of bromobenzene in 100 cc. of ether. Refluxing started immediately, and the solution was stirred for three hours. After standing overnight, decomposition was effected with ammonium chloride. A tertiary carbinol (15.4 g.) was obtained on evaporation of the ether which melted at 100–101° after recrystallization from methanol and petroleum ether.[10] As described by Blicke,[10] this carbinol gave a yellow color with sulfuric acid which disappeared on dilution, and a yellow coloration with hydrochloric acid in acetic acid.

Benzyl Isodurylate.—To sodium isodurylate (23 g.) was added 20 cc. of benzyl bromide and 100 cc. of toluene. The mixture was refluxed and stirred mechanically for eight hours. The precipitated salt gave only a slight cloudiness on acidification. The toluene layer was fractionated, and 21 g. of the ester distilled at 175–180° (6–8 mm.).

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.33; H, 7.08.

Summary

1. It has been shown that allylic esters with greatly hindered carbonyl groups are cleaved by the Grignard reagent to give magnesium salts and hydrocarbons.

2. It is believed that the mechanism of this cleavage is comparable to that of acetomesitylene and the Grignard reagent.

MINNEAPOLIS, MINNESOTA

RECEIVED SEPTEMBER 29, 1941

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[10] Blicke and Weinkauff, THIS JOURNAL, **54**, 1446 (1932).

[CONTRIBUTION NO. 252 FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Identification of Organic Compounds. IV. Chlorosulfonic Acid as a Reagent for Identification of Alkylbenzenes

BY ERNEST H. HUNTRESS AND JOHN S. AUTENRIETH[1,2]

The use of chlorosulfonic acid as a tool for the characterization of organic compounds, whose application to the identification of aryl halides[3a] and aromatic ethers[3b] was reported in the first two papers of this series, has now been extended to a substantial group of alkylbenzenes.

The principle employed involves two stages, *viz.*, direct introduction of one sulfonyl chloride group into the aromatic nucleus by direct treatment with excess chlorosulfonic acid in chloroform followed by conversion of the resultant sulfonyl chlorides into the corresponding sulfonamides.

The specific application to these hydrocarbons was similar to that designated in the earlier paper[3a] as Procedure I. However, the amount of chlorosulfonic acid employed was 5 ml. (instead of 5 g.), and the chlorosulfonylation product was stirred forty-five minutes before pouring it onto ice. Conversion of the sulfonyl chloride was effected with solid ammonium carbonate substantially as in Procedure B[3a] of the first paper.

The structures of the ultimate sulfonamides from the monoalkylated benzenes were established by permanganate oxidation of the side chain. The resultant *p*-sulfamidobenzoic acid indicated that chlorosulfonylation had occurred para to the single side chain. For the polyalkylbenzene derivatives this oxidation was infeasible and the structures of the products have been inferred from previous work.

The various sulfonamides were subjected to combustion analyses for nitrogen and gave satisfactory values. In the interest of space economy their details are not reported. They served as evidence, however, that only one sulfonamido group was introduced under the conditions employed.

Experimental Work

The melting points reported in this paper are uncorrected. They were determined on a standard rod form 360° melting point thermometer in a copper block of the Berl and Kullmann type as described by Morton.[4]

The chlorosulfonic acid was obtained by fractional distillation of commercial material through a large bore six-foot column of about 40 theoretical plates. The colorless fraction boiling at 150.2° cor. was preserved in small colored glass sealed bottles.

The solvent chloroform was prepared from U. S. P. product by thorough washing with dilute aqueous sodium bicarbonate solution, then with distilled water, drying over phosphorus pentoxide and distilling from a fresh sample of the same agent. The fraction boiling at 61.5–62° was collected in lightly stoppered brown bottles and stored in a dark place.

The alkylbenzenes were obtained from a variety of

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[1] This paper is constructed from part of a dissertation submitted in March, 1941, by John S. Autenrieth to the Faculty of the Massachusetts Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Present address: Hercules Powder Company, Wilmington, Delaware.

[3] (a) Huntress and Carten, THIS JOURNAL, **62**, 511 (1940); (b) **62**, 603 (1940).

[4] Morton, "Laboratory Technique in Organic Chemistry," first ed., McGraw-Hill Book Company, New York, N. Y., 1938, pp. 32–33.

sources and where necessary were carefully purified by careful fractional distillation in a three-foot jacketed column of about 20 theoretical plates or by recrystallization. The authors express particular thanks to Professor Lee I. Smith and Professor Dorothy Nightingale for samples of some of the less common individuals.

After reprecipitation from their alkaline solutions the various sulfonamides were recrystallized either from ethanol–water or benzene–ligroin mixtures, the dilute alcohol solvent usually being preferred for products melting above 100°, the hydrocarbon solvent for those below 100°. It proved desirable to recrystallize the low melting individuals from dilute solutions since otherwise they frequently separated as oils. When necessary decolorizing carbon was employed to remove traces of discoloration. The results are collected in Table I.

TABLE I

SULFONAMIDES FROM ALKYLBENZENES

-Benzene	-Benzenesulfonamide-1	Yield, %	M. p. obsd. (uncor.), °C.
H-	...	23	150.0–150.5
Me-	4-Me-	36–44	135.5–136[a]
Et-	4-Et-	73–95	109–110[b]
1,2-Di-Me-	3,4-Di-Me-	67	143–144[c,d]
1,3-Di-Me-	2,4-Di-Me-	78	136.5–137[a,c,e]
1,4-Di-Me-	2,5-Di-Me-	84	145.5–146.5[d,e]
n-Pr-	4-*n*-Pr-	65–95	107–108[f]
i-Pr-	4-*i*-Pr-	82–88	104.5–105.5[f,g]
1,2,4-Tri-Me-	2,4,5-Tri-Me-	52	175–176
1,3,5-Tri-Me-	2,4,6-Tri-Me-	57	141.5–142.5
n-Bu-	4-*n*-Bu-	80	94.5–95[h,i,n]
s-Bu-	4-*s*-Bu-	63–72	81.0–82.5[j]
t-Bu-	4-*t*-Bu-	100	136–137[a]
i-Bu-	4-*i*-Bu-	82	84–85[j]
1-Me-4-*i*-Pr-	2-Me-5 *i*-Pr-	84–87	114.5–115.5
1,3-Di-Et-	2,4-Di-Et-(?)	57–58	98–99[h]
1,3-Di-Me-4-Et-	2,4-Di-Me-5-Et-(?)	80–85	147–148
1,2,3,4-Tetra-Me-	2,3,4,5-Tetra-Me-	85	183.5–184.0
1,2,3,5-Tetra-Me-	2,3,4,6-Tetra-Me-	82	141.5–142
1,2,4,5-Tetra-Me-	2,3,5,6-Tetra-Me-	...	153–154
n-Am-	4-*n*-Am-	80–100	85.5–86.5[k]
t-Am-	4-*t*-Am-	89–90	83–84[k,o]
1,3-Di-Me-4-*n*-Pr-	2,4-Di-Me-5-*n*-Pr-(?)	79–82	90–93
1,3-Di-Me-4-*i*-Pr-	2,4-Di-Me-5-*i*-Pr-(?)	68	155.5–156
1,3,5-Tri-Me-2-Et-	2,4,6-Tri-Me-3-Et-	64–71	131–132
Penta-Me-	Penta-Me-	90–92	182–183
n-Hexyl-	4-*n*-Hexyl-	81	85–85.5[p]
1,3-Di-Me-4-*t*-Bu-	.....	81	128–130[l,q]
1,3-Di-Me-5-*t*-Bu-	2,4-Di-Me-6-*t*-Bu-(?)	86	132–133[l]
1,3,5-Tri-Et-	2,4,6-Tri-Et-	94	118–118.5
1,4-Di-*t*-Bu-	2,5-Di-*t*-Bu-	...	135.5–136.5[a,r]
n-Nonyl-	4-*n*-Nonyl-	54–67	94.5–95[h,i,s]
n-Undecyl-	4-*n*-Undecyl-	... .	95.7–96.2[h]
Cyclohexyl-	4-Cyclohexyl-	85–87	160–160.5[t]
1,2,4,5-Tetra-*i*-Pr-	2,3,5,6-Tetra-*i*-Pr-	60–85	154.5–155[m]

[a] The m. p. m. (melting point of a mixture) of the sulfonamides (m. p. 135.5–136.5° uncor.) from 1,4-di-*t*-Bu-benzene and that (m. p. 136–137° uncor.) from *t*-Bu-benzene was not depressed, *i. e.*, m. p. 135.5–136.5 uncor. However, each of these compounds when mixed with *p*-toluenesulfonamide (m. p. 136° uncor.) or with *m*-xylenesulfonamide-4 (m. p. 136.5–137° uncor.) showed substantial depression to 95–115°. [b] The m. p. m. of this product with the corresponding sulfone (m. p. 97.5–98°) was 75–95°. [c] The m. p. m. of the sulfonamides from *o*-xylene and *m*-xylene was 112–115°. [d] The m. p. m. of the sulfonamides from *o*-xylene and *p*-xylene was 114–120°. [e] The m. p. m. of the sulfonamides from *m*-xylene and *p*-xylene was 108–112°. [f] The m. p. m. of the sulfonamides from *n*-Pr-benzene and *i*-Pr-benzene was 83–93°. [g] The m. p. m. of this sulfonamide and the corresponding sulfone (m. p. 105–107° uncor.) was 75–86°. [h] The m. p. m. of the sulfonamide of *n*-undecylbenzene with that from *n*-nonylbenzene was 85–91°; with that from *n*-butylbenzene 60–84°; with that from *m*-diethylbenzene 70–80°. [i] The m. p. m. of the sulfonamides from *n*-butylbenzene and *n*-nonylbenzene was 86–94°. [j] The m. p. m. of the sulfonamides from *s*-butyl- and *i*-butylbenzenes was 80–84°. [k] The m. p. m. of the sulfonamides from *n*-amyl- and *t*-amylbenzenes was 55–75°. [l] The m. p. m. of the sulfonamides from 1,3-di-Me-4-*t*-Bu-benzene and 1,3-di-Me-5-*t*-Bu-benzene varied in the range between the values for the two individuals. [m] This product could not be obtained from the sulfonyl chloride *via* the ammonium carbonate method but only by long treatment of the dry ligroin solution with gaseous ammonia. Recrystallization of the sulfonyl chloride from dilute methanol yielded the methyl ester, m. p. 126–126.5° uncor., or from dilute ethanol the ethyl ester, m. p. 99–99.5° uncor. The analogous behavior of pentaethylbenzenesulfonyl chloride was reported during the progress of this work by Smith and Guss, THIS JOURNAL, **62**, 2634 (1940).

ANALYSES

Ref.	Formula	Nitrogen, % Calcd.	Nitrogen, % Found	
n	$C_{10}H_{15}O_2NS$	6.57	6.62	6.78
o	$C_{11}H_{17}O_2NS$	6.16	6.45	6.34
p	$C_{12}H_{19}O_2NS$	5.80	6.05	6.02
q	$C_{12}H_{19}O_2NS$	5.80	5.59	5.63
r	$C_{14}H_{23}O_2NS$	5.20	5.51	5.62
s	$C_{15}H_{25}O_2NS$	4.94	4.90	4.91
t	$C_{12}H_{17}O_2NS$	5.85	5.85	5.93

Intermediate Sulfonyl Chlorides.—In eleven of the cases studied the intermediate sulfonyl chlorides were solids. In these cases the melting point of this intermediate taken in conjunction with the corresponding value for the final sulfonamide affords additional evidence in the identification of the material without any extra work.

Recrystallization of intermediate solid sulfonyl chlorides was best effected from dry ether, ligroin, or petroleum ether. The results are collected in Table II.

TABLE II

SOLID SULFONYL CHLORIDES FROM CERTAIN ALKYLBENZENES

Hydrocarbon, -benzene	Sulfonyl chloride, -benzenesulfonyl chloride-1	Yield, %	M. p., °C. uncor.
Me-	4-Me-	61–65	64–66
1,2-Di-Me-	3,4-Di-Me-	74–86	52
1,3,5-Tri-Me-	2,4,6-Tri-Me-	65–72	50–53
t-Bu-	4-*t*-Bu-	100	80–82
1,2,3,4-Tetra-Me-	2,3,4,5-Tetra-Me-	95	72–73
1,2,4,5-Tetra-Me-	2,3,5,6-Tetra-Me-	100	98–99
Penta-Me-	Penta-Me-	98	77–78.5
1,3-Di-Me-5-*t*-Bu-	2,4-Di-Me-6-*t*-Bu-(?)	97	65–67
Cyclohexyl-	4-Cyclohexyl-	..	51–52.5
1,2,4,5-Tetra-*i*-Pr-	2,3,5,6-Tetra-*i*-Pr-	77–86	141.5–142

Sulfones Obtained during Chlorosulfonylation.—To detect any sulfone which might have been simultaneously formed each sulfonamide was treated with cold aqueous 6 *N* sodium hydroxide. Any sulfone remaining was filtered off, the dissolved sulfonamide being reprecipitated from its alkaline solution upon acidification and subsequently recrystallized to constant melting point.

The amount of sulfone formation was considerable (27%) only in the case of benzene. In various runs toluene gave 1–10%, ethylbenzene 1–6% and isopropylbenzene 2–3% but the other hydrocarbons gave no evidence of corresponding products.

Other Hydrocarbons.—Occasion having arisen to study this procedure on hydrindene and tetrahydronaphthalene these results are included here.

Hydrindene gave 65–70% yield of indane-5-sulfonamide, flakes from dilute ethanol, m. p. 132.5–133.5° uncor.

1,2,3,4-Tetrahydronaphthalene gave a 75% yield of 5,6,7,8-tetrahydronaphthalenesulfonamide-2, flakes from dilute ethanol, m. p. 134.5–135° uncor. In this case the intermediate sulfonyl chloride separated as a wax-like solid recrystallization of which from ligroin gave flakes, m. p. 58.0–58.5° uncor.

Summary

1. The use of chlorosulfonic acid as a means of identification has been extended to thirty-seven aromatic hydrocarbons, most of which are alkylated benzenes.

CAMBRIDGE, MASS. RECEIVED SEPTEMBER 3, 1941

[CONTRIBUTION FROM THE DIVISION OF PLANT BIOLOGY, CARNEGIE INSTITUTION OF WASHINGTON]

Isomerizations of Polyene Acids and Carotenoids. Preparation of β-Eleostearic and β-Licanic Acids

BY HAROLD H. STRAIN

As a preliminary step in the interpretation of chemical and biochemical transformations of the polyene pigments,[1] the effects of several catalysts on the isomerization of unsaturated aliphatic acids and carotenoids have been compared. Isomerization of olefinic acids is catalyzed by a variety of substances such as sulfur,[2] selenium,[3] phosphorus,[4] halogens,[5,6] oxides of nitrogen[7,8] and oxides of sulfur.[9] With these catalysts and in the absence of secondary reactions such as polymerization and combination with the catalyst, eleostearic and licanic acids have now been found to undergo isomerization much more rapidly than oleic acid. This greater reactivity of the polyene acids as compared to oleic acid may result, in part, from simultaneous changes about two or more conjugated double bonds, rather than from successive changes about individual double bonds in the molecule.

Under some of the conditions employed in these experiments, high yields of the beta or high-melting *trans* forms of eleostearic and licanic acids were obtained from the natural or alpha isomers. These conditions have been utilized for the rapid preparation of the beta acids.

Carotenoids with ten and eleven conjugated double bonds were altered rapidly by most of the catalysts listed above. The alteration products varied considerably with different catalysts. Reactions produced by acids[1 (p. 87), 10] resulted in the formation of pigments that were adsorbed below the unchanged carotenoids on Tswett columns of specially prepared magnesia.[1] This alteration was most rapid in the presence of strong acids and at elevated temperatures. It often led to complete decomposition of the original carotenoids. It occurred even when solutions of the carotenoids in non-polar solvents were placed in contact with solid, slightly soluble, dibasic organic acids. It was prevented by addition of organic bases such as pyridine to the solutions.

Carotenoid pigments are known to be converted reversibly into isomeric compounds by the action of either heat[1,11,12] or iodine.[12] Dihydroxyxanthophylls yield isomers that are more strongly adsorbed than the unchanged pigments, whereas monohydroxyxanthophylls and the hydrocarbon carotenes yield isomers that are not so strongly adsorbed as the native polyenes.[11,12] In the experiments described in this paper, the dihydroxyxanthophylls have been found to yield a second group of isomerization products. If the reaction with iodine was permitted to proceed for a long period, or if an excess of iodine was used, weakly

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(1) Strain, "Leaf Xanthophylls," Carnegie Inst. of Wash. Publication No. 490 (1938).

(2) Maquenne, *Compt. rend.*, **135**, 696 (1902).

(3) Bertram, *Chem. Weekblad*, **33**, 3 (1936).

(4) Rankoff, *Ber.*, **69**, 1231 (1936).

(5) Morrell and Davis, *J. Chem. Soc.*, 1481 (1936).

(6) Kappelmeier, *Chem. Abst.*, **30**, 887 (1936).

(7) Holde and Rietz, *Ber.*, **57**, 99 (1924).

(8) Griffiths and Hilditch, *J. Chem. Soc.*, 2315 (1932).

(9) Rankoff, *Ber.*, **62**, 2712 (1929).

(10) Kuhn, Winterstein and Lederer, *Z. physiol. Chem.*, **197**, 141 (1931); Quackenbush, Steenbock and Peterson, THIS JOURNAL, **60**, 2937 (1938).

(11) Carter and Gillam, *Biochem. J.*, **33**, 1325 (1939).

(12) Kuhn and Lederer, *Ber.*, **65**, 637 (1932); Zechmeister and Tuzson, *ibid.*, **72**, 1340 (1939); Zechmeister, Cholnoky and Polgar, *ibid.*, **72**, 1678, 2039 (1939)