<div style="text-align:center">REACTION OF GRIGNARD REAGENTS WITH TRIMETHYLACETAMIDE</div>

| | | | | | | | ⌐———————Derivatives of ketones———————⌐ | | |
| | | | B. p. | | | Yield, | 2,4-Dinitro-phenyl-hydrazone | Semi-carbazone | Oxime |
	RMgX	Ketone	°C.	Mm.	$n^{20}D$	%	m. p., °C.	m. p., °C.	m. p., °C.
1	Methyl	Methyl t-butyl (Pinacolone)	105	746	1.3952–1.3960	52	126–127	.....	78.5–79.5
2	Ethyl	Ethyl t-butyl	124.5	729	1.4049–1.4052	78	143.5–144.5	.....	84.5–85.5
3	n-Propyl	n-Propyl t-butyl	145	738	1.4103–1.4107	67	116–116.5^d	.....	78–78.5
4	Isopropyl	Isopropyl t-butyl	134–135	744	1.4060–1.4070	20	......	.....	143–144
5	n-Butyl	n-Butyl t-butyl	166	745	1.4162–1.4172	68	......	144.5–145	59.5–60.5^c
6	Isobutyl	i-Butyl t-butyl^a	.....	...	....	..	......	.....	......
7	s-Butyl	s-Butyl t-butyl	156–157	745	1.4158–1.4162	12	......	.....	87–88
8	t-Butyl	(Trimethylacetonitrile)^b	103.5	738	1.3792	..	......	.....	......
9	n-Amyl	n-Amyl t-butyl	184–185	745	1.4208–1.4219	42	99–100^e	140–140.5	......

^{a} Reaction 6 yielded 42% nitrile, unreacted amide, and only 1 g. of ketone from which an oxime, m. p. 72–73°, was made. ^{b} Trimethylacetonitrile was obtained in 73% yield. It was identified by conversion to ethyl t-butyl ketone with ethyl-magnesium bromide. ^{c} Anal. Calcd. for $C_9H_{19}NO$: N, 8.91. Found: 8.95. ^{d} Anal. Calcd. for $C_{14}H_{20}N_4O_4$: N, 18.18. Found: 17.99. ^{e} Anal. Calcd. for $C_{16}H_{24}N_4O_4$: N, 16.67. Found: 16.83.

Summary

1. The reaction of trimethylacetamide with normal aliphatic Grignard reagents gives good yields of t-butyl ketones.

2. The reaction of trimethylacetamide with t-butylmagnesium chloride yields chiefly tri-methylacetonitrile.

Identification of Alkyl Phenyl Sulfides, Sulfoxides, and Sulfones[1]

BY V. N. IPATIEFF AND B. S. FRIEDMAN

During the course of the study[2] of the reaction of olefins and alkyl esters of phosphoric and sulfuric acids with thiophenol, it became necessary to develop methods for identifying the resultant alkyl phenyl sulfides.

Unlike the aliphatic sulfides, alkyl phenyl sulfides coördinate very slowly, if at all, with mercuric chloride; so that this excellent method[3a] of identification was of no aid. The other mercuric salts were equally unsatisfactory. With palladous chloride, however, the coördination compounds, $(C_6H_5\text{-S-R})_2 \cdot PdCl_2$, are formed rapidly and in good yield.[2,3b] These are solid derivatives possessing desirable physical properties in all but a few cases. t-Butyl and t-amyl phenyl sulfides formed insoluble, brick red powders melting above 250°; analyses of these indicated that the compounds possess the formula, $C_6H_5\text{-S-R} \cdot 2PdCl_2$. Complexes of the $(C_6H_5\text{-S-R})_2 \cdot PdCl_2$ type could be obtained from t-butyl and t-amyl phenyl sulfides only if an excess of the sulfide was used in the preparation of the derivative. These were yellow powders, easily soluble in organic solvents,

(1) Presented before the Organic Division of the American Chemical Society, Milwaukee, Wisconsin, September 5–9, 1938.

(2) Ipatieff, Pines and Friedman, THIS JOURNAL, 60, 2731 (1938).

(3) (a) Faragher, Morrell and Comay. ibid., 51, 2774 (1929); (b) Mann and Purdie, J. Chem. Soc., 1549 (1935).

and melting at 84 and 72–73°, respectively. However, on recrystallization from any of various solvents, or upon standing, there always was obtained the brick red powder accompanied by droplets of the free t-alkyl phenyl sulfide. The following reaction apparently takes place

$$2(C_6H_5\text{-S-R})_2PdCl_2 \longrightarrow$$
$$C_6H_5\text{-S-R} \cdot 2PdCl_2 + 3C_6H_5\text{-S-R}$$
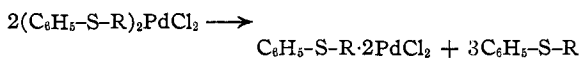
This characteristic behavior of these derivatives of t-butyl and t-amyl phenyl sulfides made possible the identification of these sulfides in mixtures with their isomers.

The palladous chloride complex of $active$-amyl phenyl sulfide was an oil, and of s-isoamyl phenyl sulfide a solid of indefinite melting point.

To identify the alkyl phenyl sulfides giving unsatisfactory palladous chloride derivatives, as well as to provide additional means for the identification of the other alkyl phenyl sulfides, this investigation was extended to include the preparation of the corresponding sulfones (I). The latter were satisfactory derivatives in only a few instances (see Table I). The sulfones, therefore, were nitrated to give m-nitrophenyl alkyl sulfones (II), most of which were then reduced to give the corresponding m-aminophenyl alkyl sulfones (III).

All the alkyl phenyl sulfones except *t*-butyl and *t*-amyl (which again behave differently) were nitrated by heating for a few minutes on the water-bath with concentrated sulfuric and nitric acids (3:1 by volume). *t*-Butyl and *t*-amyl phenyl sulfones were decomposed violently by this treatment. They were nitrated successfully at 50° by means of a special procedure.

Since even the *m*-nitrophenyl and the *m*-aminophenyl alkyl sulfones were also not entirely satis-

factory derivatives, acylation of the amines was studied. Acetylation and benzoylation gave oils which could not be induced to crystallize. When the amine was treated with *m*-bromobenzoyl bromide, solid derivatives were obtained. At room temperature in the presence of pyridine, *m*-(3-bromobenzamino)-phenyl alkyl sulfone (IV) was formed; if the reaction mixture was warmed on a water-bath or refluxed for a few minutes, two molecules of *m*-bromobenzoyl bromide reacted

TABLE I
DERIVATIVES, PROPERTIES AND ANALYSES

Alkyl	Crystalline form[a]	M.p. (uncorr.), °C.[b]	Formula	Analyses, % Calcd.	Found	Hydrogen Calcd.	Found
Alkyl Phenyl Sulfide Palladous Chloride Complexes[e]							
Ethyl	Orange needles	139–140	$C_{16}H_{20}S_2 \cdot PdCl_2$	Pd,[f] 23.55	23.60		
n-Propyl	Yellow needles	90–91	$C_{18}H_{24}S_2 \cdot PdCl_2$	22.17	22.24		
i-Propyl	Orange prisms	162	$C_{18}H_{24}S_2 \cdot PdCl_2$	22.17	22.30		
n-Butyl[b]	....	106–106.5	....	...	...		
s-Butyl	Orange needles	137–138	$C_{20}H_{28}S_2 \cdot PdCl_2$	20.93	21.00		
i-Butyl[b]	Orange prisms	92.5–93.5	....	...	...		
t-Butyl	Brick-red powder	84, >250[i]	$C_{10}H_{14}S \cdot 2PdCl_2$	40.9	38.3		
n-Amyl[b]		75–76					
i-Amyl[b]		96–97					
2-*s*-Amyl	Orange prisms	107.5–108	$C_{22}H_{32}S_2 \cdot PdCl_2$	19.87	19.91		
3-*s*-Amyl	Slender yellow prisms	101–102	$C_{22}H_{32}S_2 \cdot PdCl_2$	19.87	19.90		
Active Amyl	Oil	....		...	...		
t-Amyl	Brick-red micro-needles	72–73, >250[i]	$C_{11}H_{16}S \cdot 2PdCl_2$	39.87	39.55		
Alkyl Phenyl Sulfones[k]							
Methyl	....	(88)[c]	....	...	...		
Ethyl	....	(41–42)[d]	....	...	...		
n-Propyl	Plates	44[g]	....	...	...		
t-Butyl[b]	....	98–99	....	...	...		
n-Amyl	Slender prisms	31–32	....	...	...		
i-Amyl	Slender prisms	35.5–36.5[h]	....	C, 62.26	62.36	7.54	7.47
3-*s*-Amyl	....	46–47	....	...	...		
t-Amyl[b]	....	29–30	....				
Alkyl *m*-Nitrophenyl Sulfones[l]							
n-Propyl[b]	....	78.5–79	....	...	...		
i-Propyl[b]	....	112–113	....	...	...		
t-Amyl	Needles	93–94	$C_{11}H_{15}NO_4S$	N, 5.45	5.26		
Alkyl *m*-Aminophenyl Sulfones							
i-Butyl[m]	Clusters of prisms	83.5–84	$C_{10}H_{15}NO_2S$	C, 56.33	56.48	7.04	7.03
3-*s*-Amyl[l]	Needles	76–77	$C_{11}H_{17}NO_2S$	N, 6.16	6.33	..	..
s-*i*-Amyl[b]	....	93.5–94.5	....			..	..
Alkyl *m*-(3-Bromobenzoylamino)-phenyl Sulfones[l]							
n-Butyl	Prisms	130.5–131.5	$C_{17}H_{18}BrNO_3S$	C, 51.89	51.73	4.54	4.73
s-Butyl	Prisms	115–116	$C_{17}H_{18}BrNO_3S$	C, 51.89	51.93	4.54	4.74
n-Amyl	Prisms	120.5–121	$C_{18}H_{20}BrNO_3S$	C, 52.68	52.74	4.87	4.79
Alkyl *m*-(4-Bromobenzoylamino)-phenyl Sulfones[l]							
s-Butyl	Prisms	141–142	$C_{17}H_{18}BrNO_3S$	N, 3.53	3.66		
n-Amyl	Prisms	165–166	$C_{18}H_{20}BrNO_3S$	N, 3.43	3.51		
i-Amyl	Prisms	168–168.5	$C_{18}H_{20}BrNO_3S$	N, 3.43	3.51		
2-*s*-Amyl	Prisms	137–138	$C_{18}H_{20}BrNO_3S$	N, 3.43	3.32		
3-*s*-Amyl	Prisms	158–159	$C_{18}H_{20}BrNO_3S$	N, 3.43	3.58		
s-*i*-Amyl	Prisms	128.5–129.5	$C_{18}H_{20}BrNO_3S$	N, 3.43	3.53		

| Alkyl | Crystalline form[a] | M.p.(uncorr.), °C.[b] | Formula | Analyses, % | | Hydrogen | |
				Calcd.	Found	Calcd.	Found
			Alkyl *m*-(Di-3-bromobenzoylamino)-phenyl Sulfones[f]				
n-Butyl	Needles	200.5–201.5	$C_{24}H_{21}Br_2NO_4S$	N, 2.41	2.63		
s-Butyl	Needles	169–170	$C_{24}H_{21}Br_2NO_4S$	C, 49.74	50.04	3.62	3.48
i-Butyl	Needles	188–189	$C_{24}H_{21}Br_2NO_4S$	N, 2.41	2.47		
n-Amyl	Needles	166.5–168	$C_{25}H_{23}Br_2NO_4S$	N, 2.36	2.4		
i-Amyl	Needles	190.5–191.5	$C_{25}H_{23}Br_2NO_4S$	C, 50.59	50.75	3.87	4.02
				N, 2.36	2.46		
2-*s*-Amyl	Needles	163.5–164.5	$C_{25}H_{23}Br_2NO_4S$	N, 2.36	2.31		
Active Amyl	Needles	175–176.5	$C_{25}H_{23}Br_2NO_4S$	N, 2.36	2.46		
s-*i*-Amyl	Needles	161–162	$C_{25}H_{23}Br_2NO_4S$	N, 2.36	2.2		

[a] Colorless unless otherwise stated. [b] Values given in previous paper[1] are included here; values in parentheses are those reported by other workers. [c] Otto and Artmann, *Ann.*, **284**, 301 (1895). [d] Otto, *Ber.*, **13**, 1274 (1880). [e] See experimental part for directions for recrystallizing these complexes. [f] Weighed as metal. [g] Otto and Otto, *Ber.*, **21**, 998 (1888), report 44°. [h] Reference *c*, page 303, reports 37°. [i] The low melting derivatives of probable formula, $(C_6H_5S–R)_2·PdCl_2$, were not analyzed. On recrystallization, or on standing, these were always converted to brick-red powders which did not melt below 250° and which analyzed correctly for $C_6H_5–S–R·2PdCl_2$. [j] From 95% ethanol. [k] From hexane. [l] Ethanol. [m] Benzene–cyclohexane.

with the amine to form the N,N-dibromobenzoyl derivative (V).

However, the preparation of these derivatives in the presence of pyridine had to be abandoned, since it was found that the newly purchased as well as some old lots of *m*-bromobenzoyl bromide reacted with pyridine to yield a difficultly soluble compound which interfered with the isolation of the desired derivatives. The structure of this compound was established as *m*-bromobenzoic anhydride, identical with a specimen obtained by the reaction of potassium *m*-bromobenzoate with *m*-bromobenzoyl bromide. *p*-Bromobenzoic anhydride was formed by treating *p*-bromobenzoyl chloride with pyridine

$$p\text{-BrC}_6H_4COCl + p\text{-BrC}_6H_4COOH[4] + C_5H_5N \longrightarrow$$
$$C_5H_5N·HCl + (p\text{-BrC}_6H_4CO)_2O$$
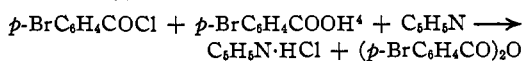
The formation of anhydrides by this type of reaction has been observed previously.[5]

This difficulty was avoided by use of dilute alkali instead of pyridine, but in all cases only the N,N-dibromobenzoyl derivative was obtained when *m*-bromobenzoyl bromide was used. For several of the compounds the melting points of this derivative are too close together; so still another derivative, the *m*-(4-bromobenzamino)-phenyl alkyl sulfone (VI), was prepared for these by the Schotten–Baumann reaction using *p*-bromobenzoyl chloride instead of *m*-bromobenzoyl bromide. It is interesting to note that under

exactly the same conditions *p*-bromobenzoyl chloride gave only the mono acyl derivative, whereas *m*-bromobenzoyl bromide gave only the diacyl derivative.
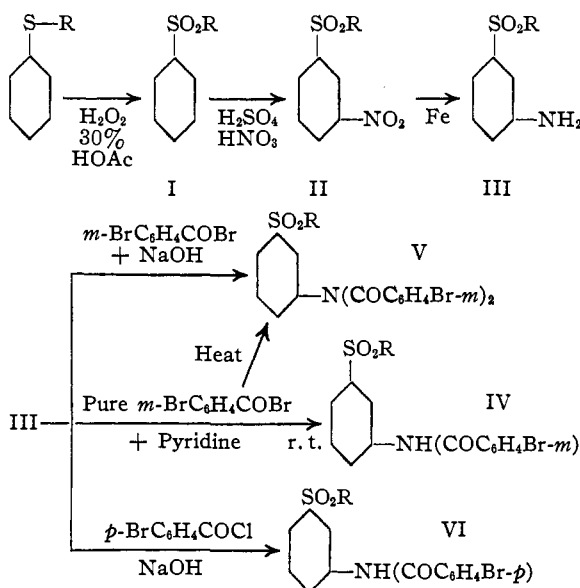
It is obvious that not only alkyl phenyl sulfides but also alkyl phenyl sulfones and sulfoxides may be identified by means of these derivatives. The sulfoxides readily can be oxidized[6] to sulfones by means of hydrogen peroxide or potassium permanganate, or reduced[6] to sulfides by zinc dust in the presence of acetic acid.

In connection with the proof of structure of the anhydride obtained from the reaction of *m*-bromo-

(4) Present as impurity.
(5) (a) Losanitsch, *Monatsh.*, **35**, 318 (1914), with 3-nitrobenzoyl chloride; (b) Rule and Paterson, *J. Chem. Soc.*, **125**, 2161 (1924), with *o*-methoxybenzoyl chloride; (c) Benary, Reiter and Soenderop, *Ber.*, **50**, 73 (1917), with 4-bromobenzoyl chloride and quinoline.

(6) Hickinbottom, "Reactions of Organic Compounds," Longmans, Green and Company, New York, N. Y., 1936, p. 401.

benzoyl bromide and pyridine, an attempt was made to convert m-bromobenzoic acid to the anhydride by following the procedure used by Rule and Paterson[5b] in the preparation of m-chlorobenzoic anhydride. A toluene solution of the acid was boiled with an excess of phosphorus pentoxide. The product, however, was found to be 3-bromo-4'-methylbenzophenone, identical with the ketone obtained by the reaction of m-bromobenzoyl bromide on toluene in the presence of aluminum chloride. The ability of phosphorus pentoxide to promote aroylation of benzene and toluene was reported long ago.[7] The use of other solvents, such as paraffins, is to be recommended in the preparation of anhydrides by the action of phosphorus pentoxide.

Experimental

Procedure for Preparing Derivatives

Palladous Chloride Complexes of Alkyl Phenyl Sulfides.—These were prepared according to directions previously given.[2]

t-Butyl phenyl sulfide was detected easily in a mixture containing 0.05 cc. of the t-butyl and 0.95 cc. of i-butyl phenyl sulfides. The synthetic mixture was converted into the palladous chloride complex as usual and the crude product dissolved in cold acetone and filtered by gravity. Water was added until the solution was faintly turbid, and the turbidity was removed with a few drops of acetone. The solution was allowed to stand. Orange prisms, appearing more red in color than the pure crystals, soon appeared. These were separated by filtration and extracted on the filter paper with acetone until the filtrate was colorless. This treatment removed the soluble i-butyl derivative and left the easily recognized red powder consisting of the insoluble t-butyl isomer. This powder, when heated in a capillary melting point tube above 250°, decomposed, leaving a black residue with droplets of liquid gathered a centimeter or two up the tube.

By a slight modification of this method t-amyl phenyl sulfide–palladous chloride complex was separated from the isoamyl derivative. A mixture of 0.05 cc. of the t- and 0.95 cc. of isoamyl phenyl sulfides was converted into the palladous chloride derivative and recrystallized from acetone and water. The needles were separated by filtration and leached with acetone, leaving undissolved a small amount of the brick red, insoluble powder characteristic of the t-amyl palladous chloride complex. The acetone extract was diluted with water and allowed to stand. The yellow needles which formed were covered with red dots. These crystals were removed by filtration and leached with acetone. There remained undissolved on the filter paper a much larger amount of the red micro-crystalline needles of the t-amyl derivative than was obtained from the first crop of crystals.

The Alkyl Phenyl Sulfones (I).—Two cc. each of 30% hydrogen peroxide and glacial acetic acid was added to 1

cc. of alkyl phenyl sulfide, and the mixture was heated in a 50-cc. beaker on a water-bath in a hood until the acetic acid and water were evaporated. (When the fumes no longer bleached or affected the color of a strip of moist blue litmus paper held over the top of the beaker, the heating was stopped.) The beaker was cooled in dry ice-acetone mixture and scratched with a stirring rod to induce crystallization of the sulfone, which was recrystallized from hexane or dilute alcohol; or the crude sulfone was taken directly for nitration to form m-nitrophenyl alkyl sulfones.

m-Nitrophenyl Alkyl Sulfones (II). A.—As a preliminary test, one drop of the sulfone was added to 0.5 cc. of nitrating mixture (3 parts concentrated sulfuric acid, 1 part concentrated nitric acid) and heated on a water-bath. If violent decomposition as evidenced by frothing and excessive evolution of brown oxides of nitrogen occurred, indicating a t-alkyl phenyl sulfone, the nitration was carried out according to procedure (B). If no decomposition occurred, the balance of the crude sulfone (from 1 cc. of the sulfide) was mixed with 3 cc. of the nitrating mixture and gradually warmed on the water-bath with occasional stirring. The reaction mixture was then heated on the water-bath for five minutes more, after which it was poured on crushed ice and extracted with ether. The ether solution was washed with water, dried over anhydrous sodium sulfate and evaporated on the water-bath.

If the m-nitrophenyl alkyl sulfone solidified on cooling to −80° and scratching, it was recrystallized from dilute alcohol; or the crude product was used for preparing the corresponding m-aminophenyl alkyl sulfone.

B.—Alkyl phenyl sulfones which decomposed when treated with the nitrating mixture at 100° were added dropwise with rapid stirring to the nitrating mixture heated by a bath kept at 50°. After the addition was complete, the reaction mixture was stirred for an additional five minutes at 50°. The product was then poured on crushed ice and isolated as in procedure (A).

m-Aminophenyl Sulfones (III).—The reduction of nitrophenyl alkyl sulfones was carried out according to the directions previously given.[2] Crystallization of the amine was difficult; the best solvent was hexane. Usually the crude amine was dissolved in about 10–15 cc. of ether, and this solution used in the preparation of the derivatives described below.

m-(Di-3-bromobenzoylamino)-phenyl Alkyl Sulfones (V).—To one-half of the ether solution of the amine in an Erlenmeyer flask was added 0.5 cc. of m-bromobenzoyl bromide[8] and 50 cc. of 10% potassium hydroxide. The mixture was shaken until the odor of the bromide could no longer be detected (about ten minutes). The acetylated compound was quite insoluble in ether and separated out after the mixture had been shaken for five minutes or so. The ether was removed by applying a slight vacuum to the flask, or by use of a gentle air blast. The colorless precipitate was separated by filtration, washed first thoroughly with water, and then with a small amount of ether, and recrystallized from 95% ethanol.

m-(4-Bromobenzamino)-phenyl Alkyl Sulfones (VI).—This derivative was prepared by treating the other half of the ether solution of the amino sulfone with 0.5 g. of p-bromobenzoyl bromide[8] in the presence of 50 cc. of 10%

(7) Hoolarits and Merg, *Ber.*, **6**, 537 (1873).

(8) Eastman Kodak Co. product,

potassium hydroxide. The crude product was washed with water and recrystallized from dilute ethanol.

The Use of Pyridine in Aroylation of m-Aminophenyl Sulfones.—If pyridine is to be used in the aroylation of the m-aminophenyl alkyl sulfones, a "blank" test must be run on the aroyl halide to determine whether it contains free acid which will lead to the formation of an anhydride in the presence of pyridine. About 0.5 cc. of the aroyl halide is warmed slightly with 5 cc. of anhydrous pyridine. The mixture is poured into an excess of 5% sulfuric acid and is then extracted with ether. The ether solution is washed with water, alkali, water again, and dried. If a residue (anhydride) remains after removal of the ether by evaporation on the water-bath, it must be concluded that the aroylation may not be carried out in the presence of pyridine.

If no residue remains, the aroyl halide may be used in the following procedure. The aminosulfone is dissolved in 10 cc. of anhydrous pyridine, and the solution is divided into two equal portions, to each of which is added 0.5 cc. of m-bromobenzoyl bromide. One portion is heated on the water-bath for two or three minutes to prepare the diacyl derivative; the other portion is stirred at room temperature for five minutes to prepare the mono-acyl compound. Each one is added to 400 cc. of 5% sulfuric acid. The diacyl compound is separated by filtration and washed thoroughly with alkali and with water, and then once or twice with ether, and recrystallized from 95% ethanol. The mono acyl derivative is taken up with ether; the ether solution is washed with alkali and water, dried, and evaporated on a water-bath. The residue is recrystallized from dilute ethanol.

m- and p-Bromobenzoic Acid Anhydrides.—These were prepared in good yield from the corresponding aroyl halides and pyridine by following the directions given above for the "blank" test. m-Bromobenzoic anhydride formed colorless glistening flakes when recrystallized from benzene and heptane, m. p. 97–98.0°. Anal. Calcd. for $C_{14}H_8Br_2O_3$: Br, 41.66. Found: Br, 41.61.

This compound was also prepared as follows. Two hundred sixty mg. of potassium m-bromobenzoate and 0.2 cc. of m-bromobenzoyl bromide were heated at 190–200° for one hour. The resulting solid was treated with 20 cc. of ether; the ether solution was washed with alkali and water, and dried over anhydrous potassium carbonate. On rapid evaporation of the ether solution to one-half its volume, the anhydride separated as colorless glistening flakes, m. p. 98–98.5°,[9] mixed m. p. with specimen prepared as above was 97–98°.

p-Bromobenzoic anhydride was prepared from p-bromobenzoyl chloride and pyridine. Since it was quite insoluble in ether, it was separated and washed with alkali and water on the suction filter. It formed colorless feathery needles from carbon tetrachloride, m. p. 213–213.5°.[10]

3-Bromo-4'-methylbenzophenone. (A).—The directions given by Rule and Paterson[5b] for preparing the anhydrides of m-chlorobenzoic acid were followed in an attempt to

prepare the anhydride of m-bromobenzoic acid. A solution of the acid in toluene (10 parts) was boiled for four hours with an excess of phosphoric anhydride. The product was extracted with ether, the ether solution was shaken with alkali, washed with water, dried over anhydrous sodium sulfate, and evaporated to one-third its volume on the water-bath. Two volumes of heptane was added and the solution cooled. The colorless precipitate which appeared was separated by filtration and dissolved in boiling heptane from which it crystallized to give colorless flakes, m. p. 107–108.5°. The substance was identified as 3-bromo-4'-methylbenzophenone by compairson with the ketone prepared by the Friedel–Crafts reaction (see B). Anal. Calcd. for $C_{14}H_{11}OBr$: C, 61.09; H, 4.00. Found: C, 60.97; H, 4.15.

B.—Two grams of aluminum chloride was added in portions to a mixture of 1 g. of m-bromobenzoyl bromide and 2 g. of toluene. The reaction mixture was allowed to stand for fifteen minutes, after which it was heated at 90° for 10 minutes. It was then cooled, treated with crushed ice and 40% alkali. The colorless precipitate was separated and washed with water on the suction filter. Recrystallized from 95% ethanol it formed colorless glistening flakes, m. p. 109–109.5°; mixed m. p. with specimen obtained in (A) was 107–108°.

Summary

Procedures are described for the preparation of solid derivatives of alkyl phenyl sulfides and sulfones by one or more of the following reactions: (1) coördination of the sulfide with palladous chloride, (2) oxidation of the sulfide to the sulfone, (3) nitration of the sulfone to form m-nitrophenyl alkyl sulfone, (4) reduction of the latter to the amino sulfone, (5) acylation of the amino sulfone with m-bromobenzoyl bromide or p-bromobenzoyl chloride.

The alkyl phenyl sulfoxides can be converted to the sulfides or sulfones and characterized by the above procedures.

Aroylation of the amino sulfones in the presence of pyridine is often unsuccessful because of the formation of the anhydride derived from the aroyl halide. In the presence of alkali m-bromobenzoyl bromide reacted with the amines to form N,N-dibromobenzoyl derivatives, whereas p-bromobenzoyl chloride gave only N-bromobenzoyl derivatives.

By means of the palladous chloride derivatives, it is possible to detect and separate small amounts of t-butyl or t-amyl phenyl sulfides in mixtures of each with its isomers.

t-Butyl and t-amyl phenyl sulfones differ from their isomers in that they decompose when they are nitrated at 100°. These must be nitrated by a special procedure.

(9) Danaila, *Bull. soc. chim.*, [7] **4**, 287 (1910), reported 148–149° for this compound.

(10) Jackson and Rolfe, *Am. Chem. J.*, **9**, 85 (1887), reported 212–213°; Claisen, *Ann.*, **291**, 89 (1896), reported 218–220°.

3-Bromo-4'-methyl-benzophenone is prepared by refluxing a toluene solution of *m*-bromo-

benzoic acid over phosphorus pentoxide.

Raman Spectra of the Hexanes and Heptanes[1]

BY E. J. ROSENBAUM, ARISTID V. GROSSE AND H. F. JACOBSON

The study of the Raman spectra of paraffin hydrocarbons is worth while both from the standpoint of the theory of molecular structure and as a practical method for the analysis and identification of paraffins in mixtures.

For many molecules, particularly those of high degree of symmetry, a satisfactory correlation has been made of the normal modes of vibration with the observed vibrational frequencies. For the vast majority of molecules, on the contrary, no such correlation is possible at present, partly because the normal vibrations are not known and partly because the experimental data are insufficient.

Among the molecules which have not yet received adequate treatment are the chain molecules, exemplified by the paraffin hydrocarbons.[2] While the recent analysis of the vibrational spectrum of ethane[3] has provided a start in the understanding of these spectra, little in detail can be said about them until the theory has been extended to more complicated cases. It can be anticipated, however, that the paraffin isomers, which contain a small number of different kinds of bonds and differ primarily in symmetry, will furnish the best test of future theoretical developments.

From a more practical point of view, the application of these Raman spectra to the *qualitative* and *semi-quantitative analysis of hydrocarbon* mixtures is of great value because the number and chemical similarity of the hexane and heptane isomers make the purely chemical analytical methods very difficult in the case of hexanes[4] and practi-

cally impossible in the case of heptanes. The results obtained in the analysis of paraffin mixtures and the identification of specific isomers will be described in a separate publication.[5]

In this paper we present the Raman spectra of all the nine possible heptane and five possible hexane isomers. Of the heptanes only the normal compound[6] has been studied previously, while data for all five of the hexanes[7] have been reported. Since this latter work seemed quite incomplete, a repetition was thought advisable.

A study of the spectra of the eighteen isomeric octanes is in progress.

Experimental

Exceptionally pure synthetic paraffins were available for this investigation due to the coöperation of G. Calingaert of the Ethyl Gasoline Corporation, Detroit, P. L. Cramer of the General Motors Corporation, Detroit, F. D. Rossini of the National Bureau of Standards, and J. Smittenberg of the N. V. de Bataafsche Petroleum Maatschappij, The Hague. For a sample of 2-methylpentane from natural gas we are indebted to J. H. Bruun of the Sun Oil Company.

We wish to express our thanks for the opportunity of working with these samples.

Six paraffins were available from two independent sources and one was available from three.

The sources of the individual preparations are given in Table I, in which the tube numbers marked with an asterisk refer to samples used in obtaining the spectra reported here. The indices of refraction of all samples used were determined and found to be practically identical with the best literature values (see Table I). The close agreement between the values for hydrocarbons from two or three sources is a further proof of their purity. In addition, it is important to stress the fact that the spectra of the same paraffins from different sources were identical.

The spectra were excited by four low-voltage mercury arcs. Photographs were taken with a Steinheil spectrograph whose dispersion varies from 6 Å./mm. at 4000 Å.

(1) A preliminary account of this work was presented to the Petroleum Division at the Milwaukee meeting, September, 1938. Tables V–XVIII, furnishing additional data, have been issued through Auxiliary Publication, and may be obtained from American Documentation Institute, c/o Offices of Science Service, 2101 Constitution Ave., Washington, D. C., by ordering Document 1158, remitting 24¢ for copy in microfilm, or $1.60 for copy in photoprints legible without mechanical aid.

(2) The most ambitious theoretical attempt in this direction was that of Kassel, *J. Chem. Phys.*, **3**, 326 (1935).

(3) Crawford, Avery and Linnett, *ibid.*, **6**, 682 (1938); Schäfer, *Z. physik. Chem.*, **40**, 357 (1938).

(4) A. V. Grosse and V. N. Ipatieff, papers presented before the 94th Meeting of the American Chemical Society at Rochester, N. Y., Sept., 1937, Petroleum Division, O, p. 11.

(5) See E. J. Rosenbaum, A. V. Grosse and H. F. Jacobson, paper presented before the 96th Meeting of the American Chemical Society at Milwaukee, Wis., Sept., 1938, Petroleum Division, O, pp. 10 and 11.

(6) Most recently by Kohlrausch and Köppl, *Z. physik. Chem.*, **B26**, 209 (1934).

(7) Andant, Lambert and Lecomte, *Compt. rend.*, **198**, 1306 (1934).