286. The Thermal 2 + 2-Addition of N-(2-Phenylallyl),N-(3-phenyl-allyl)-toluenesulfonamide: Stereochemical and Kinetic Evidence for a Diradical Intermediate

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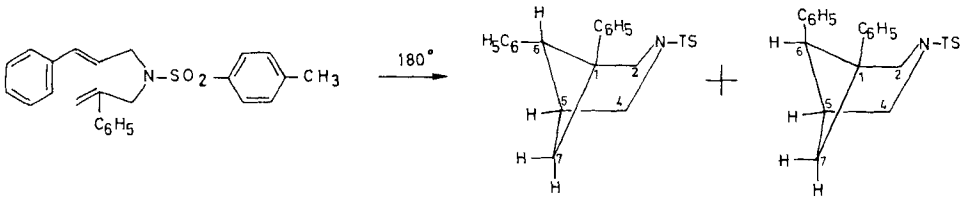
(28. X. 74)

Zusammenfassung. Durch Thermolyse der *trans*- und *cis*-Bis-styryl Derivate **1a** und **1b** erhält man unabhängig von der Konfiguration des Ausgangsmaterials die Produkte **2** und **3** im gleichen Verhältnis. Die Verbindungen **1a**, **2** und **3** lassen sich unter den Reaktionsbedingungen ineinander überführen. Diese Resultate sprechen für einen reversiblen Cycloadditionsprozess unter Beteiligung des diradikalischen Zwischenproduktes **4**. Eine der Addukt-Bildung vorgelagerte rasche *cis*/*trans*-Isomerisierung **1b** → **1a** verläuft offensichtlich über das gleiche Diradikal. Übereinstimmungsgemäss erfolgt die *cis*/*trans*-Isomerisierung des Mono-styryl Derivates **5** zu **6** wesentlich langsamer als die Isomerisierung **1b** → **1a**.

The thermolysis of the simple bis-styryl derivative **1a** to yield exclusively the 2 + 2-adducts **2** and **3** (*Scheme 1*) has been described in the preceding communication [1].

Scheme 1



1a **2** **3**

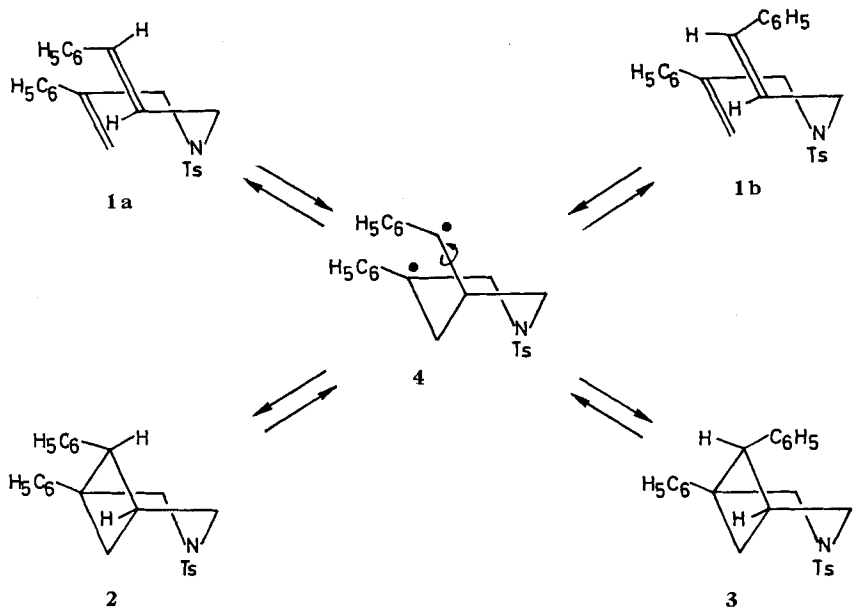
This reaction appears to be unusual, since thermal 2 + 2-cycloaddition reactions of olefins to give cyclobutanes are not common [2]. Some of the known examples involve either biradical or 1,4-dipolar intermediates [3] as illustrated by the addition of difluoroalkenes to conjugated or isolated olefins [4] and by the addition of tetracyanoethylene to electron-rich olefins [5]. Apart from these stepwise reactions, a symmetry allowed concerted [π^2s + π^2a]-process, requiring orthogonal approach of the reactants, seems to be restricted to comulenes or strongly twisted olefins [2]. In order to elucidate the mechanism of the reaction **1a** → **2** + **3**, the N-(*cis*-3-phenylallyl),N-(2-phenylallyl)-toluenesulfonamide **1b** was prepared from *cis*-cinnamylamine and its thermolysis compared with that of the *trans*-diene (Table 1).

The fact, that both, *cis*- and *trans*-dienes **1a** and **1b** gave similar product mixtures after different reaction times (Table 1, run 1–4) is consistent with a stepwise diradical rather than a concerted [π^2s + π^2a]-process (*Scheme 2*). Stabilisation of both radical sites in the postulated intermediate **4** also explains the observed regioselectivity.

Table 1. *Thermolysis of the dienes* **1a**, **1b** *and of the aza[3.1.1]bicycloheptanes* **2** *and* **3**; *product composition as determined by* ^1H*–NMR. analysis*

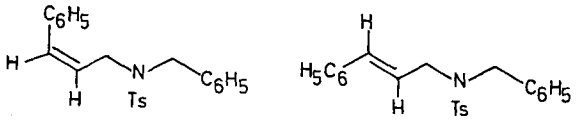
Run	Starting material	Reaction conditions	% *trans*-diene **1a**	% *cis*-diene **1b**	% adduct **2**	% adduct **3**	Total material recovered
1	**1a**	180°/70 h	4	–	48	48	92%
2	**1b**	180°/70 h	4	–	46	50	86%
3	**1a**	180°/6.5 h	56	–	31	13	97%
4	**1b**	180°/6.5 h	43	–	36	21	100%
5	**1b**	180°/0.5 h	46	54	< 5	< 5	82%
6	**2**	180°/70 h	9	–	57	34	88%
7	**3**	180°/70 h	4	–	23	71	98%
8	**2**	220°/24 h	9	–	27	64	83%
9	**3**	220°/24 h	12	–	30	58	88%

Scheme 2



Further insight into the nature of this transformation was provided by the clean thermal interconvertibility of the compounds **1a**, **2** and **3**. Heating both adducts **2** and **3** to 220° for 24 h led to the same equilibrium mixture of the compounds **1a**, **2** and **3**, in which the latter one predominates (runs 8 and 9). By contrast, kinetic control favors the formation of the adduct **2** (runs 3 and 4). Consequently all the individual reaction steps shown in *Scheme 2* must be reversible. Additional evidence for the intermediacy of the diradical **4** was found on heating the *cis*-diene **1b** for a limited period of time in boiling dichlorobenzene. Thus, after 30 min reaction time none of the adducts **2** and **3** could be detected, whereas the recovered diene was a 1:1-mixture of *cis*- and *trans*-isomer **1b** and **1a**; after 6.5 h only pure *trans*-diene **1a** and no *cis*-diene **1b** was left.

Scheme 3



5 6

In a control experiment only 8% of the N-benzyl, N-(*cis*-3-phenylallyl)-toluenesulfonamide **5** was converted to its *trans*-isomer **6**, after heating for 30 min in boiling dichlorobenzene. This suggests, that the isomerisation **1b** → **1a** proceeds *via* the initially formed biradical **4**. This intermediate after rotation of the benzylic fragment may cleave to either diene or close to the adducts. Since the rate of the *cis*/*trans*-isomerisation exceeds significantly the rate of adduct formation, clearly the rotation and cleavage of the biradical **4** proceeds faster than ring closure. This result is in perfect accord with the proposed biradical mechanism and militates against the intermediacy of a 1,4-dipole[1]).

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Experimental Part[2])

(in collaboration with *G. Würtele*)

N-(cis-*3-Phenyl-2-propenyl*)-*trifluoroacetamide*. To a stirred mixture of 10 g of *cis*-cinnamylamine hydrochloride [6], 10.3 g of pyridine and 200 ml of CH_2Cl_2 was added dropwise at 0° 13.7 g of trifluoroacetic anhydride. After 0.5 h at room temperature the reaction mixture was shaken 3 times with 10% aqueous citric acid, once with saturated $NaHCO_3$ sol., dried and evaporated. The oily residue yielded after crystallisation from pentane at –30° 9.5 g of crystals, m.p.: 26–31°. – IR. (film): 3300, 1710, no band at 960. – ^{1}H–NMR. (60 MHz): 4.2 (2 H, *t*, J = 5.5 Hz); 5.6 (1 H, $d \times t$, J = 11.5 Hz and 6.5 Hz); 6.6 (1 H, $d \times t$, J = 11.5 Hz and 1.5 Hz); 6.8–7.2 (6 H).

N-(*2-Phenylallyl*), *N*-(cis-*3-phenylallyl*)-*toluenesulfonamide* (**1b**). Following the procedure described for the preparation of N-(2-phenylallyl), N-(*trans*-3-phenylallyl)-toluenesulfonamide (**1a**) [1] 4.4 g of N-(*cis*-3-phenyl-2-propenyl)-trifluoroacetamide was alkylated with 3-bromo-2-phenyl-propene to give 3.6 g of oily N-(2-phenylallyl), N-(*cis*-3-phenylallyl)-trifluoroacetamide. 2.5 g of this amide yielded after alkaline saponification 1.5 g of oily N-(2-phenylallyl), N-(*cis*-3-phenylallyl)-amine. (· HCl: m.p. = 137–140° after crystallisation from methanol/ether). 1.0 g of the free amine was acylated with toluenesulfonylchloride to give after crystallisation from ether 0.62 g of crystals: m.p.: 78–80°. – IR. (Nujol): 1640 w, 1330, 1170, no band at 960. – ^{1}H–NMR. (100 MHz): 2.4 (3 H, *s*); 4.0 (2 H, $d \times d$, J = 1 Hz and 3.5 Hz); 4.2 (2 H *s*,); 5.0 (1 H, *s*); 5.2 (1 H, *s*); 5.4 (1 H, $d \times t$, J = 11.5 Hz and 6 Hz); 6.4 (1 H, *d* br., J = 11.5 Hz); 6.9–7.4 (12 H); 7.6 (2 H, *d*, J = 8 Hz).

N-Benzyl, *N*-(cis-*3-phenylallyl*)-*toluenesulfonamide* (**5**). To a stirred mixture of 0.5 g of *cis*-cinnamylamine hydrochloride, 1.25 g of pyridine and 5 ml of CH_2Cl_2 was added dropwise a solution of 0.565 g of toluenesulfonylchloride. The reaction mixture was kept at room temperature for 19 g to give after usual workup and chromatography (silica gel C_6H_6/EtOAc 9:1) 0.41 g of N-(*cis*-3-phenylallyl)-toluenesulfonamide as a viscous oil. 0.2 g of this material was added to a suspension of 20 mg of 80% sodium hydride in 0.7 ml of hexamethylphosphoramide. After 1 h 0.10 g of benzyl bromide in 0.7 ml of hexamethylphosphoramide was added to the mixture, which then was kept at room temperature for 3 h to furnish after usual workup and chromatography

[1]) In apolar solvents, due to the operation of coulombic forces rotation about single bonds is much more restricted in 1,4-dipoles compared to 1,4-diradicals [3] [5].

[2]) For generalities see [1].

(silica gel, C_6H_6/EtOAc 9:1) 0.11 g of oily N-benzyl, N-(*cis-3*-phenylallyl)-toluenesulfonamide (**5**). – IR. (Nujol): 1350, 1170, no band at 940. – ^{1}H–NMR. (100 MHz): 2.41 (3 H, *s*); 3.98 (2 H, *d* × *d*, J = 2 Hz and 6.5 Hz); 4.26 (2 H, *s*); 5.38 (1 H, *d* × *t*, J = 11.5 Hz and 6.5 Hz); 6.42 (1 H, *d* × *t*, J = 11.5 Hz and 1.5 Hz); 6.8–7.4 (12 H); 7.66 (2 H, *d*, J = 8 Hz).

N-Benzyl, N-(trans-*3-phenylallyl)-toluenesulfonamide* (**6**). Following the procedure described for the preparation of N-(2-phenylallyl), N-(*trans*-3-phenylallyl)-toluenesulfonamide (**1**) [1] 0.5 g of N-(*trans*-3-phenyl-2-propenyl)-trifluoroacetamide was alkylated with benzylbromide to give 0.9 g of crude N-benzyl, N-(*trans*-3-phenylallyl)-trifluoroacetamide. After saponification the resulting N-benzyl, N-(*trans*-3-phenylallyl)-amine was converted to its crystalline hydrochloride, m.p. 209–212° (0.25 g after crystallisation from methanol/ether). Treatment of the amine-hydrochloride (0.25 g) with 0.27 g of toluenesulfonyl chloride and 0.4 g of pyridine followed by the usual workup furnished after crystallisation from ether/hexane 0.054 g of crystals: m.p.: 78–80°. – IR. (Nujol): 1350, 1170, 940. – ^{1}H–NMR. (100 MHz): 2.41 (3 H, *s*); 3.88 (2 H, *d*, J = 6.5 Hz); 4.36 (2 H, *s*); 5.74 (1 H, *d* × *t*, J = 16 Hz and 6.5 Hz); 6.2 (1 H, *d*, J = 16 Hz); 7.0–7.5 (12 H); 7.75 (2 H, *d*, J = 8 Hz).

Thermolysis Experiments (Table 1). 0.04 to 0.25 g of purified compound **1a**, **1b**, **2**, **3**, **5** and **6**, respectively, was heated in 5 ml of refluxing *o*-dichlorobenzene (runs 1–7), or in toluene, using a sealed tube (runs 8–9) for the indicated time. After evaporation and chromatographic removal of apolar and strongly polar impurities (silica gel/benzene) the recovered mixture was analysed by ^{1}H–NMR. spectroscopy (runs 1, 2, 5 and 6). In the experiments run 3, 4, 7, 8 and 9 chromatography of the crude reaction mixture (silica gel/benzene/pentane) afforded 2 fractions (the first one containing the less polar dienes **1a** and **1b** and the second one containing the adducts **2** and **3**), each of which was subjected to ^{1}H–NMR. analysis. From the mixture obtained in run 2 all 3 components **1a**, **2** and **3** were isolated by chromatography and crystallisation and identified by comparison of their ^{1}H–NMR. spectra and melting points.

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287. Synthesis of New Xanthones, I

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(17. X. 74)

Summary. Condensation of salicylic acid and C-methylphloroglucinol gave the already known 1,3-dihydroxy-2-methylxanthone (**1**) along with two new compounds: 1,3-dihydroxy-4-methylxanthone (**2**) and a second one tentatively presented as being 1,3-dihydroxy-2-methyl-4-(2-hydroxybenzoyl)xanthone (**3**). The UV., IR., NMR. and mass spectra for the two first compounds