Organic Sulfur Mechanisms. 13. Sulfene Formation by a Reverse Diels–Alder Reaction

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Received April 4, 1973

Dimethyl 2,2-dioxido-4-phenyl-2-thiabicyclo[2.2.2]octa-5,7-diene-5,6-dicarboxylate (**5**), a molecule purposely designed to undergo a thermal reverse Diels–Alder reaction to form sulfene and an aromatic co-fragment, has been synthesized. Thermolysis of **5** gave dimethyl biphenyl-2,3-dicarboxylate (**7**) and, in addition, (*a*) in the presence of an enamine (**6**) gave the appropriate sulfene–enamine adduct (**8**), and (*b*) with an excess of *p*-toluidine gave methanesulfon-*p*-toluidide (**10**), in agreement with the above expectation. In the absence of sulfene traps the only product identified, in addition to **7**, was sulfur dioxide; further experiments failed to determine the fate of the methylene group but serve to exclude certain possibilities, including fragmentation of sulfene to sulfur dioxide and a trappable carbenoid species.

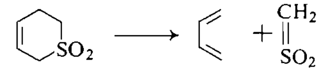
On a synthétisé le dioxydo-2,2 phényl-4 thia-2 bicyclo[2.2.2] octadiène-5,7 dicarboxylate-5,6 de diméthyle (**5**), afin d'étudier spécifiquement sa transformation thermique, selon une réaction inverse de Diels–Alder, en sulfène et en un fragment aromatique. La thermolyse de **5** a conduit au biphényl dicarboxylate-2,3 de diméthyle (**7**) et a conduit, en plus, (*a*) en présence d'une énamine (**6**) au composé d'addition prévu sulfène–énamine (**8**) et (*b*) en présence d'un excès de *p*-toluidine au méthanesulfon-*p*-toluidine (**10**) ce qui est en accord avec les prévisions énoncées antérieurement. En absence de sulfène, le seul produit identifié, en plus de **7**, a été l'anhydride sulfureux (SO_2); d'autres expériences n'ont pas réussi à montrer ce qu'il advient du groupe méthylène mais ont cependant permis de rejeter certaines hypothèses, en particulier celle qui impliquerait la fragmentation du sulfène en anhydride sulfureux et en une espèce carbènoide isolable. [Traduit par le journal]

Can. J. Chem., 51, 3044 (1973)

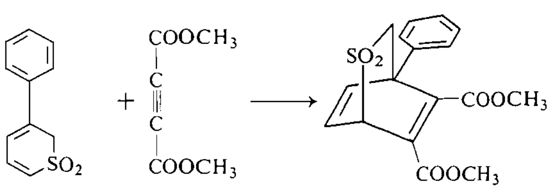
Introduction

For some time we have been engaged in the study of the formation of sulfenes by thermolysis (1–3). Our goal in continuing this work has been to find a particularly mild, general route to sulfenes in which by-products or co-products would be either absent or unreactive toward the sulfene. This paper presents the details of one of our recent approaches to the problem which has employed the reverse Diels–Alder reaction (4); a preliminary report has already appeared (5).

The simplest reaction leading to formation of a sulfene by a reverse Diels–Alder reaction would be **1** → **2** + **3**. A rough thermochemical estimate indicates that the reaction **1** → **2** + **3** would be endothermic by about 40 to 50 kcal/mol,[1] but a molecule so constituted that the diene is part of an incipient aromatic system (*e.g.* **5**) would be expected to react more readily. Using essentially the method of Benson *et al.* (8), we estimate that for the fragmentation of bicyclo[2.2.2]octadiene into benzene and ethylene $\Delta H^0 \approx +1$ kcal/mol or lower,[2] whereas $\Delta H^0 = +39.7$ kcal/mol for the conversion of cyclohexene into butadiene and



1 **2** **3**



4 **5**

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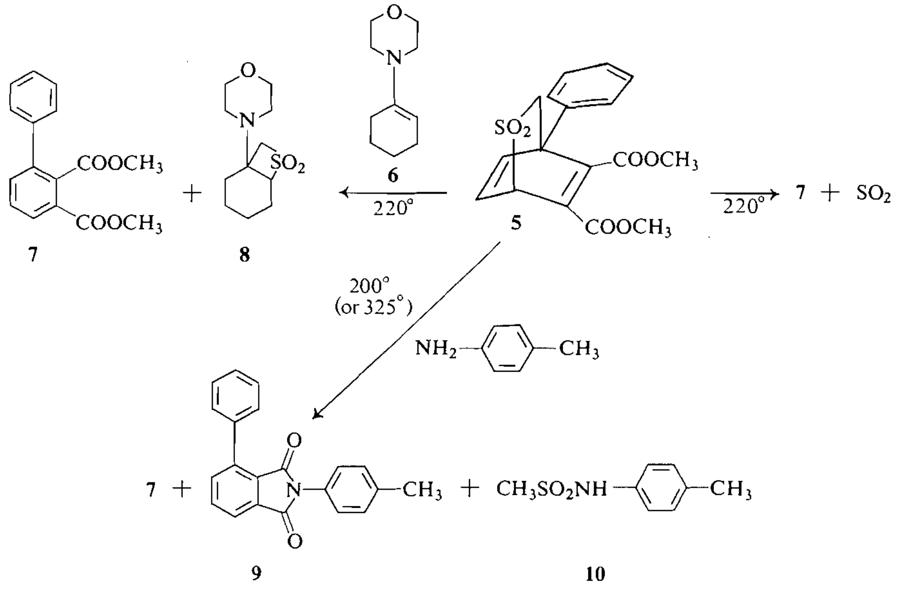
[1] In simple average bond energy terms ΔH for the reaction **1** → **2** + **3** would be given by $E(\text{C—C}) + E(\text{C—SO}_2) - E_\pi(\text{C=C}) - E_\pi(\text{C=SO}_2)$, where $E_\pi(\text{C=C}) = E(\text{C=C}) - E(\text{C—C})$ and $E_\pi(\text{C=SO}_2) = E(\text{C=SO}_2) - E(\text{C—SO}_2)$. We take $E(\text{C—C}) = 82.6$ kcal/mol and $E(\text{C=C}) = 145.8$ kcal/mol (6) (and so $E_\pi(\text{C=C}) = 63.2$ kcal/mol), $E(\text{C—SO}_2) = 62$ kcal/mol (average of the values deduced by Mackle (7)), and estimate (see Appendix) a value for $E_\pi(\text{C=SO}_2)$ of $\sim 35 \pm 5$ kcal/mol.

[2] Without correcting for steric strain we estimate $\Delta H^0 = +10.5$ kcal/mol. No estimate of the steric strain in the bicyclic diene itself is at hand but the corresponding correction for bicyclo[2.2.2]octane may be obtained by comparing the experimental $\Delta H_f = -24.09$ kcal/mol (9) with the value -33.5 kcal/mol derived by addition of Benson's group energies. The value so obtained, 9.4 kcal/mol, may be regarded as a lower limit for bicyclo[2.2.2]octadiene since the latter is almost certainly more strained than its saturated analog.



SCHEME 1

ethylene. In addition, as has been pointed out by Kwart and King (4), such a fragmentation process would be expected to be accompanied by an increase in entropy and hence be favored by an increase in temperature.

Results and Discussion

Synthesis of the Material to be Thermolyzed

The simplest bicyclic sulfone that would give sulfene and an aromatic co-product is 2-thiabicyclo[2.2.2]octa-5,7-diene 2,2-dioxide, but our attempts to obtain it from the monocyclic sulfide 1-thiacyclohexa-2,4-diene (10) having proved fruitless we explored the formation of the [2.2.2]bicyclo system using the substituted cyclohexadienic sulfone **4** (11). Dimethyl acetylenedicarboxylate with the sulfone **4** under mild conditions gave no reaction, but a 46% yield of **5** was obtained by heating the reagents at 140° for 68 h; small amounts of both starting material and thermolysis product were detectable in the reaction mixture. The product (**5**) was a solid melting at 210–211° for which the structure is established by the full agreement of the mode of synthesis and analytical and spectroscopic data. The n.m.r. spectrum is particularly indicative: in addition to phenyl hydrogens at 7.1 to 7.5 and two methyl groups 3.34 and 3.80, there is an AB quartet at 3.01 and 3.40 ($J = 11.0$) due to the methylene group and an ABX pattern, δ_A 6.84, δ_B 6.64, δ_X 5.30 p.p.m., J_{AB} 7.6, J_{AX} 6.6, and J_{BX} 1.6 Hz, arising from the olefinic plus bridgehead hydrogens.

Thermolysis of 5 in the Presence of Sulfene Traps

The thermolyses of **5** are summarized in Scheme 1. At 220° in the presence of the enamine **6** the biphenyldicarboxylic ester **7** and the enamine adduct **8** were obtained in 80% and 38% yields, respectively. The products were identical with authentic specimens synthesized essentially as described respectively by Heilbron and coworkers (12) and by Borowitz (13). An improvement in one step of the synthesis of the biphenyl diester (**7**) seems worth noting. Conventional esterification of 3-nitrophthalic acid stops at the monoester and whereas the earlier workers used a silver salt procedure to effect complete esterification, we found that sodium hydride in dimethylformamide followed by treatment with methyl iodide gave the diester in good yield.

The formation of **7** and **8** is clearly in agreement with a reverse Diels–Alder process as originally expected. Confirmation of this was obtained by the finding that methanesulfon-*p*-toluidide is the principal product (52% yield) when **5** is heated at 325° for 1.5 min with excess *p*-toluidine; a slightly lower yield of the sulfonamide (39%) was obtained when the reaction was carried out at 200° for 15 min. The biphenyl diester (**7**) was obtained in 49% yield at 325° (45% at 200°); some of the biphenyl portion appeared as the imide **9** (17% yield at 325°, 30% at 200°). The imide (**9**) can be prepared by heating the biphenyl ester (**7**) with *p*-toluidine, and presumably some of the imide in the reaction product from **5** is so formed or else arises from a precursor derived from reaction of **5** with *p*-toluidine before the reverse Diels–Alder reaction takes place.

Thermolysis of 5 in the Absence of Sulfene Traps: The Fate of the Sulfene

One of the aims of this study, as pointed out in the Introduction, was to find a general method of making a sulfene in which neither the starting material nor the co-products would react with sulfene.[3] Such a reaction might make it possible to perform certain experiments on sulfenes not hitherto feasible, for example, performance of direct observations on sulfenes under conditions rather more convenient than the -196 to $< -160°$ range to which such experiments have been restricted to date (2). Since the results described above strongly indicated that sulfene was formed in at least 50% yield from **5**, it was felt that its thermolysis in the absence of the usual sulfene traps should be looked at.

An attempt at flash thermolysis (cf. refs. 2 and 3) at 700° and $< 1\ \mu$, carried out by Dr. R. A. Marty of this department, proved disappointing because the sulfone **5** proved almost involatile in the flash thermolysis apparatus and was induced to sublime into the hot tube only with great difficulty. The result is that it is unclear whether thermal decomposition actually takes place in the hot tube in the gas phase or merely during the heating of the material to induce sublimation. The infrared spectrum of the product on the cold finger at $-196°$ showed very weak bands of 1230 and 1330 cm^{-1} corresponding to the strongest bands previously observed for sulfene (2), but the weakness of the spectrum of the material from **5** precludes an unambiguous conclusion.

Simply heating **5** in the melt at 220° gave **7** in 95% yield. The only co-product that we have identified is sulfur dioxide which is formed in about 80% yield; the fate of the methylene carbon is unclear. The formation of sulfur dioxide would seem to point to the fragmentation of sulfene into methylene and sulfur dioxide, but when the thermolysis was carried out in the presence of a large excess of cyclooctene, there was no sign of the methylene adduct, bicyclo[6.1.0]nonane, even though an estimated 5% conversion to the methylene adduct would have been clearly detectable. It is noteworthy that a number of authors (one of us included) have suggested and looked for fragmentation of a sulfene to carbene and sulfur dioxide, and in no instance has any evidence for such a reaction been obtained (14). A simple estimate suggests that the reaction $CH_2{=}SO_2 \rightarrow CH_2 + SO_2$ is endothermic by 55 to 60 kcal/mol.[4]

Two other possibilities for the decomposition of the sulfene were explored and discarded. Under flash thermolysis conditions above 700—800°, sulfenes undergo desulfinylation, *i.e.* loss of sulfur monoxide with formation of the aldehyde or ketone (3). Even though the nearly quantitative conversion of sulfur monoxide to sulfur dioxide under these conditions seemed improbable, we made attempts to detect formation of formaldehyde. None was observed; control experiments indicated that a 10% yield would have been readily detectable. Another possibility was that the sulfene had dimerized to form Opitz' sulfene dimer, 1,3-dithietane 1,1,3,3-tetroxide. Under conditions of flash thermolysis this compound gives some sulfur dioxide, ethylene, and formaldehyde (16). No sign of ethylene was found in the gaseous products from **5**, thereby rendering it unlikely that the sulfur dioxide observed arises via Opitz' sulfene dimer.

Having excluded the above possibilities the question remains: where does the CH_2 go? With the comparatively modest supplies of **5** that were available the thermolyses were normally carried out on quantities of the order of 50 mg and the actual mass represented by the methylene group is thus only 2 mg. A small quantity of intractable, apparently polymeric material remained on the wall of the Carius tube after these reactions and

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[3] It should perhaps be specifically pointed out that no such method was known at the outset of this study. The present work and the recently discovered sulfo-Cope rearrangement (1) come closest at present, and these are not ideal owing to the relatively high temperatures required.

[4] Using average bond energies $\Delta H = E_\pi(C{=}SO_2) + E(\dot{C}{-}\dot{S}O_2)$. We used for the former 35 kcal/mol (see Appendix) and for the latter the average of the estimated bond dissociation energies of a number of radicals of the type $R{-}\dot{S}O_2$, *viz.* 22 kcal/mol (7). Approximate similarity of $D(\dot{C}H_2{-}\dot{S}O_2)$ and $D(CH_3{-}\dot{S}O_2)$ is to be expected in view of the similarity of $D(CH_3{-}H)$ and $D(\dot{C}H_2{-}H)$, which are reported to be 104 and 106 kcal/mol, respectively (15).

small amounts of unidentified materials were seen in the crude products; either (or both) of these materials could perhaps originate from the "lost" methylene. It would appear that **5**, though it has proved very useful in demonstrating the possibility of generating sulfenes by such a reverse Diels–Alder reaction, is not the ideal substrate either for flash thermolysis or determining what happens to the sulfene fragment in the absence of added traps. We intend to continue study of the latter points with another substrate when the opportunity presents itself.

Experimental

Melting points were taken in capillary tubes with a Gallenkamp apparatus and are uncorrected. Unless stated otherwise recrystallizations were effected from CH_2Cl_2–hexane, analytical t.l.c. was performed with microscope slides coated with silica gel, and preparative t.l.c. with 20 × 20 cm or 10 × 20 cm glass plates bearing 20 or 10 g of silica gel, respectively. T.l.c. plates were developed with CH_2Cl_2, analytical plates being visualized with iodine vapor and preparative plates by means of the u.v. phosphor in the silica gel; compounds were extracted from preparative plates using CH_2Cl_2–MeOH (100:15, v/v). In aqueous work-ups, dichloromethane solutions were run through a small plug of cotton wool (previously washed with dichloromethane to remove fats) before evaporation, which simultaneously removed the remaining trace of water azeotropically. I.r. spectra were measured with a Beckman IR20A, and n.m.r. spectra with Varian T-60 or HA-100 spectrometers.

Synthesis of Dimethyl 2,2-Dioxido-4-phenyl-2-thiabicyclo[2.2.2]octa-5,7-diene-5,6-dicarboxylate (5)

A solution of sulfone **4** (11) (80 mg, 0.39 mmol) and dimethyl acetylenedicarboxylate (77 mg, 0.54 mmol) in xylene (5 ml) in a 10 ml round-bottomed flask was flushed with nitrogen for 10 min. The flask was then sealed with a wired-on serum cap and heated at 140° for 68 h. The bright-yellow solution was evaporated (rotary evaporator connected to an oil pump) to give a mixture of oil and crystalline solid, 153 mg. T.l.c. indicated that starting **4** was only a minor component of this reaction mixture. Recrystallization readily gave the adduct **5** as very pale-yellow, elongated prisms, m.p. 203–206°, 52 mg; a second crop of 10 mg was obtained (total yield 62 mg, 46%). Examination by n.m.r. of the material remaining in the mother liquors showed them to contain virtually no adduct. (The biphenyl **7** was a major component.) Similar results were obtained when the reaction was scaled up by a factor of about 10. Recrystallization gave an analytical sample as rosettes of colorless, elongated prisms, m.p. 210–211.5°, darkening right after melting.

I.r.: 1731, 1316, 1125 cm^{-1}; n.m.r.: 7.1–7.5 (m, 5H); an ABX pattern (3H, δ_A 6.84, δ_B 6.64, δ_X 5.30, J_{AB} 7.6, J_{AX} 6.6, J_{BX} 1.6), an AB quartet (2H, δ_A 3.40, δ_B 3.01, J 11.0 Hz), 3.34 (3H), 3.30 p.p.m. (3H).

Anal. Calcd. for $C_{17}H_{16}O_6S$: C, 58.60; H, 4.63; S, 9.20. Found: C, 58.83; H, 4.68; S, 9.06.

Thermolysis of 5

(a) In the Absence of Added Reagents

The adduct **5** (50 mg) was sealed under nitrogen in a 10 × 150 mm Pyrex tube, and the tube was immersed in an oil bath at 220° for 7 min; the compound melted, went brown, and effervesced. The tube was cooled under tapwater and opened; it was noted that the colorless gas in the tube smelled like sulfur dioxide and was acidic to moist p*H* test paper. The thermolyzate was an orange-brown gum, 48 mg, readily soluble in $CDCl_3$, the n.m.r. spectrum of which solution showed it to be essentially the biphenyl diester **7**; there was some absorption at δ 3.0–3.4. T.l.c. showed, besides the biphenyl **7**, a spot corresponding to less mobile material which was not further studied.

A dichloromethane solution of the thermolyzate was passed through a 5 × 15 mm column of neutral alumina (Woelm, activity I) and evaporated to give **7** as a clear, light-brown oil, 37 mg (95% yield), estimated by n.m.r. to be 95–99% pure. Two recrystallizations gave colorless rosettes, m.p. 95–95.5°; with authentic **7** (12) of m.p. 95–96°, the mixed m.p. was 95–96°. The two materials were indistinguishable by t.l.c., and their i.r. spectra were identical.

The yield of sulfur dioxide was found by thermolyzing the adduct **5** (50 mg) in a 12 × 100 mm Pyrex tube connected to a 45 × 110 mm gas cell, the apparatus having been previously evacuated and closed off. The thermolysis tube was almost completely immersed in an oil bath at 220° for 7 min; a little of the **5** appeared to distil rather than decompose. I.r. examination of the material in the gas cell showed it to be virtually only sulfur dioxide. The yield of sulfur dioxide and the upper limit to possible ethylene formation were found by comparing the i.r. spectrum of the gaseous thermolysis products with a series of spectra of known amounts of sulfur dioxide and of ethylene. These standard spectra were obtained by injecting through a serum cap from a syringe known volumes of the gases (at atmospheric pressure and room temperature) into the evacuated thermolysis tube – i.r. cell apparatus. The yield of sulfur dioxide was 82 ± 10%, and the yield of ethylene (of which there was no definite indication) was < 5%. The spectrum showed only very weak bands which might be ascribed to C—H or C=O groups. Sulfur dioxide was also identified by thermolyzing the adduct under a slow stream of nitrogen and sweeping the gaseous products into a trap cooled in Dry Ice. Dichloromethane was added and the u.v. spectrum of the solution was taken: there was no indication of anything besides sulfur dioxide (λ_{max} (CH_2Cl_2) 287 mμ).

Preparative t.l.c. of the thermolyzate residue (brownish solid) led to the recovery of 8% starting adduct **5** and the isolation of 81% of the biphenyl **7** (the yields of sulfur dioxide and the biphenyl were calculated taking into account the recovered adduct).

(b) Attempt to Detect a Carbenoid Species in the Thermolysis of 5

The adduct **5** (50 mg) and cyclooctene (1.0 ml) were heated under nitrogen in a sealed tube for *ca.* 10 min at 220°. The reaction mixture was filtered and the filtrate was distilled in an evacuated L-shaped tube (one arm heated in a waterbath, the other cooled in Dry Ice). The distillate was checked by v.p.c. (10% SE-30 on Chromosorp W, 6 ft × 1/4 in. copper column, 92°, helium flow *ca.* 60 ml/min); only a peak corresponding to cyclooctene was seen. By injecting known mixtures of cyclooctene and bicyclo[6.1.0]nonane it was shown that a 5% yield of bicyclo[6.1.0]nonane would have been detectable.

(c) Attempt to Detect Formaldehyde from the Thermolysis of 5

In one arm of an L-shaped tube was placed a solution of dimedone (20 mg) in about 0.5 ml of methanol, and a micro stirring bar. In the other arm was placed the adduct **5** (25 mg). The tube was sealed and the arm holding the adduct was heated at 220° for 7 min while the dimedone solution was stirred and cooled in ice. The whole length of the apparatus above the solution was then warmed with a flame to drive any formaldehyde (which might have condensed as paraformaldehyde) into the dimedone solution. The solution was then checked by t.l.c.: there was no trace of the dimedone adduct. A control experiment treating paraformaldehyde in the same way as the adduct **5** indicated that a 10% yield of formaldehyde would have been readily detectable.

Thermolysis of 5 in the Presence of Enamine 6

The adduct **5** (100 mg, 0.29 mmol) and the enamine (1.0 ml; 6.0 mmol) from cyclohexanone and morpholine (**6**) (24) were sealed under nitrogen in a 10 × 140 mm Pyrex tube holding a micro stirring bar. The mixture was stirred and heated at 200° for 25 min. The clear solution was evaporated and thoroughly evacuated to give an oil, 157 mg. The oil was dissolved in 10 ml of dichloromethane, extracted with 3 × 5 ml of 1 *N* HCl, and the HCl was then basified (*ca.* 25 ml of 10% NaOH) and extracted with 3 × 5 ml of dichloromethane, evaporation of which gave the sulfene–enamine adduct **8**, 32.6 mg (47%); this was estimated by n.m.r. to be *ca.* 80% pure, making the yield of adduct about 38%. A control experiment showed that this procedure for isolating the sulfene-enamine adduct led to its recovery in 97% yield. The crude **8** was recrystallized twice to give colorless prisms, m.p. 136–138°; with authentic **8** (11) of m.p. 138–140°, the mixed m.p. was 136–138°. The two materials were indistinguishable on t.l.c. (CH_2Cl_2–MeOH, 100:2 and 100:3, v/v) and showed identical i.r. spectra.

The acid-insoluble materials were obtained by evaporating the dichloromethane solution from which **8** had been removed as described. Preparative t.l.c. gave the biphenyl **7**, 62 mg (80%), identified by direct comparison with authentic material (mixed m.p., t.l.c., and i.r. spectra). In addition, a more polar material (19 mg), showing ν_{max} (CH_2Cl_2) 1729, 1315, 1128 cm^{-1}, was isolated but not further investigated.

Thermolysis of 5 in p-Toluidine

The adduct **5** (50 mg) and *p*-toluidine (200 mg) were sealed under nitrogen in a 10 × 150 mm Pyrex tube. The tube was briefly warmed on the steambath and agitated to produce a solution which was then allowed to cool and set to a solid mass. The reaction mixture was immersed for 1.5 min in an oil bath at 325°, then quickly cooled under the tap. The contents of the tube were dissolved in 10 ml of CH_2Cl_2, washed with 10 ml of 1 *N* HCl and then 4 × 10 ml of water and evaporated to give a yellow oil, 53 mg. This was dissolved in 10 ml of CH_2Cl_2 and extracted with 4 × 5 ml of 5% NaOH. The NaOH extracts were acidified (*ca.* 2 ml of concentrated HCl), extracted with 4 × 5 ml of CH_2Cl_2, and the CH_2Cl_2 was evaporated to give the sulfonamide **10** as a colorless solid, 12.5 mg (52%, taking into account recovered **5**). A control experiment showed that this procedure led to virtually quantitative recovery of the sulfonamide. Two recrystallizations gave colorless platelets, m.p. 100–101°; with authentic sulfonamide **10** (25) of m.p. 101–102.5°, the mixed m.p. was 101–102°. The two materials were indistinguishable on t.l.c. (CH_2Cl_2–MeOH, 100:2, v/v; both silica gel and neutral alumina), and their i.r. spectra were identical.

Evaporation of the CH_2Cl_2 solution from which the sulfonamide had been extracted gave the base-insoluble material as a yellow oil, 39.4 mg. Preparative t.l.c. (plate run three times) gave five bands. The two minor bands, 1.8 mg and 3.1 mg, were not investigated. The least mobile band (4.7 mg) was indistinguishable from starting adduct **5** on t.l.c. (analytical plate run four times). The next most mobile band (21.1 mg) was shown by n.m.r. to be *ca.* 90% pure biphenyl **7** (49% yield, if 90% pure). The most mobile band, 7.7 mg, was shown by n.m.r. to be *ca.* 95% pure biphenyl imide derivative **9** (17% yield, if 95% pure). The combined yield of biphenyl products was thus 66%.

That the material designated as the biphenyl **7** was in fact this compound was rigorously shown in another experiment in which the analogous band gave, after further purification (again subjected to preparative t.l.c., treated with decolorizing charcoal, and run through a 5 × 10 mm column of Woelm activity I neutral alumina with CH_2Cl_2, then recrystallized twice), colorless rosettes, m.p. 95–96°; with authentic biphenyl diester of m.p. 95–96°, the mixed m.p. was 95–96°. The two materials were indistinguishable on t.l.c., and their i.r. spectra were identical.

The material designated as the imide **9** was assigned this structure by comparison with authentic imide (*vide infra*) of the analogous band in another experiment: two recrystallizations (ethyl acetate – hexane) gave colorless needles, m.p. 175–176.5°; with authentic imide of m.p. 175–176°, the mixed m.p. was 175.5–176.5°. The two materials were indistinguishable on t.l.c., and their i.r. spectra were identical.

Thermolysis of the adduct **5** with *p*-toluidine at lower temperatures (200°/15 min) gave somewhat lower yields of sulfonamide (39%) and higher yields of the imide **9** (30%); the yield of biphenyl diester was about the same (45%).

Preparation of Dimethyl Biphenyl-2,3-dicarboxylate (7): a Simple Method for Esterification of 3-Nitrophthalic Acid

The synthesis of the biphenyl diester **7** by reaction of benzene with diazotized dimethyl 3-aminophthalate was carried out essentially as described by Heilbron and coworkers (12). One step in this synthesis, namely the formation of dimethyl 3-nitrophthalic acid, was modified as follows.

In a 100 ml round-bottomed flask was placed sodium hydride (57% dispersion in mineral oil, 406 mg, 9.7 mmol). The flask was flushed with nitrogen, fitted with a stirring bar and a serum cap, and the sodium hydride dispersion was washed twice with pentane by stirring briefly, letting the NaH settle, and removing the supernatant pentane (syringe technique). Dimethylformamide (DMF, 50 ml) was then added, and a solution of 3-nitrophthalic acid (1.0 g, 4.17 mmol) in DMF (4.0 ml) was added fairly quickly (brisk effervescence, the H_2 was allowed to escape through a syringe needle); the syringe was rinsed with 2×2 ml of DMF. After stirring for 20 min at 25°, methyl iodide (2.0 ml, 4.55 g, 32 mmol) was added to the suspension over 30 s, and stirring was continued for 23 h. The light-yellow suspension was poured into 300 ml of water, extracted with 3×50 ml of CH_2Cl_2, and the CH_2Cl_2 extracts were washed with 4×150 ml of water and evaporated to give an oil which on evacuation overnight crystallized to a light-yellow solid, m.p. 66–68° (lit. (12) 67–68°), 0.92 g (81%); one spot on t.l.c. Recrystallization (CH_2Cl_2 : CCl_4 : hexane) gave colorless prisms, m.p. 69–70°. The structure was confirmed by the infrared (ν_{max} (CH_2Cl_2) *no* OH, 1737, 1538, 1350, 1280 cm^{-1}) and n.m.r. (δ 8.32, d, $J = 8.0$ Hz, 2H; 7.67, t, $J = 8.0$ Hz, 1H; 4.03, s, 3H; 3.97, s, 3H) spectra.

Attempts at esterification of 3-nitrophthalic acid using acidic catalysts (HCl, concentrated H_2SO_4, or BF_3-etherate (26)) gave the monoester alone or a mixture of the mono- and diesters.

Preparation of Authentic Biphenyl Imide 9

The biphenyl diester **7** (51 mg) and *p*-toluidine (298 mg) were heated at 200° for 20 min under nitrogen in a sealed 10×150 mm Pyrex tube. The reaction mixture was dissolved in 10 ml of CH_2Cl_2, washed with 10 ml of 1 *N* HCl, then with 4×10 ml of water, and evaporated to give a pale-yellow oil, 50 mg. The n.m.r. spectrum showed this material to consist of diester : imide in the molar ratio 4.2 : 1.0. This reaction mixture was treated with *p*-toluidine (429 mg) and methanesulfonic acid (2.2 mg) at 200° for 20 min, as before. Workup gave a light-yellow oil, 47 mg, the n.m.r. spectrum of which showed it to consist of diester **7** and imide **9** in the molar ratio 1.3 : 1.0. Preparative t.l.c. led to the isolation of the biphenyl diester **7** (24 mg) and the imide **9** (white solid, m.p. 172–173°, 21 mg, 68% on the basis of reacted diester). The assigned structure **9** is supported by spectra and microanalysis. ν_{max} (CH_2Cl_2) 1778 w, 1721, 1515 m, 1381 cm^{-1}; this compares well with the i.r. spectrum of *N*-methyl phthalimide (prepared from phthalimide, sodium hydride, and methyl iodide in DMF), ν_{max} (CH_2Cl_2) 1773 w–m, 1713 cm^{-1}. The n.m.r. spectrum showed δ ($CDCl_3$) 8.1–7.2 (m, 12H), 2.38 (s, 3H). Recrystallization (ethyl acetate – hexane) gave colorless needles, m.p. 175–176°.

Anal. Calcd. for $C_{21}H_{15}NO_2$: C, 80.49; H, 4.82; N, 4.47. Found: C, 80.42; H, 4.72; N, 4.60.

We thank the National Research Council of Canada for financial assistance and Dr. R. A. Marty for carrying out the flash thermolysis experiments.

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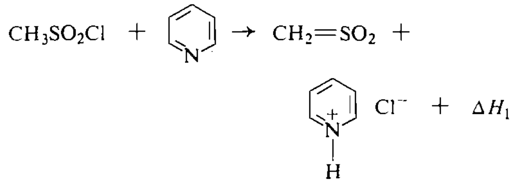
Appendix

Estimate of the "π-Bond Energy" of Sulfene

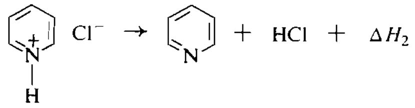
Our estimate of the "π-bond energy" of sulfene, $E_\pi(C{=}SO_2)$ (defined as $E(C{=}SO_2) - E(C{-}SO_2)$) was obtained by averaging an upper and a lower limit for $E_\pi(C{=}SO_2)$, each obtained by a slightly roundabout argument as follows.

It is evident from eqs. 1 to 3 that $\Delta H_1 + \Delta H_2 = \Delta H_3$ and $\Delta H_3 = E(C{-}H) + E(SO_2{-}Cl) - E_\pi(C{=}SO_2) - E(HCl)$, and so $E_\pi(C{=}SO_2) = E(C{-}H) + E(SO_2{-}Cl) - E(HCl) - \Delta H_1 - \Delta H_2$.

[1]



[2]



[3] $CH_3SO_2Cl \rightarrow CH_2{=}SO_2 + HCl + \Delta H_3$

E(C—H) and E(HCl), respectively 98.7 and 103.1 kcal/mol, are readily available (6) but E(SO_2—Cl) is surprisingly uncertain; we use the value 58 ± 6 kcal/mol (17). An estimate of the heat of neutralization of pyridine with hydrogen chloride ($-\Delta H_2$) in acetonitrile of -19 kcal/mol may be made from data on the reaction of pyridine and hydrogen bromide taken with a comparison of the values of ΔH for the reactions of hydrogen bromide and hydrogen chloride with 1,3-diphenylguanidine (18). The corresponding data are not available for the reaction in 1,2-dimethoxyethane, the solvent for which we make an estimate of ΔH_1, but it seems probable that the variation in heat of neutralization on changing from one not very polar solvent to another is less than the uncertainties in the other parameters employed here. (With tributylamine and 2,4-dinitrophenol, for example, the variation in ΔH has been found to be <3 kcal/mol over a range of solvents including dibutyl ether, benzene, and fluorobenzene (19).)

The value of ΔH_1 is not known but a rough limit of <4 kcal/mol may be set as follows: (*a*) One may estimate $\Delta H_1^{\ddagger} = 8.7$ kcal/mol from the rate constants for reaction 1 in dimethoxyethane at 20.0 and 40.0° (20), and obviously ΔH_1 must be $<\Delta H_1^{\ddagger}$. (*b*) The magnitude of $\Delta H_1^{\ddagger} - \Delta H_1$ is unknown but a lower limit may be found from the following: (i) The amount of reversal of [1] in D_2O must be very small since the amount of $CH_2DSO_3^-$ that is formed is $<0.5\%$ (and that can be formed by other mechanisms than reversal of [1]) (21). (ii) In the reaction of methanesulfonyl chloride, piperidine, and water (molar ratio 1:2:30) in dimethoxyethane, a 98% yield of the piperidine was obtained (22). In order to account for the selectivities of water trapping *vs.* reversal of [1] and piperidine *vs.* water trapping, the activation barrier to reversal must be at least 5 kcal/mol greater than that for piperidine. Even if the latter barrier were zero (which is unlikely), ΔH_1 must therefore be <4 kcal/mol. Inserting all of these values in the expression above we obtain $E_\pi(C{=}SO_2) > 31$ kcal/mol.

An *upper* limit to $E_\pi(C{=}SO_2)$ may be deduced from the observation (23) that of the two ways of removing HCl from β-chloroethanesulfonyl chloride, that which gives the carbon–carbon double bond predominates, probably by a large amount, but at least by enough to lead to a 72% isolated yield of ethenesulfonyl chloride under one set of conditions (23); at the very least $\Delta G_5^{\ddagger} - \Delta G_4^{\ddagger} > 0$ kcal/mol.

[4] $ClCH_2CH_2SO_2Cl + R_3N \rightarrow CH_2{=}CHSO_2Cl + R_3\overset{+}{N}H\ Cl^- + \Delta H_4$

[5] $ClCH_2CH_2SO_2Cl + R_3N \rightarrow Cl{-}CH_2{-}CH{=}SO_2 + R_3\overset{+}{N}H\ Cl^- + \Delta H_5$

The two reactions involve a common attack of base on an α-hydrogen, and the (developing) charge in the α-carbon at some point proceeds to displace one of the chlorine atoms, either the one on the sulfur or the one on the carbon. In view of the probable similarity of the energy profiles it seems highly likely that the difference $\Delta G_5^{\ddagger} - \Delta G_4^{\ddagger}$ is a reflection of the difference $\Delta H_5 - \Delta H_4$, and also that $\Delta G_5^{\ddagger} - \Delta G_4^{\ddagger}$ is smaller than $\Delta H_5 - \Delta H_4$ because the bonds that lead to the energy difference are not fully formed and would not show the energy difference in full at the transition state stage. Since $\Delta H_5 - \Delta H_4 = E_\pi(C{=}C) + E(SO_2{-}Cl) - E_\pi(C{=}SO_2) - E(C{-}Cl)$, and $E_\pi(C{=}C) = E(C{=}C) - E(C{-}C) = 63.2$ kcal/mol (6), $E(C{-}Cl) = 81$ kcal/mol (6), and $E(SO_2{-}Cl) = 58$ kcal/mol (16), $\Delta H_5 - \Delta H_4 > \Delta G_5^{\ddagger} - \Delta G_4^{\ddagger} > 0$, then $E_\pi(C{=}SO_2) < 40$ kcal/mol.

Taking a number between the upper and lower limits, we obtain $E_\pi(C{=}SO_2) = 35 \pm 5$ kcal/mol. This number depends on a highly uncertain value for $E(SO_2{-}Cl)$ and a change in the latter would similarly change $E_\pi(C{=}SO_2)$. The value is clearly only rough but we believe that until a better one is obtained it can be useful in constructing energy diagrams for the reactions of sulfenes, and for the approximate thermochemical estimates of the kind made in this paper.