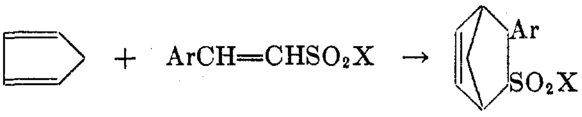
[Contribution from the Department of Chemistry, University of Michigan]

UNSATURATED SULFONIC ACIDS. II. REVERSIBILITY OF THE DIELS-ALDER REACTION WITH SULFONYL CHLORIDES AND SULFONAMIDES[1]

CHRISTIAN S. RONDESTVEDT, Jr. and JAMES C. WYGANT[2]

Received March 6, 1952

In the first paper of this series (1), it was shown that methyl 2-phenylethene-1-sulfonate (Ia) and methyl 2-*p*-nitrophenylethene-1-sulfonate (IIa) would form adducts with cyclopentadiene at 155°. The corresponding sodium salt (Ib), the sulfonyl chlorides (Ic, IIc), and the sulfonamides (Id, IIe) failed to produce isolable adducts and were largely recovered when heated with dienes at temperatures from 100–150°.



III

I; Ar = C_6H_5
a; X = OCH_3
c; X = Cl
e; X = $N(C_2H_5)_2$

II; Ar = p-$NO_2C_6H_4$
b; X = ONa
d; X = NH_2

A priori, it had been expected that the reactivities would fall in the orders II > I—since the nitro group would enhance the electrophilic character of the double bond — and $-SO_2Cl > -SO_2OR > -SO_2NR_2 > -SO_2ONa$ — since the electron-attracting powers of the group X are known to decrease in that sequence. Lambert and Rose (2) observed that methyl ethenesulfonate reacted with cyclopentadiene at 150° (by implication, not at lower temperatures); Snyder, Anderson, and Hallada (3) reported recently that ethenesulfonyl chloride formed adducts readily with several dienes at temperatures below 50°. From their results, it appeared that the predicted reactivities were actually correct, and that the previous failure to obtain adducts from the chlorides and amides might have been caused by an unfavorable equilibrium at the high temperatures used, not by lack of reactivity. The Diels-Alder reactions of ethenesulfonyl chloride were exothermic (3); hence the adduct would be favored at lower temperatures.

Adducts did form when Ic, IIc, and IIe were kept with cyclopentadiene for several days at 45° — in 63, 76, and 87% crude yields, respectively, based on unrecovered starting materials. No solid adduct could be isolated from Ia as the dienophile at 45°, but a 1% yield of bromosultone (compared to 9% at 155°)

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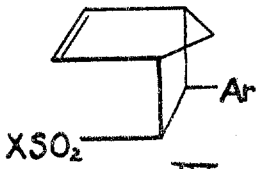
[1] A portion of this work was supported by a grant from the Faculty Research Fund of the University of Michigan.

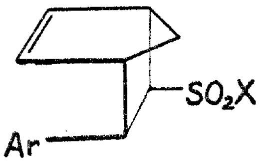
[2] Abbott Laboratories Fellow, 1950–1951.

after hydrolysis and bromination proved that a trace of adduct was formed (1). The nitro ester IIa refused to react at temperatures below 130° (1), but satisfactory yields were obtained at 155°. The structures (III) of the adducts are assigned on the basis of elementary analyses, saponification equivalents, and bromine titers.

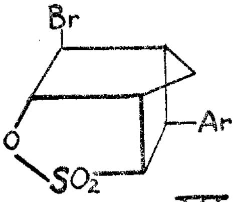
Since the starting sulfonyl compounds are *trans* (1), mixtures of stereoisomers IV and V were obtained. Separation of the mixtures by crystallization was laborious and only partially successful. Chromatography of the adduct from the ester IIa on alumina led to ester cleavage, with formation of aluminum salts, but the adduct from IIe could be separated on alumina into a crystalline solid and an oil. In the adducts from Ic and IIc, the fraction present as stereoisomer IV was estimated by conversion to the bromosultone VI. Configuration IV finds the sulfo group close to the double bond; in V, sultone formation is prevented by the methylene bridge. Hydrolysis of the sulfonamido group in the adduct from IIe without disruption of the molecule was impractical, so that sultonization was not feasible. Since with the other adducts of proved configuration, the *endo* form IV is higher-melting and less soluble than the *exo* form V, configuration IV is assigned to the solid adduct from IIe on the basis of this analogy.



IV



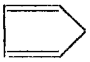
V



VI

The steric course of the Diels-Alder reaction is governed by the principle of "maximum accumulation of double bonds" (4, 5). A recent discussion (6) in more modern terminology emphasizes the preferential stabilization of one of the two possible transition states resulting from the overlapping of the electronic orbitals of the diene with the unsaturation electrons of the dienophile's "activating groups." An alternative picture invokes simple electrostatic interaction in the transition state between the "positive" diene and the "negative" substituents on the dienophile (7). In applying these ideas to the *trans* dienophiles under consideration, it is apparent that both transition states, leading to IV and V, will be benefited by these interactions. Both products would be expected; both are formed. Since IV predominates, it appears that the sulfonyl group interacts more effectively than aryl. The ability of a substituent to interact with the double bonds of the diene seems to be related to its electron-attracting power; hence, it would be expected that the percentage of adduct in configuration IV would decrease in the same order — $SO_2Cl > SO_2OR > SO_2NR_2$. Examination of Table I shows that the experimental results support this prediction. In comparing the effect of different aryl groups on the same basis, the more negative nitrophenyl group should produce a higher percentage of V than should unsubstituted phenyl; the reverse is seen to be true.[3]

TABLE I

ArCH=CHSO$_2$X +  $\xrightarrow{45°}$ IV + V

DIENOPHILE	YIELD[a], % IV + V	ADDUCT, % as IV	RECOVERY OF DIENOPHILE, %
Ia	1[b]; 9[b, c]	[b]	78
Ic	63	59	33
Id[d]	0	0	92[d]
IIa	68[c]	65[c]	0
IIc	76	74	0
IIe	87[e]	54	50

[a] Yields are based on unrecovered dienophile. [b] No solid adduct; figures are based on bromosultone VI. [c] Run at 155°; see ref. (1). [d] Reaction with butadiene at 150° for 9 hours. [e] Combined solid and oily fractions.

EXPERIMENTAL PART[4]

The dienophiles were prepared as previously described (1). Cyclopentadiene was distilled from iron filings (8) and collected in cold toluene.

2-p-Nitrophenyl-3,6-endomethano-1,2,3,6-tetrahydrobenzenesulfonyl chloride. A mixture of 4.0 g. of 2-*p*-nitrophenylethene-1-sulfonyl chloride (IIc) and 2.1 g. of cyclopentadiene in 200 ml. of toluene was maintained at 45° for 3½ days. The toluene and unreacted diene were largely removed at reduced pressure. The solution was diluted with petroleum ether and chilled. There was obtained 3.86 g. (76%) of crude adduct, m.p. 105–116°, which gave a saponification equivalent of 158 (calc'd 157). Bromine titration of the hydrolyzate gave a molecular weight of 322 (calc'd 324), and the solid bromosultone corresponded to 74% in configuration IV. After five recrystallizations from benzene-petroleum ether, the adduct melted at 116–121.5°, and it gave 85% of the bromosultone.

Anal. Calc'd for $C_{13}H_{12}ClNO_4S$: C, 49.76; H, 3.86.
Found: C, 50.05; H, 3.66.

The sultone and the benzylthiuronium salt from this adduct were identical with those obtained from the adduct of IIa and cyclopentadiene (1).

2-Phenyl-3,6-endomethano-1,2,3,6-tetrahydrobenzenesulfonyl chloride. A mixture of 3.0 g. of 2-phenylethene-1-sulfonyl chloride (Ic) and 1.95 g. of cyclopentadiene in 200 ml. of toluene was kept for 3½ days at 45°. Most of the toluene and excess cyclopentadiene were removed under reduced pressure, and the solution was diluted with petroleum ether. On chilling, 0.98 g. (33%) of the starting material was recovered. Complete removal of the solvent in an air jet left an oil which solidified. After pressing on porous plate, 1.70 g. of solid (63%)[5] remained, m.p. 48–60°. Recrystallization from petroleum ether gave 1.27 g. (48%),[5] m.p. 63–72°; saponification number 132 (calc'd 134) and bromine titer 334 (calc'd 338); and 59% of bromosultone was obtained. The analytical sample was prepared by two

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[3] It would be of interest to compare the steric course of the reaction of substituted *trans*-cinnamic acid derivatives with cyclopentadiene to these results. This investigation is now underway.

[4] Melting points are uncorrected. Microanalyses are by Clark Microanalytical Laboratories, Urbana, Illinois.

[5] Yield based on unrecovered starting material.

more recrystallizations, which raised the melting point to 62.5–72.5°; this material gave 73% of bromosultone. The sultone was identical with that prepared previously from the adduct of Ia and cyclopentadiene (1).

Anal. Calc'd for $C_{13}H_{13}ClO_2S$: C, 58.10; H, 4.87.
Found: C, 57.64; H, 4.65.

The *benzylthiuronium salt*, prepared in the usual way, was recrystallized from water-alcohol; m.p. 180–182°.

Anal. Calc'd for $C_{21}H_{24}N_2O_3S_2$: C, 60.55; H, 5.81.
Found: C, 60.71; H, 5.92.

2-p-Nitrophenyl-3,6-endomethano-1,2,3,6-tetrahydro-N,N-diethylbenzenesulfonamide. A mixture of 4.0 g. of N,N-diethyl-2-*p*-nitrophenylethene-1-sulfonamide (IIe) and 0.34 g. of cyclopentadiene was kept in 200 ml. of toluene for five days at 45°. The solution was concentrated under reduced pressure. On chilling, 1.65 g. of starting material was recovered. After further evaporation, a solid remained, which was shown to be a mixture of IIe plus adduct by the elementary analysis. Separation could not be effected by crystallization from petroleum ether. A sample of mixed stereoisomeric sulfonamides was prepared independently from the adduct of IIc by reaction with diethylamine; its solubility in common solvents was similar to that of IIe.

The impure adduct in benzene was chromatographed on alumina and eluted with benzene containing 2% acetone. The first fraction, on evaporation, left 1.18 g. (47%)[5] of adduct, m.p. 117–120°; mixture m.p. with IIe was strongly depressed. The material from the intermediate fractions was oily, 1.01 g. Continued development eluted an additional 0.33 g. of IIe; total recovery of starting material 1.98 g. (50%).

Further recrystallization of the adduct gave material melting at 118.3–120.0°.[6] It slowly decolorized bromine in acetic acid.

Anal. Calc'd for $C_{17}H_{22}N_2O_4S$: C, 58.26; H, 6.33.
Found: C, 58.65, 58.54; H, 5.93, 6.04.

An attempt to obtain solids from the intermediate oily fractions by rechromatographing on Magnesol-Celite failed.

Methyl 2-phenyl-3,6-endomethano-1,2,3,6-tetrahydrobenzenesulfonate. A mixture of 1.2 g. of methyl 2-phenylethene-1-sulfonate (Ia) and 0.8 g. of cyclopentadiene in 100 ml. of toluene was kept at 45° for three days. The solution was concentrated under reduced pressure. On chilling, 0.93 g. (78%) of Ia was recovered. No solid adduct could be isolated from the filtrate by evaporation and attempted crystallization. The residue was hydrolyzed and brominated, giving 20 mg. (1%) of bromosultone, identical with that previously prepared (1).

Acknowledgment. We are indebted to Mr. Charles VerNooy for the preparation of certain starting materials.

SUMMARY

2-Phenylethene-1-sulfonyl chloride, 2-*p*-nitrophenylethene-1-sulfonyl chloride, and N,N-diethyl-2-*p*-nitrophenylethene-1-sulfonamide form adducts with cyclopentadiene at 45°, but not at 100–155°. This result has been interpreted as a reversal of the equilibrium at the higher temperature.

The adducts are mixtures of stereoisomers. In one isomer, the sulfo group is located so close to the double bond that a bromosultone can be formed, and this reaction was used to estimate the amount of this isomer in the mixture. A correlation between the electron-attracting power of the substituent X in

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[6] The adduct turns yellow on standing, perhaps because of reactions induced by light or oxygen.

$ArCH{=}CHSO_2X$ and the relative amounts of the two stereoisomers has been noted.

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