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THE REACTION OF BENZENESULFONYL AZIDE WITH *cis–endo* AND *cis–exo* NORBORNENE-5,6-DICARBOXYLIC ACID ANHYDRIDES AND METHYL ESTERS. THE FORMATION OF *endo* AZIRIDINES FROM *exo* TRIAZOLINES[1]

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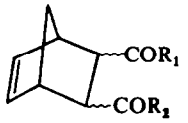
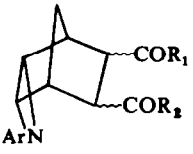
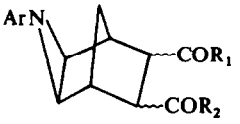
Abstract—Benzenesulfonyl azide reacts with *cis–endo* (Ia) and *cis–exo*-norbornene-5,6-dicarboxylic anhydrides (IIa) and with the corresponding *cis–exo*-dimethyl ester (IIb) in refluxing carbon tetrachloride to give predominantly *endo* aziridines. Under identical conditions the *cis–endo* dimethyl ester (Ib) gives exclusively the *exo* aziridine and under photolytic conditions the *cis–exo* and *cis–endo* anhydrides and dimethyl esters give almost exclusively *exo* aziridines. At room temperature, the *cis–exo* dimethyl ester IIb gives predominantly the *exo* aziridine, and p-methoxybenzenesulfonyl azide reacts with the *endo*-anhydride Ia in refluxing carbon tetrachloride to give an even greater ratio of the *endo* aziridine. The *exo*-1,2,3-Δ^2-triazoline XIIIa prepared from the *exo* anhydride and phenyl azide, on pyrolysis in decalin, gives an almost 1:1 ratio of the *exo* and *endo* aziridine.

A mechanism is proposed to account for the above observations which involves the conversion of *exo*-1,2,3-Δ^2-triazolines to *endo* aziridines via a 3-diazomethylcyclopentane-2-carboxaldehydeimine intermediate (XI).

IN RECENT reports[2] we have described the thermal reaction of benzenesulfonyl azide with *cis–endo* (Ia) and *cis–exo* norbornene-5,6-dicarboxylic anhydride (IIa) which, in apparent violation of Alder and Stein's[3] "*exo* addition rule" give predominantly *endo*-aziridines IIIa and IVa respectively. The reaction in each case is very clean giving an almost quantitative yield of aziridines. This result is to be contrasted with the







Ia: *endo* anhydride
$R_1 \equiv R_2 = O$
Ib: *endo*-dimethyl ester
$R_1 = R_2 = OCH_3$
IIa: *exo*-anhydride
$R_1 \equiv R_2 = O$
IIb: *exo*-dimethyl ester
$R_1 = R_2 = OCH_3$

III: Ar = ϕSO_2
a: *endo*-anhydride
b: *endo*-dimethyl ester
IV: Ar = ϕSO_2
a: *exo*-anhydride
b: *exo*-dimethyl ester

V: Ar = ϕSO_2
a: *endo*-anhydride
b: *endo*-dimethyl ester
VI: Ar = ϕSO_2
a: *exo*-anhydride
b: *exo*-dimethyl ester

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quantitative formation of *exo* aziridine in the reaction of norbornene with benzenesulfonyl azide at room temperature.[4] We have undertaken this more detailed study in order to determine why *endo* aziridines are formed in this case. This expanded study includes the corresponding esters Ib and IIb, the reaction of *p*-methoxybenzenesulfonyl azide and Ia, and the reactions of Ia, Ib, IIa and IIb with benzenesulfonyl azide under photolytic conditions; the results are presented in Table 1. A summary of the evidence supporting the assignment of *exo* or *endo* stereochemistry to the aziridine rings is presented later in the paper.

TABLE 1. *endo/exo* AZIRIDINE RATIO*

Reaction		Aziridine products *endo*	*exo*	Thermal† reaction *endo/exo* aziridine ratio	Photolytic‡ reaction *endo/exo* aziridine ratio
1. ϕSO_2N_3 +	Ia	IIIa	Va	68/32	6/94
2.	Ib	IIIb	Vb	<1/>99	<1/>99
3.	IIa	IVa	VIa	76/24	5/95
4.	IIb	IVb	VIb	70/30	10/90
5. p-$CH_3OC_6H_4SO_2N_3$ +	Ia	XVIIIb	XXI	81/5	—

* The ratio of *endo* to *exo*-aziridines was determined by GLC analysis of the product mixtures in the form of the dimethyl esters prepared from the anhydrides by the action of diazomethane in ether–methanol, on an SE 30 on Gas-Chrom Q Column; analysis by NMR gave similar but less accurate results. The pure aziridine products were also isolated for spectral and GLC analysis.[2b] In reaction 5 the thermal reaction ratio represents isolated materials. In this case the *exo* aziridine was not isolated but instead the lactone XXIa, derived from the *exo* aziridine, was isolated in 5% yield.

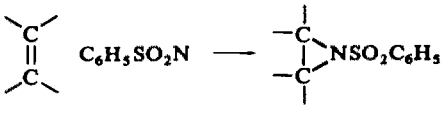
† Carried out by simultaneously refluxing the azide and olefin (1·3:1 molar ratio) samples in carbon tetrachloride for 42 hours. The *endo/exo* aziridine ratio was essentially invariant from 14 to 63 hr. Previously [2b] the total yield of aziridines from Ia and Ib was reported as somewhat less than quantitative but as shown later in this paper the *exo* aziridines Va and Vb are readily transformed into lactones and when this is taken into account the yields of aziridines in these cases are also essentially quantitative.

‡ Carried out by irradiation of the azide-olefin mixtures (1·3:1) at −5° in carbon tetrachloride using a 200 W Hanovia lamp with a Pyrex filter for three hours.

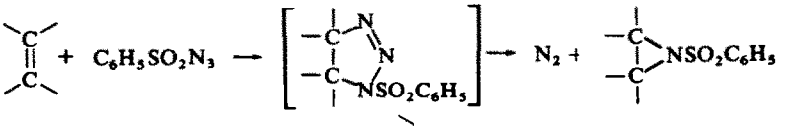
In any consideration of the mechanism of the thermal reaction, one immediately wishes to determine whether the reaction involves nitrene intermediates (Scheme 1-A) or whether the reaction proceeds via a 1,3-dipolar cycloaddition mechanism involving unstable 1,2,3-Δ^2-triazoline intermediates (Scheme 1-B). Benzenesulfonyl azide

SCHEME 1

A. $C_6H_5SO_2N_3 \rightarrow N_2 + C_6H_5SO_2N$



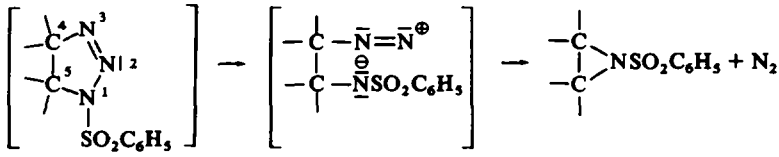
B.



was found not to evolve nitrogen on heating under the thermal reaction conditions in carbon tetrachloride alone or in the presence of dihydro-Ia or dihydro-IIa. Thus a mechanism involving intermediate nitrenes or induced decomposition of the azide by the anhydride moiety is not indicated. Likewise, the fact that diester IIb gives essentially the same ratio of *endo*:*exo* aziridine products as anhydrides Ia and IIa suggests that the anhydride ring plays no unique role as previously thought.[2] Also, the fact that photolysis gives almost exclusively *exo* aziridines further suggests that mechanism A (Scheme 1) is not operable in the thermal reaction.

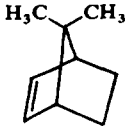
We have discussed previously[4a] the evidence which indicates that the reaction of norbornene with benzenesulfonyl azide proceeds by the now ubiquitous 1,3-dipolar cycloaddition mechanism to give an unstable and yet unisolable 1,2,3-Δ^2-triazoline intermediate. Likewise Huisgen[5] has recently presented evidence which shows that arylsulfonyl azides react with norbornene by a cycloaddition reaction and Bailey and White[6] showed similar results with picryl azides. The instability of the 1,2,3-Δ^2-triazoline ring arises because of the electron withdrawing power of the benzenesulfonyl group which stabilizes the well established[4, 5-7] diazonium-betaine inter mediate (Scheme 2). There is no reason to assume a change in mechanism for the

SCHEME 2

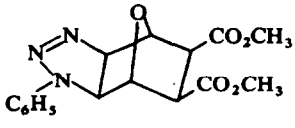


compounds listed in Table 1. As previously reported,[2b] the relative rates of evolution of nitrogen in the thermal reactions with benzenesulfonyl azide are norbornene (100), IIa (10), Ia (1). A similar relative order of reactivity of IIa and Ia has been reported in their epoxidation[8] and is ascribed to a field effect which is greater for the *endo* anhydride because of the closer proximity of the *endo* anhydride group to the double bond. A field effect has also been reported in the reaction of Ia with picryl azide.[6] It is interesting that evidence has recently been presented[9] which suggests a 1,3 dipolar cycloaddition mechanism for peracid epoxidation also.

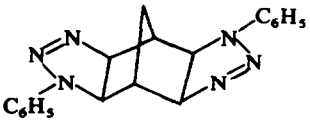
If one accepts that the aziridines produced in the thermal reaction of the olefins listed in Table 1 with benzenesulfonyl azide arise via the unstable 1,2,3Δ^2-triazoline, then the next question is whether the *endo* aziridines arise from *endo* triazolines. This does not seem likely. Alder and Stein first pointed out that azide additions to norbornene systems take place with *exclusive exo* orientation.[2, 10, 11] These authors also found that what is today referred to as cycloaddition fails if *exo* attack is sterically hindered by substituents at the methylene bridge as in apobornylene (VII). It was



VII



VIII

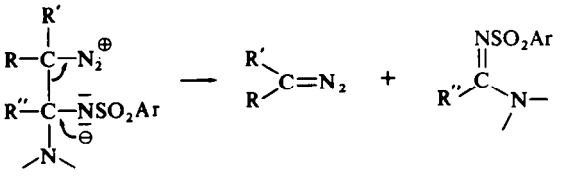


IX

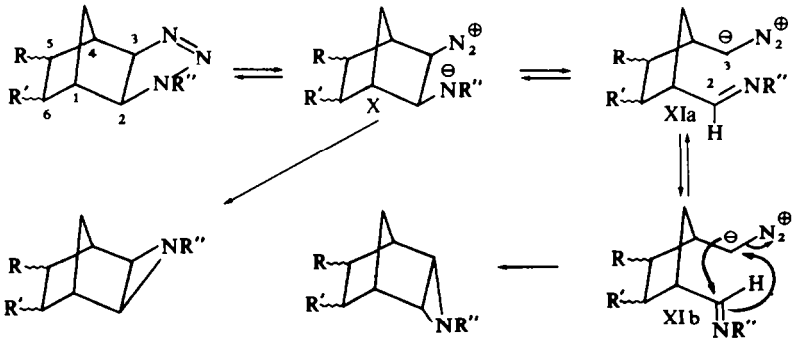
this work that led to the postulation of the "*exo* addition rule" and Huisgen[10] has reported conclusive proof of this selectivity in the reaction of phenyl azide with norbornylene. In spite of the fact that thorough investigations have recently been made of the reaction of norbornene with aryl azides[12] and of 7-oxabicyclo(2.2.1)-heptene derivatives[13] with phenyl azide *no endo* triazolines have been detected. Thus pure crystalline VIII was isolated in 97% yield.[13] Even in the case of norbornadiene, a 96% yield of the *exo*:*exo* bisadduct IX is obtained.[5] It should be noted that in the reaction of norbornadiene with the first molar equivalent of phenyl azide there are no *endo* hydrogens at C-5 and C-6 which could offer steric hindrance to *endo* attack by the azide. Therefore, there seems to be no reason to expect arylsulfonyl azides to react with IIa or IIb from the *endo* side and certainly the *endo* side of Ia and Ib should be extremely hindered. We, therefore, are led to the conclusion that both *endo* and *exo* aziridines arise from *exo* triazolines in the cases under consideration.

A consideration of the requirement for conversion of an *exo*-1,2,3-Δ^2-triazoline to an *endo* aziridine immediately leads to the conclusion that cleavage of the C-4, C-5 bond of the 1,2,3-Δ^2-triazoline ring must occur, followed at some stage by regeneration of this carbon–carbon bond. There is precedence for C—C bond cleavage in the decomposition of 1,2,3-Δ^2-triazolines. Thus, Fusco *et al.*[14] report that the reaction of certain enamines with arylsulfonyl azides results in cleavage of the C-4, C-5 bond of the 1,2,3-Δ^2-triazoline via the diazonium-betaine intermediate (Scheme 2) as indicated in Scheme 3. This fragmentation is particularly facile when R = $\underset{\underset{O}{\|}}{CR}$ and is the basis of the synthesis of α-diazobutyraldehyde (R = CHO, R′ = Et), the first reported aliphatic α-diazoaldehyde.[15] When R and R″ (Scheme 3) are part of the

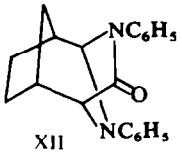
SCHEME 3



SCHEME 4



same molecular ring system then the diazo and imino groups, because of their close proximity, can react with each other. Thus, the formation of the *endo* aziridines observed in this study could be explained as outlined in Scheme 4. Baldwin *et al.*[16] first proposed the existence of an intermediate such as XIa in order to explain the formation of XII from the pyrolysis of the norbornene-phenyl azide adduct in the presence of phenyl isocyanate.



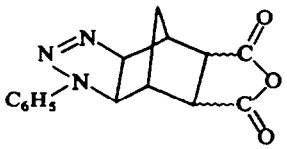
XII

Although the *exo* aziridines could likewise arise via intermediate XI, it does not seem likely that such an intermediate is involved in the reaction of norbornene with benzenesulfonyl azide since, if it were, one would not expect exclusive formation of the *exo* aziridine. In the cases under consideration here (R,R′ = $\overset{O}{\overset{\|}{C}}—O—\overset{O}{\overset{\|}{C}}—$; R = R′ = CO_2Me, Scheme 4), the strong electron-withdrawing groups at C-5 and C-6 would be expected to stabilize the negative charge at C-3 in XI and thus facilitate the formation of this intermediate. The conversion of X into XI would be expected to be less facile at lower temperatures. Indeed, we have observed that in the reaction of IIb with benzenesulfonyl azide, the *endo*:*exo* aziridine ratio drops to 30:70 at room temperature; under these conditions, as expected, the rate of reaction is very low. This observation is consistent with the preponderant formation of *exo* aziridines via intermediate X.

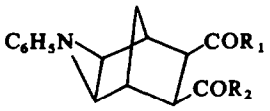
An examination of the thermal reaction data in Table 1 shows that Ib is clearly different in its behavior from Ia, IIa, and IIb. We believe the low *endo*:*exo* aziridine ratio observed for Ib is a result of steric inhibition and unfavorable entropy, which results in a low population of the conformer XIb, the intermediate for *endo* aziridine formation.* The preponderant formation of *endo* aziridines from Ia, IIa and IIb (Table 1) is more difficult to explain. This may be an indication of the greater stability of XIb relative to XIa, in these cases, because of the eclipsing of the groups at C-2 and C-3 in XIa.

In order to obtain additional evidence in support of the mechanism outlined in Scheme 4 we investigated the pyrolysis of a stable *exo*-1,2,3-Δ^2-triazoline, namely XIIIa, prepared by the reaction of IIa and phenyl azide. The exo anhydride IIa was chosen instead of the endo anhydride Ia when it was found that the anhydride ring participated in the thermal reaction of the adduct from Ia. The thermolysis of XIIIa was found to be greatly influenced by the nature of the solvent; thus heating XIIIa in diethylene glycol diethyl ether led to a complex mixture, whereas heating in decalin at 160 ± 5° gave only aziridines XIVa and XVa in a ratio of 46:54. *exo*

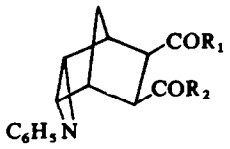
* *A priori*, it does not appear likely that the formation of *endo* aziridine from XIb should be substantially faster than *exo* aziridine formation from X or XIa hence this is not a violation of the Curtin–Hammett principle.



XIII a: *exo* anhydride
b: *endo* anhydride



XIV a: $R_1 \equiv R_2 = O$
b: $R_1 = R_2 = OCH_3$



XV a: $R_1 \equiv R_2 = O$
b: $R_1 = R_2 = OCH_3$

Aziridine XIVa and its dimethyl ester XIVb, prepared by treatment of XIVa with diazomethane in ether–methanol, showed identical physical properties with those previously reported for these compounds.[2,17] The previously unreported *endo* aziridine XVa showed the characteristic aziridine absorption[18] in the infrared (1200 cm^{-1}) and was readily converted into the corresponding dimethyl ester which showed similar aziridine absorption (1195 cm^{-1}).

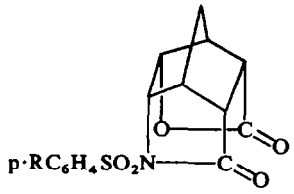
That XVb, and therefore XVa, contained an *endo* aziridine ring was apparent from its NMR spectrum. Thus the *exo* protons at C-2 (H_2) and C-3 (H_3) gave an ill-defined triplet at δ 2·80 with a half-height width ($W_{\frac{1}{2}h}$) of 6 c/s which was superimposed on the signal arising from the bridgehead protons ($H_1 + H_4$) in $CDCl_3$. However, in benzene the two signals were clearly separated. The width of the H_2, H_3 signal is clearly indicative of *exo* protons and therefore of an *endo* aziridine ring as shown in Table 2. Thus *endo* aziridines IIIb and IVb show a similar broad signal for the H_2, H_3

TABLE 2. NMR SPECTRA OF AZIRIDINES

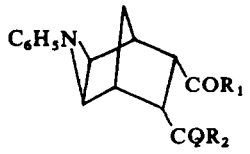
Compound	Half-height width of H_2, H_3 signal	$\delta_{7\,anti}$	$\delta_{7\,syn}$
Vb	2·5 ± 0·5	0·90	1·70
VIb	2·5 ± 0·5	1·47	1·75
XVIIb	2·5 ± 0·5	0·84	1·92
XIVb	2·5 ± 0·5	1·73	1·73
IIIb	6·5 ± 0·5	2·00	1·53
IVb	6·5 ± 0·5	2·32	1·92
XVb	6·5 ± 0·5	2·28	1·82
XVIIIa	6·0 ± 0·5	2·07	1·71
XVIIIb	6·0 ± 0·5	1·85	1·44

* All spectra except for those of XVIIb and XVIIIa, which were run in DMSO, were run in $CDCl_3$.

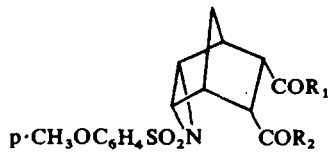
protons (Table 2). The structure of IIIa and therefore IIIb has been well established[2a] by its conversion to XVI. Likewise the structure of IVa, and therefore IVb, is known since the former has been chemically degraded to the 2-*endo* benzenesulfonamidobicyclo(2.2.1)heptane.[2] By contrast, the isomeric *exo* aziridines Vb, VIb and XIVb show narrow signals for H_2, H_3 with $W_{\frac{1}{2}h}$ 2·5 ± 0·5 c/s (Table 2), which are known to be characteristic of *exo* aziridines.[2,4] As an additional example, *exo* aziridine XVIIb was prepared by addition of phenyl azide to anhydride Ia to give the known *exo* triazoline[11] XIIIb which was photolyzed to give the previously reported[11] *exo*



XVI: R = H
XX: R = OCH_3



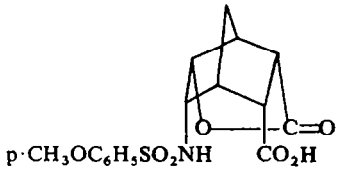
XVII a: $R_1 \equiv R_2 = O$
b: $R_1 = R_2 = OCH_3$



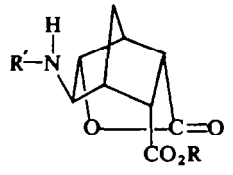
XVIII a: $R_1 \equiv R_2 = O$
b: $R_1 = R_2 = OCH_3$

aziridine XVIIa which in turn was treated with diazomethane to give the known[11] XVIIb. Alder and Stein[11] also prepared XVIIb by a similar route, but using pyrolysis rather than photolysis to convert the triazoline to the aziridine. Scheiner[19] has shown that photolysis of 1,2,3-Δ^2-triazolines yields aziridines in excellent yields with a negligible amount of rearrangement. As indicated in Table 2, XVIIb shows the characteristic narrow signal for H_2, H_3 observed in *exo* aziridines. Tori[18] has shown that an *exo* aziridine produces an anisotropic shielding effect on the 7-*anti* proton in a norbornyl system and this effect can be used to assign *exo* or *endo* configuration to an aziridine ring. This shielding is illustrated by Vb and XVIIb in Table 2, where the 7-*anti* protons appear 0·8–1·1 ppm upfield from the 7-*syn* protons. However this method cannot be used with VIb and XIVb since these substances contain C-2 and C-3 *exo* carbomethoxy groups which deshield the 7-*anti* protons.

The reaction of Ia with *p*-methoxybenzenesulfonyl azide under the previously described thermal reaction conditions led to an 81% yield of the *endo* aziridine XVIIIa which was converted into the corresponding dimethyl ester XVIIIb. The NMR spectra of XVIIIa and XVIIIb are consistent with the assignment of *endo* configurations to the aziridine rings of XVIIIa and XVIIIb as indicated in Table 2. That XVIIIa did indeed contain an *endo* aziridine ring was shown by its conversion in sodium hydroxide to XIX as previously described for IIIa[2a] and pyrolysis of XIX gave XX. In addition to XVIIIb, there was obtained on chromatography of the crude



XIX



XXIa: R′ = $CH_3OC_6H_4SO_2$, R = CH_3
b: R′ = $C_6H_5SO_2$, R = CH_3
XXIIa: R′ = C_6H_5, R = H
b: R′ = C_6H_5, R = CH_3

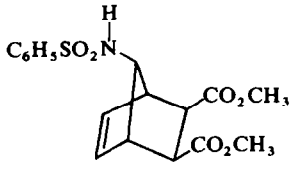
methylated product from the reaction of Ia with *p*-methoxybenzenesulfonyl azide, a 5% yield of XXIa, which undoubtedly arises from the *exo* aziridine, which was not isolated. Similarly, in the thermal reaction of Ib with benzenesulfonyl azide a corresponding lactone (XXIb) was formed on prolonged refluxing of the reaction mixture. Thus after 42 hr reflux the ratio of the lactone to *exo* aziridine was 0·46 : 1 while after

63 hr the ratio had increased to 1·25 : 1. Likewise, in the photolysis of Ib and benzenesulfonyl azide, large amounts of lactone XXIb were isolated if the reaction products were not isolated immediately and the pyrolysis of XIIIa in diethylene glycol diethyl ether gave lactone XXIIa.

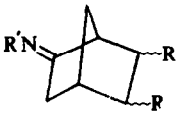
The effect of solvent in the pyrolysis of XIIIa and the increase in *endo* : *exo* aziridine ratio in the reaction of Ia with *p*-methoxybenzenesulfonyl azide provide additional support for the mechanism proposed in Scheme 4. Thus, a non-polar solvent such as decalin would favor less charge separation as in XI and thus facilitate the conversion of X to XI and hence increase the amount of *endo* aziridine produced. The electron-releasing methoxy group should destabilize X and thus also favor XI.

The photolytic reaction can be visualized as occurring by one of three pathways: (1) an initial thermal addition of azide to give preferentially *exo* triazoline, followed by photochemical decomposition to yield *exo* aziridine; (2) photochemical addition of azide to give *exo* triazoline followed by photochemical decomposition to yield *exo* aziridine; (3) photochemical generation of a nitrene followed by reaction with the alkene from the less hindered *exo* side to give *exo* aziridine. The first possibility is eliminated because the reaction is much too fast to involve initial thermal 1,2-dipolar cycloaddition (Table 1). With the evidence available at present, it is not possible to state with certainty whether the photochemical reaction proceeds by pathway (2) or (3) but the isolation of an insertion product, presumed to be XXIII, lends support to pathway (3). The photodecomposition of *exo* 1,2,3-Δ^2-triazolines is known to lead to almost exclusive formation of *exo* aziridines.[4, 5, 19, 20]

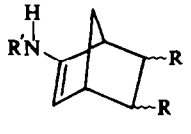
It is interesting that in the pyrolysis of XIIIa in decalin and in the reactions of I and II with benzenesulfonyl azide and the reaction of Ia with *p*-methoxybenzenesulfonyl azide, no imines such as XXIV were observed. This is to be contrasted with the results of Oehlschlager[21] in the pyrolysis of the triazoline adduct formed in the reaction of norbornene with phenyl azide. The latter workers have observed that the amount of imine increases in more polar solvents. Thus, the imine may be produced by loss of nitrogen from an intermediate such as X to give a carbonium ion followed by proton transfer from C-2 to the nitrogen anion X to give an enamine type structure XXV which could equilibrate to XXIV.[22] Such a process would be more facile in more polar solvents and would be hindered by electron-withdrawing groups (R in XXIV) such as the anhydride moiety and carbomethoxy groups on the norbornyl ring system. Likewise, Oehlschlager, *et al.* observed rearranged products such as *syn*-7-N-phenylaminobicyclo(2.2.1)hept-2-ene and 3-N-phenylaminotricyclo(2.2.1.$0^{2,6}$)-heptane which were not observed in those examples mentioned in this study and which could arise via the above mentioned carbonium ion mechanism.



XXIII

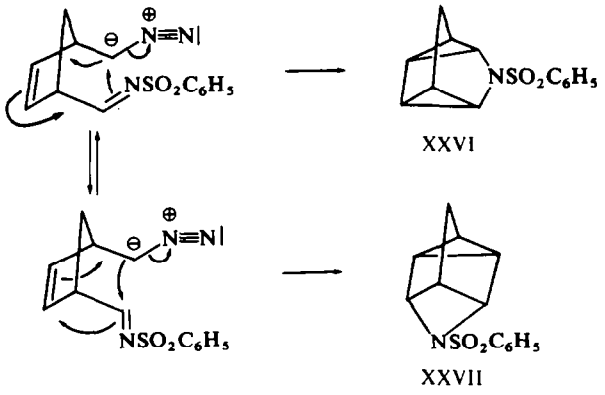


XXIV



XXV

The mechanism proposed in Scheme 4 readily accounts for the minor product reported by Franz and Osuch[23] in the reaction of norbornadiene with benzenesulfonyl azide regardless of whether this product possesses structure XXVI or XXVII.



Finally, the work of Oehlschlager and McDaniel,[21] who have independently observed the conversion of *exo* triazolines to *endo* aziridines, further supports the mechanism shown in Scheme 4. In thier work, which involved the triazoline adduct from norbornene and phenyl azide, the *endo* aziridine was only a minor product (a maximum of 9% in decalin). This is consistent with the decreased stability of XI in the absence of electron-withdrawing groups (R,R′ Scheme 4) on the norbornyl ring.

EXPERIMENTAL

M.ps were taken on a Thomas–Hoover apparatus and are uncorrected. IR spectra were recorded with a Perkin–Elmer 237B spectrophotometer. NMR spectra were obtained with a Varian A-60 spectrometer using $CDCl_3$ as solvent and TMS as an internal standard ($\delta = 0$). Gas chromatographs were obtained using an F & M Biomedical Gas Chromatograph model 400 containing glass columns and a hydrogen flame detector. Photolyses were performed using a Hanovia 200 W lamp with a Pyrex filter.

Thermal reaction of benzenesulfonyl azide with bicyclo {2.2.1} *5-heptene*-endo–cis (Ia) *and* exo–cis (IIa)-*anhydrides and dimethyl esters* (Ib *and* IIb). Benzenesulfonyl azide was prepared as previously described.[24] The *endo* anhydride Ia (m.p. 163–165°) was obtained commercially (Eastman) while the *exo* anhydride IIa (m.p. 142–144°) was prepared by the method of Craig.[25] The corresponding dimethyl esters Ib and IIb were prepared by treatment of methanol solns of the anhydrides with ethereal diazomethane. The four reactions were run simultaneously under identical conditions (6·1 mmoles of olefin and 8·2 mmoles of benzenesulfonyl azide in 20 ml CCl_4 refluxed on the steam bath). After addition of chloroform to dissolve precipitated products, samples were analyzed by gas chromatography using a 0·125-in diam by 4-ft long glass column of 3·8% SE-30 on 80/100 mesh Diatoport S at a column temp of 238° and a He flow rate of 80 cc/min. The anhydride reaction mixtures were treated with MeOH and ethereal diazomethane prior to analysis to convert the anhydrides to dimethyl esters. Authentic samples for comparisons were obtained as previously described[2] and gave the following retention times under the conditions specified above: IIIb, 2·7 min; IVb, 4·3 min; Vb, 5·1 min; VIb, 5·9 min. The ratios of *endo* to *exo* aziridine products after 42 h are given in Table 1. The ratios were determined by measuring GLC peak areas with a planimeter.

While Ia, IIa and IIb gave only *endo* and *exo* aziridines in a ratio of between 2 and 3:1, Ib gave almost exclusively *exo* aziridine Vb in the early stages of the reaction. In addition, a third product (XXII) was observed, with a GLC retention time of 7·2 min which increased as the reaction proceeded. At 42 hr the ratio XXII:Vb was 0·46 and after 63 hr the ratio had increased to 1·25, i.e. XXII was the major product. After 24 months at room temp the conversion of Vb to XXII was complete; crystallization of this solid product from acetone gave pure XXII in essentially quantitative yield. The analytical sample was obtained after recrystallizationn from acetone and gave m.p. 167–169°. (Found: C, 54·44; H, 4·63. Calc. for $C_{16}H_{17}O_6NS$: C, 54·5; H, 5·23%); ν_{max}^{KBr} 3230, 1780, 1730 cm^{-1}; NMR (d_6-acetone) δ 1·70 (d, $J = 12$ c/s, 1H), δ 2·10 (d, $J = 12$ c/s, 1H), δ 3·54 (s, 3H), δ 3·93 (m, 1H), δ 4·60 (d, $J = 5$ c/s, 1H), δ 7·5–8·03 (m, 5H).

Reaction of benzenesulfonyl azide with exo-*dimethyl ester* IIb *at room temp.* Dimethyl ester IIb (1·28 g) and the azide 1·5 g) were dissolved in 20 ml CCl_4 in a flask protected from the light by Al foil. The reaction was left standing at room temp and N_2 was slowly evolved. After 4 weeks, a considerable amount of crystalline solid had formed and filtration gave 0·4 g of *exo* aziridine VIb, m.p. 147–149°. The solvent was then removed *in vacuo* at room temp to give 2·1 g of a gummy residue. Chromatography on alumina of 1·6 g of this material gave in the benzene eluate (850 ml), 0·21 g of a mixture of the starting materials and in the chloroform:benzene (1:1) eluate (125 ml) 0·31 g of solid material which was found by GLC analysis (6-ft by 0·125-in column of 10% SE-30 on 100/120 mesh Gas-Chrom Q at 250° and He flow of 110 ml/min) to contain 36% *exo* aziridine VIb and 63% *endo* aziridine IVb. Elution with 125 ml chloroform gave 0·15 g of solid consisting of 73% VIb and 24% IVb. Elution with an additional 375 ml of chloroform gave 0·02 g of pure VIb. Calculation then gives an *endo*:*exo* aziridine ratio of 30:70.

Photolytic reaction of benzenesulfonyl azide with bicyclo{2.2.1} *5-heptene*-endo–cis (Ia) *and* exo–cis (IIa)-*dicarboxylic anhydrides and dimethyl esters* (Ib *and* IIb). The four reactions were run simultaneously by dissolving the reactants (6·1 mmoles of olefin and 8·2 mmoles of azide) in 50 ml CCl_4, cooling the solns to −5° (whereupon the olefins partially precipitated), and irradiating for 3 hr with a Pyrex-filtered 200 W Hanovia lamp. The reaction mixtures, in the case of the anhydrides, were then treated with MeOH and ethereal diazomethane and analyzed on a 0·125 in by 6 ft glass column of 2% SE-30 on 60/80 mesh Gas-Chrom Q at 238° and a He flow rate of 80 ml/min. The ratios of *endo* to *exo* aziridine products are reported in Table 1. In each case the *exo* aziridine was formed almost exclusive of the *endo* aziridine. In the reactions of the olefins containing *endo* carbonyl functions (i.e. Ia and Ib) the major product was not the *exo* aziridine but XXII formed from the *exo* aziridine. In the reaction of IIa a considerable amount of insertion product XXIII was also formed. The isolation of XXIII is described below.

Photolysis of benzenesulfonyl azide with anhydride IIa *in ethyl acetate; isolation of the insertion product* XXIII. Azide (18·3 g, 0·1 moie) was added to a soln of 16·4 g (0·1 mole) of IIa in 500 ml EtOAc. The resulting soln was cooled to 0°, deoxygenated by bubbling dry N_2 through it, and irradiated for 6 hr during which time a considerable amount of black tarry material precipitated. The solvent was removed on the rotary evaporator to give 33·6 g of a dark syrup which was dissolved in MeOH and esterified with ethereal diazomethane. After evaporation of solvent, the residue was chromatographed on Merck acid-washed alumina. Elution with 200 ml of benzene gave about 10 mg of a yellow oil which showed no carbonyl or azide absorptions in the IR. Elution with an additional 500 ml benzene and 5 l of 1:1 benzene:chloroform gave 12·54 g of a solid which was recrystallized from ether to give 10·3 g of *exo* VIb (m.p. 148–149°) identical with that previously reported.[2] Analysis of the mother liquor by GLC showed the presence of *endo* IVb and the insertion product XXIII in addition to VIb. Elution with 1·2 l. chloroform gave 4·3 g material. Rechromatography of this material on silica gel and crystallization from acetone of the chloroform eluate gave 290 mg of XXIII. The analytical sample was obtained by recrystallization from acetone and gave m.p. 142–143°. (Found: C, 55·68; H, 5·40. Calc for $C_{17}H_{19}O_6NS$: C, 55·94; H, 5·25%); ν_{max}^{KBr} 3280, 1740, 1715 cm^{-1}; NMR ($CDCl_3$) δ 2·97 (S, $W_{\frac{1}{2}h}$ 6 c/s, 2H), δ 3·25 (S, $W_{\frac{1}{2}h}$ 5·5 c/s, 2H), δ 3·50 (d, J = 9·5 c/s, 1H, collapses to broad singlet on addition of D_2O), δ 3·54 (S, 3H), δ 5·42 (d, J = 9·5 c/s, 1H, disappears on addition of D_2O), δ 6·12 (S. 2H), δ 7·4–7·9 (m, 5H).

Preparation and pyrolysis of the phenyl azide adduct of exo *anhydride* IIa. Phenyl azide was prepared from phenylhydrazine and nitrous acid as described in the lit.[26] The azide (6 g) was added to a soln of IIa (8·2 g) in 250 ml CCl_4 and the mixture was refluxed on the steam bath for 3 hr during which time XIIIa (11 g, 79%) precipitated as a white powder, m.p. 95–96° (lit.[11] 220° dec) ν_{max}^{KBr} 1850, 1770, 1600 cm^{-1}. Triazoline XIIIa (14·2 g) was added to 500 ml of dry, freshly distilled diethylene glycol diethyl ether (Eastman) and the mixture was placed in an oil bath at 160 ± 5°. As the mixture warmed, the solid dissolved and vigorous evolution of N_2 occurred. After 30 min, the rate of gas evolution was very low and heating was discontinued. The soln was evaporated on the steam bath at 0·05 mm to a volume of about 150 ml and cooled to room temp, whereupon 4·12 g of the *exo* XIVa crystallized. Recrystallization from acetone gave a sample, m.p. 217–219° (lit[3] 219°) which was shown by IR spectra and GLC to be identical with XIVa obtained by pyrolysis of XIIIa in decalin as described below. The mother liquor was examined by GLC and found to be a very complex mixture and was not further investigated.

Triazoline XIIa (11 g) was added to 500 ml of freshly distilled decalin (Eastman) and heated in an oil bath at 160 ± 5° for 3·3 hr. The mixture had not become homogeneous and 3·2 g of starting material was filtered from the hot reaction mixture. The filtrate was analyzed by GLC using a 0·125 in by 6 ft glass column of 10% SE-30 on 100/120 mesh Gas-Chrom Q at 173° and a He flow rate of 93 cc/min. Under these conditions, two peaks only were observed at retention times of 12·3 min (54%) and 13·4 min (46%). After standing

in the refrigerator 48 hr a solid (6·83 g) had crystallized and was filtered. The filtrate was evaporated at 32° and 0·025 mm to give an additional 0·46 g of solid. A portion (2·4 g) of the combined solids was fractionally crystallized from acetone. The first crystals were pure *exo* XIVa which had a retention time of 13·4 min under the conditions described above. The analytical sample was obtained by recrystallization from acetone and gave m.p. 218–220° (Found: C, 70·59; H, 5·09. Calc. for $C_{15}H_{13}O_3N$: C, 70·65; H, 5·14%); ν_{max}^{KBr} 1848, 1775, 1231 cm^{-1}. After several fractions were crystallized as mixtures the residue left upon evaporation of the mother liquor was *endo* XVa with a GLC retention time of 12·3 min. The *L*analytical sample was obtained by recrystallization from acetone and gave m.p. 165–167°. (Found: C, 69·75; H, 5·00. Calc. for $C_{13}H_{15}O_3N$: C, 70·65; H, 5·14%; ν_{max}^{KBr} 1860, 1785, 1200 cm^{-1}. Treatment of a MeOH soln of 4·4 g of the solid reaction product with ethereal diazomethane followed by fractional crystallization from hexane resulted in the isolation of XIVb and XVb. Esterification of the pure XIVa and XVa also gave XIVb and XVb, respectively. The analytical sample of XIVb was obtained by recrystallization from hexane and gave m.p. 134–136° (lit.[3] 138°) (Found: C, 67·61; H, 6·35. Calc. for $C_{17}H_{19}O_4N$: C, 67·83; H, 6·36%); ν_{max}^{KBr} 1733, 1208 cm^{-1}; NMR ($CDCl_3$) δ 1·73 (S, $W_{\frac{1}{2}h}$ 5 c/s, 2H), δ 2·34 (S, $W_{\frac{1}{2}h}$, 2·5 c/s, 2H), δ 2·73 (S, $W_{\frac{1}{2}h}$ 3 c/s, 2H), δ 2·91 (S, $W_{\frac{1}{2}h}$ 4 c/s, 2H), δ 3·67 (S, 6H), δ 6·7–7·4 (m, 5H). The analytical sample of XVb was obtained by recrystallization from hexane and gave m.p. 87–89°. (Found: C, 67·66, H, 6·42. Calc. for $C_{17}H_{19}O_4N$: C, 67·83; H, 6·36%); ν_{max}^{KBr} 1744, 1195 cm^{-1}, NMR ($CDCl_3$) δ 1·83 (d, J = 10 c/s, 1H), δ 2·27 (d, J = 10 c/s, 1H), δ 2·78 (S, 2H), overlapping half of triplet (J = 2 c/s, 2H) at δ 2·81, δ 3·12 (d, J = 1·6 c/s, 2H), δ 3·60 (S, 6H), δ 6·8–7·4 (M, 5H); NMR (C_6H_6) δ 2·42 (m, $W_{\frac{1}{2}h}$ 6·5 c/s), δ 2·58 (m, $W_{\frac{1}{2}h}$, 4·5 c/s).

Preparation and pyrolysis of the phenyl azide adduct XIIIb *of* endo *anhydride* Ia. Phenyl azide (11·9 g, 0·1 mole) was added to a soln of 16·4 g (0·1 mole) of Ia in 200 ml EtOAc and stirred at room temp. The *exo* XIIIb precipitated as the reaction proceeded and was filtered after 19 days to give 17·9 g of XIIIb, m.p. 232–234° dec. (lit.[27] 225 dec); ν_{max}^{KBr} 1860, 1780, 1600 cm^{-1}.

Pyrolysis of XIIIb in diethylene glycol diethyl ether (Eastman) at 160 ± 5° for 2 hr gave a complex mixture from which four unidentified crystalline products have been isolated by chromatography on alumina. In addition, two other products crystallized directly from the reaction mixture upon concentration. One of these, isolated in 7·5% yield, has been identified as XXIIa. The analytical sample was obtained by recrystallization from acetone and gave m.p. 233–235° (lit.[11] 236°). (Found: C, 66·16; H, 5·70. Calc. for $C_{15}H_{15}O_4N$: C, 65·93; H, 5·49%); ν_{max}^{KBr} 3400, 2800–3650 (broad), 1780, 1700 cm^{-1}. Treatment of MeOH soln of XXIIa with ethereal diazomethane gave the ester XXIIb, m.p. 208–210° (lit.[11] 204); ν_{max}^{KBr} 3395, 1776, 1726 cm^{-1}. None of the compounds isolated were aziridines. The structures of the other five products are currently under investigation.

In order to prepare the *exo* XVIIb 4·3 g of XIIIb was suspended in 500 ml EtOAc and irradiated at 16° for 2·5 hr with a Hanovia 200 W lamp fitted with a quartz filter. The soln was then concentrated, whereupon 2·04 g (84%) of XVIIa crystallized as fine white platelets, m.p. 160–162°; ν_{max}^{KBr} 1860, 1780, 1220 cm^{-1}. Treatment of XVIIa with ethereal diazomethane and MeOH followed by evaporation of the solvent and recrystallization of the residue from ether gave XVIIb, m.p. 83–84° (lit.[11] 86°): NMR (CCl_4) δ 0·84 (d, J = 11 c/s, 1 HO, δ 1·92 (d, J = 11 c/s, 1H), δ 2·78 (S, $W_{\frac{1}{2}h}$, 2·5 c/s, 2H), δ 2·87 (S, $W_{\frac{1}{2}h}$ 5 c/s, 2H), δ 2·98 (S, $W_{\frac{1}{2}h}$ 3·5 c/s, 2H), δ 3·62 (S, 6H), δ 6·7–7·3 (m, 5H). After standing 24 months this solid material was analyzed by GLC and found to have undergone a significant (40%) change to XXIIb. Recrystallization from CH_2Cl_2 gave crystalline XXIIb, m.p. 208–210° (no depression on admixture with XXIIb obtained in the pyrolysis of XIIIb). These compounds also showed identical retention times by GLC (6·7 min on a 6-ft by 0·125-in column of 3% SE-30 on 100/120 mesh Gas-Chrom Q at 210° and a He flow of 95 ml/min) and gave identical IR spectra. Analysis by GLC of the mother liquor after four days at room temp gave only one peak corresponding to XXIIb. The NMR (d_6-acetone) of XXIIb was very similar to that of XXIb showing peaks at δ 1·76 (d, J = 11 c/s, 1H), δ 2·26 (d, J = 11 c/s, 1H), δ 3·69 (S, 3H), δ 4·00 (m, 1H), δ 4·52 (d, J = 5 c/s, 1H), δ 6·5–7·4 (m, 5H).

Reaction of p*-methoxybenzenesulfonyl azide with anhydride* Ia. The azide was prepared by addition of an acetone soln of *p*-methoxybenzenesulfonyl chloride (Aldrich) to aqueous sodium azide according to the published procedure for *m*-nitrobenzoyl azide.[28] The azide was purified by recrystallization from methanol and gave m.p. 50–55° (lit.[29] 49–51°); ν_{max}^{KBr} 2340, 2130, 1580 cm^{-1}; NMR (CCl_4) δ 7·42 (d, J = 8·5 c/s, 2H), δ 6·60 (d, J = 8·5 c/s, 2H), δ 3·52 (S, 3H). The azide (4 g, 18·8 mmoles) and anhydride Ia (3 g, 18·3 mmoles) were dissolved in 100 ml CH_2Cl_2 and stirred at room temp. After 60 hr no apparent reaction had occurred (no decrease in intensity of azide band in IR) and the soln was then refluxed on the steam bath 56 hr. Upon cooling to room temp, 3·61 g of XVIIIa (m.p. 200–210°) crystallized. Concentration of the filtrate to about ½ its volume led to crystallization of an additional 1·39 g (m.p. 220–224°). The combined solids were re-

crystallized from CH_2Cl_2 to give the analytical sample of XVIIIa, m.p. 226–228°. (Found: C, 55·04; H, 4·46. Calc. for $C_{16}H_{15}O_6NS$: C, 55·01; H, 4·30%); ν_{max}^{KBr} 1845, 1775, 1155, 1310, 1325 cm^{-1}; NMR (d_6, —DMSO) 1·71 (d, J = 9 c/s, 1H), δ 2·07 (d, J = 9 c/s, 1H), δ 2·72 (S, $W_{\frac{1}{2}h}$ 7 c/s, 2H), δ 3·23 (S, $W_{\frac{1}{2}h}$, 6 c/s, 2H), δ 3·43 (S, $W_{\frac{1}{2}h}$ 6 c/s, 2H), δ 3·58 (S, 3H), δ 6·59 (d, J = 8 c/s, 2H), δ 7·17 (d, J = 8 c/s, 2H). The filtrate was evaporated and the residue dissolved in MeOH and treated with ethereal diazomethane. After evaporation of the solvent 3·0 g of a yellow gum was obtained which was then chromatographed on Merck acid-washed alumina (activity III). Elution with 0·25 l. benzene gave 0·2 g oil which could not be crystallized. Further elution with 1·25 l. benzene gave a fraction (0·5 g) which was crystallized from ether to give 0·35 g of XVIIIb (m.p. 191–192°) identical (m.p., IR spectra) to XVIIIb obtained by treatment of a MeOH soln of XVIIIa with ethereal diazomethane. The analytical sample was obtained by recrystallization from acetone and gave m.p. 191–192°. (Found: C, 54·73; H, 5·37. Calc. for $C_{18}H_{21}O_7NS$: C, 54·50; H, 5·72%); ν_{max}^{KBr} 1738, 1595, 1165, 1175 cm^{-1}; NMR ($CDCl_3$) δ 1·44 (d, J = 10 c/s, 1H), δ 1·85 (d, J = 10 c/s, 1H), δ 2·59 (S, $W_{\frac{1}{2}h}$ 4 c/s, 2H), δ 2·70 (S, $W_{\frac{1}{2}h}$ 4 c/s, 2H), δ 3·25 (S, 6H) overlapping δ 3·28 (S, $W_{\frac{1}{2}h}$ 6 c/s, 2H), δ 3·58 (S, 3H), δ 6·44 (d, J = 8 c/s, 2H), δ 7·17 (d, J = 8 c/s, 2H). After elution with 4 l. $C_6H_6CHCl_3$ mixtures a fraction was eluted with $CHCl_3$–C_6H_6 through 3:1 to MeOH–$CHCl_3$ (1:4) and crystallized from acetone to give 0·34 g of XXIa. The analytical sample was obtained by recrystallization from acetone and gave m.p. 210–212°. (Found: C, 53·33; H, 5·15. Calc. for $C_{17}H_{19}O_7NS$: C, 53·33; H, 5·36%); ν_{max}^{KBr} 3222, 1760, 1727, 1157 cm^{-1}; NMR (d_6-acetone) δ 1·67 (d, J = 12 c/s, 1H), δ 2·12 (d, J = 12 c/s, 1H), δ 3·59 (S, 3H), δ 3·91 (s, 3H), δ 4·59 (d, J = 5 c/s, 1H), δ 7·13 (d, J = 9 c/s, 2H), δ 7·83 (d, J = 9 c/s, 2H).

Preparation of endo-5-*hydroxy*-endo-6-(p-*methoxybensulfonamido*) endo–cis-2,3-*dicarboxybicyclo*{2.2.1}-*heptane* γ-*lactone* (XIX). A mixture of 0·88 g of XVIIIa and 2 ml 1·35 N NaOH was heated on the steam bath for 6 hr during which time the solid XVIIIa dissolved. After cooling, the soln was extracted with $CHCl_3$. Drying over $MgSO_4$ and evaporation of the $CHCl_3$ extract gave no residue. Upon the addition of conc HCl (5 ml) to the aqueous soln a colorless oil separated. The aqueous soln was then extracted with $CHCl_3$ and the extract was combined with the oil. Drying over $MgSO_4$ and evaporation of the $CHCl_3$ gave 0·83 g oil which crystallized to give XIX, m.p. 219–222° dec (vigorous bubbling). Recrystallization from acetone gave the analytical sample, m.p. 223–225° (dec). (Found: C, 52·55; H, 4·74. Calc. for $C_{16}H_{17}O_7NS$: C, 52·32; H, 4·63%); ; ν_{max}^{KBr} 3225, 1777, 1767, 1705 cm^{-1}; NMR (d_6- DMSO) δ 1·55 (S, 2H), δ 3·87 (S, 3H), δ 5·38 (S, 1H).

Preparation of endo-5-*hydroxy*-endo-6-(p-*methoxybenzenesulfonamido*) endo–cis-2,3-*dicarboxybicyclo*-{2.2.1}*heptane* γ-*lactone*-γ-*lactam* (XX). The lactone XIX (0·14 g, m.p. 223–235°) was heated at 225° until vigorous bubbling had ceased and then the flask was evacuated to 0·5 mm and heated an additional 5 min. The resulting glassy solid (0·13 g) was recrystallized from acetone to give the analytical sample of XX, m.p. 204–205°. (Found: C, 55·16; H, 4·41. Calc. for $C_{16}H_{15}O_6NS$: C, 55·06; H, 4·33%). ν_{max}^{KBr} 1730, 1780 cm^{-1}; NMR (d_6-DMSO) δ 1·78 (S, 2H), δ 2·93 (S, 2H), δ 3·88 (S, 3H).

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