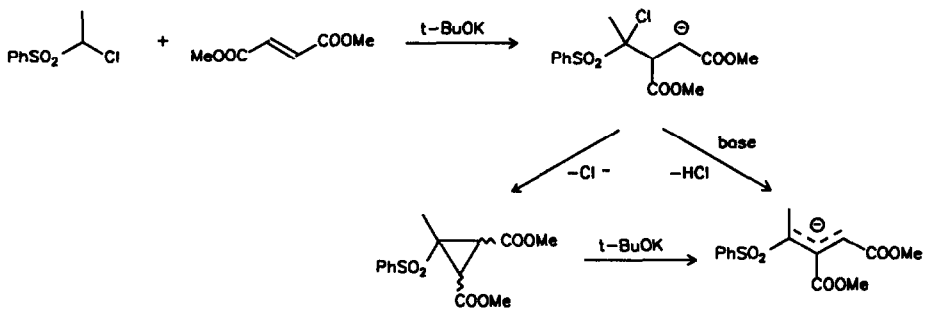
As it was mentioned earlier, sufficient stabilization of the negative charge in the anionic adducts needed for the VNS of hydrogen can be achieved only by nitro group or when two geminal electron withdrawing groups activate the double bond in the alkene. However, there is another possibility to promote the elimination process when the intermediate carbanion is not sufficiently stabilized, namely by activation of the hydrogen atom to be abstracted. This can be accomplished by introducing an electron withdrawing group at the β-position of the alkene, as it is in maleic or fumaric acid derivatives. Thus, dimethyl maleate and fumarate react with some carbanions bearing leaving groups to form expected products of the VNS reaction (table 4).

TABLE 4. Reactions of carbanions with dimethyl fumarate and maleate.

ENTRY	ALKENE	C-H ACID	*t*-BuOK EQUIV.	FINAL TEMP. °C	PRODUCT No.	PRODUCT STRUCTURE		YIELD %
1			2.5	-75	32		*a)*	77
2	"		2.5	-20	33		*b)*	57
3	"	"	1	+10	34			38
					33			38
4	"		2.5	-50	35		*c)*	46
5		$CHCl_3$	2.5	-70	36			44

a) *E* isomer[19]
b) *Z* isomer[20]
c) 2:1 mixture of stereoisomers[13]

The mechanism of the reaction can be undoubtedly considered as an addition - base promoted elimination scheme (VNS) only when the methoxy substituent - reluctant toward S_N2 process - acts as the leaving group. For the reactions of the α-chloro carbanions a ring opening reaction of the cyclopropane intermediate should also be considered because it would lead to the same products as the "direct" VNS process (scheme 5).



SCHEME 5

Several different conditions (amount of base, temperature) were used for the reaction of 1-chloroethyl phenyl sulphone with dimethyl fumarate to found the cyclopropane intermediate. However, even when only equimolar amount of the base was used for generation of the sulphone anion the reaction furnished equimolar mixture of the adduct 34 and the final substitution product 33 (entry 3). The expected cyclization of the initially formed addition product did not occur. Apparently this is caused by the fact, that the adduct exists in the reaction mixture in protonated form, rather than by its inability to cyclize. Formation of the VNS product in this reaction accords with this explanation, because the elimination reaction leading to 32 requires a base, the role of which can play the anion of the adduct. As a consequence of these processes the anion of the adduct is partially protonated and both products - 33 and 34 are formed in equimolar amounts.

Although the VNS scheme explains the results obtained, the cyclisation - ring opening reaction sequence for the formation of the substitution products cannot be definitely excluded.

The results presented in this paper along with some others reported earlier show, that the vicarious nucleophilic substitution scheme,

originally formulated for nitroaromatic compounds, is also fully applicable to strongly electrophilic alkenes. However, due to lack of strong driving force for HX elimination from the Michael adducts - such as rearomatization energy of σ-complexes in the case of aromatic systems - the scope of the aliphatic VNS reaction seems to be much more limited.

EXPERIMENTAL

Melting points are uncorrected. IR spectra were recorded in $CHCl_3$ on Beckmann IR 4240 spectrometer (only characteristic bands are given). ^{1}H-NMR spectra were taken in $CDCl_3$ unless noted otherwise (chemical shifts are given in δ ppm refered to TMS) on Varian EM-300 (60 MHz), Bruker AM-500 (500 MHz) and Varian Gemini 200 (200 MHz) spectrometers. ^{13}C-NMR spectra were recorded on Bruker AM-500 (125 MHz). Mass spectra were obtained on Finnigan 8200(70eV) spectrometer. Column chromatography was performed using silica gel 230-400 mesh (E.Merck).

The following reagents were prepared according to the known methods: Chloromethyl phenyl sulphone,[23] 1-chloroethyl phenyl sulphone,[24] 1-chloropropyl phenyl sulphone,[25] 2-chloro-3-metyl-butanenitrile,[26] methoxy(phenyl)acetonitrile,[27] 1-nitrocyclohexene,[28] (3-phenyl-2-propenylidene)propanedinitrile,[29] substituted methylenemalonic acid derivatives and nitrostyrenes.[30] The other reagents were commercial.

General procedure for VNS of hydrogen in electrophilic alkenes.

Method A: To a stirred solution of potassium *tert*-butoxide (550 mg, 5 mmol) in THF (15 mL) a solution of the carbanion precursor (2 mmol) in THF (3mL) was added dropwise at -78°C under nitrogen. The mixture was stirred for 5 min and the alkene (2 mmol) in THF (3mL) was added slowly. After stirring for 10 min below -70°C the cooling bath was removed and the reaction mixture was allowed to warm up to the temperature specified in the apropriate table, and kept at that temperature for 10 min. The mixture was then poured into cold NH_4Cl solution, slightly acidified with diluted hydrochlorid acid and extracted three times with methylene chloride. The combined extracts were washed with water and dried with anhydrous $MgSO_4$. The solvent was evaporated *in vacuo* and the products were isolated from the residue by crystallization or column chromatography as described for particular cases:

1-Nitro-2-phenyl-3-(phenylsulphonyl)propene (1):
Crystallized from ethanol, mp 107-110°C, ^{1}H-NMR(60MHz): 5.14(s, 2H); 7.2-8.2(m, 11H). ^{13}C-NMR: 56.6(t), 127.5, 128.1, 129.6, 130.9(d), 134.1(d), 134.7, 138.6, 138.7, 139.5(d). IR. 1350, 1530 cm^{-1}(=C-NO_2). Anal. calcd. for $C_{15}H_{13}NO_4S$: C - 59.37, N - 4.31, H - 4.27%. Found: C - 59.39, N - 4.61, H - 4.32%.

1-Nitro-2-phenyl-3-(phenylsulphonyl)-2-pentene (3):
Column chromatography (hexane/AcOEt 6:1), recryst. from methanol, mp 83°C, ^{1}H-NMR(60MHz): 0 84(t, J = 7.5Hz, 3H); 2.25(q, J = 7.5Hz, 2H); 6.1(s, 2H); 7.1-8.3(m, 10H) IR: 1565, 1385 cm^{-1}(-NO_2). Anal. calcd. for $C_{17}H_{17}NO_4S$: C - 61.62, H - 5.17, N - 4.23, S - 9 67% Found: C - 61.57, H - 5.09, N - 4.22, S - 9.52%.

4-Nitro-1,3-diphenyl-2-buten-1-one (4):
Column chromatography (hexane/AcOEt 5·1), pale yellow oil. ^{1}H-NMR(500 MHz)· 6.00(s, 2H); 7.45-7 65(m, 9H); 8.00-8.05(m, 2H). IR: 1665 (C=O),1560, 1375 cm^{-1} (-NO_2). High-resolution mass spectrum calcd.for $C_{16}H_{13}O$ (M^+ - NO_2) 221.0993, found 221.0966.

4-Nitro-2,3-diphenyl-2-butenenitrile (10):
Short column chromatography (hexane/AcOEt/CH_2Cl_2 5:1:2), oil, a 1:1 mixture of two stereoisomers. ^{1}H-NMR (60 MHz): *E*- 5 36(s, 2H); 7.5(s, 10H). *Z*- 5.7(s, 2H); 7.0-

7.7(m, 10H). Pure E isomer was isolated from the mixture by crystallization and recrystallization from methanol, mp 145°C. IR: 2220 (CN), 1565, 1375 cm^{-1} (NO_2). High-resolution mass spectrum calcd. for $C_{16}H_{12}N_2O_2$ 264.0899, found 264.0898.

1-Nitro-2-(3,4-dimethoxyphenyl)-3-(phenylsulphonyl)propene (11):
Column chromatography (hexane/AcOEt 2:1), recryst. from methanol, yellow crystals mp 128-130°C. ^{1}H-NMR (500 MHz): 3.93(s, 6H); 5.14(s, 2H); 6.91(d, J = 8.5 Hz, 1H); 7.8(d, J = 2.3 Hz, 1H); 7.16(dd, J = 8.5, 2.3 Hz, 1H); 7.38(s, 1H); 7.53(m, 2H); 7.66(m, 2H); 7.89(m, 1H). IR: 1525, 1340(=C-NO_2). Anal. calcd. for $C_{17}H_{17}NO_6S$· C - 56.19, H - 4.72, N - 3.85%. Found: C - 56.20, H - 4.54, N - 4.03%.

[1-Phenyl-2-(phenylsulphonyl)ethylidene]propanedinitrile (13):
Column chromatography (hexane/AcOEt 2:1), recryst. from methanol, mp 123-124°C. ^{1}H-NMR (60 MHz): 4.67(s, 2H); 7.3-7.9(m, 10H). IR: 2250 cm^{-1}(CN). Anal. calcd. for $C_{17}H_{12}N_2SO_2$: C - 66.22, H - 3.92, N - 9.08%. Found: C - 66.26, H - 3.86, N - 9.04%.

Methyl 2-cyano-3-phenyl-4-phenylsulphonyl-2-butenoate (15):
Column chromatography (hexane/AcOEt 4:1 to 2:1), oil. ^{1}H-NMR (60 MHz): 3.8(s, 3H); 5.3(s, 2H); 7.3-8.0(m, 10H). Anal. calcd. for $C_{18}H_{15}NO_5S$: C - 63.33, H - 4.43, N - 4.10%. Found: C - 63.21, H - 4.38, N - 4.02%.

Methyl 4-chloro-2-cyano-3-phenyl-4-(phenylsulphonyl)butanoate (16):
Column chromatography (hexane/AcOEt 4:1 to 2:1), recryst. from ethanol, mp 167°C, a 1 1.7 mixture of two diastereomers. ^{1}H-NMR (500 MHz); *major isomer*- 3.65(s, 3H); 4.28(dd, J = 5.9, 9.8 Hz, 1H); 4.94(d, J = 5.9 Hz, 1H); 5.29(d, J = 9.8 Hz, 1H); 7.2-8.0(m, 10H); *minor isomer*- 3.66(s, 3H); 4.41(d, J = 8.5 Hz, 1H); 4.46(dd, J = 8.5, 5.6 Hz, 1H); 5.51(d, J = 5.6 Hz, 1H); 7.2-8.0(m, 10H). High-resolution mass spectrum calcd. for $C_{18}H_{16}NO_4SCl$ 377 0489, found 377.0490

[1-[(Phenylsulphonyl)methyl]-3-phenyl-2-propenylidene]propanedinitrile (17):
Column chromatography (CH_2Cl_2), recryst. from ethanol, mp 148°C (dec.). ^{1}H-NMR (60 MHz): 4.7(s, 2H); 7.4-8.0(m, 7H); 8.2(d, J = 6 Hz, 2H). IR: 2230 (CN), 1530, 1355 cm^{-1} (-NO_2). Anal. calcd. for $C_{17}H_{11}N_3O_4S$· C - 57.78, H - 3.14, N - 11.89, S - 9.07%. Found: C - 57.38, H - 2.70, N - 11.75, S - 8 82%. High-resolution mass spectrum calcd. 353.0470, found 353.0466.

[1-[(Phenylsulphonyl)methyl]-3-phenyl-2-propenylidene]propanedinitrile (18):
The crude product was treated with hexane/AcOEt 2:1, the solid was filtered off and recrystalized from CH_3CN, mp 190°C (dec.). ^{1}H-NMR (500 MHz): 4.72(s, 2H); 7.29(d, J = 15.8 Hz, 1H), 7.36(d, J = 15.8 Hz, 1H); 7.40-7.75(m, 8H); 4.94-4.98(m, 2H). IR: 2240 (CN), 1620, 1540 cm^{-1}. Anal. calcd. for $C_{19}H_{14}N_2SO_2$: C - 68.24, H - 4.22, N - 8.38, S - 9 59%. Found: C - 67.93, H - 3.95, N - 8.28, S - 9.43%.

2,2-Dimethyl-5-(1-phenyl-2-phenylsulphonyl)ethylidene-1,3-dioxane-4,6-dione (21):
Cryst. and recryst. from ethanol, mp 152°C (dec.). ^{1}H-NMR (60 MHz): 2.0(s, 6H); 5.27(s, 2H); 7.2-8.0(m, 10H). IR: 1780, 1740, 1610 cm^{-1}. High-resolution mass spectrum calcd. for $C_{20}H_{18}O_6S$ 371.0597, found 371.0589.

Dimethyl 2-[(phenylsulphonyl)methyl]-2-butenedioate (32):
Column chromatography (hexane/AcOEt 3.1), recryst. from CCl_4/hexane, mp 64°C. ^{1}H-NMR (60 MHz): 3.56(s, 3H); 3.65(s, 3H); 4.83(s, 2H); 6.82(s, 1H); 7 3-8.0(m, 5H) ^{13}C-NMR· 52.1(q), 53.0(q), 53.3(td, $J_{C-C=C-H}$ = 8 2 Hz), 128.7(d), 128.9(d), 132.1(d), 133 7(d), 134.2(s), 138.6(s), 164.6(s), 165 1(s). IR: 1736 cm^{-1}, MS m/e: 298(7), 267(11), 157(38), 126(100), 98(24). Anal. calcd. for $C_{13}H_{14}SO_6$: C - 52.31, H - 4.73, S - 10.75%. Found: C - 52.27, H - 4.63, S - 10.11%.

Dimethyl 2-[1-(phenylsulphonyl)ethyl]-2-butenedioate (33):
Column chromatography (hexane/AcOEt 2:1), oil. ^{1}H-NMR (500 MHz): 1.55(d, J = 7.2 Hz, 3H); 3 68(s, 3H); 3.76(s, 3H); 4.35(qd, J = 7.2, 0.8 Hz, 1H); 6.17(d, J = 0.8 Hz, 1H); 7.54-7.59(m, 2H); 7.66-7.69(m, 1H); 7.85-7.88(m, 2H). ^{13}C-NMR: 13.1(q), 52.1(q), 52.5(q), 61.3(dqd, $J_{C-C=C-H}$=5.5 Hz) 129.0(d), 129.6(d), 134.2(d), 136.1(s), 137.8(s), 165.3(s),

165.8(s). IR: 1740 cm^{-1}. MS m/e: 312(26), 281(95), 171(39), 139(100), 111(23). Anal. calcd. for $C_{14}H_{16}SO_6$: C - 53.84, N - 5.16%. Found: C - 53.94, N - 5.11%.

Dimethyl 2-(α-cyanobenzylidene)butanedioate (35):
Column chromatography (hexane/AcOEt 5:1), oil, a 2·1 mixture of stereoisomers. ^{1}H-NMR (60 MHz): *major isomer*- 3 33(s, 2H); 3.60(s, 3H); 3.82(s, 3H); 7.31(s, 3H); *minor isomer*- 3.43(s, 2H); 3.66(s, 3H); 3.72(s, 3H); 7.25(s, 5H). IR: 2235, 1750 cm^{-1}. Anal. calcd. for $C_{14}H_{13}NO_4$: C - 64.85, H - 5.05, N - 5.45%. Found: C - 64.83, H - 5.02, N - 5.09%.

Method B: The same as method ***A*** except that both reagents - the carbanion precursor (2.2 mmol) and the alkene (2 mmol) dissolved in THF (5 mL) were added to a solution of potassium *tert*-butoxide (220 mg, 2 mmol) in THF, maintaining the temperature below -70°C.

1,1-Dichloro-3-nitro-2-phenylpropene (7):
Column chromatography (hexane/AcOEt 20:1), oil. ^{1}H-NMR(60 MHz): 5.3(s, 2H); 7.35(s,5H) IR: 1568, 1375 cm^{-1} (-NO_2). High-resolution mass spectrum calcd. for $C_9H_8NO_2Cl_2$ 230.9854, found 230.9858.

2-Methyl-4-nitro-3-phenyl-2-butenenitrile (8):[22]
Column chromatography (hexane/EtOAc 3:1); *E-isomer*: oil, ^{1}H-NMR(60 MHz): 1.95(s, 3H); 5.4(s, 2H); 7.0-7.5(m, 5H). *Z-isomer*: oil, ^{1}H-NMR(60 MHz). 2.1(s, 3H), 5.26(s, 2H); 7.3(s, 5H). The products very unstable.

(E,Z)-2-(1-Methylethyl)-4-nitro-3-phenyl-2-butenenitrile (9):[22]
Column chromatography (hexane/AcOEt 5:1); *E-isomer*: oil, ^{1}H-NMR (200 MHz): 1.16(d, J = 6.7 Hz, 6H); 2.68(sep, J = 6.7 Hz, 1H); 5.50(s, 2H); 7 1-7 2(m, 2H); 7.40-7.45(m, 3H). *Z-isomer*: oil, ^{1}H-NMR (200 MHz): 1.29(d, J = 6.7 Hz, 6H); 2.95(sep, J = 6.7 Hz, 1H), 5.41(s, 2H); 7.30-7.45(m, 5H). High-resolution mass spectrum calcd. for $C_{13}H_{14}N_2O_2$ (M^+ - CH_3) 230.1051, found 230.1055.

2-Cyano-4,4-dichloro-3-phenyl-2-butenenitrile (22):
Column chromatography (hexane/AcOEt 10:1), recryst. from hexane, mp 55°C. ^{1}H-NMR (60 MHz). 6 8(s, 1H); 7.41(s, 5H). IR: 2240 cm^{-1}(CN). Anal. calcd. for $C_{11}H_6N_2Cl_2$: C - 55.73, H - 2 55, N - 11.82, Cl - 29.91%. Found: C - 55.71, H - 2.27, N - 11.82, Cl - 29 76%.

[1-(Dichloromethyl)-3-phenyl-2-propenylidene]propanedinitrile (23):
Short column chromatography ($CHCl_3$), recryst. from hexane/ethanol, mp 150°C. (dec.). ^{1}H-NMR (500 MHz): 6 92(d, J = 1 Hz, 2H); 7.14(dd, J = 16.4, 1 Hz, 1H); 7.45-7.52(m, 3H); 7.64-7.67(m, 2H); 8.10(d, J = 16.4 Hz, 1H). IR: 2220 cm^{-1}. High-resolution mass spectrum calcd. for $C_{13}H_8N_2Cl_2$ 262.0065, found 262.0063.

Dimethyl 2-(dichloromethylene)butanedioate (36):[31]
Column chromatography (hexane/AcOEt 5:1), oil. ^{1}H-NMR (60 MHz) 3.53(s, 2H); 3.7(s, 3H); 3.8(s, 3H). IR 1750 cm^{-1}

Method C; preparation of ***1-Nitro-2-[(phenylsulphonyl)methyl]cyclohexene*** (12):

To a stirred solution of chloromethyl phenyl sulphone (950 mg, 5 mmol) in dry THF (10 mL), butyllithium (5.5 mmol) in hexane was added at - 70°C under nitrogen After 15 min stirring 1-nitrocyclohexene (630 mg, 5 mmol) in THF (5 mL) was added dropwise. The mixture was stirred for 30 min and a solution of potassium *tert*-butoxide (825 mg, 7 5 mmol,) in THF (10 mL) was slowly added. The cooling bath was removed and the mixture was allowed to warm up to 0°C, then poured into NH_4Claq, acidified with diluted HCl and extracted with methylene chloride. The extract was washed with water, dried ($MgSO_4$) and the solvent was evaporated. The residue was passed through a 5cm SiO_2 pad as a solution in CCl_4. The product obtained (1.0 g, 71%) was recrystalized from methanol to furnish white crystals (0.6 g, 46%) of 12:
Mp 95°C, ^{1}H-NMR(500 MHz): 1.69(m, 2H), 1.75(m, 2H); 2.55(m, 4H); 4.40(s, 2H); 7.56(m, 2H), 7 67(m, 1H); 7.87(m, 2H). IR· 1530, 1330 cm^{-1} (=C-NO_2). Anal calcd. for $C_{13}H_{15}NSO_4$· C -

55.50,, H - 5.37, N - 4.98%. Found: C - 55.52, H - 5.34, N - 5.02%.

Preparation of the adducts.

Compounds 2, 5, 19, 20 and 24 where obtained in reactions following the method *A*, described for the VNS reactions.

3-Chloro-1-nitro-2-phenyl-3-(phenylsulphonyl)pentane (2):
Recryst. from ethanol, mp 133°C. ^{1}H-NMR(500 MHz): 0.82(t, J = 7.4 Hz, 3H); 1.64(dq, J = 15.4, 7.4 Hz, 1H); 1.77(dq, J = 15.4, 7.4 Hz, 1H); 4.72(dd, J = 3.5, 11.0 Hz, 1H); 5.04(dd, J = 11.0, 13.6 Hz, 1H); 5.69(dd, J = 3.5, 13.6 Hz, 1H); 7.25-7.35(m, 3H); 7.44-7.47(m, 2H); 7.61-7.65(m, 2H); 7.74-7.77(m, 1H); 8 05-8.08(m, 2H). IR: 1565, 1385 cm^{-1}(-NO_2). Anal. calcd. for $C_{17}H_{18}NSO_4Cl$: C - 55.51, H - 4.93, N - 3.81, S - 8.72, Cl - 9.64%. Found: C - 55.21, H - 4.80, N - 3.64, S - 8.59, Cl - 9.52%.

Diethyl [2-chloro-1-phenyl-2-(phenylsulphonyl)ethyl]malonate (19):
Recryst. from methanol, mp 98°C. ^{1}H-NMR (500 MHz): 0.91(t, J = 7.1 Hz, 3H); 1.26(t, J = 7.1 Hz, 3H); 3.87(q, J = 7.1 Hz, 2H); 4.10(d, J = 11.3 Hz, 1H); 4.20(dq, J = 7.1, 10.8 Hz, 1H); 4.24(dq, J = 7.1, 10.8 Hz, 1H); 4.69(dd, J = 3.4, 11.3 Hz, 1H); 5.58(d, J = 3.4 Hz, 1H); 7.25-7.3(m, 3H); 7.45-7.5(m, 4H); 6.6(m, 1H); 7.77-7.8(m, 2H). Anal. calcd. for $C_{21}H_{23}O_6SCl$: C - 57.47, H - 5.28, S - 7.30, Cl - 8.08%. Found: C - 57.14, H - 5 13, S - 7.12, Cl - 8.00%.

Diethyl [2-chloro-1-(4-nitrophenyl)-2-(phenylsulphonyl)ethyl]malonate (20):
Recryst. from methanol, mp 138°C. ^{1}H-NMR (500 MHz): 0.98(t, J = 7.1 Hz, 3H); 1.27(t, J = 7.1 Hz, 3H); 3.92(q, J = 7.1 Hz, 2H); 4.13(d, J = 11.4 Hz, 1H); 4.23(m, 2H); 4.86(dd, J = 3 3, 11.3 Hz, 1H); 5.55(d, J = 3.3 Hz, 1H); 7.5-7.56(m, 2H); 7.60-7.70(m, 3H); 7 83-7.9(m, 2H); 8.15-8.20(m, 2H). Anal. calcd. for $C_{21}H_{22}NO_8SCl$: C - 52.12, H - 4.58, N - 2.86, S - 6.97, Cl - 7.23%. Found: C - 52.17, H - 4.28, N - 2.86, S - 6.97, Cl - 7.23%.

4-Cyano-2-methoxy-2,3-diphenylpentanedinitrile (24):
Column chromatography (hexane/AcOEt 4:1), mp 109-110°C, a 2.1 mixture of diastereoisomers. ^{1}H-NMR (500 MHz): *major isomer*- 3.46(s, 3H); 3.67(d, J = 6.2 Hz, 1H); 4.42(d, J = 6.2 Hz, 1H); 7.18-7.40(m, 10H); *minor isomer*- 3.43(s, 3H), 3.61(d, J = 6.5 Hz, 1H); 4.68(d, J = 6.5 Hz, 1H); 7 18-7.40(m, 10H). IR: 2230 cm^{-1}(CN). Anal. calcd. for $C_{19}H_{15}N_3O$: C - 75.73, H - 5.02, N - 13.94%. Found: C - 75.67, H - 4.90, N - 13.98%.

The adducts 5, 14 and the cyclopropane derivative 6 were obtained following the method *A* except that 1 equiv. (220 mg, 2 mmol) of potassium *tert*-butoxide was used.

2-Chloro-4-nitro-1,3-diphenylbutan-1-one (5):
Column chromatography (hexane/AcOEt 10:1), recryst. from methanol, mp 92-93°C. ^{1}H-NMR(500 MHz): 4.40(ddd, J = 9.4, 8.5, 4.3 Hz, 1H); 4.98(dd, J = 13.2, 9.5 Hz, 1H); 5.18(dd, J = 13.2, 4.3 Hz, 1H); 5.49(d, J = 8.5 Hz, 1H); 7.23-7.28(m, 5H); 7.43-7.47(m, 2H), 7.57-7.59(m, 1H); 7.85-7.88(m, 2H). IR· 1700 (C=O), 1560, 1380 cm^{-1} (-NO_2). Anal. calcd. for $C_{16}H_{14}NO_3Cl$: C - 63.27, H - 4.65, N - 4.61%. Found: C - 63.40, H - 4.64, N - 4.44%.

[2-chloro-1-phenyl-2-(phenylsulphonyl)ethyl]propanedinitrile (14):
Cryst. and recryst. from ethanol, mp 150-151°C, a 1 : 1.1 mixture of diastereoisomers. ^{1}H-NMR (500 MHz): *major isomer* - 4.25(dd, J = 4.2, 5.9 Hz, 1H); 4.88(d, J = 4.2 Hz, 1H); 5.19(d, J = 5.9 Hz, 1H); 7.4-7.95(m, 10H); *minor isomer* - 4.19(dd, J = 6.7, 8.6 Hz, 1H), 5.05(d, J = 6.7 Hz, 1H), 5.20(d, J = 8.6 Hz, 1H), 7 4-7.95(m, 10H). Anal.calcd for: $C_{17}H_{13}N_2O_2SCl$. C - 59.22, H - 3.80, N - 8.12, S - 9 30, Cl - 10 28% Found: C - 58.96, H - 3.57, N - 8.04, S - 9.1, Cl - 10.02%

(cis)-1-Benzoyl-(trans)-2-nitro-3-phenylcyclopropane (6):
Column chromatography (hexane/AcOEt 5:1), recryst. from ethanol, mp 99°C. ^{1}H-NMR (500 MHz). 3.91(dd, J = 11.4, 4.8 Hz, 1H); 4.13(dd, J = 11.4, 3.7 Hz, 1H); 5.50(dd, J = 4.8, 3.7 Hz, 1H); 7.14-7.25(m, 5H); 7.46-7.50(m, 2H); 7.58-7.60(m, 1H), 7.95-7.97(m, 2H). IR: 1675 (C=O), 1555, 1370 cm^{-1} (-NO_2). Anal. calcd. for $C_{16}H_{13}NO_3$: C - 71 90, H - 4.90, N - 5.24%.

Found: C - 71.47, H - 4.73, N - 5.08%.

General procedure for reactions of phenacyl chloride with methylenemalonic acid derivatives.
To a stirred solution of potassium *tert*-butoxide (220 mg, 2 mmol or 550 mg, 5 mmol - as specified in table 3) in THF (3 mL) phenacyl chloride (308 mg, 2 mmol) in THF (2 mL) was added dropwise at -78°C. After 5 min a solution of the alkene (2 mmol) in THF (3 mL) was added slowly, maintaining the temperature below -70°C and the mixture was stirred for 10 min. The cooling bath was then removed and the mixture was allowed to warm up to the final temperature specified in table 3, then poured into water acidified with HCl and extracted with methylene chloride. The extract was washed with water, dried ($MgSO_4$) and the solvent was evaporated. The product was isolated by column chromatography or simply recrystallized - as indicated for the particular cases.

***(1-Benzoyl-2-phenylethylidene)propanedinitrile* (25):**
Recryst. from ethanol, mp 106°C. ^{1}H-NMR(60 MHz): 4.23(s, 2H); 7.25-7.8(m, 10H). IR: 2240 (CN), 1680 cm^{-1} (C=O). Anal. calcd. for $C_{18}H_{12}N_2O$: C - 79.39, H - 4.44, N - 10.29%. Found: C - 79.05, H - 4.13, N - 10.36%.

***Diethyl (1-benzoyl-2-phenylethylidene)malonate* (26):**
Column chromatography (hexane/AcOEt 5:1), oil. ^{1}H-NMR (60 MHz): 1.2(t, J = 7 Hz, 6H); 4.13(q, J = 7 Hz, 4H); 4.6(s, 1H); 6.8-7.7(m, 10H). IR: 1735, 1745, 1650 cm^{-1}. High-resolution mass spectrum calcd. for $C_{22}H_{22}O_5$ 366.1467, found 366.1460.

***Diethyl 2-benzoyl-3-phenyl-1,1-cyclopropanedicarboxylate* (27):**[32]
Column chromatography (hexane/AcOEt 30:1 to 15:1), two stereoisomers separated as oils. ^{1}H-NMR (500 MHz): *cis*- 1.10(t, J = 7.1 Hz, 3H); 1.33(t, J = 7 1 Hz, 3H); 3.45(d, J = 9.9 Hz, 1H); 3.85(d, J = 9.9 Hz, 1H); 4.09(dq, J = 7.1, 10.8 Hz, 1H); 4.16(dq, J = 7.1, 10.8 Hz, 1H); 4.29(dq, J = 7.1, 10.8 Hz, 1H); 4.35(dq, J = 7.1, 10.8 Hz, 1H); 7.20-7.35(m, 5H); 7.55-7.65(m, 1H); 8.02-8.06(m, 2H); *trans*- 0.99(t, J = 7.1 Hz, 3H); 1.11(t, J = 7.1 Hz, 3H); 3.89(d, J = 7.7 Hz, 1H); 4.01(q, 7.1 Hz, 2H); 4.12(d, J = 7.7 Hz, 1H); 4.14(q, J = 7.1 Hz, 2H); 7.2-7.35(m, 5H); 7.48-7.53(m, 2H); 7.59-7.65(m, 1H), 8.1-8.13(m, 2H). Anal. calcd. for $C_{22}H_{22}O_5$: C - 72.11, H - 6.05%. Found: C - 72.06, H - 6 11%.

***(1-Benzoyl-3-methylbutylidene)propanedinitrile* (28):**
Column chromatography (hexane/AcOEt 4:1), recryst. from methanol, mp 77-79°C. ^{1}H-NMR (200 MHz): 1.04(d, J = 6,7 Hz, 6H); 1.92(m, 1H); 2.79(d, J = 7.1 Hz, 2H); 7.5-7.9(m, 5H). IR: 2240 (CN), 1680 cm^{-1} (C=O). Anal.calcd. for $C_{15}H_{14}N_2O$. C - 75.60, H - 5.92, N - 11.76% Found: C - 75.38, H - 5.68, N - 11.92%.

***2-Benzoyl-3-(1-methylethyl)-1,1-cyclopropanecarbodinitrile* (29):**[33]
Recryst. from ethanol, mp 156-157°C. ^{1}H-NMR (200 MHz): 1.15(d, J = 6.7 Hz, 3H); 1.28(d, J = 6.5 Hz, 3H); 1.65(m, 1H); 2.46(dd, J = 7.6, 10.6 Hz, 1H); 3.40(d, J = 7.6 Hz, 1H); 7.5-7.8(m, 3H); 8.0-8.1(m, 2H). Anal.calcd. for $C_{15}H_{14}N_2O$: C - 75 60, H - 5.92, N - 11.76%. Found: C -75.62, H - 5.78, N - 11.75%.

***Diethyl 1-benzoyl-3-methyl-1-butenylmalonate* (30):**
Column chromatography (hexane/AcOEt 20:1), oil. ^{1}H-NMR (500 MHz): 0.87(d, J = 6.5 Hz, 6H); 1.23(t, J = 7.1 Hz, 6H); 2.21(dsep, J = 6.5, 10.9 Hz, 1H); 4.22(q, J = 7.1 Hz, 4H); 4.46(d, J = 0.9 Hz, 1H); 5.84(dd, J = 0.9, 10,9 Hz, 1H); 7.44-7.48(m, 2H); 7.54-7.56(m, 1H); 7.93-7.95(m, 2H). IR: 1745, 1735, 1655 cm^{-1}. High-resolution mass spectrum calcd. for $C_{19}H_{24}O_5$ 332.1624, found 332.1630.

***Diethyl 2-benzoyl-3-(1-methylethyl)-1,1-cyclopropanedicarboxylate* (31):**[32]
Column chromatography (hexane/AcOEt 20:1), oil, 2:1 *cis/trans* mixture. ^{1}H-NMR (500 MHz): *cis*- 0.81(d, J = 6.7 Hz, 3H); 1.21(d, J = 6.5 Hz, 3H); 1.26(t, J = 7.1 Hz, 3H), 1.29(t, J = 7 1 Hz, 3H); 1.85(dd, J = 9.8, 10.8 Hz, 1H); 2.26(dsep, J = 6 6, 10.8 Hz, 1H); 3.55(d, J = 9.8 Hz, 1H); 4.16-1.32(m, 4H); 7.45-7.50(m, 2H); 7.54-7.57(m, 1H), 7.96-7.99(m, 2H). *trans*- 1.04(d, J = 6.7 Hz, 3H); 1.05(d, J = 6.7 Hz, 3H); 1.09(t, J = 7.1 Hz, 3H); 2.18(t, J = 7.1 Hz, 3H); 1.54(dsep, J = 6.7, 10.5 Hz, 1H); 2.38(dd, J = 10.5, 7.3 Hz, 1H); 3 50(d, J = 7.3 Hz, 1H); 4.07(dq, J = 10.8, 7.1 Hz, 1H); 4.10(dq, J = 10.8, 7.1 Hz, 1H); 4.16-

4.30(m, 2H); 7.45-7.50(m, 2H); 7.54-7.57(m, 1H); 8.0-8.06(m, 2H). Anal. calcd. for $C_{19}H_{24}O_5$: C - 68.66, H - 7.28%. Found: C - 68.68, H - 7.42%.

Reaction of 1-chloroethyl phenyl sulphone with diethyl fumarate.

The reaction was carried out according to the method ***A***, described for the VNS process, except that 1 eqiv. (220 mg, 2.0 mmol) of potassium *tert*-butoxide was used. The crude mixture of the reaction products was separated by column chromatography (hexane/AcOEt 5:1 to 2:1) to give 235 mg (38%) of 33 and 265 mg (38%) of the adduct 34.

Dimethyl 2-[1-chloro-1-(phenylsulphonyl)ethyl]butanedioate **(34):**

Oil, a 2·1 mixture of diastereomeres. ^{1}H-NMR(500 MHz): *major isomer*: 1.83(s, 3H); 3.09(dd, J = 11.3, 17 1 Hz, 1H); 3.20(dd, J = 3.1, 17 1 Hz, 1H); 3.68(s, 3H); 3.75(dd, J = 3.1, 11.3 Hz, 1H); 3.81(s, 3H); 7.60-7.63(m, 2H); 7.71-7.76(m, 1H); 8.02-8.04(m, 2H); *minor isomer:* 1.99((s. 3H); 3.04(dd, J = 11.9, 16.9 Hz, 1H); 3.39(dd, J = 2.8, 16.9 Hz, 1H), 3.70(s, 3H); 3.74(s, 3H); 3.77(dd, J = 2.8, 11.9 Hz, 1H); 7.60-7.63(m, 2H); 7.70-7.75(m, 1H); 7.96-8.00(m, 2H). Anal. calcd. for $C_{14}H_{17}O_6SCl$: C - 48.21, H - 4.91, S - 9.19, Cl - 10.16%. Found: C - 48.10, H - 4.98, S - 9.33, Cl - 10.08%.

Acknowledgement: This work was supported by Polish Academy of Sciences, Grant CPBP 01.13.

References and notes

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