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LINEAR FREE ENERGY RELATIONSHIPS—II[a]
SYNTHESIS AND SPECTRAL CHARACTERIZATION OF SOME NEW SOLVATOCHROMICS: 5'-SUBSTITUTED-2'-HYDROXY-4-STILBAZOLE DERIVATIVES

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Abstract—A series of 5'-substituted-2'-hydroxy-4-stilbazolium methiodides was prepared by reaction of 5-substituted salicylaldehydes and 4-picoline methiodide. Reaction of these with base leads to the corresponding betaines, which are highly solvatochromic. In addition, 1:1 complexes of the methiodide salts and the betaines were isolated from the initial reaction.

The energies of the long wavelength transitions of the salts, the betaines and the 1:1 complexes of these are directly proportional to the electrophilic substituent constants (σ^+) and the slopes are positive. Hence, the transitions appear to involve electron transfer from the salicyl ring to the pyridyl moiety.

The solvatochromisms of the betaines and the complexes are directly proportional to the solvent polarity parameter, E_T. The slopes are positive, meaning the dipole moments decrease upon excitation, again consistent with the charge transfer transition mentioned above. The relative slopes are rationalized on the basis of substituent effects.

INTRODUCTION

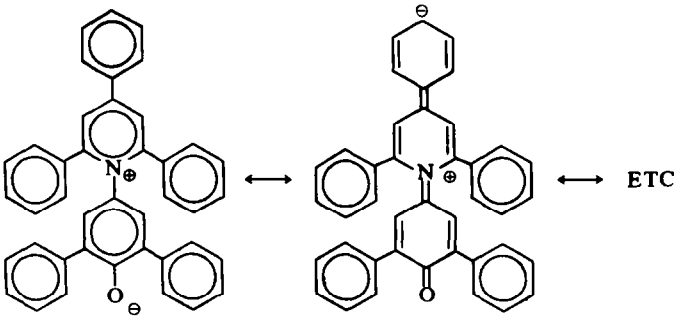
Solvatochromic compounds undergo 'color' changes, i.e., shifts in absorption wavelength, when the solvent is changed. To some extent, all compounds are solvatochromic inasmuch as spectral shifts occur in passing through the gas, liquid, solid and solution phases.[1a] These spectral shifts arise because of variable intermolecular interactions between solutes and 'solvents' in the condensed phases.

The solvatochromic compounds that undergo large shifts may generally be described in terms of two extreme resonance contributors: one of these is quinoidal or delocalized; the other is a non-quinoidal or polarized form. The change in absorption wavelength with solvent does not arise from coexistence of two tautomers, but rather from variation in the contribution of these extreme resonance forms to the resonance hybrid.[2] Thus, as solvent polarity is varied in a mixture of solvents, the absorption maximum moves continuously; there is no isosbestic point. A striking example of solvatochromism is provided by compound 1 which has λ_{max} 453 nm (yellow) in water and λ_{max} 810 nm (blue-green) in diphenyl ether.[3]

Quite a number of solvatochromatic compounds which undergo substantial color changes have been reported. The most extensive work seems to be that of Brooker and colleagues.[4] Their work dealt with merocyanines prepared by condensation reactions of active methyl substituted heterocycles. An examples of this type is compound 2.

The main interest in solvatochromics has been their use as empirical solvent polarity indicators.[5,6]

*Ref. 7 is considered Paper I of this series.



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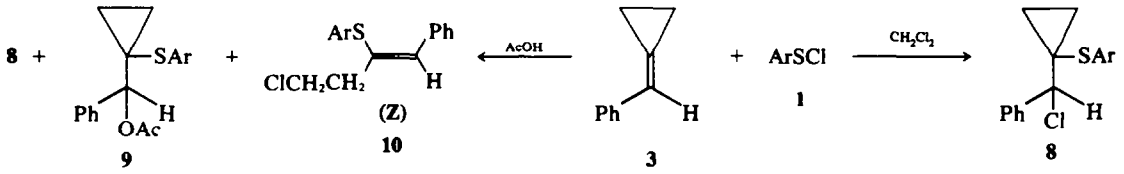
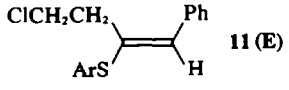


of **7**. In AcOH, after 1 h, a mixture of **6** and the rearranged chlorosulphide **7**, in an approximate ratio of 1:1, was obtained. After 5 h, practically all of **6** was transformed to **7**. By conducting the reaction in a NMR tube in CD_3COOD, it could be shown that both **6** and **7** were formed simultaneously and that **6** rearranged slowly to **7**.

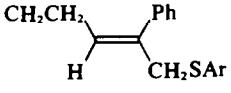
Addition of **1** to **3** in CH_2Cl_2 gave only the normal adduct **8**. In the reaction in AcOH—three major products were formed: **8**, **9**, and **10** in a ratio of 67:13:20. The ratio (average of three experiments) was established by NMR of the crude reaction mixture (some additional very small signals in the NMR spectrum were not identified). All three compounds are primary products as shown by performing a reaction in a NMR tube in CD_3COOD. The ratio of **8**:**9**:**10** remained approximately constant. The **Z** configuration of **10** was assigned according to the mechanism of the ring opening (see discussion). It may be that a small amount of the **E** isomer (**11**) was also formed.



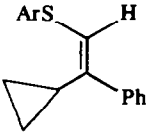
11 (E)

The reaction of **4** with **1** in CH_2Cl_2 or in AcOH gave two isomeric products **12** and **13**. The ratio of **12**:**13** in CH_2Cl_2 (after 1 h) was 1:2 and changed gradually to a constant ratio of 1:1 (average of three experiments). The ratio of **12**:**13** in AcOH was from the start (after 1 h) 1:1. The equilibration of the two isomers is probably acid catilized. Pure samples of **12** and **13** were prepared by careful column chromatography of the mixture on silica with subsequent crystalization. The stereochemistry of the two isomers was assigned on the basis of the chemical shift of the vinylic protons in **12** and **13**.[12] The isomer with the proton at δ 5·97 *cis* to the phenyl ring has the **Z** configuration, whereas the second isomer with the vinylic proton at δ 5·64 *trans* to the phenyl ring has the **E** configuration. In contrast to the mainly normal addition of **1** to **2** and **3**; only rearranged products were formed from **4**. However, in all three cases the –SAr substituted ring was relatively stable towards ring-cleavage, in particular when the reaction was performed in CH_2Cl_2.

In order to acquire more information about the preferential ring-opening of the unsubstituted ring in **4**, we investigated the addition of **1** to **5** in which the cyclopropyl ring will remain unsubstituted during the entire reaction. In CH_2Cl_2 two main products (85%) were obtained in an 1:1 ratio (three experiments) according to the NMR of the crude reaction mixture. In CH_3NO_2– the ratio was 2:1 and in AcOH only **14** was formed. The two products were isolated by TLC and subsequent crystalization. The reaction was stereospecific in all cases, the stereoisomers **16** and **17** were absent. In order to establish the stereochemistry of **14** and **15** we tried to prepare the second isomer in each case. Irradiation of **14** in benzene gave a mixture of **14** and **16**, however, in low yield. Separation by TLC

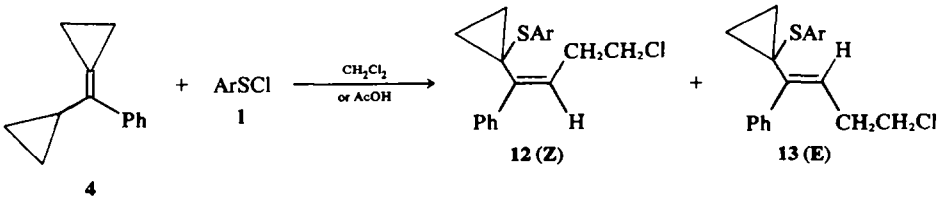


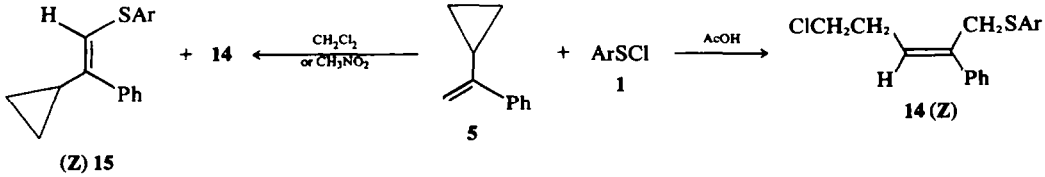
16 (E)



17 (E)

was very difficult and only a crude sample of **16** could be obtained (other attempts to isomerize **14** failed). Comparison of the chemical shift of the vinylic proton[12] at δ 6·07 *cis* to the phenyl group



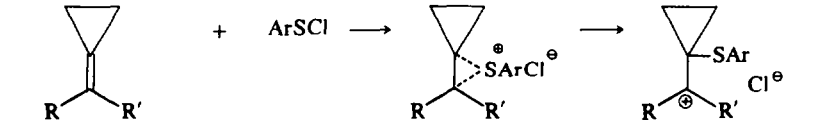


and the corresponding signal at δ 5·92 *trans* to the phenyl ring, established the **Z** configuration for **14** and the **E** configuration for **16**. Irradiation of **15** in MeOH gave a clean mixture of **15** and **17** in a ratio of 2:1. Separation by TLC gave pure **17**. Comparison of the NMR[12] of **15** and **17** established the **Z** configuration for **15** (vinylic proton at δ 6·18) and the **E** configuration for **17** (vinylic proton at δ 6·24).

DISCUSSION

There are three main points which are clearly evident from above results: (A) Most important—the different behaviour of the methylenecyclopropane system *versus* the vinylcyclopropane system; (B) the influence of the solvent; (C) the stereochemistry of the rearrangements.

(A) Comparison of the addition in CH_2Cl_2, of **1** to **2** and **3** and on the other hand to **4** and **5** shows that only the methylenecyclopropanes add **1** normally. The reason for this is the attachment of the –SAr group on the cyclopropyl ring. The first step in the addition of **1** to **2**, **3** and **4** involves a bridged transition state which may lead to the intermediate carbonium ion **19** either *via* the episulfonium ion **18**

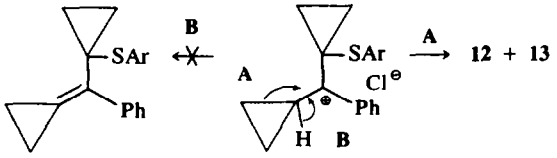


2: R = R′ = Ph
3: R = Ph; R′ = H
4: R = Ph; R′ = c.C$_3$H$_5$

18

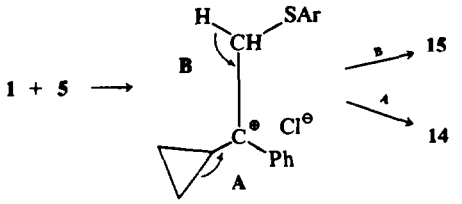
19
a: R = R′ = Ph
b: R = Ph; R′ = H

or directly.[8] The cyclopropyl ring, due to its high strain, undergoes the cyclopropylcarbinyl carbonium ion rearrangement to the homoallylic carbonium ion if possible.[9,13] This rearrangement involves the donation of a pair of electrons from the ring to form the double bond in the homoallyl system. The attachment of electronegative 2,4-dinitrobenzenesulfenyl group on the ring prevents this process—therefore, the reaction is terminated by attack of the chloride ion on **18** or **19** to yield the normal addition products. When R′ is cyclopropyl (**4**), the positive charge in the carbonium **20** is



21 **20**

adjacent to both rings. The –SAr substituted ring remains intact whereas the second ring undergoes the expected ring cleavage to yield **12** + **13**. A similar inhibition of ring opening by the electronegative effect of chlorine was observed in the solvolysis of *gem*-dichlorocyclopropylcarbinyl chloride.[14]



22

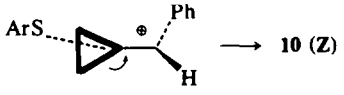
The addition of **1** to **5** involves the carbonium ion **22** (*via* an episulfonium ion or directly) which is the product determining step. The intermediate **22** may either undergo a cyclopropylcarbinyl carbonium ion rearrangement (path **A**) or loose a proton (path **B**). Both routes are observed and the ratio between them is solvent dependent. In the case of **20**—Path **A** takes place preferentially because path **B** would lead to the strained methylenecyclopropane **21**. A few cases of vinyl sulfide formation, during the addition of sulfenyl chlorides to olefins, have been observed.[6,15,16] This fact has been viewed as evidence for the participation of an intermediate carbonium ion.[6,16] The rearrangment with ring opening[9,13] is, in particular, a characteristic reaction of the cyclopropylcarbinyl carbonium ion—thus confirming the participation of carbonium ions **19**, **20** and **22** in addition of **1** to **2**, **3**, and specially to **4** and **5**.

(B) The solvent, CH_2Cl_2 or AcOH, has a relative strong influence on the character of the addition reactions of **1**, in particular on the addition to **5**. CH_2Cl_2 is an aprotic solvent whereas AcOH is a more ionizing and protic solvent which may promote the disassociation of **6** for example. In addition, AcOH can reduce the nucleophilicity of the chloride ion by solvation and increase the lifetime of the corresponding carbonium ion.[7] In the case of **2** and **3**, AcOH promotes ring cleavage due to the reasons mentioned. In this solvent pure **6**, rearranges, *via* **19a**, slowly to **7** whereas **8** does not rearrange at the same conditions (24 h at r.t.). This difference may be the result of the more facile disassociation of **6** than of **8**. A very pronounced solvent effect has been found in the addition of **1** to **5**. AcOH inhibits completely the stabilization of **22** by path **B**. The tendency of the intermediate **22** to loose a proton is diminished by enhanced acidity of the solvent in the order:

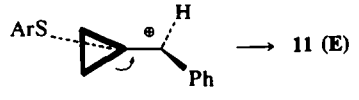
$$AcOH \gg CH_3NO_2 > CH_2Cl_2.$$

It is of interest that in all cases [except in the case of **3** which gave a small amount of unrearranged acetate (**9**)] no participation of AcOH, in the addition reactions, has been found. All rearranged products: **7**, **10**, **12**, **13** and **14** were formed by attack of chloride ion on the corresponding homoallylic carbonium ions. This observation is in contrast to the report of Cristol and Jarvis[7]—in which addition of phenylsulfenyl chloride to dibenzobicyclo-[2,2,2]octatriene in AcOH resulted in formation of the rearranged acetate. The different behaviour of the two systems is a result of different ion pairs formed. In our case an "intimate" ion pair participates which collapses by internal return[17] to yield rearranged chlorides. In the case of dibenzobicyclo[2,2,2]octatriene a solvent separated ion pair is formed which reacts with a solvent molecule[17] to yield rearranged acetate.[7]

(C) The formation of **10** and in particular **14** and **15** is stereospecific, also the initial ratio of **12** and **13** 1:2 (in CH_2Cl_2) shows some preference for the formation of the E isomer (**13**). The conformation of all the cyclopropylcarbinyl carbonium ions will be bisected due to the large energy stabilization of this conformation;[9] the prefered spatial arrangement in all cases will place the more bulky substituents as far as possible—thus controlling the subsequent ring opening and stereochemistry of the olefinic products. Starting from **3**—the carbonium ion (**19b**) may have conformation **23** or **24**.

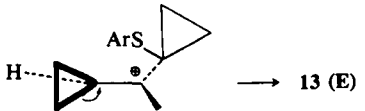


23



24

Inspection of Dreiding models shows that **23** has less steric crowding than **24**—therefore the isomer (**10**) will be formed preferentially. This conclusion is in accord with the fact that the cyclopropyl ring is the largest group and the SAr group has a small steric influence because of the long C–S bond which keeps the 2,4 - dinitrophenyl group away from the phenyl ring. In the case of the carbonium ion **20** the two conformations **25** and **26** have similar energies with some preference for **25** in which the two cyclopropyl rings are *trans*. The strongest influence of the conformation of the cyclopropylcarbinyl carbonium ion on the stereochemistry of the products is demonstrated in the case of **5**. The prefered spatial arrangement of **22** will place the phenyl and SAr groups as far as possible from the



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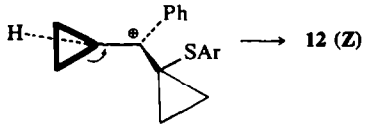

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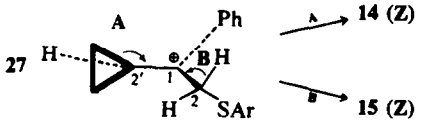

cyclopropyl ring therefore conformation **27** will be favoured (Dreiding models). This conformation will lead by path **A** to **14**. The configuration of the double bond of **15** will be controlled by the conformation of the C_1C_2 unit. The leaving proton will be eclipsed with the empty orbital of the carbonium ion (path **B**).

EXPERIMENTAL

Microanalysis were performed by Mrs. M. Goldstein of the micro-analytical laboratory of the Hebrew University. B.ps and m.ps are uncorrected. NMR spectra were recorded on Varian EM-360 and HA-100 spectrometers with TMS as internal standard. They are reported in δ units, ppm multiplicity (number of hydrogens). IR spectra were measured on a Perkin-Elmer Infracord 337 machine and UV spectra were recorded on a Unicam SP-800 spectrometer. Mass spectra were recorded on an Atlas Mat CH4 spectrometer. TLC was carried out on 2 mm Merck Kieselgel 60 F_{254} plates. For column chromatography Merck Kieselgel 60 (70–230 mesh) was used. Irradiations were performed in a pyrex vessel with a 75 Watt Hanovia lamp. The IR spectra of all addition products are very similar, therefore, they are not reported.

Starting materials. Compound **1** puriss. p.a. (Fluka) was used without further purification. Compounds **2** and **3** were prepared according to the procedure of Utimoto *et al.*[10] Compound **4** was prepared from 3 - bromopropyltriphenylphosphonium bromide and cyclopropylphenyl ketone similar to **2** and **3**.[10] The crude product b.p. 80–90%, 2 mm, was purified by column chromotography and redistilled in a kugelrohr at 100–110/0·2 mm, yield 55%. IR (neat) 3000 br, 1670, 1600, 1495, 1445, 960, 760, 690 cm^{-1}, NMR (CCl_4): 7·70/m (2H); 7·20/m(3H); 1·70/m(1H); 1·20/bs(4H); 0·80/m(4H). UV: λ_{max}^{EtOH} (nm) 251 (ϵ 10600), 270 (ϵ 5400) shoulder. MS: M^+ 170 *m/e*. (Found: C, 91·9; H, 8·3. Calc. for $C_{13}H_{14}$: C, 91·8; H, 8·2%). Compound **5** was prepared from methyltriphenylphosphonium bromide and cyclopropylphenyl ketone by the procedure of Zimmermann *et al*[11] in 75%, b.p. 50–55/0·4 mm (lit[18] b.p. 92–94/3 mm).

Addition of **1** *to diphenylmethylenecyclopropane* (**2**)

(a) A mixture of **1** (1·17 g, 5 mmol) and **2** (1·03 g,

5 mmol) in CH_2Cl_2 (20 ml) was stirred magnetically for 1 h at r.t. The mixture was concentrated and dried on high *vacuo*. The NMR showed the presence of **6** with traces of **7**. Crystallization from CH_2Cl_2 + hexane gave 80–90% of **6** m.p. 139–141° with preliminary softening. A second crystallization from cyclohexane gave an analytical sample m.p. 153–154°. NMR ($CDCl_3$): 8·79/d, J = 2 (1H); 7·81/dxd, J_1 = 9; J_2 = 2 (1H); 7·60/m(4H); 7·25/m(6H); 7·02/d, J = 9 (1H); 2·00/m(2H); 1·36/m(2H). UV: λ_{max}^{EtOH} (nm) 350 (ε 10800), 275 (9000) shoulder. (Found: C, 60·1; H, 3·9; Cl, 8·3; N, 6·2; S, 7·1. Calc. for $C_{22}H_{17}ClN_2O_4S$: C, 59·9; H, 3·8; Cl, 8·0; N, 6·3; S, 7·2%). The same reaction was run for 20 h with the same results.

(b) A mixture of **2** (1·03 g, 5 mmol) and **1** (1·17 g, 5 mmol) in AcOH (20 ml) was stirred at r.t. for 20 h; concentrated and dried on high *vacuo*. NMR showed the presence of one product namely **7**. Crystallization from ethyl acetate + hexane gave 60–70% of **7**, m.p. 173–175°. NMR ($CDCl_3$): 8·97/d, J = 2 (1H); 8·39/dxd, J_1 = 9; J_2 = 2 (1H); 7·80/d, J = 9 (1H); 7·36/m(4H); 7·20/bs (6H); 3·69/t, J = 7 (2H); 2·86/t, J = 7 (2H). UV: λ_{max}^{EtOH} (nm) 353 (ε 10000); 275 (ε 10400) shoulder. (Found: C, 59·9; H, 3·6; Cl, 8·1; N, 6·2; S, 7·4. Calc. for $C_{22}H_{17}ClN_2O_4S$: C, 59·9; H, 3·8; Cl, 8·0; N, 6·3; S, 7·2%). When the same reaction was run for 1 h a mixture of **6** and **7** in a ratio of 1:1 was obtained (NMR). The transformation of **6**→**7** in CD_3COOD was checked periodically by NMR.

Addition of **1** *to benzylidenecyclopropane* (**3**)

(a) A mixture of **3** (0·65 g, 5 mmol) and **1** (1·17 g, 5 mmol) in CH_2Cl_2 (20 ml) was stirred under N_2 at r.t. for 1 h. Solid impurities were filtered off and the filtrate was concentrated and dried. The NMR showed the presence of **8** accompanied by traces of other products. Crystallization from ethyl acetate + hexane gave 70–80% of **8**, m.p. 135–136°. NMR ($CDCl_3$): 8·96/d, J = 2 (1H); 8·08/dxd, J_1 = 9; J_2 = 2 (1H); 7·53/d, J = 9 (1H); 7·34/m(5H); 4·96/s(1H); 1·9–1·1/m(4H). UV: λ_{max}^{EtOH} (mm) 331 (ε 11000); 275 (ε 6000) shoulder. (Found: C, 53·0; H, 3·6; Cl, 9·6; N, 7·5; S, 8·7. Calc. for $C_{16}H_{13}ClN_2O_4S$: C, 52·7; H, 3·6; Cl, 9·7; N, 7·7; S, 8·8%). The same reaction was run for 4 h with the same results.

(b) The same reaction as above in 20 ml AcOH gave a crude residue which was dissolved in CH_2Cl. Small amounts of solid material were filtered off and the filtrate was concentrated to dryness and analysed by NMR. Three main products were present **8**, **9** and **10** in a ratio of 67:13:20 (3 experiments). The same ratio was obtained after 20 h. Crystallization from ethyl acetate + hexane gave 0·82 g (45%) of **8**. The residue was submitted to preparative TLC with ethyl acetate 1: hexane 4 as eluent. Products **9** and **10** were isolated along with a third product which was not identified. Crystallization from MeOH + H_2O gave acetate (**9**), m.p. 163–164° with preliminary softening. IR (CCl_4): 1735 cm^{-1} (acetate). NMR ($CDCl_3$): 8·96/d, J = 2 (1H); 8·18/dxd, J_1 = 9, J_2 = 2 (1H); 7·82/d, J = 9 (1H); 7·30/bs (5H); 5·83/s(1H); 2·10/s(3H); 1·55–1·10/m(4H). (Found: C, 55·5; H, 4·4. Calc. for $C_{18}H_{16}N_2O_6S$: C, 55·7; H, 4·1%). Crystallization of **10** from MeOH + H_2O gave a sample with m.p. 100–101°. NMR ($CDCl_3$): 9·06/d, J = 2 (1H); 8·32/dxd, J_1 = 9, J_2 = 2 (1H); 7·67/d, J = 9 (1H); 7·44/bs(5H); 7·25/s(1H); 3·72/t, J = 7 (2H); 3·01/5, J = 7 (2H). (Found: C, 53·0; H, 3·9. Calc. for $C_{16}H_{13}ClN_2O_4S$: C, 52·7; H, 3·6%).

Addition of **1** *to α-cyclopropylbenzylidenecyclopropane* (**4**)

(a) A mixture of **4** (0·85 g, 5 mmol) and **1** (1·17 g, 5 mmol) in CH_2Cl_2 (20 ml) was stirred at r.t. under N_2 for 1 h; solid impurities were filtered off and the filtrate was concentrated and dried. The NMR showed the presence of **12** and **13** in the ratio of 1:2. When the crude mixture was left for 20 h the ratio changed to approximately 1:1, Crystalization from MeOH + H_2O gave 80–90% of a mixture of **12** + **13**. Chromatography of 1 g mixture on 200 g SiO_2 and elution with hexane + 10% ethyl acetate gave a small amount of the **Z** isomer (**12**); m.p. 130–132° (MeOH + H_2O). NMR ($CDCl_3$): 9·00/d, J = 2 (1H); 8·36/dxd, J_1 = 9, J_2 = 2 (1H); 8·14/d, J = 9 (1H); 7·40–7·00/m(5H); 5·97/t, J = 7 (1H); 3·41/t, J = 7 (2H); 2·28/q, J = 7 (2H); 1·80–1·20/m(4H). A main fraction of a mixture of **12** + **13** and finally a small sample of the **E** isomer (**13**); m.p. 127–129 (MeOH + H_2O). NMR ($CDCl_3$: 8·85/d, J = 2 (1H); 8·05/dxd, J_1 = 9, J_2 = 2 (1H); 7·80/d, J = 9 (1H); 7·24/bs(5H); 5·64/t, J = 7 (1H); 3·69/t, J = 7 (2H); 3·01/q, J = 7 (2H); 1·8–1·1/m(4H). (Found: C, 56·5; H, 4·3; Cl, 8·6; N, 6·7; S, 7·6. Calc. for $C_{19}H_{17}ClN_2O_4S$ (**12** + **13**): C, 56·4; H, 4·2; Cl, 8·8; N, 6·9; S, 7·9%).

(b) When the same reaction was run in AcOH, a mixture of **12**:**13** in an approximate ratio of 1:1 was obtained. Crystallization from MeOH + H_2O gave 70–80% yield of the mixture.

Addition of **1** *to α-cyclopropylstyrene* (**5**)

(a) A mixture of **5** (0·72 g, 5 mmol) and **1** (1·17 g, 5 mmol) in CH_2Cl_2 (20 ml) was stirred, at r.t. under N_2 for 1 h, concentrated and dried. According to NMR two main products, **14** and **15** in an approximate ratio of 1:1 were obtained. Separation by TLC with ethyl acetate 1: hexane 4 as eluent gave **14** and **15** in 44% and 41% yield. Crystallization from MeOH gave pure **14**, m.p. 139–140°. UV: λ_{max}^{EtOH} (nm): 335 (ε 12000); 240 (ε 100000). NMR ($CDCl_3$): 9·03/d, J = 2 (1H); 8·37/dxd, J_1 = 9, J_2 = 2 (1H); 7·60/d, J = 9 (1H); 7·33/m(5H); 6·07/t, J = 7 (1H); 4·13/s(2H); 368/t, J = 7 (2H); 2·82/q, J = 7 (2H); MS: M^+ 380, 378 *m/e*. (Found: C, 53·9; H, 3·7; Cl, 12·5; N, 7·9; S, 11·4. Calc. for $C_{17}H_{13}ClN_2O_4S$: C, 54·0; H, 3·9; Cl, 12·8; N, 7·6; S, 11·5%). Crystallization of **15** from MeOH gave a sample with m.p. 129–130°. UV: λ_{max}^{EtOH} (nm): 350 (ε 12000); 255 (ε 14000) shoulder. NMR ($CDCl_3$): 8·98/d, J = 2 (1H); 8·34/dxd, J_1 = 9, J_2 = 2 (1H); 7·73/d, J = 9 (1H); 7·28/m(5H); 6·18/s(1H); 1·91/m(1H); 0·85–0·55/m(4H). MS: M^- 342 *m/e*. (Found: C, 59·5; H, 4·1; N, 8·0; S, 9·2. Calc. for $C_{17}H_{14}N_2O_4S$: C, 59·6; H, 4·1; N, 8·2; S, 9·3%).

(b) The same reaction in CH_3NO_2 gave a mixture of **14** + **15** in a ratio of 2:1 (NMR).

(c) When the same reaction was run in AcOH (double volume),—**14** was the only product (NMR). Crystallization from MeOH gave a 75–80% yield.

Irradiation of **14**. The **Z** isomer (**14**) (100 mg) in benzene (200 ml) was irradiated for 18 h, brown material precipitated and was filtered off. The clear filtrate was concentrated and dried. According to NMR, a mixture of **14** and the **E** isomer (**16**) in an approximate ratio of 3:7 accompanied by some impurities, was obtained. Attempts to prepare an analytical sample, by TLC, silica or silver nitrate impregnated plates, failed. NMR ($CDCl_3$) of a crude sample: 8·97/d, J = 2 (1H); 8·27/dxd, J_1 = 9, J_2 = 2 (1H); 7·56/d, J = 9 (1H); 7·25/m(5H); 5·96/t, J = 7 (1H); 3·99/s (2H); 3·47/t, J = 7 (2H); 2·46/q, J = 7 (2H). MS: M^+ 380, 378 *m/e*.

Irradiation of **15**. The **Z** isomer (**15**) (200 mg) in MeOH (200 ml) was irradiated for 7 h to yield quantitatively, a mixture of **15** and the **E** isomer (**17**) in a ratio of 2:1. TLC separation with ethyl acetate 1:hexane 4 as eluent and subsequent crystallization from MeOH gave a pure sam-

ple of **17**, m.p. 104–105°. UV: λ_{max}^{EtOH} (nm): 360 (ϵ 12000); 275 (ϵ 13000) shoulder. NMR ($CDCl_3$): 9·01/d, J = 2 (1H); 8·30/dxd, $J_1 = 9$, $J_2 = 2$ (1H); 7·71/d, J = 9 (1H); 7·32/bs(5H); 6·24/s(1H); 2·20/m(1H); 1·00–0·75/m(4H). MS: M^+ 342 *m/e*. (Found: C, 59·2; H, 4·0. Calc. for $C_{17}H_{14}N_2O_4S$: C, 59·6; H, 4·1%).

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