Reactions of Dimethoxycarbene with *N*-Tosylated Imines

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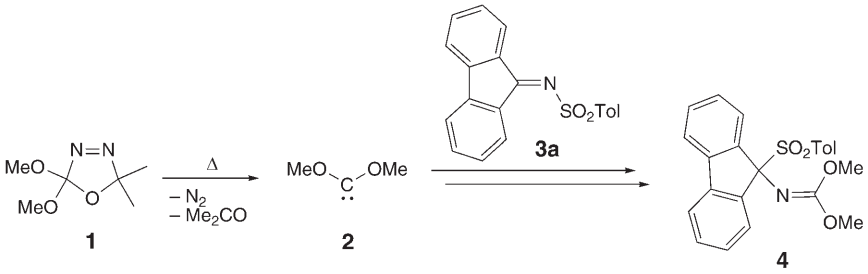
Dedicated to Professor *Günther Maier* (Giessen) on the occasion of his 75th birthday

The reactions of dimethoxycarbene (DMC; **2**), which was generated *in situ* by thermal decomposition of 2,5-dihydro-2,2-dimethoxy-5,5-dimethyl-1,3,4-oxadiazole (**1**), with *N*-tosylated imines of xanthone and 2,3:6,7-dibenzosuberenone, **3a** and **3d**, respectively, led to different adducts with rearranged skeletons. In the case of **3a**, the 1:1 adduct **5** as well as the 2:1 adduct **6** were obtained (*Scheme 2*). The formation of both products can be explained by a migration of a MeO group of the DMC fragment in a zwitterionic intermediate. On the other hand, migration of a Me group of DMC is necessary for the formation of the two 1:1 adducts **13** and **14** of **2** and **3d** (*Scheme 5*). The structures of all products have been established by X-ray crystallography.

1. Introduction. – The thermal decomposition of 2,5-dihydro-2,2-dimethoxy-5,5-dimethyl-1,3,4-oxadiazole (**1**), elaborated by *Warkentin* and co-workers [1][2], is a convenient method for the generation of dimethoxycarbene (**2**), which enabled the exploration of this nucleophilic carbene for synthetic purposes. Similarly to other carbenes, the reactions with diverse multiple bonds are of special interest. In the case of **2**, the reactions with C=C bonds are limited to ethenes, which are activated by electron-withdrawing groups. Whereas, with dimethyl dicyanofumarate, a multistep reaction leads to a 2,2-dimethoxy-2,3-dihydrofuran derivative [3], dicyanomethylidene-substituted adamantane and 9*H*-fluorene yield the corresponding cyclopropanes [4]. The reactions of **2** with cycloaliphatic ketones lead either to spirocyclic 2,2-dimethoxyoxiranes or to ring-enlarged 2,2-dimethoxy ketones [2][5][6]. Cycloaliphatic thioketones react efficiently with **2** to give dimethoxythiiranes [6][7].

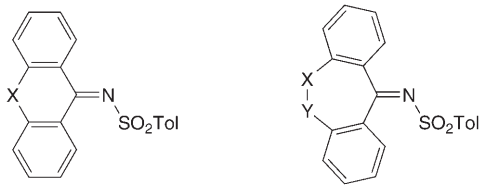
The reactions of **2** with C=N-containing compounds have been examined with isocyanates only [8]. Recently, we reported the first example of a successful conversion of **2** with 9*H*-fluorene-9-imine **3a**, which is activated by a toluenesulfonyl substituent (*Scheme 1*). The isolated product **4** is formed in a multi-step reaction, in which the sulfonyl group has migrated from the N- to the C-atom [9].

Scheme 1



The detailed reaction mechanism is not known to date, but the presence of an aziridine and/or an azomethine ylide as key intermediate is likely. The influence of the fluorene system is decisive, as neither the analogous benzaldehyde *N*-tosylimine nor benzophenone *N*-tosylimine reacted with **2**.

The present study is aimed at the explanation of the influence of the structure of the *N*-tosylated imine of type **3** on the reactivity towards **2**. For this reason, the corresponding imines **3b**–**3e** were prepared and used as potential substrates in the reactions with the carbene **2** generated by thermal decomposition of **1**.

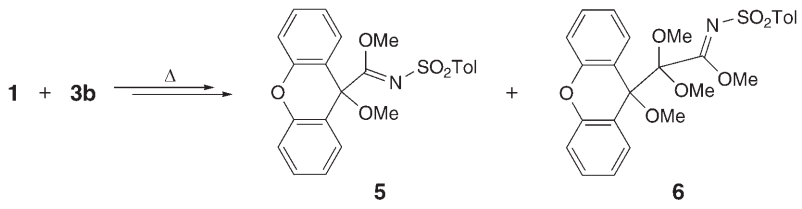


3b X = O
3c X = S

3d X–Y = CH=CH
3e X–Y = CH_2–CH_2

2. Results and Discussion. – 2.1. *Reactions of* **2** *with* **3b** *and* **3c**. A solution of **3b** and 3 equiv. of **1** in toluene was heated under reflux for 8 h. The ^{1}H-NMR spectrum of the mixture showed the presence of two products **5** and **6** (Me signals of the Ts residue at 2.40 and 2.35 ppm, resp.; *Scheme 2*) along with the starting imine **3b** (Me signal at 2.45 ppm). Then, 2 additional equiv. of **1** were added, and the heating was continued for another 6 h, until **3b** was consumed completely. The ^{1}H-NMR analysis of the mixture confirmed the presence of **5** and **6**, and the ratio of both products, established on the basis of the intensity of the Me signals for the Ts residue, was *ca.* 1:3.

Scheme 2



The products were separated by preparative layer chromatography, and the less-polar fraction gave the minor product **5** as a colorless, crystalline material. The ^{1}H-NMR spectrum showed three *singlet*s for Me groups at 2.40, 3.00, and 3.45 ppm in a 1:1:1 ratio. The ^{13}C-NMR signal at 170.7 ppm, as well as an intensive absorption in the IR spectrum at 1637 cm^{-1}, revealed the presence of a C=N group. The ESI-MS with *m*/*z* 462 and 446 ($[M+K]^+$ and $[M+Na]^+$, resp.) indicated that **5** is a 1:1 product. However, the two non-equivalent MeO groups suggested that, similar to the reaction with **3a**, the isolated product **5** is not an aziridine derivative. Based on these data, a structure analogous to **4** could tentatively be formulated. Finally, an X-ray crystal structure determination established unambiguously structure **5** with the two MeO groups located at two different C-atoms (*Scheme 2* and *Fig. 1*). In contrast to **4**, the formation of **5** requires a migration of one MeO group of the carbene fragment.

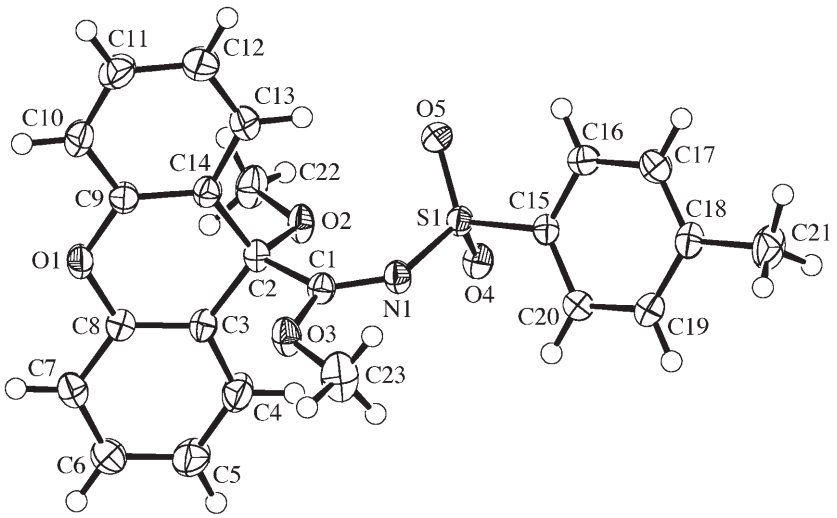


Fig. 1. *ORTEP Plot* [10] *of the molecular structure of* **5** (arbitrary numbering of the atoms; 50% probability ellipsoids)

The more-polar fraction was also obtained as a colorless crystalline substance. In this case, the ^{1}H-NMR spectrum showed one signal for an aromatic Me group (2.35 ppm) and three signals for MeO groups located at 2.95, 3.35, and 3.45 ppm in the ratio of 1:2:1. The ESI-MS with *m*/*z* 536 and 520 ($[M+K]^+$ and $[M+Na]^+$, resp.) showed that this product corresponds to a 2:1 stoichiometry with respect to **2** and **3b**. Again, the ^{13}C-NMR spectrum as well as the IR spectrum confirmed the presence of a C=N group (165.8 ppm and 1633 cm^{-1}, resp.). The structure **6** was also established by X-ray crystallography (*Fig. 2*).

The structures of the isolated products **5** and **6** indicate a different pathway of the reaction of dimethoxycarbene (**2**) and **3b** compared with that of **2** and **3a**. Whereas, in the case of **3a**, the intermediate rearranges by a N → C migration of the sulfonyl group to give **4**, the intermediate formed from **2** and **3b** undergoes a C → C migration of a MeO group. The formation of the aziridine **7**, most likely *via* the initially formed zwitterion **B**, followed by the cleavage of the N–C(9) bond to give **8**, offers a plausible

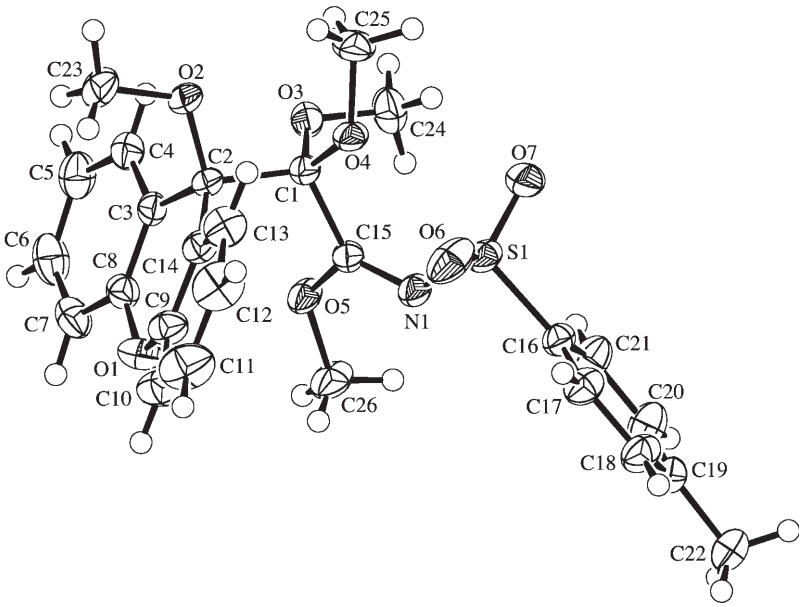


Fig. 2. *ORTEP Plot* [10] *of the molecular structure of* **6** (arbitrary numbering of the atoms; 50% probability ellipsoids)

explanation for the sequence of the atoms in **5**. The latter is formed *via* a 1,2-shift of a MeO group (*Scheme 3*). Whether this shift occurs as a concerted process or *via* the ion pair **9** cannot be answered.

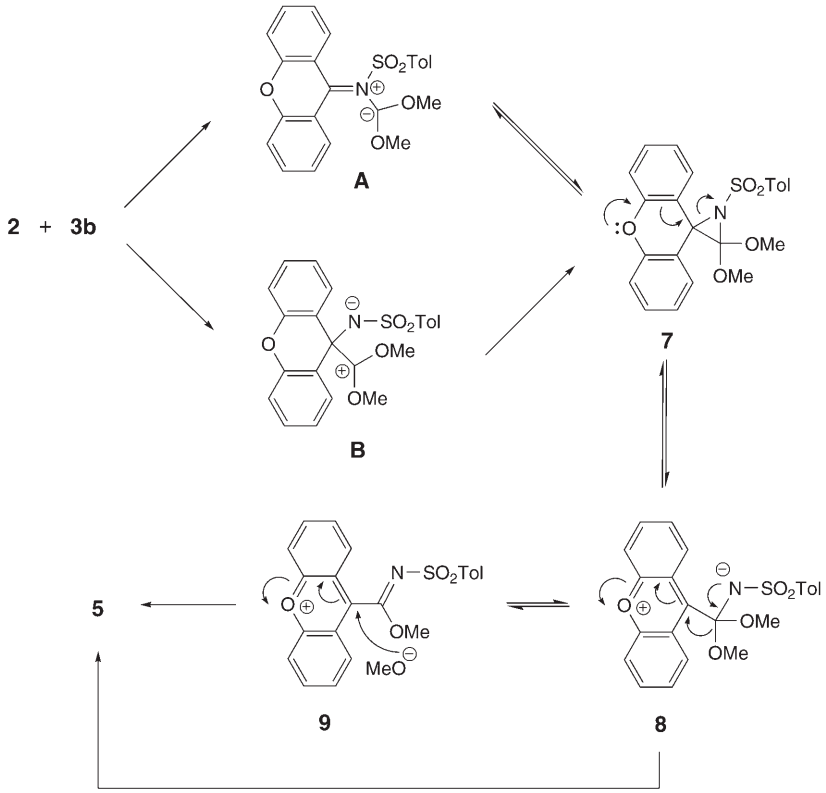
The structure of **6** shows that this product was formed either from **5** or from an intermediate precursor of **5** *via* insertion of a second carbene **2** into a C,C bond. However, a control experiment with **5** and **1** in boiling toluene evidenced that no **6** was formed and, therefore, **5** is not an intermediate in the formation of **6**.

In some reactions of dimethoxycarbene (**2**), the tetramethoxyethene (dimer of **2**), formed *in situ*, is proposed to react with electron-deficient π-systems to yield the four-membered [2+2] cycloadducts [8b]. In the reaction with **3b**, which requires a large excess of the carbene precursor **1**, the [2+2] cycloaddition with tetramethoxyethene would lead to the azetidine derivative **10**. The negative result of a control experiment with **3b** and tetramethoxyethene, carried out in boiling toluene, showed that **3b** was inert under these conditions.

Taking into account the results of both control experiments, a plausible explanation for the formation of **6** is based on the assumption that the initially formed zwitterion **B** reacts with a second molecule of **2** to give a new zwitterion **C**, which subsequently undergoes ring closure to yield the azetidine **10**. The ring opening of the latter results in the formation of the isomeric zwitterion **11**, which is converted to the final product **6** *via* migration of a MeO group. Again, this MeO migration may occur in two steps *via* an ion pair or *via* two consecutive 1,2-shifts of MeO groups.

Another candidate for the reaction with the second molecule of **2** may be the cation of the ion pair **9**. The nucleophilic attack of **2** onto **9** could lead to the intermediate **12**,

Scheme 3

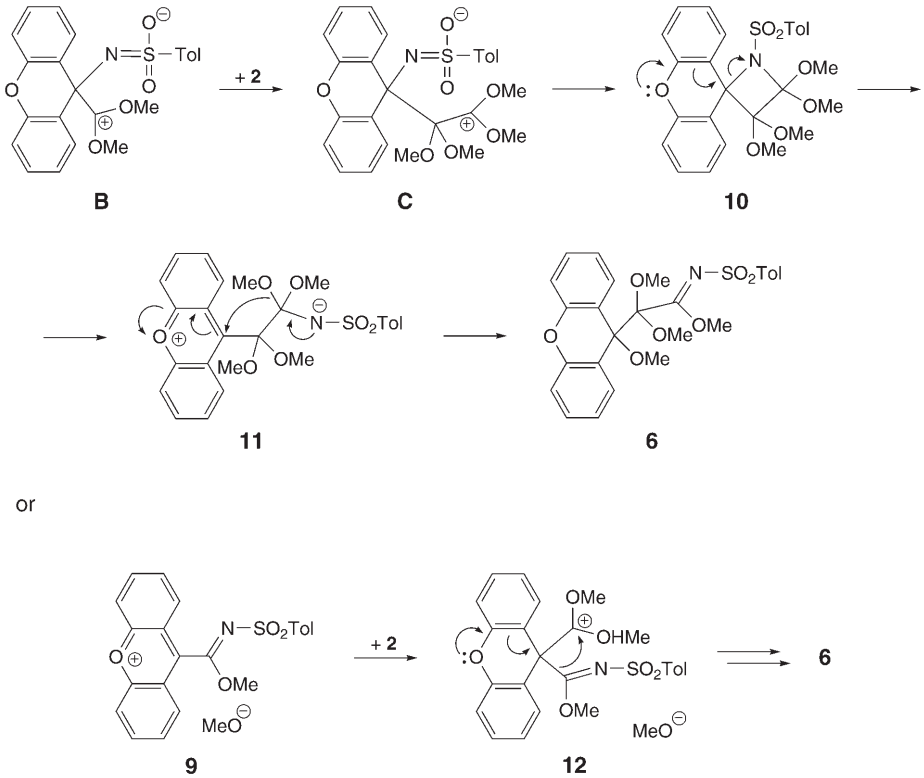


which undergoes a 1,2-shift of the imido ester group. The isolated product **6** is then formed by addition of methoxide (*Scheme 4*).

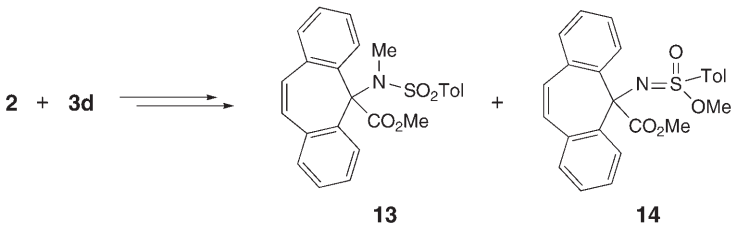
The analogous reaction of the thioxanthone imine **3c** and **1** led to a complex mixture of products, which, after consumption of **3c**, showed absorption signals of MeO groups between 3 and 4 ppm. However, the separation of the products by fractional crystallization was unsuccessful, and the attempted chromatographic separation led to decomposition of the products.

2.2. *Reactions of* **2** *with* **3d** *and* **3e**. The complete consumption of **3d** in boiling toluene was achieved with a threefold excess of **1**. After evaporation of the solvent, trituration of the residue with Et_2O led to a crystalline, colorless material. The ^{1}H-NMR spectrum showed a signal for an aromatic Me group at 2.39 ppm, and two signals at 2.68 and 4.08 ppm in a ratio of 1:1:1. Only the latter is a typical shift for a MeO group. Surprisingly, the IR spectrum of this product showed a strong absorption band at 1736 cm^{-1}, indicating the presence of a C=O group instead of the C=N group. This conclusion was confirmed by the signal at 172.3 ppm in the ^{13}C-NMR spectrum. These data suggest the presence of a methyl ester. Finally, the structure of the ester **13** was established by X-ray crystallography (*Scheme 5* and *Fig. 3*).

Scheme 4



Scheme 5



The analysis of the mother liquor by ^{1}H-NMR spectroscopy showed that, along with traces of **13**, a second product was present, which also displayed three Me signals at 2.48, 3.54, and 3.56 ppm in a ratio of 1 : 1 : 1. Whereas the first one is characteristic for the Me group of the tolyl residue, the others are in the range of MeO groups. In the IR spectrum (KBr), the absorption of a C=O group was located at 1737 cm^{-1}, almost identical with that of **13**. The presence of an ester group was confirmed by the ^{13}C-NMR spectrum, in which the C=O signal appeared at 171.8 ppm. Furthermore, the

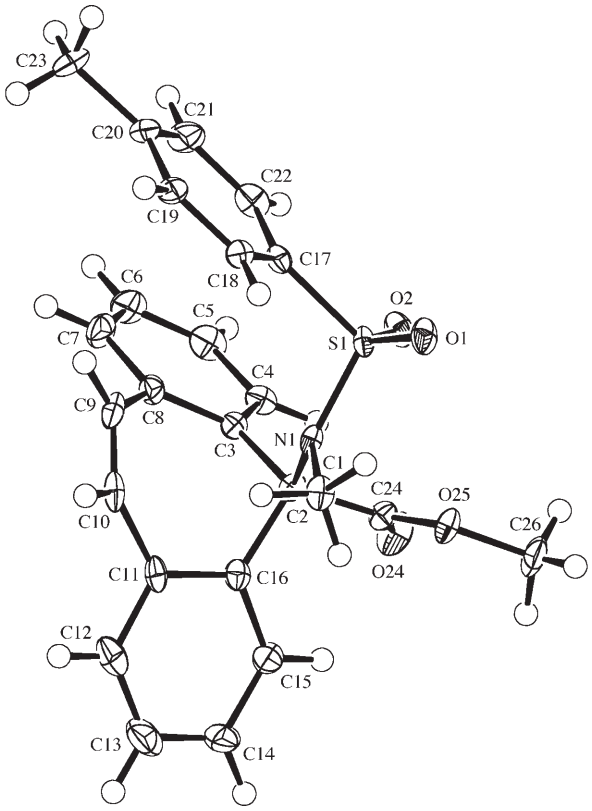


Fig. 3. *ORTEP Plot* [10] *of the molecular structure of* **13** (arbitrary numbering of the atoms; 50% probability ellipsoids)

ESI-MS showed that the product is an isomer of **13** (*m*/*z* 456, $[M+\mathrm{Na}]^+$). Unexpectedly, the X-ray crystal-structure determination revealed the structure **14**, which contains a methyl carboxylate and a methyl iminosulfonate (*Scheme 5* and *Fig. 4*).

To test their thermal stability, the separated products **13** and **14** were heated in refluxing toluene. After 4 h, no isomerization was observed, and each substance was recovered from the solution unchanged. This result is consistent with the observation that the ratio of **13** and **14**, determined in the crude reaction mixture of **1** and **3d** after different lengths of heating time, was constant.

The structures of **13** and **14** show that both compounds are formed *via* migration of a Me group. To the best of our knowledge, this is the first case in which an intermediate, formed by the addition of dimethoxycarbene (**2**), is stabilized by a Me and not a MeO shift (*cf.* [11]). A plausible reaction pathway is depicted in *Scheme 6*. The zwitterion **B′** is probably the crucial intermediate for the formation of both products. However, the labile aziridine **15** can also be involved in the reaction. The formation of **13** from **B′** can be rationalized by an O → N Me shift. In principle, this reaction could occur by either

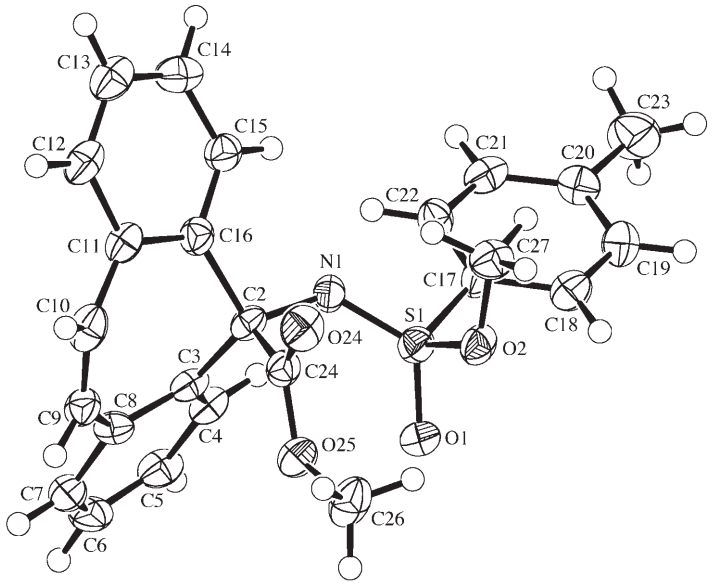


Fig. 4. *ORTEP Plot* [10] *of the molecular structure of one of the two symmetry-independent molecules of* **14** (arbitrary numbering of the atoms; 50% probability ellipsoids)

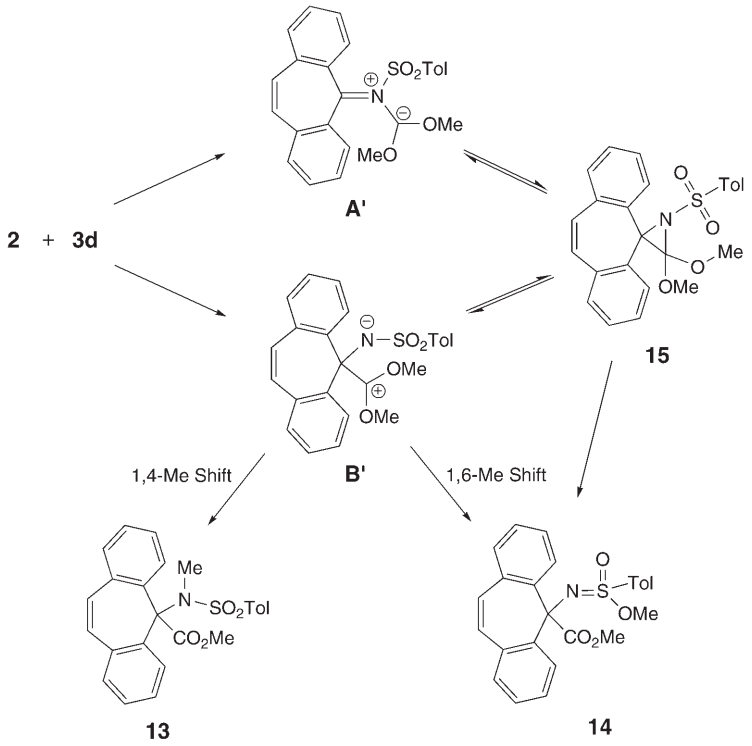
an intra- or intermolecular process, but neither of them is favorable. Whereas the intramolecular 5-*endo-tet* transition state is disfavored in terms of the *Baldwin* rules [12] (*cf.* also [13]), the intermolecular pathway seems unlikely because of the low concentration of the reactive intermediate [11]. In spite of this fact, intermolecular transfers of the Me group are reported for certain systems [14].

The intermediate **B′** can also be proposed as the precursor of **14**. In this case, the observed O → O migration of the Me group corresponds to a 1,6-shift, which involves a seven-membered transition state. According to the *Baldwin* rules, this is a favored process (however, see [13b]). Nonetheless, an intermolecular transfer of the Me group cannot be excluded. Upon the assumption that the aziridine **15** is an intermediate, the Me shift **15** → **14** can be recognized as a *retro*-ene reaction (*Scheme 6*).

Under the conditions applied for the reaction of **1** and **3d**, the 2,3:6,7-dibenzosuberone derivative **3e** did not react with **2**, and, after chromatographic separation, it was recovered almost quantitatively. This result shows again that small structural differences in the *N*-sulfonylated imines influence the outcome of the reaction with **2** significantly.

3. Conclusions. – In addition to the reaction of **2** with *N*-tosylated 9*H*-fluoren-9-one imine **3a** described earlier [9], the present study shows that the corresponding imines, derived from 9*H*-xanthen-9-one **3b** and 2,3:6,7-dibenzosuberenone **3d**, are able to react with **2** to give 1:1 or 1:2 adducts. The course of the reaction depends strongly on the structure of the imine used. In none of the cases studied, could the aziridine derivatives, which might be expected as typical carbene adducts to the C=N bond, be

Scheme 6



isolated or detected. Nevertheless, the intermediacy of these heterocycles offers a plausible explanation of the mechanisms leading to the final products. Depending on the nature of the imine, each of the three bonds of the aziridine can be broken under the reaction conditions. Whereas, in the case of **3a**, the final product can be formed *via* formation of an azomethine ylide (cleavage *a*; *Fig. 5*), in the cases of **3b** and **3d**, the alternative cleavages of a C–N bond are observed (cleavage *b* and *c*, resp.).

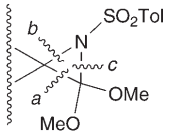


Fig. 5. *Cleavage possibilities*

We thank Mrs. *M. Celeda*, University of Łódź, for technical assistance, and Dr. *M. Wörle*, ETH-Zürich, for collecting the diffraction data for **6**. *G. M.* thanks the *Polish Ministry of Education and Science* for a grant (No. PBZ-KBN-126/T09/12), and *H. H.* acknowledges financial support by *F. Hoffmann-La Roche AG*, Basel.

Experimental Part

1. *General*. M.p.: in capillary with a *Meltemp 2* apparatus; uncorrected. IR Spectra: in KBr pellets with a *Nexus FT-IR* spectrophotometer; in cm^{-1}. ^1H- and ^{13}C-NMR spectra: *Bruker 200* and *400* spectrometer, resp. (200 and 100 MHz, resp.) with TMS (=0 ppm) as an internal standard; δ in ppm, J in Hz. CI-MS: *Finnigan MAT-90* spectrometer; in *m/z* (rel.). Elemental analyses were performed in the Analytical Laboratory of the University of Zürich.

2. *Starting Materials. 2,2-Dimethoxy-5,5-dimethyl-2,5-dihydro-1,3,4-oxadiazole* (**1**) was prepared and purified according to the procedure published by *Warkentin* and co-workers [1]. The sulfonylated imines **3b**–**3e** were prepared from the corresponding commercially available ketones and 4-methylbenzenesulfonamide by heating in 1,2-dichloroethane soln. in the presence of Et_3N and $TiCl_4$ according to [15]. Crystalline products were obtained in good yields (70–90%) and were purified by crystallization or column chromatography (CC).

4-Methyl-N-*(9*H-*xanthen-9-ylidene)benzenesulfonamide* (**3b**). Pale yellow crystals. M.p. 174–176° (MeOH/CH_2Cl_2) ([16]: 170–171°).

4-Methyl-N-*(9*H-*thioxanthen-9-ylidene)benzenesulfonamide* (**3c**). Pale yellow crystals. M.p. 207–210° (MeOH/CH_2Cl_2) ([17]: 212°).

N-(*5*H-*Dibenzo[*a,d*]cyclohepten-5-ylidene)-4-methylbenzenesulfonamide* (**3d**). Pale yellow crystals. M.p. 156–159° (purified by CC (SiO_2; CH_2Cl_2/petroleum ether 4:1)). IR (KBr): 1599*s*, 1574v*s* (C=N), 1548*m*, 1319v*s*, 153v*s*, 1090*s*, 843*s*, 804*s*, 788*s*, 673*s*, 566*s*. ^1H-NMR ($CDCl_3$): 8.10–7.05 (*m*, 12 arom. H); 6.96 (*s*, CH=CH); 2.30 (*s*, Me). Anal. calc. for $C_{22}H_{17}NO_2S$ (359.45): C 73.51, H 4.77, N 3.90, S 8.90; found: C 73.38, H 4.69, N 3.68, S 8.79.

N-*(10,11-Dihydro-5*H-*dibenzo[*a,d*]cyclohepten-5-ylidene)-4-methylbenzenesulfonamide* (**3e**). Pale yellow crystals. M.p. 112–115° (purified by CC (SiO_2; petroleum ether with increasing amount of CH_2Cl_2)). IR (KBr): 1595v*s*, 1564v*s* (C=N), 1323v*s*, 1155v*s*, 1091*s*, 838*s*, 750v*s*, 670*s*, 561v*s*. ^1H-NMR ($CDCl_3$): 7.90–7.60 (*m*, 4 arom. H); 7.40–7.00 (*m*, 8 arom. H); 3.02 (*s*, 2 CH_2); 2.35 (*s*, Me). Anal. calc. for $C_{22}H_{19}NO_2S$ (361.47): C 73.10, H 5.30, N 3.87, S 8.85; found: C 69.87, H 5.28, N 3.72, S 8.69.

3. *Reactions of DMC* (**2**) *with* **3b**–**3e**. *General Procedure.* A soln. of **1** (480 mg, 3 mmol) and the corresponding imine **3** (1 mmol) in abs. toluene (4 ml) was heated to reflux for 8 h under Ar. When the imine **3** was completely consumed, the solvent was evaporated, and the crude residue was analyzed by ^1H-NMR spectroscopy. In the case of **3e**, after 8 h of heating, the major component of the mixture was identified as the starting material (TLC; ^1H-NMR: *m* at 7.90–7.60 ppm and *s* for 2 CH_2 at 3.02 ppm). The mixtures obtained with **3b**, **3c**, and **3d** were separated by CC (SiO_2). However, the products formed with **3c** decomposed during the attempted chromatographic separation and subsequent crystallization. Separation of the crude mixtures obtained with **3b** and **3d** yielded two products in each case.

Reaction with **3b**. In this case, 800 mg (5.0 mmol) of **1**, added in two portions, were used to achieve complete conversion of **3b** after 14 h of heating. Prep. layer chromatography (PLC) on plates coated with SiO_2 (CH_2Cl_2/petroleum ether 8:2) was applied to separate the products **5** and **6**.

*(*E*)*-N-*[Methoxy(9-methoxy-9*H-*xanthen-9-yl)methylidene]-4-methylbenzenesulfonamide* (**5**). Less-polar fraction. Yield: 84 mg (20%). Colorless crystals. M.p. 192–194° (MeOH). IR (KBr): 1637v*s* (C=N), 1481*m*, 1447*s*, 1322*s*, 1299*m*, 1155*s*, 1092*m*, 756*s*, 676v*s*, 608*s*. ^1H-NMR ($CDCl_3$): 7.85 (*d*, ^3J = 7.0, 2 arom. H); 7.72 (*d*, ^3J = 7.0, 2 arom. H); 7.42–7.15 (*m*, 8 arom. H); 3.45, 3.00 (2*s*, 2 MeO); 2.40 (*s*, Me). ^{13}C-NMR: 170.7 (*s*, C=N); 151.5 (*s*, 2 arom. C); 142.1, 142.0 (2*s*, 2 arom. C); 130.4, 129.1, 128.4, 126.2, 123.6 (5*d*, 2 arom. CH each); 118.6 (*s*, 2 arom. C); 116.8 (*d*, 2 arom. CH); 77.4 (*s*, C(9″)); 56.1, 51.0 (2*q*, 2 MeO); 21.6 (*q*, Me). ESI-MS: 462 (9, $[M+K]^+$), 446 (62, $[M+Na]^+$), 392 (100, $[M-MeO]^+$). Anal. calc. for $C_{23}H_{21}NO_5S$ (423.48): C 65.23, H 5.00, N 3.31, S 7.57; found: C 64.94, H 4.83, N 3.15, S 7.54.

*(*E*)-4-Methyl*-N-*[1,2,2-trimethoxy-2-(9-methoxy-9*H-*xanthen-9-yl)ethylidene]benzenesulfonamide* (**6**). More-polar fraction. Yield: 250 mg (50%). Colorless crystals. M.p. 143–145°. IR (KBr): 1633v*s* (C=N), 1477*m*, 1447*s*, 1314*s*, 1241*m*, 1161v*s*, 1093v*s*, 757*m*, 674*s*, 607*m*. ^1H-NMR ($CDCl_3$): 7.69–7.08 (*m*, 12 arom. H); 3.45 (*s*, MeO); 3.35 (*s*, 2 MeO); 2.95 (*s*, MeO); 2.35 (*s*, Me). ^{13}C-NMR ($CDCl_3$): 165.8 (*s*, C=N); 152.6 (*s*, 2 arom. C); 141.9, 141.7 (2*s*, 2 arom. C); 130.1, 129.5, 129.0, 125.9, 122.4, 115.9 (6*d*, 2 arom. CH each); 118.8 (*s*, 2 arom. C); 105.3 (*s*, C(2′)); 80.5 (*s*, C(9″)); 55.7 (*q*, MeO); 52.7 (*q*, 2 MeO);

51.3 (*q*, MeO); 21.5 (*q*, Me). ESI-MS: 536 (44, $[M+K]^+$), 520 (100, $[M+Na]^+$), 466 (34, $[M-MeO]^+$). Anal. calc. for $C_{22}H_{27}NO_7S$ (497.56): C 62.76, H 5.47, N 2.82, S 6.44; found: C 62.66, H 5.72, N 2.72, S 6.39.

Reaction with **3d**. After heating for 7 h, no starting material was detected (TLC) in the soln. Toluene was evaporated to dryness, and separation of **13** and **14** was achieved either by trituration of the oily residue with Et_2O at r.t. (in this case, **13** precipitated from the solution), or by PLC (SiO_2) with petroleum ether/AcOEt 8:2 as the eluent. Anal. pure products were obtained by crystallization.

*Methyl 5-[Methyl(4-methylphenylsulfonyl)amino]-5*H*-dibenzo[*a,d*]cycloheptene-5-carboxylate* (**13**). Less-polar fraction. Yield: 135 mg (31%). Colorless crystals. M.p. 233–235° ($MeOH/CH_2Cl_2$). IR (KBr): 1736v*s* (C=O), 1632*m* (br.), 1332v*s*, 1243*s*, 1156*s*, 1011*m*, 972*m*, 839*s*, 795*s*, 671*m*, 594*s*, 553*m*. ^{1}H-NMR ($CDCl_3$): 7.95 (br. *s*, 2 arom. H); 7.33 (*t*-like, 2 arom. H); 7.21 (*t*-like, 2 arom. H); 7.08–6.98 (*m*, 4 arom. H); 6.82 (*d*-like, 2 arom. H); 6.45 (br. *s*, CH=CH); 4.08 (*s*, MeO); 2.68 (*s*, MeN); 2.39 (*s*, Me). ^{13}C-NMR ($CDCl_3$): 172.3 (*s*, C=O); 142.3, 138.9, 134.7, 128.1 (4 br. *s*, 6 arom. C); 134.9, 131.5 (2 br. *s*, 4 CH); 129.5, 128.7, 128.4, 127.4, 126.5 (5*d*, 12 CH); 75.9 (*s*, C(5)); 52.9 (*q*, MeO); 37.6 (*q*, MeN); 21.6 (*q*, Me). ESI-MS: 472 (85, $[M+K]^+$), 456 (100, $[M+Na]^+$), 249 (50). Anal. calc. for $C_{25}H_{23}NO_4S$ (433.53): C 69.26, H 5.35, N 3.23, S 7.40; found: C 69.34, H 5.32, N 3.21, S 7.49.

Methyl N-*[5-(Methoxycarbonyl)-5*H*-dibenzo[*a,d*]cyclohepten-5-yl]-4-methylbenzenesulfonimidate* (**14**). More-polar fraction. Yield: 152 mg (35%). Colorless crystals. M.p. 171–173° (MeOH). IR (KBr): 1737v*s* (C=O), 1629*m* (br.), 1332v*s* (br.), 1210*s* (br.), 1014*m*, 982*m*, 807*m*, 765*m*, 729*m*, 669*m*, 580*m*. ^{1}H-NMR ($CDCl_3$): 8.25–7.82 (*m*, 4 arom. H); 7.55–7.15 (*m*, 6 arom. H); 7.03 (*s*, CH=CH); 3.56, 3.54 (2*s*, 2 MeO); 2.48 (*s*, Me). ^{13}C-NMR ($CDCl_3$): 171.8 (*s*, CO); 143.8, 141.0, 140.4, 135.9 (4*s*, 6 arom. C); 132.9, 131.0, 129.7, 127.9, 127.7, 126.4, 124.7 (7*d*, 12 arom. CH, CH=CH); 70.5 (*s*, C(5)); 56.5, 52.5 (2*q*, 2 MeO); 21.6 (*q*, Me). ESI-MS: 472 (6, $[M+K]^+$), 456 (100, $[M+Na]^+$), 249 (10). Anal. calc. for $C_{25}H_{23}NO_4S$ (433.53): C 69.26, H 5.35, N 3.23, S 7.40; found: C 69.27, H 5.43, N 3.11, S 7.35.

4. *Control Experiments. a*) A soln. of **5** (30 mg, 0.07 mmol) and **1** (22 mg, 0.14 mmol) in toluene (0.5 ml) was heated under reflux for 8 h. After evaporation of the solvent, the colorless residue was analyzed by ^{1}H-NMR spectroscopy, which evidenced the presence of unchanged **5**, exclusively.

b) A soln. of **1** (80 mg, 0.5 mmol) in toluene (1 ml) was heated under reflux for 8 h. Then, the soln. was cooled to r.t., and, after addition of **3b** (139 mg, 0.4 mmol), heating under reflux was continued for 6 h. The solvent was evaporated, and the residue was analyzed by ^{1}H-NMR spectroscopy, which showed the presence of unchanged **3b**. No traces of either **5** or **6** were detected in the spectrum.

5. *X-Ray Crystal-Structure Determination of* **5**, **6**, **13**, *and* **14** (*Table* and *Figs. 1–4*)[1]). All measurements for **5**, **13**, and **14** were performed on a *Nonius KappaCCD* area-detector diffractometer [18] using graphite-monochromated MoK_α radiation (λ 0.71073 Å) and an *Oxford Cryosystems Cryostream 700* cooler. Data reduction was performed with *HKL Denzo* and *Scalepack* [19]. In the case of **6**, all measurements were performed on a *BRUKER SMART-CCD* area-detector diffractometer using graphite-monochromated MoK_α radiation. Data reduction was performed with the *Bruker* SAINT software [20]. For each data set, the intensities were corrected for *Lorentz* and polarization effects, and an absorption correction based on the multi-scan method [21] was applied. The data collection and refinement parameters are given in the *Table*, and views of the molecules are shown in *Figs. 1–4*. Each structure was solved by direct methods using SIR92 [22], which revealed the positions of all non-H-atoms. In the case of **14**, there are two symmetry-independent molecules in the asymmetric unit. The atomic coordinates of the two molecules were tested carefully for a relationship from a higher symmetry space group using the program PLATON [23], but none could be found. For each structure, the non-H-atoms were refined anisotropically. All of the H-atoms were placed in geometrically calculated positions and refined using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2 U_{eq} of its parent C-atom (1.5 U_{eq} for the Me groups). The refinement of each structure was carried out on F^2 using full-matrix least-squares procedures, which minimized the function $\Sigma w(F_o^2 - F_c^2)^2$. A correction for secondary extinction was applied in the cases of **5** and **14**. For **13**, the refinement of the absolute structure parameter [24] yielded a value of 0.04(9), which confidently

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[1]) CCDC-656139–656142 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the *Cambridge Crystallographic Data Centre via* http://www.ccdc.cam.ac.uk/data_request/cif.

confirms that the refined model corresponds with the true enantiomorph. For **14**, the absolute structure parameter of 0.60(11) suggests that the structure may be an inversion twin. The absolute structure of the model was chosen arbitrarily. In the case of **14**, two reflections, whose intensities were considered to be extreme outliers, were omitted from the final refinement. Neutral atom scattering factors for non-H-atoms were taken from [25], and the scattering factors for H-atoms were taken from [26]. Anomalous dispersion effects were included in F_c [27]; the values for f' and f'' were those of [28]. The values of the mass attenuation coefficients are those of [29]. All calculations were performed using the SHELXL97 program [30].

Table. *Crystallographic Data for Compounds* **5**, **6**, **13**, *and* **14**

	5	**6**	**13**	**14**
Crystallized from	EtOH	hexane/CH_2Cl_2	MeOH	MeOH
Empirical formula	$C_{23}H_{21}NO_5S$	$C_{26}H_{27}NO_7S_2$	$C_{25}H_{23}NO_4S$	$C_{25}H_{23}NO_4S$
Formula weight	423.48	497.56	433.52	433.52
Crystal color, habit	colorless, prism	colorless, prism	colorless, prism	colorless, tablet
Crystal dimensions [mm]	$0.12 \times 0.22 \times 0.28$	$0.40 \times 0.40 \times 0.50$	$0.17 \times 0.25 \times 0.28$	$0.12 \times 0.22 \times 0.25$
Temp. [K]	160(1)	233(1)	160(1)	160(1)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1$	Cc
Z	4	4	2	8
Reflections for cell determination	26834	985	20737	92876
2θ Range for cell determination [°]	4–60	5–60	4–55	4–50
Unit cell parameters:				
a [Å]	10.8564(2)	11.4689(9)	7.6740(1)	13.1687(3)
b [Å]	8.9071(2)	17.107(1)	12.7363(3)	12.9675(4)
c [Å]	21.6690(5)	13.078(1)	11.0467(2)	25.5922(8)
β [°]	98.673(1)	106.404(2)	103.012(1)	101.091(2)
V [Å^3]	2071.41(8)	2461.3(3)	1051.96(3)	4288.6(2)
D_x [g cm^{-3}]	1.358	1.343	1.369	1.343
μ(MoK_α) [mm^{-1}]	0.191	0.178	0.187	0.183
Scan type	ϕ and ω	ω	ϕ and ω	ϕ and ω
$2\theta_{(max)}$ [°]	60	61	55	50
Transmission factors [min; max]	0.867; 0.978	0.840; 1.000	0.841; 0.974	0.841; 0.990
Total reflections measured	54323	33531	22909	31147
Symmetry independent reflections	6040	7531	4773	7243
Reflections with $I > 2\sigma(I)$	3912	4901	4272	5151
Reflections used in refinement	6040	7531	4773	7241
Parameters refined; restraints	275; 0	321; 0	283; 1	566; 2
Final $R(F)$ ($I > 2\sigma(I)$ reflections)	0.0497	0.0460	0.0592	0.0639
$wR(F^2)$ (all data)	0.1366	0.1196	0.1533	0.1553
Weighting parameters (a; b)[a]	0.064; 0.7213	0.056; 0.4736	0.0938; 0.5154	0.0734; 5.7909
Goodness-of-fit	1.023	1.007	1.097	1.045
Secondary extinction coefficient	0.025(2)	–	–	0.0046(4)
Final Δ_{max}/σ	0.001	0.001	0.001	0.001
$\Delta\rho$ (max; min) [e Å^{-3}]	0.44; −0.33	0.33; −0.27	0.49; −0.59	0.44; −0.36

[a]) $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = (F_o^2 + 2F_c^2)/3$.

REFERENCES

[1] M. El-Saidi, K. Kassam, D. L. Pole, T. Tadey, J. Warkentin, *J. Am. Chem. Soc.* **1992**, *114*, 8751; K. Kassam, D. L. Pole, M. El-Saidi, J. Warkentin, *J. Am. Chem. Soc.* **1994**, *116*, 1161; P. Conture, M. El-Saidi, J. Warkentin, *Can. J. Chem.* **1997**, *75*, 326.

[2] J. Warkentin, *J. Chem. Soc., Perkin Trans. 1* **2000**, 2161.

[3] H. W. Zhou, G. Mlostoń, J. Warkentin, *Org. Lett.* **2005**, *7*, 487; A. Śliwińska, W. Czardybon, G. Mlostoń, J. Warkentin, *Can. J. Chem.* **2007**, *85*, in press.

[4] A. Śliwińska, W. Czardybon, J. Warkentin, *Org. Lett.* **2007**, *9*, 695.

[5] P. C. Venneri, J. Warkentin, *Can. J. Chem.* **2000**, *78*, 1194.

[6] J. Romański, G. Mlostoń, H. Heimgartner, *Helv. Chim. Acta* **2007**, *90*, 1279.

[7] M. Dawid, G. Mlostoń, J. Warkentin, *Org. Lett*. **2001**, *3*, 2455; M. Dawid, G. Mlostoń, J. Warkentin, *Chem. – Eur. J.* **2002**, *8*, 2184.

[8] a) J. H. Rigby, P. J. Burke, *Heterocycles* **2006**, *67*, 643; b) J. H. Rigby, J.-C. Brouet, P. J. Burke, S. Rohach, S. Sidique, M. J. Heeg, *Org. Lett*. **2006**, *8*, 3121.

[9] G. Mlostoń, H. Heimgartner, *Helv. Chim. Acta* **2007**, *90*, 1758.

[10] C. K. Johnson, 'ORTEPII', Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1976.

[11] D. L. Pole, J. Warkentin, *J. Org. Chem.* **1997**, *62*, 4065.

[12] J. E. Baldwin, *J. Chem. Soc., Chem. Commun.* **1976**, 734.

[13] a) L. Tenud, S. Farooq, J. Seibl, A. Eschenmoser, *Helv. Chim. Acta* **1970**, *53*, 2059; b) J. F. King, M. J. McGarrity, *J. Chem. Soc., Chem. Commun.* **1979**, 1140; c) J. F. King, M. J. McGarrity, *J. Chem. Soc., Chem. Commun.* **1982**, 175.

[14] E. Schaumann, T. Marr, H. Nimmesgern, S. Sieveking, *Chem. Ber.* **1987**, *120*, 335; E. Schaumann, J. Dietz, E. Kausch, G. C. Schmerse, *Chem. Ber.* **1987**, *120*, 339.

[15] R. N. Ram, A. A. Kahn, *Synth. Commun.* **2001**, *31*, 841.

[16] M. M. Campbell, M. M. Evgenios, *J. Chem. Soc., Perkin Trans. 1* **1973**, 2866.

[17] Y. Tamura, Y. Nishikawa, K. Sumato, M. Ikeda, *J. Org. Chem.* **1977**, *42*, 3226.

[18] R. Hooft, KappaCCD Collect Software, *Nonius BV*, Delft, 1999.

[19] Z. Otwinowski, W. Minor, in 'Methods in Enzymology', Vol. 276, 'Macromolecular Crystallography', Part A, Eds. C. W. Carter Jr., R. M. Sweet, Academic Press, New York, 1997, pp. 307 – 326.

[20] SAINT (Version 6.02a), *Bruker AXS Inc.*, Madison, Wisconsin, 1999.

[21] R. H. Blessing, *Acta Crystallogr., Sect. A* **1995**, *51*, 33.

[22] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, SIR92, *J. Appl. Crystallogr.* **1994**, *27*, 435.

[23] A. L. Spek, PLATON, Program for the Analysis of Molecular Geometry, University of Utrecht, Utrecht, 2006.

[24] H. D. Flack, G. Bernardinelli, *Acta Crystallogr., Sect. A* **1999**, *55*, 908; H. D. Flack, G. Bernardinelli, *J. Appl. Crystallogr.* **2000**, *33*, 1143.

[25] E. N. Maslen, A. G. Fox, M. A. O'Keefe, in 'International Tables for Crystallography', Ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, 1992, Vol. C, Table 6.1.1.1, pp. 477 – 486.

[26] R. F. Stewart, E. R. Davidson, W. T. Simpson, *J. Chem. Phys.* **1965**, *42*, 3175.

[27] J. A. Ibers, W. C. Hamilton, *Acta Crystallogr.* **1964**, *17*, 781.

[28] D. C. Creagh, W. J. McAuley, in 'International Tables for Crystallography', Ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, 1992, Vol. C, Table 4.2.6.8, pp. 219 – 222.

[29] D. C. Creagh, J. H. Hubbell, in 'International Tables for Crystallography', Ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, 1992, Vol. C, Table 4.2.4.3, pp. 200 – 206.

[30] G. M. Sheldrick, SHELXL97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen, 1997.

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