[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

Derivatives of Sulfenic Acids. II. Characterization of Olefins with 2,4-Dinitrobenzenesulfenyl Chloride[1]

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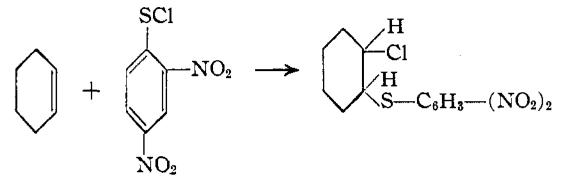
In the first paper of this series,[3] it was shown that 2,4-dinitrobenzenesulfenyl chloride adds to cyclohexene to yield 2-chlorocyclohexyl 2',4'-dinitrophenyl sulfide.



We have now found that this reaction can be considerably extended, and that 2,4-dinitrobenzenesulfenyl chloride may be recommended as a useful reagent for the characterization of olefins.

The results of our studies with a selected list of olefins are summarized in Table I. Formation of the 1:1 adduct, as shown above for cyclohexene, was generally observed. In a few cases, as with 1,1-diphenylethylene and with bicyclic olefins such as camphene, the reaction of addition was accompanied by elimination of hydrogen chloride. In these instances, the resulting products were equally suitable for purposes of characterization. With the *d* and *l*-limonenes, diadducts resulted if sufficient sulfenyl chloride was used. The adduct to anethole underwent solvolysis with particular ease. If the reaction of anethole with 2,4-dinitrobenzenesulfenyl chloride was carried out in benzene or in carbon tetrachloride, the expected chlorine-containing adduct (m. p. 133–134°) resulted. On attempted recrystallization of this from absolute ethanol or methanol, a corresponding ethoxy or methoxy derivative was obtained. If the reaction with anethole was effected in glacial acetic acid, or if the 1:1 adduct was treated with the acid, the acetoxy derivative was found.[4] The adducts with other olefins did not display this pronounced lability of the chlorine atom.

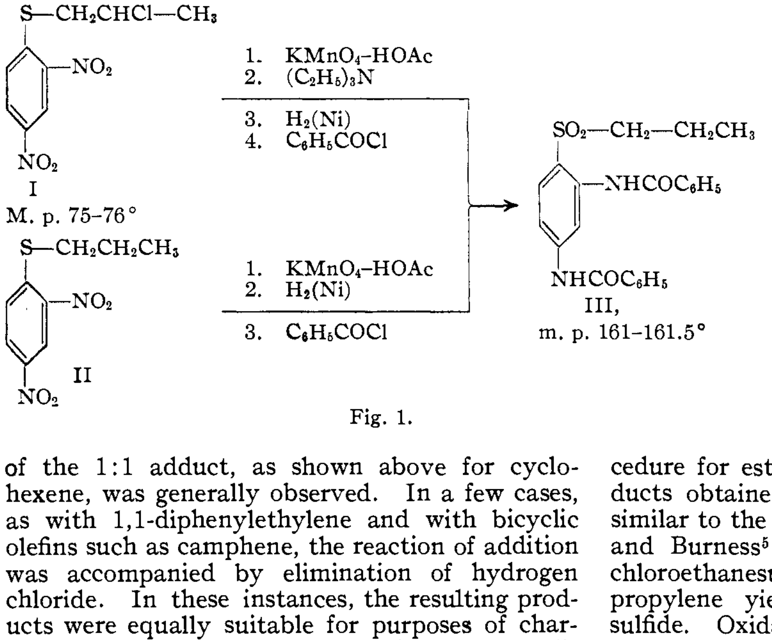


Fig. 1.

The reactions of the reagent with symmetrical olefins led to the isolation of single products only. This was also found to be the case with styrene. With olefins such as propylene and pentene-2, however, two distinct adducts were observed. Of the two adducts to propylene, the one isolated in higher yield (65%, m. p. 75–76°) is the isomer predicted by Markownikoff's rule, considering the polarity of the sulfenyl chloride to be RS^+Cl^-. The proof of structure for this product, 2-chloropropyl 2',4'-dinitrophenyl sulfide, was accomplished by the sequence of reactions shown in Fig. 1, whereby I and II were independently converted to III.

The structure of the non-Markownikoff adduct to propylene (isolated in 15% yield) was established in a similar manner. The adduct (I', 2,4-dinitrophenyl 1'-methyl-2'-chloroethyl sulfide, m. p. 108.5–109.5°) was converted to 2,4-dibenzamidophenyl isopropyl sulfone (III', m. p. 212–213°), and this sulfone was then synthesized independently from 2,4-dinitrophenyl isopropyl sulfide (II') by the same steps as shown in Fig. 1 for the *n*-propyl isomer. This procedure for establishing the structures of the adducts obtained with propylene in this study is similar to the method employed by Fuson, Price and Burness[5] to prove that the addition of 2-chloroethanesulfenyl chloride ($ClCH_2CH_2SCl$) to propylene yields 2-chloroethyl 2'-chloropropyl sulfide. Oxidation of the β-chloro sulfides (I, I')

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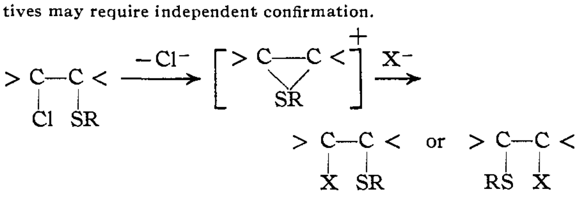
(1) Presented in part before the Organic Division of the American Chemical Society, New York, September, 1947.

(2) Abbott Laboratories Research Fellow, 1947–1948.

(3) N. Kharasch, H. L. Wehrmeister and H. Tigerman, THIS JOURNAL, **69**, 1612 (1947).

(4) In view of the possible occurrence of rearrangements in nucleophilic displacement reactions on β-chlorosulfides, in the manner shown below, the structures of the acetoxy, ethoxy, and methoxy derivatives may require independent confirmation.



(5) R. C. Fuson, C. C. Price and D. M. Burness, *J. Org. Chem.*, **11**, 475 (1946).

TABLE I

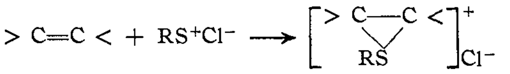
ADDUCTS OF 2,4-DINITROBENZENESULFENYL CHLORIDE WITH OLEFINS

Olefin	Product[a] (R = 2,4-dinitrophenyl)	M. p., °C.[b]	Analyses, % Carbon		Hydrogen	
			Calcd.	Found	Calcd.	Found
Ethylene	$RSCH_2CH_2Cl$	94–94.5[c]	36.58	36.62	2.69	2.73
Propylene	$RSCH_2CHClCH_3$ (65%)	75–76	39.06	39.42	3.28	3.38
	$RSCH(CH_3)CH_2Cl$ (15%)[d]	108.5–109.5	39.06	39.55	3.28	3.56
				39.42		3.65
Butene-1[e]	$C_{10}H_{11}ClN_2O_4S$	77.5–78.5	41.31	42.03	3.81	4.07
				41.95		4.42
Butene-2	$C_{10}H_{11}ClN_2O_4S$	128–129	41.31	41.51	3.81	3.96
Isobutylene	$C_{10}H_{11}ClN_2O_4S$[f]	86–87	41.31	41.36	3.81	3.65
Pentene-2	$C_{11}H_{13}ClN_2O_4S$[g]	116–118	43.35	43.77	4.30	4.39
Hexene-1	$C_{12}H_{15}ClN_2O_4S$[h]	61–62	45.21	45.53	4.74	5.07
2-Methylheptene-1	$C_{14}H_{19}ClN_2O_4S$[i]	47–48	48.48	48.52	5.52	5.65
Cyclohexene	$C_{12}H_{13}ClN_2O_4S$[j]	117–118	45.50	45.84	4.14	4.31
1-Methylcyclohexene	$C_{13}H_{15}ClN_2O_4S$	139–140	47.20	47.35	4.57	4.80
Styrene	$C_{14}H_{11}ClN_2O_4S$[k]	143–143.5	49.63	50.09	3.27	3.55
				50.29		3.33
1,1-Diphenylethylene	$(C_6H_5)_2C{=}CHSR$[l]	135.5–136.5	63.47	63.70	3.73	3.55
Acenaphthylene	$C_{18}H_{11}ClN_2O_4S$[m]	187–189 dec.	55.89	56.05	2.87	2.89
Anethole	$C_{18}H_{20}N_2O_4S$[n]	128–129	55.09	55.18	5.14	5.15
d or *l*-Limonene	$C_{22}H_{22}Cl_2N_4O_8S_2$[o]	195–196	43.64	43.93	3.66	3.86
Camphene	$C_{16}H_{18}N_2O_4S$[p]	121–122	57.47	57.57	5.42	5.24

[a] Unless otherwise specified the products were recrystallized from absolute alcohol, yielding excellent yellow or orange solids. [b] All melting points reported in this paper are uncorrected. [c] G. M. Bennett and E. M. Whincop, *J. Chem. Soc.*, **119**, 1864 (1921), report the melting point of 2,4-dinitrophenyl 2′-chloroethyl sulfide as 97°. Repeated crystallization of our product failed to raise its melting point above 94.5°. [d] Chlorine analysis. Calcd.: Cl, 12.82. Found: Cl, 12.59. [e] The adduct listed is the isomer less soluble in a mixture of absolute alcohol (80 vols.)-petroleum ether (20 vols.). The second carbon-hydrogen analysis reported was made on a separately prepared product. Chlorine analysis. Calcd.: Cl, 12.20. Found: Cl, 11.99. [f] Recrystallized from 95% ethyl alcohol. [g] Adduct listed is the isomer less soluble in absolute ethyl alcohol; obtained in 32% crude yield. The other isomer was isolated in 36% crude yield, and melted at 89–90° after purification. [h] The adduct listed is the isomer less soluble in 95% ethyl alcohol. [i] Recrystallized from equal volumes of ethyl alcohol-petroleum ether. [j] Previously reported in reference 3. [k] Sulfur analysis. Calcd.: S, 9.47. Found: S, 9.58. [l] Product is the vinyl sulfide; recrystallized from benzene. [m] Recrystallized from benzene. [n] The product listed is the ethoxy derivative obtained by recrystallization of the 1:1 adduct from absolute ethyl alcohol. *Cf.* experimental section for details. [o] The products are the diadducts, formed by using a 2:1 molar ratio of the reagent to the limonene. The analysis reported is for the *d*-limonene adduct. The sample of pure *d*-limonene was kindly supplied by Dr. Herman Pines. [p] Hydrogen chloride is eliminated. NOTE ADDED IN PROOF: Since the addition of the reagent to *cis* and *trans* olefin pairs appears to be stereo-specific (private communication from Dr. D. J. Cram) a complete investigation of the reactions with authentic samples of pure *cis* and *trans* olefins has been undertaken.

to the corresponding sulfones, prior to dehydrochlorination with triethylamine, assures that the proofs of structure are rigorous, since this precludes any possibility for rearrangement of the original sulfide to an isomeric structure *via* a cyclic sulfonium intermediate, as was shown to be possible by Fuson, Price and Burness.

The detailed proofs of structure for the adducts to other unsymmetrical olefins are not reported in the present study. It would appear reasonable to assume, in accord with the results of Fuson and co-workers[5] and with the conclusions of Turner and Connor,[6] that the structures of the major products from the reactions of 2,4-dinitrobenzenesulfenyl chloride with unsymmetrical olefins such as butene-1 and hexene-1 may be predicted by Markownikoff's rule, and that this rule may also be used to anticipate the structures of the single products obtained with olefins such as styrene. Subject to our further studies of the mechanism of these additions, we conceive of the reactions as proceeding *via* a resonating cyclic sulfonium ion intermediate.



This formulation is convenient for representing all of the observations described in this paper. The sulfonium ion may (1) add the chloride ion to yield the β-chloro sulfide, (2) eliminate a proton to form the vinyl sulfide, or (3) react with the solvent, for example acetic acid, to form the β-acetoxy sulfide.

Studies concerning the effects of peroxides on the reactions of sulfenyl chlorides, sulfenyl bromides, and sulfenyl thiocyanates with olefins are now in progress in this Laboratory. The direction of addition of 2,4-dinitrobenzenesulfenyl chloride to styrene was not affected by catalytic amounts of benzoyl peroxide or acetyl peroxide in glacial acetic acid, benzene, or carbon tetrachloride. Neither was the ratio of the two adducts to

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(6) R. A. Turner and R. Connor, THIS JOURNAL, **69**, 1009 (1947), concluded that the structure of the adduct of 2-nitro-4-chlorobenzenesulfenyl chloride to isobutylene corresponds to the isomer predicted by Markownikoff's rule, namely, 2-chloro-2-methylpropyl 2′-nitro-4′-chlorophenyl sulfide.

propylene noticeably affected by the presence of benzoyl peroxide in glacial acetic acid. With propylene, in carbon tetrachloride solution at room temperature, addition of the reagent was incomplete in a period of two weeks, both in the presence or absence of benzoyl peroxide. In the case of 2,4-dinitrobenzenesulfenyl chloride, it was established that the peroxide oxidizes the sulfenyl chloride to 2,4-dinitrobenzenesulfonyl chloride, and it appears that this oxidation reaction predominates over any tendency which may exist for non-Markownikoff addition via a peroxide-catalyzed mechanism.

Since molecular weights for sulfenyl halides have not been previously reported, it was considered desirable to determine the molecular weight of 2,4-dinitrobenzenesulfenyl chloride. As expected it was found to be a monomer in benzene solution.

Experimental

2,4-Dinitrobenzenesulfenyl chloride, m. p. 95–96°, was prepared by chlorinolysis of 2,4-dinitrophenyl disulfide[3] in yields of 60–70%. *sym*-Tetrachloroethane was found to be an equally good solvent for the preparation as ethylene bromide. The molecular weight of the sulfenyl chloride was determined by the cryoscopic method in benzene. Calcd. for $C_6H_3ClN_2O_4S$: mol. wt., 234.6. Found: mol. wt., 234.

Addition of 2,4-Dinitrobenzenesulfenyl Chloride to Olefins.—The reactions for characterization of olefins with 2,4-dinitrobenzenesulfenyl chloride can be readily effected. Glacial acetic acid was found to be the best general medium for this purpose. It is a good mutual solvent for the reactants, does not itself react with the reagent, and it promotes a marked increase in the rates of addition in comparison with the rates in inert solvents. Since the products are obtained in high yields, and are generally easy to purify by recrystallization, only small quantities of reagents need be employed. A useful test to ascertain whether the addition of the reagent has gone to completion is to add a few drops of the reaction solution to aqueous potassium iodide. The presence of unreacted reagent is immediately revealed by liberation of iodine: $2RSCl + 2I^- \rightarrow RSSR + I_2 + 2Cl^-$. Directions for a suitable general procedure for the characterization of olefins are given at the end of this section.

The keeping qualities of the reagent are satisfactory. 2,4-Dinitrobenzenesulfenyl chloride, prepared by the chlorinolysis of the disulfide,[3] when used for several months without special storage precautions showed only slight decomposition. The traces of decomposition products are insoluble in hot carbon tetrachloride and may be removed by one recrystallization from this solvent. The efficiency of the reagent is, however, not noticeably affected by their presence.

2,4-Dinitrobenzenesulfenyl chloride shows good selectivity in characterizing closely related olefins. This is nicely shown in the considerably different values for the melting points of the adducts obtained from the isomeric butylenes, and the generally good spread of melting points recorded in Table I. The reagent fails, however, to add to olefins which are highly substituted with negative groups. Thus, addition was not effected with stilbene, tetrachloroethylene, acrylonitrile, or sorbic acid. It is of interest to note, however, that the reagent adds with ease to 1,2-diphenylpropene.

The products in Table I were obtained by procedures corresponding to those illustrated below. The gaseous olefins used were the C. P. reagents supplied by the Matheson Company.

Ethylene.—One gram of 2,4-dinitrobenzenesulfenyl chloride in 25 ml. of glacial acetic acid was shaken at room temperature, for sixteen hours, under 20 lb./sq. in. pressure of ethylene. The crude adduct was precipitated by pouring the reaction mixture into 200 ml. of water. Recrystallization from a hot mixture of absolute ethyl alcohol and acetone gave a 64% yield of 2-chloroethyl 2,4-dinitrophenyl sulfide, m. p. 94–94.5°.

Propylene.—Propylene was bubbled through a solution of 10.00 g. of the chloride in 200 ml. of glacial acetic acid for twenty minutes. The resulting solution was allowed to stand sixteen hours. Absence of unreacted reagent was indicated by non-liberation of iodine on testing a sample of the solution with 5% aqueous potassium iodide. The solution was poured into one liter of water. The solid which precipitated was dissolved in a minimum of hot absolute alcohol. On cooling, 9.5 g. of yellow solid, melting at 72–79°, was collected. This was washed, with gentle suction, with 100 ml. of absolute alcohol at 60°. The undissolved residue was recrystallized from absolute alcohol, yielding 1.89 g. (15%) of yellow crystals, m. p. 108.5–109.5°. The filtrate from the above separation was concentrated to about 50 ml. volume, and refrigerated. There was thus obtained 7.67 g. of product melting at 72–75°; yield 65%. Recrystallization from ethyl alcohol raised the melting range to 75–76°.

Other Gaseous Olefins.—The adducts to isobutylene and butene-2 were obtained by similar procedures as described for propylene. In both of these cases, only one product was isolated. In the case of butene-1, a second isomer was probably formed, but was not isolated in spite of a definite attempt to do so.

Anethole.—The adduct of 2,4-dinitrobenzenesulfenyl chloride to anethole represented a rather special case, in that the chlorine atom in the adduct was particularly subject to solvolysis. The 1:1 adduct (A) was obtained by reaction of anethole with the sulfenyl chloride in inert solvents such as benzene or carbon tetrachloride, m. p. 133–134°.[7]

Anal. Calcd. for $C_{16}H_{15}ClN_2O_5S$: Cl, 9.26. Found: Cl, 9.59.

When anethole reacted with 2,4-dinitrobenzenesulfenyl chloride in glacial acetic acid, there was obtained the acetoxy derivative of (A), m. p. 160–161°. This identical compound was also obtained by recrystallizing the 1:1 adduct (A) from glacial acetic acid. This product did not contain chlorine.

Anal. Calcd. for $C_{18}H_{18}N_2O_7S$: C, 53.19; H, 4.46; S, 7.89. Found: C, 53.57; H, 4.97; S, 7.55.

If the 1:1 adduct (A) was recrystallized from absolute alcohol, the ethoxy group displaced the chlorine, yielding an excellent product melting at 128–129°.

Anal. Calcd. for $C_{18}H_{20}N_2O_6S$: C, 55.09; H, 5.14. Found: C, 55.18; H, 5.15.

A methoxy derivative was obtained by recrystallization of adduct A from methanol; m. p. 127–128°; mixed melting point with the ethoxy derivative 111–116° (*cf.* also footnote 4).

***d*- and *l*-Limonene.**—Reaction of *d*-limonene with 2,4-dinitrobenzenesulfenyl chloride in glacial acetic acid at room temperature (molar ratio 1:2) yielded a diadduct, m. p. 195–196°. An identical procedure with *l*-limonene gave a similar product, also melting at 195–196°. The mixed melting point of these two products showed a distinct depression. Dipentene gave a product which melted over a considerable range, which was observed to vary depending on the exact conditions of crystallization.

Other Olefins.—The additions of 2,4-dinitrobenzenesulfenyl chloride to other liquid or solid olefins listed in Table I were effected by using one gram of the chloride in glacial acetic acid at room temperatures and employing a 10 to 100% molar excess of the olefin in each case. Completion of reaction was generally tested for by means of aqueous potassium iodide solution. The crude product was usually obtained by pouring the reaction mixture into 150–200 ml. of water. Recrystallization was generally effected from

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[7] This product is most likely 1-*p*-methoxyphenyl-1-chloro-2-(2′,4′-dinitrophenylthio)propane.

absolute ethyl alcohol. The yields of products obtained were very satisfactory. Addition of the reagent to stilbene, acrylonitrile, tetrachloroethylene and sorbic acid could not be effected under a variety of conditions. With 1,2-diphenylpropene, however, the 1:1 adduct, m. p. 153–155°, was readily obtained.

Anal. Calcd. for $C_{21}H_{17}ClN_2O_4S$: Cl, 8.27. Found: Cl, 8.56.

General Procedure for the Characterization of Olefins.—The following procedure was found to be a generally satisfactory one for the rapid characterization of small quantities of liquid and solid olefins. A solution of 0.2 g. of 2,4-dinitrobenzenesulfenyl chloride and 0.2–0.3 g. of the olefin in 5 ml. of glacial acetic acid is heated on a steam-bath for fifteen minutes (or until the potassium iodide test shows that the reaction is complete). The reaction mixture is refrigerated. If the product precipitates, it may be collected by filtration. If an inadequate amount or no product at all is obtained in this manner, the reaction solution or filtrate is poured onto 5–10 g. of crushed ice. The resulting solid or oil is crystallized from ethyl alcohol, or sometimes from another solvent as shown in Table I.

2,4-Dibenzamidophenyl *n*-Propyl Sulfone

The preparation of this sulfone (III, Fig. 1) was effected by two alternate procedures, thus proving that the adduct of 2,4-dinitrobenzenesulfenyl chloride which melts at 75–76° (I, Fig. 1) is the isomer to be expected by Markownikoff's rule.

2,4-Dinitrophenyl *n*-propyl sulfide was prepared from *n*-propyl bromide and 2,4-dinitrothiophenol; m. p. 81–82°. It was observed that the yield was improved and a better crystalline product resulted if the reaction mixture was allowed to stand at room temperature for two days, instead of being heated as directed in the literature.[8]

2,4-Dinitrophenyl *n*-propyl sulfone was obtained from the above sulfide by oxidation with potassium permanganate by the method of Bost, Turner and Norton,[9] yielding a product which melted at 126–127° after recrystallization from ethyl alcohol. The value recorded in reference 9 is 127.5°.

A solution of 0.50 g. of 2,4-dinitrophenyl *n*-propyl sulfone in 30 ml. of benzene was shaken for three hours in the Parr–Burgess hydrogenator under 20 lb./sq. in. hydrogen pressure, in the presence of approximately 0.2 g. of Raney nickel catalyst. The catalyst and water formed in the reaction were removed, a fresh sample of catalyst was added, the bottle recharged with hydrogen, and the shaking was continued for an additional hour. After removal of the catalyst, 1.0 ml. of benzoyl chloride was added to the filtrate, and the resulting solution was refluxed for fifteen minutes. This was then concentrated to approximately 10 ml., and 35 ml. of absolute ethyl alcohol was added. On standing overnight, 0.45 g. (58% of theoretical yield) of well-formed, but slightly colored crystals was collected. After charcoaling and recrystallizing from ethyl alcohol, a 39% yield of 2,4-dibenzamidophenyl *n*-propyl sulfone, melting at 161–161.5° was obtained.

Anal. Calcd. for $C_{23}H_{22}N_2O_4S$: C, 65.38; H, 5.25; S, 7.59. Found: C, 65.42; H, 5.26; S, 7.40.

The alternate preparation of 2,4-dibenzamidophenyl *n*-propyl sulfone, starting from the adduct of 2,4-dinitrobenzenesulfenyl chloride to propylene, melting at 75–76° (*cf.* Fig. 1), was achieved as follows.

1. **Oxidation to the Sulfone.**—Three grams of the adduct (I, Fig. 1) was dissolved in 50 ml. of glacial acetic acid and to this there was added slowly a solution of 3.0 g. of potassium permanganate in 500 ml. of water. Sufficient glacial acetic acid was added as required to prevent the sulfide from precipitating from the solution. The mixture was diluted and cooled, by addition of crushed ice, whereupon some of the sulfone precipitated and was separated by filtration. A considerable quantity of residual product in the aqueous filtrate was extracted with benzene. A troublesome emulsion was encountered during this extraction process, but it was found to separate on standing overnight. The benzene extracts were washed with water, and the solvent was evaporated in an air-stream. The crude product was recrystallized from ethyl alcohol, yielding 49% of 2-chloropropyl 2′,4′-dinitrophenyl sulfone, m. p. 94–94.5°. The analyses indicate that the product may contain a small amount of 2,4-dinitrophenyl 1-propenyl sulfone.

Anal. Calcd. for $C_9H_9ClN_2O_6S$: C, 35.01; H, 2.94. Found: C, 35.62, 35.62; H, 3.15, 3.23. The second analysis was made on a newly prepared sample, which gave the following chlorine analysis. Calcd.: Cl, 11.49. Found: Cl, 11.22.

2. **Dehydrochlorination.**—2,4-Dinitrophenyl 1-propenyl sulfone was prepared by removal of hydrogen chloride from 2-chloropropyl 2′,4′-dinitrophenyl sulfone. A solution of 0.39 g. of the latter in 20 ml. of benzene was treated with 1.0 ml. of triethylamine, whereupon triethylammonium chloride separated immediately. The mixture was allowed to stand overnight, and the precipitate then collected, dried, and found to weigh 0.16 g. The benzene filtrate was washed with water, with dilute hydrochloric acid, and twice again with water. It was then dried over anhydrous calcium chloride and, after concentrating to about 5 ml., diluted with 15 ml. of carbon tetrachloride. This solution was treated with activated charcoal, filtered, and allowed to stand overnight. There was thus obtained 0.14 g. of a product which melted at 126–127°. Concentration of the mother liquor led to the isolation of an additional 0.07 g. of the product. The crude yields were combined and recrystallized from *n*-heptane, yielding 0.19 g. of 2,4-dinitrophenyl 1-propenyl sulfone, m. p. 133–134°; yield, 55%.

Anal. Calcd. for $C_9H_8N_2O_6S$: C, 39.71; H, 2.96. Found: C, 40.04; H, 3.11.

3. **Reduction and Benzoylation.**—2,4-Dibenzamidophenyl *n*-propyl sulfone was obtained from 2,4-dinitrophenyl 1-propenyl sulfone by hydrogenation and subsequent benzoylation. 2,4-Dinitrophenyl 1-propenyl sulfone (0.13 g.) was dissolved in 25 ml. of benzene and shaken for three hours in the presence of approximately 0.2 g. of Raney nickel catalyst, under a pressure of 35 lb./sq. in. of hydrogen. The treatment was then repeated with a fresh sample of catalyst for one hour. After the catalyst was removed 0.50 g. of benzoyl chloride was added and the resulting solution was refluxed for thirty minutes. The solution was shaken successively with aqueous potassium carbonate, water, dilute hydrochloric acid, and twice again with water. The solution was concentrated to 5 ml. and about 5 ml. of *n*-heptane was added. After standing overnight there was collected 0.09 g. of crystals melting at 158–159°. Recrystallization of this product from ethyl alcohol raised the melting range to 161–161.5°. A mixed melting point determination with product III showed no depression.

Preparation of 2,4-Dibenzamidophenyl Isopropyl Sulfone

This sulfone was synthesized, starting from the adduct of 2,4-dinitrobenzenesulfenyl chloride to propylene which melted at 108.5–109.5°; and also from 2,4-dinitrophenyl isopropyl sulfide. The syntheses were carried out by the same procedures as described above for the *n*-propyl isomer. The identity of the product obtained *via* both routes proves that the structure of the higher-melting adduct to propylene corresponds to 2,4-dinitrophenyl 1′-methyl-2′-chloroethyl sulfide, the non-Markownikoff adduct.

2,4-Dinitrophenyl isopropyl sulfide was obtained from potassium 2,4-dinitrothiophenoxide and isopropyl bromide; m. p. 93–94°; yield, 48%. Oxidation with potassium permanganate yielded 2,4-dinitrophenyl isopropyl sulfone; m. p. 138–139°; yield, 65%.[9] Hydrogenation, as above, and benzoylation, followed by similar working up of the product, led to 2,4-dibenzamidophenyl isopropyl sulfone, m. p. 212–213°.

Anal. Calcd. for $C_{23}H_{23}N_2O_4S$: C, 65.38; H, 5.25. Found: C, 65.61; H, 5.19.

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[8] C. Willgerodt, *Ber.*, **18**, 328–331 (1885).

[9] R. W. Bost, J. C. Turner and R. D. Norton, This Journal, **54**, 1985 (1932).

The identical product was also obtained as follows. The adduct to propylene formed in the lower yield, 0.75 g., m. p. 108–108.5° was oxidized to 0.45 g. (55% yield) of 2,4-dinitrophenyl 1′-methyl-2′-chloroethyl sulfone, m. p. 97–97.5°.

Anal. Calcd. for $C_9H_9N_2O_6SCl$: C, 35.01; H, 2.94. Found: C, 35.02; H, 3.00.

The latter product, 0.354 g., was dehydrochlorinated with triethylamine (dried by distillation from potassium hydroxide), yielding 0.22 g. (71%) of 2,4-dinitrophenyl isopropenyl sulfone, m. p. 129–129.5° (recrystallized from carbon tetrachloride).

Anal. Calcd. for $C_9H_8N_2O_6S$: C, 39.71; H, 2.96. Found: C, 40.10; H, 3.01.

The 2,4-dinitrophenyl *iso*propenyl sulfone (0.120 g.) was hydrogenated, then benzoylated, yielding 0.158 g. (85%) of a slightly colored product which melted at 204–206°. Repeated treatment with activated charcoal in ethyl alcohol resulted in colorless crystals. These melted at 212–213°, and showed no depression in a mixed melting point determination with the 2,4-dibenzamidophenyl isopropyl sulfone obtained by the alternate route from 2,4-dinitrophenyl isopropyl sulfide.

Effect of Peroxides.—A solution of 0.45 g. of 2,4-dinitrobenzenesulfenyl chloride, 0.02 g. of dibenzoyl peroxide, and 1 ml. of styrene in 10 ml. of benzene was allowed to stand for four hours and then concentrated by evaporation with an air-stream. The yellow solid which separated was recrystallized from benzene, dried, and found to melt at 141–142°. It did not depress the melting point of the adduct to styrene obtained in the absence of peroxides.

The percentage of the two adducts to propylene, using 1.00 g. of 2,4-dinitrobenzenesulfenyl chloride in glacial acetic acid, was not noticeably affected by the presence of 0.03 g. of benzoyl peroxide. The addition to propylene in carbon tetrachloride was not completely effected in two weeks either in the presence or in the absence of benzoyl peroxide or acetyl peroxide.

In the above experiments, the amounts of peroxides employed were not sufficient to permit recovery of the suspected product of the oxidation of 2,4-dinitrobenzenesulfenyl chloride. That the peroxide oxidizes the reagent to 2,4-dinitrobenzenesulfonyl chloride was shown by permitting a solution of 0.10 g. of 2,4-dinitrobenzenesulfenyl chloride and 0.30 g. of benzoyl peroxide, in 10 ml. of carbon tetrachloride, to stand at room temperature for four hours. On concentrating the solution in an air-stream, 2,4-dinitrobenzenesulfonyl chloride separated in nearly colorless crystals, m. p. 101–102°. The reported value for this compound is 102°.[10]

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Summary

2,4-Dinitrobenzenesulfenyl chloride promises to be a most versatile reagent for the characterization of various classes of organic compounds. The present study reports the characterization of a series of olefins with this reagent.

The additions of 2,4-dinitrobenzenesulfenyl chloride to symmetrical olefins or negatively substituted olefins, such as styrene, yield single adducts. Other olefins, such as propylene and pentene-2, yield mixtures of isomeric adducts. Of the two isomeric adducts to propylene, the product isolated in 65% yield was proved to be the one predictable by Markownikoff's rule. The structure of the other isomer (isolated in 15% yield) was also established in an unambiguous manner.

In a few instances, as with 1,1-diphenylethylene, addition of the reagent is accompanied by dehydrohalogenation, yielding vinyl sulfides rather than the usually observed β-chloro sulfides.

The presence of peroxides was found not to affect the mode of addition to propylene or styrene. Benzoyl peroxide oxidizes 2,4-dinitrobenzenesulfenyl chloride to 2,4-dinitrobenzenesulfonyl chloride.

(10) J. M. Sprague and T. B. Johnson, THIS JOURNAL, **59**, 2439 (1937).

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF DELAWARE]

Polymerization of Fatty Acid Esters of 3-Butene-1,2-diol. I.[1]

BY ELIZABETH DYER, THOMAS G. CUSTER[2] AND WILLIAM C. MEISENHELDER[3]

The formation of polymers from the higher fatty acid esters of monohydric unsaturated alcohols, such as vinyl, allyl, and substituted allyl, has been reported,[4,5,6,7] but there is no published work on the polymerization of such esters of a dihydric unsaturated alcohol. In this paper a report is made of the polymerization of the acetic and palmitic esters of the unsaturated glycol 3-butene-1,2-diol (erythrol). A study of the oleic and linoleic esters of erythrol is in progress. Erythrol is obtainable through hydrolysis of 3,4-epoxy-1-butene[8] (butadiene monoxide).

Erythryl dipalmitate and diacetate were most conveniently obtained by the reactions of the corresponding acid chloride with erythrol in pyridine. The diacetate was previously prepared by Henninger[9] from erythrol and acetic anhydride, the dipalmitate from the successive reactions of butadiene monoxide with one equivalent of palmitic acid in the presence of ferric chloride and with one equivalent of palmitoyl chloride.[10]

(1) From the Master's Theses of Thomas G. Custer and William C. Meisenhelder, University of Delaware, 1948.

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(4) Powers, *Ind. Eng. Chem.*, **38**, 837 (1946).

(5) Dean, U. S. Patent 2,374,081, April 17, 1945.

(6) Swern, Billen and Knight, THIS JOURNAL, **69**, 2439 (1947).

(7) Swern and Jordan, *ibid.* **70**, 2334 (1948).

(8) Pariselle, *Ann. chim. phys.*, [8] **24**, 392 (1911).

(9) Henninger, *ibid.*, [6] **7**, 214 (1886).

(10) Unpublished work of Whitmore and Krems, Brooklyn Polytechnic Institute.