Pergamon

Tetrahedron Vol. 51, No. 33, pp. 9223-9240, 1995

0040-4020/95 $9.50+0.00

0040-4020(95)00527-7

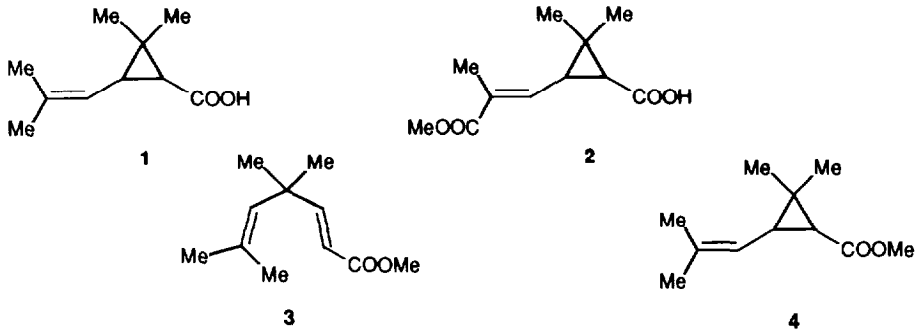
A New Photochemical Synthesis of Cyclopropanecarboxylic Acids Present in Pyrethroids by the Aza-di-π-methane Rearrangement

Diego Armesto,* Mar G. Gallego, William M. Horspool and Antonia R. Agarrabeitia

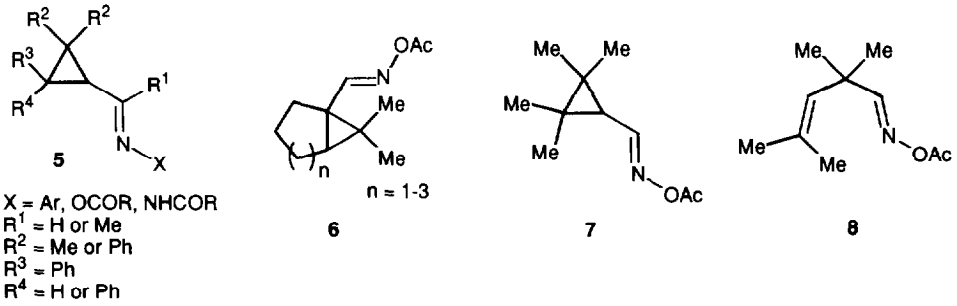
Departamento de Química Orgánica I, Facultad de Ciencias Químicas, Universidad Complutense, 28040-Madrid, Spain.

Abstract: *A novel synthetic route to chrysanthemic acid, 2-cyclopentylidenmethyl-3,3-dimethylcyclopropanecarboxylic acid, fluorenespiro-2,2-dimethylcyclopropanecarboxylic acid and indenespiro-2,2-dimethylcyclopropanecarboxylic acid, all of them present in pyrethroids of known insecticidal activity, is described. The key step in the synthesis is the aza-di-π-methane rearrangement of some 1-aza-1,4,6-trienes and some 1-aza-1,4-dienes, using triplet sensitization.*

As a result of the increasing deterioration of the environment and the strictness of the legislation governing control of pollution the consumption of ecologically safe insecticides has increased dramatically in the last decade. The two most important lines of research at present in this area are centred in the synthesis of insect hormones (pheromones, juvenile hormones, etc.), and particularly in the synthesis of pyrethrins and pyrethroids.[1, 2] The industrial importance of such insecticides is shown by the growing consumption of synthetic pyrethroids from 12,000 tonnes in 1985 (15-20% of the world market in insecticides) to an estimated market share of 30-35% in 1995.[1] The pyrethroids are compounds structurally related to the natural pyrethrins that have insecticidal activity that has been known for centuries. These compounds are esters of chrysanthemic acid (**1**) and pyrethric acid (**2**) with substituted cyclopentenolones and are obtained from the flowers of *Chrysanthemum cinerafolis* and *Chrysanthemum coccineum*.[1] Pyrethrins and pyrethroids are lipophilic insecticides that act on the nervous system of the insect and are characterized by high efficiency, low toxicity to mammals in general and humans in particular and are biodegradable.[1, 2] The key step in the synthesis of pyrethroids is the construction of the substituted cyclopropanecarboxylic acid that is then esterified with the appropriate alcohol. There are many routes for the syntheses of these acids and most of them have been patented.[1] However, none of the synthetic routes that have been described so far can be considered as general. Among them, the addition of ethyl diazoacetate to differently substituted buta-1,3-dienes and the addition of sulphur or phosphorus ylides to methyl penta-2,4-dienoates[3] have been widely used to obtain the most common vinylcyclopropanecarboxylic acids, but all of these routes have limitations and can be used for the synthesis of only a few pyrethroids. Another problem to take into consideration regarding these synthetic procedures is that in some cases the starting materials for these syntheses are difficult to obtain and purify. Other synthetic procedures reported in the literature for this class of compounds are limited to the synthesis of one or two specific cyclopropanecarboxylic acids.[1, 3] The only photochemical route reported for the synthesis of pyrethroids is the direct irradiation of the methyl ester **3** that gives the methyl chrysanthemate (**4**) in 12-15% yield by a di-π-methane rearrangement.[4,5]



Since the discovery of the aza-di-π-methane (ADPM) rearrangement of 1-aza-1,4-dienes about fifteen years ago the reaction has been demonstrated to be a useful synthetic process for the construction of differently substituted cyclopropyl derivatives such as **5**[6] or the bicyclic compounds **6**.[7] A few years ago we have also demonstrated the usefulness of the ADPM rearrangement for the synthesis of the cyclopropyl component of pyrethrins and pyrethroids,[8,9] as in the case of cyclopropane **7** obtained by the acetone-sensitized cyclization of the azadiene **8**.[8] This compound **7** is a precursor of the cyclopropanecarboxylic acid present in the pyrethroid *terallethrin*.

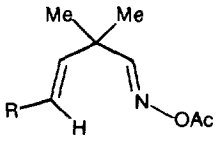


This paper extends that work and reports the application of the ADPM rearrangement to the synthesis of a variety of cyclopropanecarboxylic acids present in insecticidally-active pyrethrins and pyrethroids.

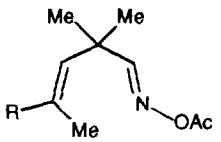
RESULTS AND DISCUSSION

In a previous publication[10] we described the influence of C5-substitution on the photochemical reactivity of a series of 1-aza-1,4-dienes **9**. The results obtained showed that C5 mono substituted oxime acetates **9a-d** do not undergo the ADPM rearrangement. The only reaction observed was the *E*/*Z*-isomerization of the C-C double bond. The failure of these oxime acetates to undergo cyclization was considered to be due to a deactivation by a free rotor effect. Support for this postulate was obtained in the acetone-sensitized irradiation of the C5 disubstituted oxime acetates **9e-g** that yield the corresponding cyclopropyl derivatives **10a-c** in reasonable yields. However, later studies[11] showed that success or failure of the reaction was not due to a free rotor effect but to the stability of the corresponding cyclopropyl 1,4-biradical intermediate **11**. Thus,

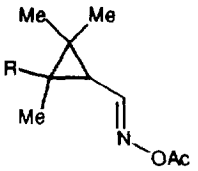
disubstitution at C5, as in **11a-e**, or conjugation with a phenyl group, as in **11f**, are effective in promoting the aza-di-π-methane rearrangement. In any other situation the reaction fails.



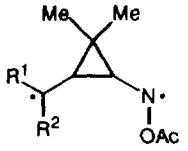
9a: R = CO_2Et
9b: R = CN
9c: R = CH_2OMe
9d: R = CH_2OCOMe



9e: R = CO_2Et
9f: R = CN
9g: R = CH_2OCOMe

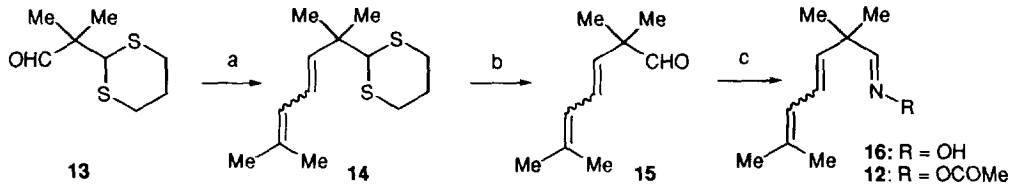


10a: R = CO_2Et
10b: R = CN
10c: R = CH_2OCOMe



11a: $R^1 = R^2$ = Ph
11b: $R^1 = R^2$ = Me
11c: R^1 = Me, $R^2 = CO_2Et$
11d: R^1 = Me, R^2 = CN
11e: R^1 = Me, $R^2 = CH_2OCOMe$
11f: R^1 = Ph, R^2 = H

Following on these results a logical extension was to examine the control which allylic stabilization could exercise on the biradical intermediate. If the ADPM rearrangement was operative a new route to pyrethrins and pyrethroids would be available. The target molecule for this study was identified as the triene **12** since this could be the precursor to chrysanthemic acid (**1**), the main cyclopropane component of natural pyrethrin. The synthetic approach to the diene involves a Wittig reaction with the protected aldehyde **13**[12] to afford the diene **14** in good yield and as a 3.5:1 mixture of isomers (Scheme 1). Their configuration was established by study of the coupling constants of the vinylic protons in the ^{1}H-NMR spectra. Deprotection is carried out readily[13] to afford the aldehyde **15**. Conversion to the corresponding oxime **16** and oxime acetate **12** is achieved by standard procedures. The identity of all the compounds was established by standard techniques.

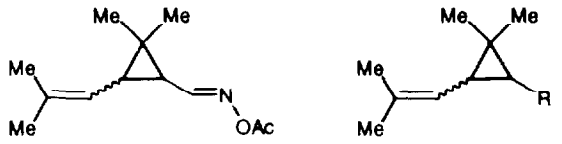


13 **14** **15**
16: R = OH
12: R = OCOMe

[a] Key: (a) $Me_2C{=}CHCH_2PPh_3^+Br^-$, *n*-BuLi; (b) HgO, $BF_3.Et_2O$; (c) Condensation with NH_2OH yielded the oxime **16**. Treatment of **16** with MeCOCl gave acetate **12**.

Scheme 1[a]

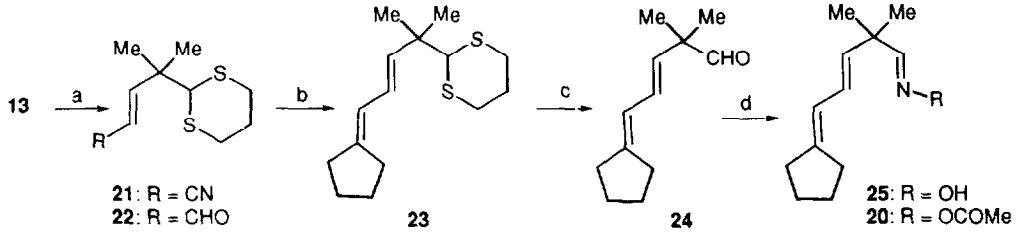
Acetophenone-sensitized irradiation of **12** in an immersion-well apparatus for 30 min brought about conversion to a single photoproduct in 45% yield. This was identified as the cyclopropane **17** which was shown by NMR spectroscopy to be a mixture of *cis:trans* diastereoisomers (ratio 1:1). The cyclopropane **17** was transformed into the corresponding nitrile **18** that was then reduced by DIBAL into the aldehyde **19**. Final proof of identity was obtained by oxidation of the aldehyde **19** into chrysanthemic acid (**1**). The spectroscopic data from this compound were identical with that obtained from an authentic sample purchased from Sigma (10453-89-1).



17 **18**: R = CN
19: R = CHO

The success of the foregoing transformation was proof that the concept of allylic stabilization of the intermediate cyclopropyl 1,4-biradical could permit the successful application of the ADPM to trienes such as **12**. As mentioned earlier there are only two other reports[4, 5] of the photochemical synthesis of a chrysanthemate. These make use of the di-π-methane rearrangement and give only very low yields of product after 30 h of irradiation. It is clear that our route has a greater synthetic potential and the following experiments have been designed to demonstrate the utility of the reaction and its application to the synthesis of a variety of differently substituted substrates that could be converted photochemically into cyclopropane components of pyrethroids with known insecticidal activity.

To show the versatility of this method for the synthesis of other alkyl-substituted vinyl cyclopropanes the azatriene **20** was prepared. The synthesis involves the use of the protected aldehyde **13** as the starting material and a six-step sequence, all of them in high yield, affords the desired product (Scheme 2).



21: R = CN
22: R = CHO

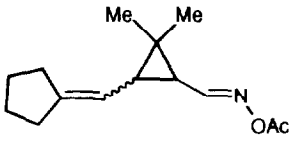
23 **24**

25: R = OH
20: R = OCOMe

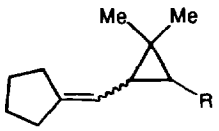
[a] Key: (a) Reaction of **13** with $(EtO)_2POCH_2CN$ and LDA yielded **21**. Treatment of **21** with DIBAL gave aldehyde **22**; (b) Cyclopentyltriphenylphosphonium bromide, *n*-BuLi; (c) HgO, $BF_3.Et_2O$; (d) Condensation with NH_2OH yielded the oxime **25**. Treatment of **25** with MeCOCl gave acetate **20**.

Scheme 2[a]

The irradiation of **20** was carried out under acetophenone-sensitization for 30 min and affords the cyclopropane **26** in 67% yield as a 3:1 mixture of *cis:trans* diastereoisomers. The predominant product was identified as the *cis*-isomer by study of the ^{1}H-NMR data and by comparison with those of related compounds.[14] Furthermore the cyclopropane **26** was converted into the nitrile **27**, and after reduction with DIBAL, into the aldehyde **28**. Oxidation of the aldehyde afforded the acid **29** component of the pyrethroid *bioethanomethrine*.[1] The success of this transformation, achieved in good yield, confirms the utility of this synthetic strategy.

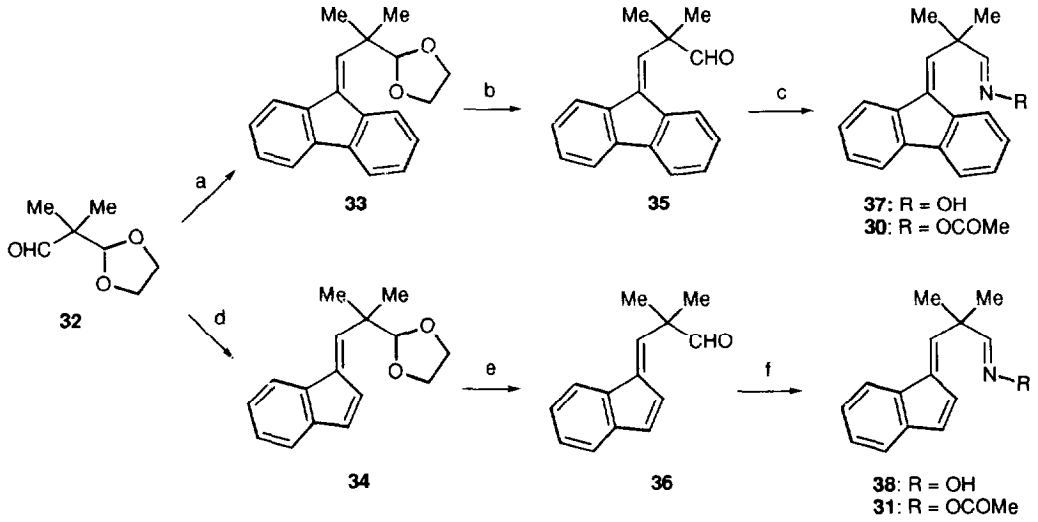


26



27: R = CN
28: R = CHO
29: R = COOH

As we noted earlier in this paper the routes to commercially available pyrethroids are not very general. Some of the reaction paths can be applied to the synthesis of a few derivatives but if major changes are required a new synthetic route has to be devised. In order to test the generality of our approach we report the application of the ADPM rearrangement to the synthesis of cyclopropanecarboxylic acid components of spirocyclic pyrethroids. The target molecules selected for this study were the azadienes **30** and **31**. The synthesis of these compounds is remarkably simple and involves the protected aldehyde **32**[15] as the starting material. Condensation of **32** with fluorenyl or indenyl anions yields the acetals **33** and **34** that were deprotected, as outlined in Scheme 3, to afford the aldehydes **35** and **36** respectively, in reasonable yields. The conversions to the appropriate azadienes **30** and **31** are readily achieved by the standard method.



32

33

34

35

36

37: R = OH
30: R = OCOMe

38: R = OH
31: R = OCOMe

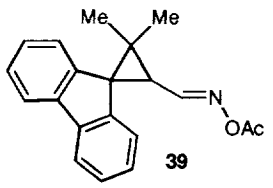
[a] Key: (a) Fluorene, *n*-BuLi; (b) HCl 50%; (c) Condensation with NH_2OH yielded the oxime **37**. Treatment of **37** with MeCOCl gave acetate **30**; (d) Indene, *n*-BuLi; (e) HCl 50%; (f) Condensation with NH_2OH yielded the oxime **38**. Treatment of **38** with MeCOCl gave acetate **31**.

Scheme 3[a]

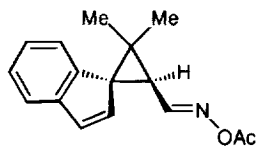
Irradiation of the azadiene **30** for 90 min, using acetophenone sensitization, afforded the corresponding cyclopropane **39** in 60% yield. Irradiation of the azadiene **31**, using *m*-methoxyacetophenone sensitization, for 15 min, gave cyclopropane **40** in 59% yield and as a 6:1 mixture of cyclopropane isomers *SR,RS* (**40a**) and *SS,RR* (**40b**) respectively. Their configurations were established by means of NOE difference measurements.

Only the major isomer **40a** gave a NOE between the indene H-2 and the oximino proton. Thus, irradiation at 6.24 ppm causes an enhancement of a 7% of the signal at 7.9 ppm. The structural assignment of **40a** and **40b** was also confirmed by comparison of the ^{1}H-NMR data with those described for related compounds.[16]

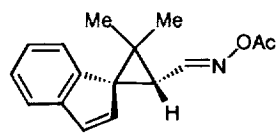
The cyclopropanes **39** and **40** were converted into the corresponding carboxylic acids **41** and **42** by means of the same procedure described previously for the synthesis of **1**. Both of these acids, **41** and **42**, are the cyclopropyl components of pyrethroids that have proven insecticidal activity.[1] The synthesis of these spiro derivatives is the first example of the formation of such systems by the ADPM rearrangement. As far as we are aware the formation of spiro compounds is uncommon in the di-π-methane or the oxa-di-π-methane rearrangements.[17, 18]



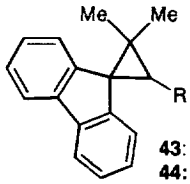
39



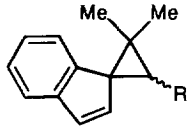
40a



40b



43: R = CN
44: R = CHO
41: R = COOH



45: R = CN
46: R = CHO
42: R = COOH

It is surprising, since the key structural feature of pyrethrins and pyrethroids is a cyclopropane carboxylic acid, that little use has been made of photochemical methods such as the di-π-methane family of reactions for the synthesis of these specific cyclopropanes.[17] Presumably the reason for this is that the di-π-methane rearrangement in compounds similar to those studied by us will take place from the singlet excited state that presents serious limitations in the type of substitution possible on the molecule. Furthermore the compounds that could be obtained by such a route would be 1,2-divinyl cyclopropanes that could be difficult to transform selectively into the cyclopropane carboxylic acid. On the other hand the oxa-di-π-methane rearrangement, that usually takes place from the triplet excited state, is unpredictable in its outcome in acyclic substrates.[18] There is no doubt from the results described above that the aza-di-π-methane rearrangement is the most convenient photochemical method for the synthesis of a variety of pyrethrins and pyrethroids because of the high chemical yields, short irradiation times and, in some cases, good stereochemical control.

EXPERIMENTAL

Melting points were determined on a Buchi 530D apparatus in open capillaries and are uncorrected. IR spectra were recorded using a Perkin-Elmer 781 spectrophotometer and band positions are reported in wavenumbers (cm^{-1}). NMR spectra were run at the Servicio de Resonancia Magnética Nuclear de la Universidad Complutense de Madrid. ^{1}H-NMR spectra were recorded in $CDCl_3$ as solvent using a Varian VXR-300S (300 MHz) or else, where stated, a Bruker AC-250F (250 MHz), and TMS as internal standard,

with chemical shifts δ expressed in ppm and coupling constants *J* are given in Hz. ^{13}C-NMR spectra were recorded in $CDCl_3$ as solvent using a Bruker AC-250F (62 MHz) as the standard or else, where stated, a Varian VXR-300S (75 MHz) and $CDCl_3$ (δ 77.0) as the internal reference. UV/visible spectra were recorded in CH_2Cl_2 solution using a Perkin Lambda 3B spectrophotometer. Mass spectra were run at the Chemistry Department, University of Dundee using a VG 11-250J mass spectrometer. Combustion analyses were carried out by the Servicio de Microanálisis de la Universidad Complutense de Madrid. Column chromatography was performed by using silica gel 60 (40-63 mm) from Merck. Commercially available starting materials and reagents were purchased from Aldrich Chemical Co.

Synthesis of Aldehydes **15**, **24**, **35** *and* **36**.

2-(1,3-*Dithian*-2-*yl*)-2,6-*dimethylhepta*-3,5-*diene* **14.** 3-Methyl-2-butenyltriphenylphosphonium bromide was made by refluxing a mixture of 1-bromo-3-methyl-2-butene (5 g, 33.5 mmol) and triphenylphosphine (8 g, 30.5 mmol) in 20 ml of toluene for 12 h. The white precipitate was filtered, washed several times with warmed toluene and dried, to yield 12.7 g (92%) of the salt (mp 235-236 °C, ethanol). To a stirred solution of 7.64 g (19 mmol) of 3-methyl-2-butenyltriphenylphosphonium bromide, in 60 ml of dry THF, under an argon atmosphere and at 0 °C, were added slowly dropwise 14.5 ml (23 mmol) of 1.6 M solution of *n*-BuLi in hexane. The red solution of the ylid was allowed to warm to RT and then 3.5 g (15 mmol) of 2-(1,3-dithian-2-yl)-2-methylpropanal **13**[12] in 50 ml of dry THF were added . The reaction mixture was stirred at RT for 24 h before being quenched with saturated NH_4Cl solution and extracted with ether. The combined organic phases were dried, filtered and concentrated to leave a residue that was purified by flash chromatography (elution with hexane/Et_2O 95:5) to afford 2.8 g (63%) of compound **14** as an oil and as a 3.5:1 mixture of *Z*:*E*-isomers; IR (neat) 1650 and 1610 (C=C) cm^{-1}; δ_H 1.2 (1.38 H, s, $2CH_3$, *E*-isomer), 1.4 (4.62 H, s, $2CH_3$, *Z*-isomer), 1.73 (2.31 H, s, CH_3C=C, *Z*-isomer), 1.75 (0.69 H, s, CH_3C=C, *E*-isomer), 1.76 (0.69 H, s, CH_3C=C, *E*-isomer), 1.8 (2.31 H, s, CH_3C=C, *Z*-isomer), 2.0-2.1 (2 H, m, CH_2), 2.8-2.9 (4 H, m, $2CH_2S$), 4.0 (0.23 H, s, CHS, *E*-isomer), 4.2 (0.77 H, s, CHS, *Z*-isomer), 5.3 (0.77 H, d, *J* = 11.5, H-5, *Z*-isomer), 5.6 (0.23 H, d, *J* = 15.3, H-3, *E*-isomer), 5.8 (0.23 H, d, *J* = 10.4, H-5, *E*-isomer) and 6.1-6.3 (1.77 H, m, H-3, H-4, *Z*-isomer and H-4, *E*-isomer); δ_C 17.6 (CH_3, *Z*-isomer), 18.4 (CH_3, *E*-isomer), 25.4 (CH_3, *E*-isomer), 25.9 (CH_2), 26.8 ($2CH_3$, *E*-isomer), 27.3 ($2CH_3$, *Z*-isomer), 29.7 (CH_3, *Z*-isomer), 31.2 ($2CH_2S$), 40.5 (quaternary C, *E*-isomer), 41.7 (quaternary C, *Z*-isomer), 59.7 (CH, *E*-isomer), 62.0 (CH, *Z*-isomer), 120.7 (C=*C*H, *Z*-isomer), 120.8 (C=*C*H, *E*-isomer), 124.8 (C=*C*H, *E*-isomer), 125.1 (C=*C*H, *Z*-isomer), 133.7 (C=*C*H, *E*-isomer), 134.1 (C=*C*H, *Z*-isomer), 139.5 (*C*=CH, *E*-isomer) and 141.0 (*C*=CH, *Z*-isomer); MS *m/z*: 242 (M^+, 2), 149 (18), 123 (100), 119 (43), 105 (12), 91 (21), 81 (40), 77 (19) and 67 (13) (Found: M^+, 242.1156. $C_{13}H_{22}S_2$ requires M, 242.1158).

2,2,6-*Trimethylhepta*-3,5-*dienal* **15.** The removal of the thioacetal group was carried out by the method of Vedejs and Fuchs.[13] To a stirred suspension of red mercuric oxide (5.5 g, 26 mmol) in 100 ml of 15% aqueous THF under an argon atmosphere, were added 3.6 g (25 mmol) of BF_3·Et_2O. Then, a solution of the protected aldehyde **14** (3.1 g, 12.7 mmol) in 20 ml of THF was added through a dropping funnel. The stirred mixture was maintained at RT for 20 min and then gently refluxed for 2 h to complete the reaction. The mixture was allowed to cool to RT and the mercuric salts were precipitated by addition of 30 ml of ether and then filtered. The filtrate was washed with saturated $NaHCO_3$ solution, then with brine and finally dried. The organic extracts

were filtered and concentrated to yield the oily aldehyde **15** (1.5 g, 78%) as a 3:1 mixture of *Z*:*E*-isomers; IR (neat) 1735 (C=O), 1660 and 1610 (C=C) cm^{-1}; δ_H 1.1 (1.5 H, s, $2CH_3$, *E*-isomer), 1.2 (4.5 H, s, $2CH_3$, *Z*-isomer), 1.67 (0.75 H, s, CH_3C=C, *E*-isomer), 1.71 (0.75 H, s, CH_3C=C, *E*-isomer), 1.73 (2.25 H, s, CH_3C=C, *Z*-isomer), 1.77 (2.25 H, s, CH_3C=C, *Z*-isomer), 5.2 (0.75 H, d, *J* = 11.4, H-5, *Z*-isomer), 5.3 (0.25 H, d, *J* = 15.5, H-3, *E*-isomer), 5.76 (0.25 H, d, *J* = 10.2, H-5, *E*-isomer), 5.80 (0.75 H, d, *J* = 11, H-3, *Z*-isomer), 6.17-6.27 (1 H, m, H-4, *Z*-isomer and H-4, *E*-isomer), 9.3 (0.25 H, s, CHO, *E*-isomer) and 9.5 (0.75 H, s, CHO, *Z*-isomer); δ_C 18.0 (CH_3, *E*-isomer), 18.4 (CH_3, *E*-isomer), 21.6 ($2CH_3$, *Z*-isomer), 23.5 ($2CH_3$, *E*-isomer), 26.1 (CH_3, *Z*-isomer), 26.5 (CH_3, *E*-isomer), 48.8 (quaternary C), 124.7 (C=*C*H, *Z*-isomer), 125.6 (C=*C*H, *E*-isomer), 127.8 (C=*C*H, *Z*-isomer), 128.0 (C=*C*H, *E*-isomer), 129.6 (C=*C*H, *E*-isomer), 131.7 (C=*C*H, *Z*-isomer), 135.8 (*C*=CH, *E*-isomer), 136.3 (*C*=CH, *Z*-isomer), 202.3 (CHO, *Z*-isomer) and 203.6 (CHO, *E*-isomer); MS *m/z*: 153 (M^++1, 32), 152 (6), 135 (47), 123 (33), 94 (100), 81 (23), 79 (26), 69 (49) and 55 (58) (Found: M^++1, 153.1276. $C_{10}H_{17}O$ requires M, 153.1275).

(E)-4-(1,3-*Dithian*-2-*yl*)-4-*methylpent*-2-*enenitrile* **21.** To a solution of 20 mmol of lithium diisopropylamide in 30 ml of dry THF (prepared from 2.8 ml, 20 mmol of diisopropylamine and 12.7 ml, 20 mmol of 1.6 M solution of *n*-BuLi in hexanes), at -78 °C under an atmosphere of argon, were added slowly dropwise 3 ml (18.0 mmol) of diethyl cyanomethylphosphonate. The mixture was stirred for 45 min and then a solution of the aldehyde **13**[12] (3.5 g, 18 mmol) in 50 ml of dry THF was added dropwise. The reaction was kept at -78 °C for 2 h, allowed to warm at room temperature and stirred for 2 h before being quenched with saturated NH_4Cl solution and extracted with ether. The combined organic phases were dried, filtered and concentrated to leave a residue that was purified by flash chromatography (elution with hexane/Et_2O 8:2) to afford 3.8 g (99%) of compound **21** as a solid: mp 70-72 °C (hexane); IR (KBr) 2220 (CN) and 1630 (C=C) cm^{-1}; δ_H (250 MHz) 1.2 (6 H, s, $2CH_3$), 1.7 (1 H, m, CH_2), 2.1 (1 H, m, CH_2), 2.8 (4 H, m, $2CH_2S$), 4.0 (1 H, s, CH), 5.3 (1 H, d, *J* = 16.6, CH=C*H*CN) and 6.8 (1 H, d, *J* = 16.6, C*H*=CHCN); δ_C 24.3 ($2CH_3$), 25.7 (CH_2), 31.2 ($2CH_2S$), 42.7 (quaternary C), 58.7 (CH), 98.6 (vinyl C), 117.5 (CN) and 161.1 (vinyl C); MS *m/z*: 213 (M^+, 94), 107 (96), 85 (24), 80 (100) and 74 (21) (Found: C, 56.7; H, 7.3; N, 6.5; S, 30.1. $C_{10}H_{15}NS_2$ requires C, 56.34; H, 7.04; N, 6.57; S, 30.05%).

(E)-4-(1,3-*Dithian*-2-*yl*)-4-*methylpent*-2-*enal* **22.** To a solution of 3.3 g (15 mmol) of (*E*)-4-(1,3-ditihian-2-yl)-4-methyl-2-pentenenitrile (**21**) in 40 ml of dry toluene at -78 °C under an argon atmosphere, were added 23 ml (23 mmol) of a 1.0 M solution of DIBAL in toluene. The reaction mixture was stirred for 90 min at -78 °C and then for 2 h at RT before being quenched with 75 ml of 10% HCl solution and extracted with ether. The organic phases were washed with saturated aqueous $NaHCO_3$ solution, then with brine and finally dried. The organic extracts were concentrated to leave a residue that was purified by flash chromatography (elution with hexane/Et_2O 9:1), to afford 3.3 g (98%) of compound **22** as a solid: mp 72-74 °C (ethanol); IR (KBr) 1670 (C=O) and 1630 (C=C) cm^{-1}; δ_H (250 MHz) 1.3 (6 H, s, $2CH_3$), 1.7 (1 H, m, CH_2), 2.0 (1 H, m, CH_2), 2.9 (4 H, m, $2CH_2S$), 4.1 (1 H, s, CH), 6.1 (1 H, dd, *J* = 15.8, 7.7, CH=C*H*CHO), 6.9 (1 H, d, *J* = 15.8, C*H*=CHCHO) and 9.5 (1 H, d, *J* = 7.7, CHO); δ_C 24.8 ($2CH_3$), 25.8 (CH_2), 31.3 ($2CH_2S$), 42.2 (quaternary C), 59.2 (CH), 130.7, 163.7 (vinyl C) and 194.3 (CHO); MS *m/z*: 216 (M^+, 7), 119 (100), 106 (12) and 41 (12) (Found: C, 55.8; H, 7.7; S, 29.6. $C_{10}H_{16}OS_2$ requires C, 55.55; H, 7.41; S, 29.63%).

(E)-5-*Cyclopentyliden*-2-(1,3-*dithian*-2-*yl*)-2-*methylpent*-3-*ene* **23.** Cyclopentyl triphenylphosphonium bromide was made by refluxing a mixture of cyclopentyl bromide (10 g, 67 mmol) and triphenylphosphine (16 g, 61 mmol) for 5 h. The white precipitate was filtered, washed several times with warmed toluene and dried, to yield 15 g (60%) of cyclopentyltriphenylphosphonium bromide (mp 168-170 °C). The corresponding ylid was made from 13.5 ml (22 mmol) of 1.6 M solution of *n*-BuLi in hexane and 8.9 g (22 mmol) of cyclopentyl triphenylphosphonium bromide in 60 ml of dry THF according to the method described for **14**. The aldehyde **22** (3.3 g, 15 mmol) in 50 ml of dry THF was added slowly dropwise to the solution of the ylid. The reaction mixture was stirred at RT for 24 h before being quenched with saturated NH_4Cl solution and extracted with ether. The combined organic phases were dried, filtered and concentrated to leave a residue that was purified by flash chromatography (elution with hexane/Et_2O 95:5) to afford 2.9 g (71%) of compound **23** as an oil; IR (neat) 1650 (C=C) cm^{-1}; δ_H (250 MHz) 1.2 (6 H, s, $2CH_3$), 1.6 (4 H, m, $2CH_2$), 1.7 (1 H, m, CH_2CH_2S), 2.1 (1 H, m, CH_2CH_2S), 2.3 (4 H, m, $2CH_2$), 2.9 (4 H, m, $2CH_2S$), 4.0 (1 H, s, CH), 5.6 (1 H, d, J = 15.2, CH=CHCH=C), 5.9 (1 H, d, J = 10.7, CH=CHCH=C) and 6.1 (1 H, dd, J = 15.2, 10.7, CH=CHCH=C); δ_C 25.5 ($2CH_3$), 26.0, 26.3, 26.5, 29.4, 31.4, 34.1 (CH_2), 41.1 (quaternary C), 60.9 (CH), 120.2, 126.0, 137.2 and 147.0 (vinyl C); MS *m/z*: 268 (M^+, 5), 149 (100), 119 (14), 107 (23) and 93 (30) (Found: M^+, 268.1316. $C_{15}H_{24}S_2$ requires M, 268.1314).

(E)-5-*Cyclopentyliden*-2,2-*dimethylpent*-3-*enal* **24.** The removal of the thioacetal group was brought about following the same procedure as in **15** using red mercuric oxide (4.5 g, 21 mmol) in 100 ml of 15% aqueous THF, 2.9 g (21 mmol) of $BF_3{\cdot}Et_2O$ and the protected aldehyde **23** (2.8 g, 10 mmol) in 20 ml of THF. Work-up afforded the aldehyde **24** (1.73 g, 93%) as an oil that was used in the next step without further purification; IR (neat) 1730 (C=O) and 1640 (C=C) cm^{-1}; δ_H (250 MHz) 1.2 (6 H, s, $2CH_3$), 1.6 (4 H, m, $2CH_2$), 2.3 (4 H, m, $2CH_2$), 5.4 (1 H, d, J = 15.4, CH=CHCH=C), 5.9 (1 H, d, J = 10.7, CH=CHCH=C), 6.1 (1 H, dd, J = 15.4, 10.7, CH=CHCH=C) and 9.3 (1 H, s, CHO); δ_C 21.6 ($2CH_3$), 26.2, 26.4, 29.5, 34.1 (CH_2), 48.0 (quaternary C), 119.9, 129.3, 130.9, 148.8 (vinyl C) and 202.3 (CHO); UV (CH_2Cl_2) λ_{max} 252 (ε 18724) nm; MS *m/z*: 149 (M^+-29, 49), 132 (22), 111 (49), 105 (20), 98 (63), 95 (40), 85 (100), 71 (41) and 67 (76) (Found: M^+-29, 149.1332. $C_{11}H_{17}$ requires, M-29, 149.1326).

Ethylene acetal of 3-(9-*fluorenylidene*)-2,2-*dimethylpropanal* **33.** To a solution of 2 g (12 mmol) of fluorene in 70 ml of dry THF at 0 °C and under an argon atmosphere, were added dropwise 8 ml (13 mmol) of a 1.6 M solution of *n*-BuLi in hexane. The deep red mixture was stirred at RT for 10 min and then, a solution of 1.8 g (12 mmol) of 2,2-dimethyl-3,3-ethanediyldioxypropanal **32**[15] in 30 ml of THF was added slowly dropwise. The reaction mixture was refluxed for 1 h, allowed to reach RT, quenched with saturated NH_4Cl solution and extracted with ether. The combined organic phases were washed with water, dried, filtered and concentrated to leave a residue that was purified by flash chromatography (elution with hexane/Et_2O 9:1) to afford 1.95 g (55%) of compound **33** as a yellowish oil; IR (neat) 1630 (C=C) cm^{-1}; δ_H 1.5 (6 H, s, $2CH_3$), 3.9-4.0 (4 H, m, $2CH_2$), 4.9 (1 H, s, CHO_2), 6.9 (1 H, s, vinyl H), 7.1-7.3 (4 H, m, aryl H), 7.4-7.7 (3 H, m, aryl H) and 7.9-8.0 (1 H, m, aryl H); δ_C (75 MHz) 21.8 ($2CH_3$), 40.0 (quaternary C), 65.7 ($2CH_2$), 110.0 (CHO_2), 119.3, 119.8, 126.9, 127.4, 127.5, 127.9 and 135.3 (vinyl and aryl C); MS *m/z*: 292 (M^+, 21), 219 (11), 202 (15), 178 (11) and 73 (100) (Found: M^+, 292.1471. $C_{20}H_{20}O_2$ requires M, 292.1458).

3-(9-*Fluorenylidene*)-2,2-*dimethylpropanal* **35.** To a solution of 1.93 g (6.6 mmol) of the acetal **33** in 50 ml of THF were added 30 ml of 50% aqueous HCl. The mixture was stirred at RT for 24 h and extracted with ether. The organic phases were washed with 10% aqueous NaOH, water, dried and concentrated to leave a residue that after flash chromatography (elution with hexane/Et_2O 9:1) afforded 1.03 g (62%) of compound **35** as an oil; IR (neat) 1725 (C=O) and 1610 (C=C) cm^{-1}; δ_H 1.4 (6 H, s, $2CH_3$), 6.6 (1 H, s, vinyl H), 7.1-7.4 (5 H, m, aryl H), 7.5-7.6 (3 H, m, aryl H) and 9.6 (1 H, s, CHO); δ_C 23.7 ($2CH_3$), 48.1 (quaternary C), 119.6, 119.9, 120.4, 126.2, 127.3, 128.5, 128.8, 131.1, 134.8, 138.6, 139.2, 139.6, 141.8 (vinyl and aryl C) and 202.9 (CHO); MS *m/z*: 248 (M^+, 1), 219 (11), 203 (19), 180 (100), 165 (45), 152 (32) and 76 (11) (Found: M^+, 248.1200. $C_{18}H_{16}O$ requires M, 248.1197).

Ethylene acetal of 3-(1-*indenylidene*)-2,2-*dimethylpropenal* **34.** Following the same procedure as in **33**, from indene (2.18 g, 18.8 mmol), 12 ml (19.5 mmol) of 1.6 M solution of *n*-BuLi in hexane and 2.71 g (18.8 mmol) of the aldehyde **32**[15] Flash chromatography of the crude product (elution with hexane/Et_2O 9:1) yielded the acetal **34** (2.24 g, 50%) as an oil; IR (neat) 1640 and 1610 (C=C) cm^{-1}; δ_H (250 MHz) 1.3 (6 H, s, $2CH_3$), 3.90 (4 H, m, $2CH_2$), 4.8 (1 H, s, CHO_2), 6.7 (1 H, s, vinyl H), 6.94 (1 H, d, J = 6.6, indene H-2), 6.96 (1 H, d, J = 6.6, indene H-3), 7.1-7.3 (3 H, m, indene H) and 7.5-7.6 (1 H, m, indene H); δ_C 24.4 ($2CH_3$), 42.0 (quaternary C), 65.5 ($2CH_2$), 109.6 (CHO_2), 118.7, 120.5, 124.8, 126.2, 127.0, 133.2, 136.4, 137.7, 139.3 and 141.0 (vinyl and indene C); MS *m/z*: 242 (M^+, 2) and 73 (100) (Found: M^+, 242.1317. $C_{16}H_{18}O_2$ requires M, 242.1304).

3-(1-*Indenylidene*)-2,2-*dimethylpropanal* **36.** Following the same procedure as in **35**, from **34** (2.0 g, 8 mmol) and 40 ml of 50% aqueous HCl. The residue was purified by flash chromatography (elution with hexane/Et_2O 9:1) to yield the aldehyde **36** (1.17 g, 74%) as an oil; IR (neat) 1730 (C=O) cm^{-1}; δ_H 1.4 (6 H, s, $2CH_3$), 6.54 (1 H, s, vinyl H), 6.55 (1 H, d, J = 5.4, indene H-2), 6.9 (1 H, dd, J = 5.4, 1.5, indene H-3), 7.16-7.28 (3 H, m, indene H), 7.55-7.58 (1 H, m, indene H) and 9.63 (1 H, s, CHO); δ_C 24.2 ($2CH_3$), 49.2 (quaternary C), 119.1, 121.1, 125.0, 125.6, 128.0, 132.1, 135.2, 137.0, 141.7, 142.0 (vinyl and indene C) and 202.0 (CHO); MS *m/z*: 198 (M^+, 12), 170 (49), 169 (100), 155 (35), 154 (38), 153 (31), 152 (25), 141 (34), 128 (30) and 115 (31) (Found: M^+, 198.1032. $C_{14}H_{14}O$ requires M, 198.1041).

General Procedure for the Synthesis of Oximes.

The corresponding aldehyde, hydroxylamine hydrochloride and pyridine were refluxed in EtOH (50 ml) for 1 h. The aldehyde/hydroxylamine/pyridine ratio was 1:1.5:1.5 for all the experiments. The solvent was evaporated and the crude product was dissolved in Et_2O, washed with 10% aqueous HCl, water and brine. The extract was dried ($MgSO_4$), filtered and evaporated to dryness. The oximes were isolated and purified by flash chromatography on silica gel.

Oxime **16.** From aldehyde **15** (1.2 g, 8 mmol) and after flash chromatography using hexane/Et_2O (9:1) as eluent the oxime **16** (0.75 g, 60%) was obtained as an oil as a 3:1 mixture of *Z*:*E*-isomers; IR (neat) 3300 (OH), 1650 (C=C) and 1620 (C=N) cm^{-1}; δ_H 1.23 (1.5 H, s, $2CH_3$, *E*-isomer), 1.29 (4.5 H, s, $2CH_3$, *Z*-isomer), 1.72 (2.25 H, s, CH_3C=C, *Z*-isomer), 1.74 (0.75 H, s, CH_3C=C, *E*-isomer), 1.76 (0.75 H, s, CH_3C=C, *E*-isomer), 1.78 (2.25 H, s, CH_3C=C, *Z*-isomer), 5.2 (0.75 H, d, J = 10.4, H-5, *Z*-isomer), 5.5

(0.25 H, d, J = 15.9, H-3, *E*-isomer), 5.8 (0.25 H, d, J = 11, H-5, *E*-isomer), 6.11-6.5 (1.75 H, m, H-3 and H-4, *Z*-isomer and H-4, *E*-isomer), 7.3 (0.25 H, s, CH=N, *E*-isomer), 7.47 (0.75 H, s, CH=N, *Z*-isomer), 8.2 (0.75 H, br s, OH, *Z*-isomer) and 8.8 (0.25 H, br s, OH, *E*-isomer); δ_C 17.6 (CH_3, *Z*-isomer), 18.2 (CH_3, *E*-isomer), 25.3 ($2CH_3$, *E*-isomer), 26.5 (CH_3, *Z*-isomer), 25.8 (CH_3, *E*-isomer), 27.1 ($2CH_3$, *Z*-isomer), 38.4 (quaternary C, *Z*-isomer), 38.9 (quaternary C, *E*-isomer), 120.3 (C=*C*H, *Z*-isomer), 124.5 (C=*C*H, *E*-isomer), 124.6 (C=*C*H, *E*-isomer), 125.9 (C=*C*H, *Z*-isomer), 132.8 (C=*C*H, *Z*-isomer), 135.0 (C=*C*H, *E*-isomer), 136.0 (*C*=CH, *E*-isomer), 137.4 (*C*=CH, *Z*-isomer), 157.1 (C=N, *E*-isomer) and 158.3 (C=N, *Z*-isomer).

Oxime **25**. From aldehyde **24** (1.7 g, 9 mmol) and after flash chromatography using hexane/Et_2O (9:1) as eluent the oxime **25** (1.8 g, 96%) was obtained as an oil; IR (neat) 3340 (OH), 1660 (C=C) and 1620 (C=N) cm^{-1}; δ_H 1.1 (6 H, s, $2CH_3$), 1.6 (4 H, m, $2CH_2$), 2.3 (4 H, m, $2CH_2$), 5.4 (1 H, d, J = 15.4, C*H*=CHCH=C), 5.8 (1 H, d, J = 10.7, CH=CHC*H*=C), 6.1 (1 H, dd, J = 15.4, 10.7, CH=C*H*CH=C), 7.2 (1 H, s, CH=N) and 8.8 (1 H, s, OH); δ_C (75 MHz) 25.5 ($2CH_3$), 26.2, 26.4, 29.4, 34.0 (CH_2), 39.0 (quaternary C), 120.0, 126.2, 135.6, 147.5 (vinyl C) and 157.3 (C=N); UV (CH_2Cl_2) λ_{max} 248 (ε 24246) nm; MS *m/z*: 193 (M^+, 63), 176 (80), 160 (44), 133 (75), 105 (78), 91 (79), 79 (100) and 67 (51) (Found: M^+, 193.1482. $C_{12}H_{19}NO$ requires M, 193.1462).

Oxime **37**. From aldehyde **35** (1 g, 4 mmol) and after flash chromatography using hexane/Et_2O (9:1) as eluent the oxime **37** (0.75 g, 72%) was obtained as an oil; IR (neat) 3310 (OH) and 1610 (C=N) cm^{-1}; δ_H (250 MHz) 1.4 (6 H, s, $2CH_3$), 6.5 (1 H, s, CH), 7.0-7.7 (9 H, m, aryl H and CH=N) and 8.9 (1 H, br s, OH); δ_C 27.7 ($2CH_3$), 38.2 (quaternary C), 119.6, 120.0, 127.8, 128.1, 128.5, 130.3, 134.9, 135.1, 139.1, 140.2, 141.5, 141.9, 142.3, 143.9 (vinyl and aryl C) and 157.8 (C=N); MS *m/z*: 263 (M^+, 5), 180 (100), 165 (27), 152 (24), 91 (13) and 76 (17) (Found: M^+, 263.1302. $C_{18}H_{17}NO$ requires M, 263.1306).

Oxime **38**. From aldehyde **36** (1.1 g, 5.4 mmol) and after flash chromatography using hexane/Et_2O (9:1) as eluent the oxime **38** (1.1 g, 98%) was obtained as yellowish crystals: mp 99-101 °C (hexane); IR (KBr) 3320 (OH), 1640 (C=C) and 1610 (C=N) cm^{-1}; δ_H 1.4 (6 H, s, $2CH_3$), 6.5 (1 H, s, vinyl H), 6.7 (1 H, d, J = 5.6, indene H-2), 6.95 (1 H, d, J = 5.6, indene H-3), 7.07-7.18 (3 H, m, indene H), 7.44-7.47 (1 H, m, indene H), 7.5 (1 H, s, CH=N) and 8.7 (1 H, s, OH); δ_C (75 MHz) 27.2 ($2CH_3$), 39.8 (quaternary C), 118.7, 120.6, 125.0, 125.2, 127.4, 134.0, 135.7, 137.0, 139.6, 141.3 (vinyl and indene C) and 157.2 (C=N); MS *m/z*: 213 (M^+, 52), 196 (97), 195 (49), 181 (79), 180 (100), 154 (23), 153 (57), 152 (45), 128 (26) and 115 (36) (Found: M^+, 213.1163. $C_{14}H_{15}NO$ requires M, 213.1150).

General Procedure for the Synthesis of Oxime Acetates.

Acetyl chloride was added to a solution of the oxime in dry pyridine (3 ml) at 0 °C. The oxime/acetyl chloride ratio was 1:1.2 for all the experiments. The mixture was stirred for 1 h at RT and then Et_2O was added. The solution was washed successively with 10% aqueous HCl, saturated aqueous solution of $NaHCO_3$ and brine. The crude extract was dried ($MgSO_4$), filtered and evaporated to dryness. The product was purified by flash chromatography on silica gel.

Oxime Acetate **12**. From oxime **16** (0.55 g, 3.3 mmol) and after flash chromatography using hexane/EtO (9:1) the oxime acetate **12** (0.43g, 62%) was obtained as an oil and as a 3:1 mixture of *Z*:*E*-isomers, that were separated by flash chromatography on silica gel (elution with hexane/Et_2O 98:2). **Z-isomer:** IR (neat) 1770 (C=O) and 1630 (C=N) cm^{-1}; δ_H 1.4 (6 H, s, $2CH_3$), 1.7 (3 H, s, CH_3C=C), 1.8 (3 H, s, CH_3C=C), 2.2 (3 H, s, CH_3CO), 5.2 (1 H, d, J = 10.4, H-5), 6.09-6.12 (2 H, m, H-3 and H-4) and 7.1 (1 H, s, CH=N); δ_C (75 MHz) 17.9 (CH_3CO), 19.8, 26.68 (CH_3), 26.9 ($2CH_3$), 39.1 (quaternary C), 120.0, 127.1, 131.8 (C=*C*H), 138.6 (*C*=CH), 165.6 (C=N) and 169.1 (C=O). ***E*-isomer:** IR (neat) 1770 (C=O) and 1630 (C=N) cm^{-1}; δ_H 1.31 (6 H, s, $2CH_3$), 1.75 (3 H, s, CH_3C=C), 1.77 (3 H, s, CH_3C=C), 2.1 (3 H, s, CH_3CO), 5.5 (1 H, d, J = 15.4, H-3), 5.8 (1 H, d, J = 10.7, H-5), 6.3 (1 H, dd, J = 15.4, 10.7, H-4) and 7.5 (1 H, s, CH=N); δ_C (75 MHz) 18.5 (CH_3CO), 19.7 (CH_3), 25.1 ($2CH_3$), 26.1 (CH_3), 39.8 (quaternary C), 124.5, 125.8, 134.9 (C=*C*H), 135.7 (*C*=CH), 164.0 (C=N) and 169.0 (C=O); UV (CH_2Cl_2) λ_{max} 243 (ε 15055) nm; MS *m/z*: 149 (M^+-60, 33), 134 (24), 107 (19), 91 (16) and 73 (26).

Oxime Acetate **20**. From (1.8 g, 7.6 mmol) of oxime **25** and after flash chromatography using hexane/Et_2O (8:2) the oxime acetate **20** (1.51 g, 85%) was obtained as an oil; IR (neat) 1770 (C=O), 1660 (C=C) and 1630 (C=N) cm^{-1}; δ_H (250 MHz) 1.1 (6 H, s, $2CH_3$), 1.5 (4 H, m, $2CH_2$), 2.0 (3 H, s, CH_3CO), 2.2 (4 H, m, $2CH_2$), 5.3 (1 H, d, J = 15.4, C*H*=CHCH=C), 5.8 (1 H, d, J = 10.7, CH=CHC*H*=C), 6.0 (1 H, dd, J = 15.4, 10.7, CH=C*H*CH=C) and 7.4 (1 H, s, CH=N); δ_C 19.7 (CH_3CO), 22.7 ($2CH_3$), 26.2, 26.4, 29.5, 34.1 (CH_2), 39.7 (quaternary C), 119.8, 127.3, 134.2, 148.4 (vinyl C), 164.0 (C=N) and 169.0 (C=O); UV (CH_2Cl_2) λ_{max} 249 (ε 22236) nm; MS *m/z*: 235 (M^+, 12), 176 (19), 164 (15), 152 (32), 148 (16), 133 (21), 123 (25), 110 (100), 105 (19), 98 (41) and 67 (44) (Found: M^+, 235.1560. $C_{14}H_{21}NO_2$ requires M, 235.1567).

Oxime Acetate **30**. From oxime **37** (0.97 g, 3.7 mmol) and after flash chromatography using hexane/Et_2O (9:1) the oxime acetate **30** (487 mg, 43%) was obtained as an oil; IR (neat) 1770 (C=O) and 1630 (C=N) cm^{-1}; δ_H (250 MHz) 1.6 (6 H, s, $2CH_3$), 2.1 (3 H, s, CH_3CO), 6.6 (1 H, s, vinyl H), 7.2-7.3 (4 H, m, aryl H), 7.5-7.6 (3 H, m, aryl H), 7.8 (1 H, s, CH=N) and 7.86-7.90 (1 H, m, aryl H); δ_C 19.7 (CH_3CO), 27.1 ($2CH_3$), 38.9 (quaternary C), 119.6, 119.8, 119.9, 127.1, 127.3, 127.8, 128.4, 128.7, 133.6, 134.6, 138.0, 139.1, 139.7, 141.8 (vinyl and aryl C), 164.4 (C=N) and 168.8 (C=O); UV (CH_2Cl_2) λ_{max} 258 (ε 12044) nm; MS *m/z*: 305 (M^+, 4), 245 (63), 230 (100), 203 (38), 180 (14) and 165 (39) (Found: M^+, 305.1403. $C_{20}H_{19}NO_2$ requires M, 305.1411).

Oxime Acetate **31**. From oxime **38** (1.12 g, 5.2 mmol) and after flash chromatography using hexane/Et_2O (9:1) the oxime acetate **31** (1.1 g, 82%) was obtained as a viscous oil; IR (neat) 1770 (C=O) and 1630 (C=N) cm^{-1}; δ_H (250 MHz) 1.5 (6 H, s, $2CH_3$), 2.2 (3 H, s, CH_3CO), 6.5 (1 H, s, vinyl H), 6.7 (1 H, d, J = 5.7, indene H-2), 6.9 (1 H, dd, J = 5.7, 1.5, indene H-3), 7.18-7.28 (3 H, m, indene H), 7.52-7.55 (1 H, m, indene H) and 7.8 (1 H, s, CH=N); δ_C 19.8 (CH_3CO), 27.3 ($2CH_3$), 40.5 (quaternary C), 119.0, 121.1, 125.0, 125.4, 127.9, 134.6, 134.9, 137.1, 140.8, 141.6 (vinyl and indene C), 164.2 (C=N) and 168.9 (C=O); UV (CH_2Cl_2) λ_{max} 255 (ε 20000) nm; MS *m/z*: 255 (M^+, 5), 213 (42), 195 (28), 180 (43), 149 (47), 131 (100), 116 (56), 115 (88), 103 (53), 71 (35), 60 (40), 45 (38) and 43 (89) (Found: M^+, 255.1256. $C_{16}H_{17}NO_2$ requires M, 255.1256).

General Procedure for Preparative Photolyses.

The photolyses were carried out in an immersion well apparatus with a Pyrex filter and a 400-W medium pressure Hg arc lamp. Solutions of the compounds in dry CH_2Cl_2 (420 ml) were purged for 1h with argon and irradiated under a positive pressure of argon. After completion of the irradiation, the solvent and the sensitizer were removed under reduced pressure and the products were separated by flash chromatography on silica gel.

Acetophenone-sensitized Irradiation of **12**. Compound **12** (300 mg, 1.4 mmol) and acetophenone (1.5 g, 12.5 mmol) were irradiated for 30 min. Flash chromatography using hexane/Et_2O (8:2) gave 65 mg (22%) of recovered starting material **12** as a 1:1 mixture of *Z:E* isomers and 135 mg (45%) of cyclopropane **17** as a 1:1 mixture of *cis:trans* diastereomers; IR (neat) 1770 (C=O), 1620 (C=C) and 1610 (C=N) cm^{-1}; δ_H 1.13 (1.5 H, s, CH_3), 1.15 (1.5 H, s, CH_3), 1.20 (1.5 H, s, CH_3), 1.22 (1.5 H, s, CH_3), 1.59 (1 H, m, CH), 1.70 (1.5 H, s, CH_3C=C), 1.72 (1.5 H, s, CH_3C=C), 1.73 (1.5 H, s, CH_3C=C), 1.75 (1.5 H, s, CH_3C=C), 1.83 (1 H, m, CH), 2.1 (3 H, s, CH_3CO), 4.9 (0.5 H, dt, J = 7.5, 1.2, vinyl H, *trans*-isomer), 5.03 (0.5 H, m, vinyl H, *cis*-isomer), 7.42 (0.5 H, d, J = 9.8, CH=N, *cis*-isomer) and 7.46 (0.5 H, d, J = 9.5, CH=N, *trans*-isomer); δ_C (75 MHz) 14.0, 16.3, 18.3, 18.4, 19.3, 21.6, 22.5, 25.3, 25.4 (CH_3), 26.4, 27.9 (quaternary C), 28.4 (CH_3), 30.8, 31.4, 32.2, 32.6 (CH), 117.2, 120.5, 135.4, 137.6 (vinyl C), 159.2, 160.3 (C=N) and 168.4 (C=O). Further elution with Et_2O afforded 53 mg (18%) of highly polar material.

Acetophenone-sensitized Irradiation of **20.** Compound **20** (340 mg, 1.5 mmol) and acetophenone (2.0 g, 17 mmol) were irradiated for 30 min. Flash chromatography using hexane/Et_2O (9:1) gave 227 mg (67%) of cyclopropane **26** as a 3:1 mixture of *cis:trans* diastereomers; IR (neat) 1770 (C=O), 1660 (C=C) and 1620 (C=N) cm^{-1}; δ_H (250 MHz) 1.14 (0.75 H, s, CH_3, *trans*-isomer), 1.17 (2.25 H, s, CH_3, *cis*-isomer), 1.19 (2.25 H, s, CH_3, *cis*-isomer), 1.20 (0.75 H, s, CH_3, *trans*-isomer), 1.6 (5 H, m, $2CH_2$ and CH), 1.9 (1 H, m, CH), 2.1 (3 H, s, CH_3CO), 2.2 (4 H, m, $2CH_2$), 5.01 (0.25 H, dt, J = 8.1, 2.3, vinyl H, *trans*-isomer), 5.16 (0.75 H, dt, J = 8.5, 2.3, vinyl H, *cis*-isomer), 7.43 (0.25 H, d, J = 9.4, CH=N, *trans*-isomer) and 7.45 (0.75 H, d, J = 9.4, CH=N, *cis*-isomer); δ_C 16.5, 19.5 (CH_3CO), 21.9, 22.8 (CH_3), 25.8 (quaternary C), 26.4, 26.5 (CH_2), 26.7 (quaternary C), 28.3, 28.7 (CH_3), 28.9 (CH), 29.4, 29.5 (CH_2), 32.5, 32.6 (CH), 33.8, 33.9 (CH_2), 34.4 (CH), 112.9 (vinyl C, *cis*-isomer), 116.2 (vinyl C, *trans*-isomer), 147.1 (vinyl C, *trans*-isomer), 149.1 (vinyl C, *cis*-isomer), 159.6 (C=N, *cis*-isomer), 160.6 (C=N, *trans*-isomer) and 168.7 (C=O). Further elution with Et_2O afforded 60 mg (20%) of highly polar material.

Acetophenone-sensitized Irradiation of **30.** Compound **30** (400 mg, 1.3 mol) and acetophenone (7 g, 58 mmol) were irradiated for 90 min. Flash chromatography using hexane/Et_2O (9:1) gave 91 mg (23%) of recovered starting material **30** and 240 mg (60%) of cyclopropane **39** as an oil; IR (neat) 1765 (C=O) and 1620 (C=N) cm^{-1}; δ_H (250 MHz) 1.60 (3 H, s, CH_3), 1.63 (3 H, s, CH_3), 2.1 (3 H, s, CH_3CO), 3.0 (1 H, d, J = 9, CH), 7.2-7.4 (6 H, m, aryl H), 7.7-7.9 (2 H, m, aryl H) and 8.2 (1 H, d, J = 9, CH=N); δ_C 19.5 (CH_3CO), 23.8 ($2CH_3$), 32.9 (quaternary C), 38.1 (CH), 46.2 (quaternary C), 120.0, 120.5, 123.0, 124.7, 126.2, 126.4, 126.8, 140.6, 142.0, 142.1, 144.0 (vinyl and aryl C), 156.0 (C=N) and 168.5 (C=O); MS *m/z*: 305 (M^+, 4), 245 (63), 230 (100), 203 (38), 180 (14), 165 (39), 79 (74), 77 (50) and 67 (100) (Found: M^+, 305.1403. $C_{20}H_{19}NO_2$ requires M^+, 305.1411). Further elution with Et_2O afforded 56 mg (14%) of highly polar material.

m-*Methoxyacetophenone-sensitized Irradiation of* **31.** Compound **31** (400 mg, 1.6 mmol) and *m*-methoxyacetophenone (5 g, 33 mmol) were irradiated for 15 min. Flash chromatography using hexane/Et_2O (95:5) gave 83 mg (21%) of recovered starting material **31** and 236 mg (59%) of cyclopropane **40** as a 6:1 mixture of *SR,RS:SS,RR* diastereomers. Treatment of this fraction with ethanol afforded the major isomer ***SR,RS* isomer (40a)** as a solid: mp 108-110 °C (ethanol); IR (KBr) 1760 (C=O) and 1640 (C=N) cm^{-1}; δ_H (250 MHz) 1.44 (3 H, s, CH_3), 1.47 (3 H, s, CH_3), 2.0 (3 H, s, CH_3CO), 2.8 (1 H, d, J = 9.6, CH), 6.2 (1 H, d, J = 5.7, indene H-2), 6.9 (1 H, d, J = 5.7, indene H-3), 7.0-7.23 (3 H, m, indene H), 7.28-7.33 (1 H, m, indene H) and 7.8 (1 H, d, J = 9.6, CH=N); δ_C 19.3 (CH_3CO), 21.4, 23.1 (CH_3), 33.9 (quaternary C), 39.2 (CH), 49.2 (quaternary C), 121.4, 121.8, 124.3, 126.2, 131.8, 133.3, 143.3, 143.8 (vinyl and indene C), 157.2 (C=N) and 168.2 (C=O).; MS *m/z*: 195 (M^+-60, 90), 180 (100), 153 (55), 149 (27) and 115 (29) (Found: M^+-60, 195.1037. $C_{14}H_{13}N$ requires M-60, 195.1044). ***SS,RR* isomer (40b)**: δ_H (250 MHz) 1.46 (3 H, s, CH_3), 1.51 (3 H, s, CH_3), 2.05 (3 H, s, CH_3CO), 2.8 (1 H, d, J = 9.6, CH), 6.25 (1 H, d, J = 5.6, indene H-2), 6.83 (1 H, d, J = 5.6, indene H-3), 7.01-7.23 (3 H, m, indene H), 7.28-7.33 (1 H, m, indene H) and 7.98 (1 H, d, J = 9.6, CH=N). Further elution with Et_2O afforded 51 mg (13%) of highly polar material.

Synthesis of Chrysanthemic Acid **1**

Nitrile **18.** A solution of **17** (135 mg, 0.7 mmol) in 20 ml of toluene was refluxed for 24 h. After removing the solvent, flash chromatography using hexane/Et_2O (9:1) gave 68 mg (70%) of nitrile **18** as a 1:1 mixture of *cis:trans* diastereomers; IR (neat) 2230 (CN) cm^{-1}; δ_H 1.05 (1.5 H, s, CH_3), 1.12 (1.5 H, s, CH_3), 1.13 (1.5 H, s, CH_3), 1.3 (1.5 H, s, CH_3), 1.4 (1 H, m, CH), 1.6 (4.5 H, s, CH_3C=C), 1.7 (1.5 H, s, CH_3C=C), 1.8 (1 H, m, CH), 4.8 (0.5 H, d, J = 8.0, vinyl H, *trans*-isomer) and 4.9 (0.5 H, dt, J = 8.0, 1.2, vinyl H, *cis*-isomer); δ_C (75 MHz) 16.6, 17.1, 17.6, 18.4, 18.6, 20.0, 23.40 (CH_3), 24.8 (quaternary C), 25.3 (CH_3), 25.4 (CH), 25.5 (quaternary C), 26.3, 29.2, 32.6 (CH), 116.9, 118.9 (CN), 119.0, 120.4, 137.6 and 138.1 (vinyl C).

Aldehyde **19.** To a solution of the nitrile **18** (60 mg, 0.4 mmol) in 20 ml of dry toluene were added slowly dropwise under argon and at -78 °C, 0.12 ml (1.2 mmol) of a 1 M solution of DIBAL in toluene. The mixture was stirred at -78 °C for 90 min, allowed to warm to RT and stirred for 2 h, before being quenched with 50 ml of 10% aqueous HCl and extracted with ether. The combined organic phases were washed with saturated $NaHCO_3$ solution, dried and concentrated to afford 40 mg (65%) of the aldehyde **19** as a 1:1 mixture of *cis:trans* diastereomers; IR (neat) 1700 (C=O) cm^{-1}; δ_H 1.11 (1.5 H, s, CH_3), 1.14 (1.5 H, s, CH_3), 1.26 (1.5 H, s, CH_3), 1.29 (1.5 H, s, CH_3), 1.60 (1 H, m, CH), 1.62 (1.5 H, s, CH_3C=C), 1.63 (1.5 H, s, CH_3C=C), 1.65 (1.5 H, s, CH_3C=C), 1.7 (1.5 H, s, CH_3C=C), 2.1 (1 H, m, CH), 4.9 (0.5 H, d, J = 7.3, vinyl H, *trans*-isomer), 5.4 (0.5 H, d, J = 7.3, vinyl H, *cis*-isomer), 9.37 (0.5 H, d, J = 6.5, CHO *cis*-isomer) and 9.40 (0.5 H, d, J = 5.5, CHO, *trans*-isomer); δ_C (75 MHz) 16.0, 18.5, 21.7, 22.3, 25.4 (CH_3), 28.7, 29.6, 31.4 (quaternary C), 34.5, 35.3, 40.8, 44.9 (CH), 117.2, 120.3, 135.9, 137.1 (vinyl C), 200.9 and 202.3 (CHO); UV (CH_2Cl_2) λ_{max} 258 (ε 5704) nm. The aldehyde **19** was identical to a sample obtained by PCC oxidation of chrysanthemyl alcohol (Aldrich 19,465-4).

Chrysanthemic Acid **1.** The aldehyde **19** (60 mg, 0.4 mmol) was added to a solution of $AgNO_3$ (150 mg, 1 mmol) and sodium hydroxide (70 mg) in water (10 ml). The mixture was stirred for 30 min and then filtered. The filtrate was washed with ether and the aqueous layer acidified with concentrated HCl. The milky solution was extracted with ether and the combined extracts were washed with water, dried over $MgSO_4$ and concentrated to give 54 mg (48%) of acid **1** as a solid: mp 50-52 °C (hexane) and as 1:1 mixture of *cis:trans* diastereomers; IR (neat) 2965 (OH) and 1695 (C=O) cm^{-1}; The NMR data of this compound were identical with those obtained from an authentic sample purchased from Sigma (10453-89-1).

Synthesis of Acid **29**

Nitrile **27.** A solution of **26** (600 mg, 2.5 mmol) in 20 ml of toluene was refluxed for 24 h. After removing the solvent, flash chromatography using hexane/Et_2O (8:2) gave 368 mg (83%) of nitrile **27** as a 3:1 mixture of *cis:trans* diastereomers; IR (neat) 2240 (CN) cm^{-1}; δ_H (250 MHz) 1.13 (0.75 H, s, CH_3, *trans*-isomer), 1.18 (2.25 H, s, CH_3, *cis*-isomer), 1.23 (2.25 H, s, CH_3, *cis*-isomer), 1.3 (0.75 H, s, CH_3, *trans*-isomer), 1.4 (1 H, d, J = 8.5, CH), 1.7 (5 H, m, $2CH_2$ and CH), 2.3 (4 H, m, $2CH_2$), 4.9 (0.25 H, dt, J = 8.5, 2.2, vinyl H, *trans*-isomer) and 5.2 (0.75 H, dt, J = 8.5, 2.2, vinyl H, *cis*-isomer); δ_C 16.9, 17.4, 17.8 (CH_3), 20.3, 23.7 (CH), 25.0, 25.6 (quaternary C), 26.5 (CH_2) 26.7 (CH_3), 29.6, 30.8, 34.0 (CH_2), 34.2 (CH), 112.7 (vinyl C, *cis*-isomer), 114.6 (vinyl C, *trans*-isomer), 119.4 (CN, *cis*-isomer), 120.9 (CN, *trans*-isomer), 149.82 (vinyl C, *trans*-isomer) and 149.84 (vinyl C, *cis*-isomer); MS *m/z*: 174 (M^+-1, 27), 160 (79), 146 (39), 132 (76), 97 (45), 91 (59), 79 (74), 77 (50) and 67 (100) (Found: M^+-1, 174.1284. $C_{12}H_{16}N$ requires M-1, 174.1279).

Aldehyde **28.** This compound was synthesized by the same procedure described for compound **19** from 2.1 ml (3.1 mmol) of a 1.5 M solution of DIBAL in toluene and the nitrile **27** (368 mg, 2.1 mmol) in 20 ml of dry toluene. Work-up afforded 335 mg (90%) of the aldehyde **28** as a 3:1 mixture of *cis:trans* diastereomers; IR (neat) 1700 (C=O) cm^{-1}; δ_H (250 MHz) 1.12 (0.75 H, s, CH_3, *trans*-isomer), 1.14 (2.25 H, s, CH_3, *cis*-isomer), 1.26 (2.25 H, s, CH_3, *cis*-isomer), 1.32 (0.75 H, s, CH_3, *trans*-isomer), 1.6 (5.25 H, m, $2CH_2$ and CH), 2.0 (0.75 H, m, CH), 2.2 (4 H, m, $2CH_2$), 5.0 (0.25 H, dt, J = 8.7, 2.3, vinyl H, *trans*-isomer), 5.4 (0.75 H, dt, J = 8.7, 2.3, vinyl H, *cis*-isomer) and 9.3 (1 H, d, J = 7.8, CHO); δ_C 16.0, 21.9, 22.3 (CH_3), 26.40, 26.50 (CH_2), 28.8 (CH_3), 29.44 (CH_2), 30.0, 31.4 (quaternary C), 33.9 (CH_2), 36.2 (CH), 37.1, 41.4, 45.3 (CH), 112.7 (vinyl C, *cis-isomer*), 115.7 (vinyl C, *trans*-isomer), 147.7 (vinyl C, *trans*-isomer), 148.7 (vinyl C, *cis*-isomer), 200.9 (CHO, *trans*-isomer) and 202.3 (CHO, *cis*-isomer); MS *m/z*: 149 (M^+-29, 12), 126 (11), 111 (100), 98 (32), 85 (61) and 67 (40) (Found: M^+-29, 149.1326. $C_{11}H_{17}$ requires M-29, 149.1326).

Acid **29.** The aldehyde **28** (300 mg, 1.7 mmol) was reacted with $AgNO_3$ (350 mg, 2 mmol) and sodium hydroxide (16 mg) in water (10 ml) following the procedure described for **1**. Work-up gave 180 mg (55%) of the acid **29** as an oil and as a 3:1 mixture of *cis:trans* diastereomers; IR (neat) 2990 (OH) and 1700 (C=O) cm^{-1}; δ_H (250 MHz) 1.0 (2.25 H, s, CH_3, *cis*-isomer), 1.1 (0.75 H, s, CH_3, *trans*-isomer), 1.15 (2.25 H, s, CH_3, *cis*-isomer), 1.21 (0.75 H, s, CH_3, *trans*-isomer), 1.6-2.0 (5 H, m, $2CH_2$ and CH), 2.2 (5 H, m, $2CH_2$ and CH), 5.0 (0.25 H, d, J = 7.1, vinyl H, *trans*-isomer), 5.3 (0.75 H, d, J = 7.0, vinyl H, *cis*-isomer) and 8.6 (1 H, br s, CO_2H); δ_C 15.7 (CH_3), 20.5, 20.9 (CH), 23.2 (CH_3), 23.5, 23.6 (CH_2), 24.4, 27.1 (CH_3), 27.2,

28.3 (quaternary C), 28.9, 29.7, 32.2 (CH_2), 32.9, 32.5 (CH), 35.0, 38.2, 38.7 (CH_2), 123.7 (vinyl C, *cis*-isomer), 124.5 (vinyl C, *trans*-isomer), 142.9 (vinyl C, *cis*-isomer), 150.4 (vinyl C, *trans*-isomer), 178.4 (C=O, *trans*-isomer) and 179.4 (C=O, *cis*-isomer); MS *m/z*: 194 (M^+, 23), 179 (16), 162 (13), 149 (27), 113 (85), 95 (94), 81 (100), 110 (100) and 69 (29) (Found: M^+, 194.1296. $C_{12}H_{18}O_2$ requires M, 194.1302).

Synthesis of Acid **41**

Nitrile **43.** A solution of **39** (218 mg, 0.7 mmol) in 20 ml of toluene was refluxed for 24 h. After removing the solvent, flash chromatography on silica gel using hexane/Et_2O (9:1) gave 123 mg (73%) of the nitrile **43** as colourless crystals: mp 129-131 °C (hexane); IR (neat) 2240 (CN) cm^{-1}; δ_H 1.5 (3 H, s, CH_3), 1.6 (3 H, s, CH_3), 2.5 (1 H, s, CH), 7.2-7.5 (5 H, m, aryl H), 7.6 (1 H, m, aryl H) and 7.7-7.8 (2 H, m, aryl H); δ_C (75 MHz) 19.9, 22.2 (CH_3), 24.8 (CH), 30.7, 43.5 (quaternary C), 116.9 (CN), 119.9, 120.0, 122.2, 124.4, 126.0, 126.5, 127.2, 140.2, 141.0, 141.1 and 142.1 (vinyl and aryl C) (Found: C, 87.6; H, 6.4; N, 5.6. $C_{18}H_{16}N$ requires C, 87.80; H, 6.50; N, 5.69%).

Aldehyde **44.** This compound was synthesized by the same procedure described for **19**, from 1.1 ml (1.48 mmol) of a 1.5 M solution of DIBAL in toluene and the nitrile **41** (193 mg, 0.9 mmol) in 20 ml of dry toluene. Work-up gave 156 mg (80%) of aldehyde **44** as an oil; IR (neat) 1690 (C=O) cm^{-1}; δ_H 1.4 (3 H, s, CH_3), 1.7 (3 H, s, CH_3), 2.7 (1 H, d, J = 5.4, CH), 7.1-7.8 (8 H, m, aryl H) and 9.9 (1 H, d, J = 5.4, CHO); δ_C (75 MHz) 18.7, 23.7 (CH_3), 26.3 (quaternary C), 34.8 (CH), 49.1 (quaternary C), 119.9, 122.6, 124.1, 126.1, 126.7, 128.8, 133.8, 134.5, 140.2, 141.3, 143.3, 144.1 (aryl C) and 198.8 (CHO).

Acid **41.** The aldehyde **44** (130 mg, 0.5 mmol) was reacted with $AgNO_3$ (110 mg, 0.6 mmol) and sodium hydroxide (50 mg) in water (10 ml) following the procedure described for **1**. Work-up gave 98 mg (71%) of acid **41** as an oil; IR (neat) 3025 (OH) and 1705 (C=O) cm^{-1}; δ_H 1.5 (3 H, s, CH_3), 1.7 (3 H, s, CH_3), 2.7 (1 H, s, CH), 7.1-7.7 (8 H, m, aryl H), 12.5 (1 H, br s, CO_2H); δ_C 18.8, 23.4 (CH_3), 26.8 (quaternary C), 34.3 (CH), 48.5 (quaternary C), 119.9, 122.5, 124.3, 126.1, 126.7, 128.4, 133.5, 134.7, 140.2, 141.0, 143.3, 144.1 (aryl C) and 177.6 (C=O); MS *m/z*: 264 (M^+, 6), 180 (97), 165 (10), 152 (29), 135 (24), 126 (15), 113 (36), 95 (94), 82 (56), 77 (21) and 67 (79) (Found: M^+, 264.11457. $C_{18}H_{16}O_2$ requires M, 264.1146).

Synthesis of Acid **42**

Nitrile **45.** A solution of **40** (300 mg, 1.18 mmol) in 20 ml of toluene was refluxed for 35 h. After removing the solvent, flash chromatography on silica gel using hexane/Et_2O (9:1) gave 205 mg (89%) of the nitrile **45** as an oil and as a 6:1 mixture of *SR,RS*:*SS,RR* diastereomers; IR (neat) 2240 (CN) cm^{-1}; δ_H 1.41 (0.42 H, s, CH_3, *SS,RR*-isomer), 1.44 (2.58 H, s, CH_3, *SR,RS*-isomer), 1.52 (0.42 H, s, CH_3, *SS,RR*-isomer), 1.54 (2.58 H, s, CH_3, *SR,RS*-isomer), 2.2 (0.86 H, s, CH, *SR,RS*-isomer), 2.3 (0.14 H, s, CH, *SS,RR*-isomer), 6.10 (0.14 H, d, J = 5.7, indene H-2, *SS,RR*-isomer), 6.37 (0.86 H, d, J = 5.7, indene H-2, *SR,RS*-isomer), 6.88 (0.14 H, d, J = 5.7, indene H-3, *SS,RR*-isomer), 6.92 (0.86 H, d, J = 5.7, indene H-3, *SR,RS*-isomer) and 7.4-7.0 (4 H, m, indene H); δ_C 21.6 (CH_3, *SS,RR*-isomer), 21.8 (CH_3, *SR,RS*-isomer), 22.6 (CH_3, *SR,RS*-isomer), 23.6 (CH_3, *SS,RR*-isomer), 24.6 (CH, *SR,RS*-isomer), 26.8 (CH, *SS,RR*-isomer), 31.1 (quaternary C, *SS,RR*-isomer), 32.0 (quaternary C, *SR,RS*-isomer), 46.8 (quaternary C, *SS,RR*-isomer), 47.3 (quaternary C, *SR,RS*-isomer), 118.6, 119.7 (CN), 121.2, 121.4, 122.3, 122.5, 124.7,

125.0, 127.1, 127.2, 132.6, 133.0, 134.3, 135.4, 142.3 and 144.6 (indene C); MS *m/z*: 195 (M^+, 67), 180 (100), 153 (50), 149 (32) and 115 (23) (Found: M^+, 195.1039. $C_{14}H_{13}N$ requires M, 195.1044).

Aldehyde **46**. This compound was synthesized by the same procedure described for **19**, from 1.1 ml (1.48 mmol) of a 1.5 M solution of DIBAL in toluene and the nitrile **45** (193 mg, 1 mmol) in 20 ml of dry toluene. Work-up gave 161 mg (82%) of the aldehyde **46** as an oil and a 6:1 mixture of *SR,RS*:*SS,RR* diastereomers; IR (neat) 1710 (C=O) cm^{-1}; δ_H (250 MHz) 1.52 (0.42 H, s, CH_3, *SS,RR*-isomer), 1.57 (2.58 H, s, CH_3, *SR,RS*-isomer), 1.65 (2.58 H, s, CH_3, *SR,RS*-isomer), 1.8 (0.42 H, s, CH_3, *SS,RR*-isomer), 2.7 (0.15 H, d, J = 6.2, CH, *SS,RR*-isomer), 2.8 (0.85 H, d, J = 5.5, CH, *SR,RS*-isomer), 6.2 (0.14 H, d, J = 5.6, indene H-2, *SS,RR*-isomer), 6.8 (0.86 H, d, J = 5.7, indene H-2, *SR,RS*-isomer), 6.90 (0.14 H, d, J = 5.6, indene H-3, *SS,RR*-isomer), 6.96 (0.86 H, d, J = 5.7, indene H-3, *SR,RS*-isomer), 7.1-7.5 (4 H, m, indene H), 9.8 (0.85 H, d, J = 5.5, CHO, *SR,RS*-isomer) and 9.9 (0.15 H, d, J = 6.2, CHO, *SS,RR*-isomer); δ_C 17.8 (CH_3, *SS,RR*-isomer), 20.7 (CH_3, *SR,RS*-isomer), 23.6 (CH_3, *SR,RS*-isomer), 27.2 (CH_3, *SS,RR*-isomer), 36.7 (quaternary C), 46.2 (CH, *SS,RR*-isomer), 50.4 (CH, *SR,RS*-isomer), 52.1 (quaternary C, *SR,RS*-isomer), 53.5 (quaternary C, *SS,RR*-isomer), 121.5, 121.9, 122.2, 124.4, 126.5, 130.5, 131.1, 133.4, 137.4, 143.2, 143.9 (indene C), 198.5 (CHO, *SS,RR*-isomer) and 198.6 (CHO, *SR,RS*-isomer); MS *m/z*: 169 (M^+-29, 7) and 149 (100) (Found: M^+-29, 169.10128. $C_{13}H_{13}$ requires M-29, 169.1014).

Acid **42.** The aldehyde **46** (144 mg, 0.76 mmol) was reacted with $AgNO_3$ (140 mg, 1 mmol) and 70 mg of sodium hydroxide in water (10 ml) following the procedure described for **1**. Work-up gave 112 mg (72%) of acid **46** as an oil and as a 6:1 mixture of *SR,RS*:*SS,RR* diastereomers. Treatment of this fraction with hexane afforded the major isomer (*SR,RS*) as a solid: mp 131-133 °C (hexane). ***SR,RS* isomer**: IR (KBr) 2970 (OH) and 1690 (C=O) cm^{-1}; δ_H 1.5 (3 H, s, CH_3), 1.6 (3 H, s, CH_3), 2.7 (1 H, s, CH), 6.91 (1 H, d, J = 6.6, indene H-2), 6.93 (1 H, d, J = 6.6, indene H-3), 7.2-7.4 (4 H, m, indene H) and 10.08 (1 H, br s, CO_2H); δ_C 20.0, 23.7 (CH_3), 35.1 (quaternary C), 40.8 (CH), 49.9 (quaternary C), 121.5, 121.9, 124.1, 126.5, 130.4, 135.3, 143.6, 144.5 (indene C) and 177.4 (CO_2H); MS *m/z*: 214 (M^+, 60), 199 (13), 169 (100), 153 (32), 115 (60) and 77 (10) (Found: M^+, 214.0992. $C_{14}H_{14}O_2$ requires M, 214.0990). ***SS,RR* isomer**: IR (KBr) 2970 (OH) and 1690 (C=O) cm^{-1}; δ_H (250 MHz) 1.5 (3 H, s, CH_3), 1.7 (3 H, s, CH_3), 2.7 (1 H, s, CH), 6.25 (1 H, d, J = 5.6, indene H-2), 7.2-7.4 (5 H, m, indene H) and 10.08 (1 H, br s, CO_2H); δ_C 16.8 , 23.6 (CH_3), 35.0 (quaternary C), 38.7 (CH), 49.9 (quaternary C), 124.4, 125.3, 126.4, 128.9, 130.6, 138.2, 143.7, 144.6 (indene C) and 177.5 (CO_2H).

ACKNOWLEDGMENTS

We thank the Dirección General de Investigación Científica y Técnica (Grant No. PB 91/0396) and the European Union (Contract no. CHRX-CT93-0151) for financial support.

REFERENCES

1. Naumann, K. *Synthetic Pyrethroid Insecticides. Chemistry and Patents*, vols. 4 and 5, Springer Verlag 1990.
2. Storck, W. J. *Chemical & Engineering News* **1987**, *65 (14)*, 11.
3. Arlt, D.; Jautelat, M.; Lantzsch, R. *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 703.
4. Bullivant, M. J.; Pattenden, G. *J. Chem. Soc., Perkin Trans. 1* **1976**, 256.
5. Baeckstrom, P. *Tetrahedron* **1978**, *34*, 3331.
6. Armesto, D.; Ortiz, M. J.; Horspool, W. M.; Ramos, A. *J. Org. Chem.* **1994**, *59*, 8115 and references cited therein.
7. Armesto, D.; Ramos, A. *Tetrahedron* **1993**, *49*, 7159.
8. Armesto, D.; Horspool, W. M.; Langa, F.; Ramos, A. *J. Chem. Soc., Perkin Trans. 1* **1991**, 223.
9. Armesto, D.; Gallego, M. G.; Horspool, W. M.; Bermejo, F. ES. P. 9100648 (13th March 1991); Patent PCT/ ES 92/ 00017 (13th February 1992).
10. Armesto, D.; Gallego, M. G.; Horspool, W. M. *Tetrahedron* **1990**, *46*, 6185.
11. Armesto, D.; Horspool, W. M.; Gallego, M. G.; Agarrabeitia, A. R. *J. Chem. Soc., Perkin Trans. 1* **1992**, 163.
12. Taylor, E. C.; La Mattina, J. L. *Tetrahedron Lett.* **1977**, *24*, 2077.
13. Vedejs, E.; Fuchs, P. L. *J. Org. Chem.* **1971**, *36*, 366.
14. Mills, R. W.; Murray, R. D. H.; Raphael, R. A. *J. Chem. Soc., Perkin Trans. 1* **1973**, 133.
15. Tsuzuki, K.; Nakayima, Y.; Watanabe, T.; Yanagiya, M.; Matsumoto, T. *Tetrahedron Lett.* **1978**, *11*, 989.
16. Baldwin, J. E.; Black, K. A. *J. Am. Chem. Soc.* **1984**, *106*, 1029.
17. Zimmerman, H. E. *Org. Photochem.*; Pawda, A. Eds.; Marcel Dekker, **1991**, *11*, 1.
18. Demuth, M. *Org. Photochem.*; Pawda, A. Eds.; Marcel Dekker, **1991**, *11*, 37.

(*Received in UK* 9 *June* 1995; *accepted* 30 *June* 1995)