2. The relative yields of sulfonyl bromide and di-aryl disulfide depend upon the nature of the aryl radical: in some cases the disulfide is the only product; in other cases it is formed in very small amounts.

3. In these reactions the sulfonyl bromide is formed first. It is subsequently reduced by the phosphorus tribromide, simultaneously formed by the dissociation of phosphorus pentabromide. The sulfonic acid salts are unaffected by phosphorus tribromide alone.

4. Aryl sulfonyl bromides are readily reduced by phosphorus tribromide; sulfonyl chlorides are reduced with much greater difficulty by the same reagent. Neither the sulfonyl chlorides nor bromides are reduced by phosphorus trichloride.

5. By the use of the bromides of phosphorus certain disulfides, otherwise difficult or impossible to prepare, are readily obtained.

6. One disulfoxide was investigated. It was reduced with extraordinary ease by phosphorus tribromide.

7. In some cases where the reaction products, containing excess phosphorus tribromide, were decomposed with water and ether, the sulfonyl compounds were reduced to the thiophenols.

8. Addition of bromine to an apparently incompletely reacted mixture in the course of an Otto synthesis of a sulfinate gave a new mixed disulfoxide.

MINNEAPOLIS, MINNESOTA

ESSENTIAL OIL IN DESERT PLANTS. II. EXAMINATION OF THE OIL OF CHRYSOTHAMNUS NAUSEOSUS

BY MAXWELL ADAMS AND LEWIS KEHOE

In a former article by one of us[1] attention has been called to the occurrence and physical properties of the essential oil of *Chrysothamnus Nauseosus*. Coulter and Nelson[2] list eighteen species and four additional varieties of *Chrysothamnus* growing in the arid plateau region of the United States. This entire group of shrubs is known to the western stock men as "Fall Rabbit Brush." Some attention was called to this plant by the work of Hall,[3] who found considerable quantities of rubber in the stems of this shrub. In our former work we collected small samples of oil from carefully selected plants of the following varieties of *Chrysothamnus: nauseosus*,

[1] Adams, THIS JOURNAL, **49**, 2895 (1927).

[2] Coulter and Nelson, "Manual of Botany of the Central Rocky Mountain Region," page 494.

[3] Harvey M. Hall and Thos. H. Goodspeed, University of California publications in Botany.

naphalodes, viridulus, hololeucus and *mohavensis*, but since these varieties grow together and can be distinguished only with difficulty, no attempt was made to segregate them in this mass collection.   The raw material consisted chiefly of *nauseosus* yet small amounts of other species were present.   There is very slight variation in the physical properties of the oils from these varieties, and the general chemical composition is doubtless very similar.   The oil occurs chiefly in the leaves and small twigs.   None was detected in the roots.   The amount of oil present in a particular specimen of *Chrysothamnus* was determined by testing a sample gathered from the same plant each month during the year.   The portion gathered in February contained the least, 0.39%, and this amount increased until it reached a maximum in October when there was 0.98% present.   The amount of oil decreases when the autumn rains begin.   A sample from plants grown on moist ground at Berkeley, California, contained only 0.2% of oil.

One sample of the oil was obtained as follows: 20 kg. of leaves and stems was distilled with steam for about twenty-four hours under pressure of about 2 lb. ($1/8$ atm.) until no more oil came over.   The oil after separation was redistilled with steam and then dried over anhydrous sodium sulfate; 200 cc. of oil (sp. gr. 0.8651) was obtained corresponding to a material yield of 0.89%.   Refraction tests of this oil showed only carbon, hydrogen and oxygen.   The oil was insoluble in water and dilute acids, soluble to 2% in solutions of sodium acid sulfate, to 13% in dilute potassium hydroxide solution, and soluble in concentrated sulfuric acid to give a deep red color. It decomposes considerably when distilled at ordinary pressure, but gives a clear distillate at pressures below 100 mm.; 140 cc. of the oil distilled at 45 mm. gave fractions with the following properties.

Fraction	Range in temp., °C.	Yield, cc.	$d^{29°}$
1	90–100	60	1.4735
2	100–110	20	1.4781
3	110–167	30	1.4838
4	167–174	20	1.4970
5	174 (residue in flask)	10	1.5190

The lowest boiling fraction gave only the qualitative color test showing the presence of a small amount of α-pinene; 100 cc. of this fraction was oxidized with alkaline potassium permanganate according to the method of Wallach[4] and yielded nopinic acid which melted at 126°.   When the alkaline permanganate residue was steam distilled, 40 cc. of oil was recovered, showing roughly that 60% of the oil had been oxidized.   This indicates the presence of about 3% of β-pinene in the original oil.

The fraction boiling between 168 and 170° at 650 mm. was redistilled three times over metallic sodium until the boiling point was practically

[4] Wallach, *Ann.,* **245,** 251 (1888); *ibid.,* **356,** 229 (1907).

constant. The volume of the liquid thus obtained was composed of hydrocarbons. This fraction had a very strong odor of the oil of lemon and was tested for limonene. A bromine addition product was prepared which melted at 120°, indicating the presence of dipentene. The fraction however had a positive rotation of 59.4, which indicates the presence of limonene. Samples of *Chrysothamnus nauseosus* gathered at various places and at different seasons of the year showed great variation in the angle of rotation. Conditions under which the limonene tetrabromide will form do not appear to be well understood. Four fairly distinct methods have been recommended.[5] None of these methods gave uniformly dependable results. The following method gave us more satisfactory results than any of the above.

The oil to be tested is gently refluxed over metallic sodium for fifteen minutes and then distilled, preferably at reduced pressure, 10 to 20 mm. A second distillation over sodium is desirable. The fraction coming over between 172–178°, 760 mm. pressure, or a corresponding temperature at the reduced pressure, is then brominated as follows.

The fraction, or any part, is dissolved in an equal volume of ether. This terpene–ether solution is then added, drop by drop, to a well-cooled solution of bromine and ether. If all the bromine is not used up, more of the terpene–ether solution is prepared and added. If all the bromine is decolorized before all the terpene–ether solution is added, it is best to stop here and not attempt to add more bromine to the reaction mixture. The reaction mixture is placed at once in a desiccator, and by means of a suction pump the excess ether is boiled away. In the meantime the solution is kept cold. As the ether evaporates, the tetrabromide crystallizes out.

Fuchsine reagent shows an aldehyde present in the oil and it was separated by preparing the phenylhydrazone according to the usual method. After standing for several days clear white crystals, which may be washed free from the mother liquor with benzene, separated out. Recrystallized from alcohol the melting point was 126°. A small amount of the phenylhydrazone was hydrolyzed with concentrated hydrochloric acid, the product was evaporated to dryness, and the residue taken up with water. This water solution gave a strong aldehyde reaction with Tollens' reagent. From the amount, melting point, solubility and other properties of the phenylhydrazone it is concluded that the oil contains about 2% of cuminic aldehyde. About 20% of the oil of *Chrysothamnus nauseosus* has a boiling point of over 200° at ordinary pressure and 167° at 45 mm. pressure, which indicates the presence of sesquiterpenes. None were identified.

The results of the work outlined in this paper show that the essential oil of *Chrysothamnus nauseosus* contains about 3% β-pinene, 30 to 40% limo-

[5] Wallach, *Ann.*, **239**, 3 (1887); Baeyer and Villiger, *Ber.*, **271**, 448; Power and Kleber, *Arch. Pharm.*, **232**, 646 (1894); Godlewsky, *Chem.-Ztg.*, **22**, 827 (1898).

nene and dipentene, 2% cuminic aldehyde and 20% sesquiterpenes.   That dipentene has been converted into caoutchouc[6] gives some interest to the fact that these two substances occur together in *Chrysothamnus* and suggests the question, may not the one be changed into the other by the plant metabolism?

[6] Gildemeister and Hoffman, I, p. 312.

RENO, NEVADA

[CONTRIBUTION FROM THE OKLAHOMA A. AND M. COLLEGE]

IDENTIFICATION OF NITRILES. PREPARATION OF ALKYL (2,4,6-TRIHYDROXYPHENYL) KETONES BY THE HOESCH SYNTHESIS ON A SEMI-MICRO SCALE

BY HENRY P. HOWELLS AND J. GLENN LITTLE[1]

In a recent attempt to find an easier means of identifying alkyl cyanides, Shriner and Turner[2] treated them with the Grignard reagent to give liquid ketones, which were converted finally to solid semicarbazones.   Although the method has been found to be satisfactory when limited amount of starting material and time are not important factors, it was thought worth while to develop here a more rapid method in which very small amounts of nitriles could be used, as is recommended by Kamm, Mulliken[3] and others in qualitative organic analysis.

The present method adapts the Hoesch synthesis on a semi-micro scale, to give yields of products comparable to those described in the literature for similar preparations using much larger amounts of starting materials. Thus a small quantity of nitrile is combined with phloroglucinol to yield readily a solid phlorophenone in sufficient amount to make identification of the former very easy.

Experimental

A typical procedure for carrying out the modified Hoesch synthesis on a semi-micro scale is illustrated by the preparation of the new ketone in the series.

n-Butyl 2,4,6-Trihydroxyphenyl Ketone (Phloro-*n*-valerophenone), $C_6H_2(OH)_3$-COC_4H_9.—A solution of 0.006 mole of anhydrous phloroglucinol in about 25 cc. of dry ether was shaken up with 0.4 g. of pulverized, fused zinc chloride.   To this was added 0.01 mole of *n*-butyl cyanide and a steady stream of dry hydrogen chloride gas about saturated with ether was passed through the mixture.   After two to three minutes the

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[1] The experimental routine of this paper was carried out largely by Mr. J. Glenn Little during an advanced course in organic preparations at Oklahoma A. and M. College.

[2] Shriner and Turner, THIS JOURNAL, **52**, 1267 (1930).

[3] O. Kamm, "Qualitative Organic Analysis," J. Wiley and Sons, 1923; Mulliken, "Identification of Pure Organic Compounds," J. Wiley and Sons, N. Y., 1905.