

bromine was completed, 49 g. (0.50 mole) of maleic anhydride was added and the stirring was continued for one hour while the mixture was still immersed in the dry ice-methanol bath. The flask was then removed and, as the solution warmed to room temperature, it turned dark red. After two hours of boiling under reflux, the ether was evaporated, leaving a gummy red solid. Recrystallization removed the heavy red oil that resulted from decomposition of the bromination product. From acetic anhydride, the solid product, *sym*-octahydrophenanthrene-9,10-dicarboxylic anhydride (IV), separated as long colorless needles; from ethyl acetate as colorless platelets, m. p. 312° (Maquenne block) (lit., 310°).⁵ The over-all yield was 10 g. (16%).

Anal. Calcd. for C₁₆H₁₆O₃: C, 74.98; H, 6.29; mol. wt., 256; sap. eq., 128. Found: C, 75.12; H, 6.45; mol. wt., 285; sap. eq., 130.

The identity of the anhydride (IV) was further established by decarboxylation with soda lime followed by dehydrogenation with selenium to yield phenanthrene, which was identified by melting point and mixed melting point.

From an experiment identical with the above except that the bromine was omitted, the starting materials, 2-cyclohexylidene cyclohexanone and maleic anhydride, were recovered.

NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
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RECEIVED AUGUST 7, 1943

Identification of Alkylbenzenes. III. The Acetamino and Benzamino Derivatives of Isobutylbenzene

BY V. N. IPATIEFF AND LOUIS SCHMERLING

In previous papers¹ the characterization of all but one of the monoalkylbenzenes from toluene

the Fittig reaction between phenyl bromide and isobutyl bromide and in 10% yield by the reaction between benzylmagnesium chloride and isopropyl bromide (Table I). That very little or no isomerization occurred during the reactions was shown by the fact that both preparations yielded identical derivatives.

The derivatives were prepared by the procedure described in the previous papers. Their properties are given in Table II. Both the mono- and the diaminoisobutylbenzene could be isolated from a single nitration product, separation being effected as usual by extracting the tin salt of the monoamine with ether.

RESEARCH LABORATORIES

UNIVERSAL OIL PRODUCTS COMPANY

RIVERSIDE, ILL.

RECEIVED SEPTEMBER 4, 1943

The Preparation of 4'-Aminobenzanilide

BY CARL E. SPENCER

During recent synthetic work, 4'-aminobenzanilide was required. Methods previously described for its preparation using tin and hydrochloric acid¹ or iron and acetic acid² proved unsatisfactory because of undesirable by-products. It was found that it could be prepared readily in excellent yield and high purity from 4'-nitrobenzanilide by reduction with hydrogen using platinum black as a catalyst.

The 4'-nitrobenzanilide was prepared from *p*-nitroaniline (Eastman Practical grade) by the method of Lettré and

TABLE I
PREPARATION OF ISOBUTYL BENZENE

| Method | Reactants, g. | Conditions | | Yield, g. | Isobutylbenzene | |
|--------|---|------------|-----------|-----------|-----------------|------------|
| | | Temp. | Time, hr. | | B. p., °C. | n_D^{20} |
| A | C ₆ H ₅ Br, ^a 31; <i>i</i> -C ₄ H ₉ Br, 27; Na, 9 | Room | 24 | 8 | 164-170 | 1.4912 |
| B | C ₆ H ₅ CH ₂ MgCl, ^b 75; <i>i</i> -C ₄ H ₉ Br, 62 | Reflux | 120 | 7 | 166-170 | 1.4891 |

^a Dissolved in 50 cc. benzene. ^b Dissolved in 275 cc. ether.

TABLE II
DERIVATIVES OF ISOBUTYL BENZENE

| Derivative | M. p., °C. (uncor.) | Crystalline appearance | Nitrogen, % | |
|---|----------------------|------------------------|-------------|-------|
| | | | Calcd. | Found |
| <i>i</i> -C ₄ H ₉ C ₆ H ₄ NHCOCH ₃ ^a | 127-128 ^b | Pearly flakes | 7.33 | 7.23 |
| <i>i</i> -C ₄ H ₉ C ₆ H ₃ (NHCOCH ₃) ₂ | 210-211 ^c | White | 11.29 | 11.54 |
| <i>i</i> -C ₄ H ₉ C ₆ H ₂ NHCOC ₂ H ₅ | 128-129 ^d | Pearly flakes | 5.53 | 5.52 |

^a Hickinbottom and Preston, *J. Chem. Soc.* 1566 (1930); see, also, Hennion and Auspos, *THIS JOURNAL*, **65**, 1605 (1943). ^b Mixed m. p. (1:1 mixture) with monoacetamino-*s*-butylbenzene (m. p. 126°), 108-112°. ^c Mixed m. p. (1:1 mixture) with diacetamino-*t*-butylbenzene (m. p. 210°) 190-195°; with diacetamino-*n*-butylbenzene (m. p. 214°), 204-206°. ^d After recrystallization from hexane. The crude derivative was rather difficultly purified. Recrystallization from alcohol usually yielded material melting at about 118-122°.

through the eight amylbenzenes was described. The mono- and diacetamino and monobenzamino derivatives of the exception, isobutylbenzene, have since been prepared and are reported here in order to make the series complete.

Isobutylbenzene was prepared in 30% yield by

(1) Ipatieff and Schmerling, *THIS JOURNAL*, **59**, 1056 (1937); **60**, 1476 (1938).

Barnbeck³ with a yield of 72%, m. p. 197-198°. Twenty-four grams of it in 100 ml. of ethanol with 1 ml. of 0.1 *M* ferrous sulfate was added to platinum black prepared by the reduction of 0.1 g. of platinum oxide in 100 ml. of ethanol by hydrogen at 50 lb. pressure. The reaction

(1) Hübner, *Ann.*, **208**, 295 (1881); Rivier and Zeltner, *Helv. Chim. Acta*, **20**, 691-704 (1937).

(2) Morgan and Mecklethwait, *J. Chem. Soc.*, **87**, 933 (1905).

(3) Lettré and Barnbeck, *Ber.*, **71**, 1227 (1938).

bottle was then heated to 56° and hydrogen at 50 lb. pressure admitted, whereupon three molecular equivalents of hydrogen were absorbed in 7.6 minutes. The solution, after filtration from the catalyst and decolorization with charcoal, was allowed to crystallize; an additional crop of crystals being obtained after concentration of the mother liquor. The crops were combined and recrystallized from ethanol. The product melted sharply at 129° (cor.) and the yield was 19 g. (90%).

DEPARTMENT OF RESEARCH AND CONTROL
UNITED DRUG COMPANY
BOSTON, MASSACHUSETTS RECEIVED AUGUST 20, 1943

American Musk. II. A Preliminary Note on the Scent Glands of the Beaver

BY PHILIP G. STEVENS

The recent discovery¹ that cyclopentadecanol and cycloheptadecanol can be obtained in good yields from the scent glands of the common muskrat has prompted an investigation of the scent glands of the beaver. These glands, similar to those of the muskrat in function and shape, but considerably larger in size, have been used for years in the preparation of perfumes. While their odor is not musk-like, the presence of large ring carbinols has not been excluded, and a search for these compounds has now been made.

Walbaum and Rosental² studied the steam-distillable fraction of the glandular extract, and obtained therefrom benzyl alcohol, acetophenone, *p*-ethyl and other phenols, benzoic acid and *l*-borneol. St. Pfau³ confirmed these results in part, but isolated as well an odoriferous lactone of unknown structure, and more recently Yost⁴ obtained besides a resin, castorin, cholesterol and an unidentified volatile oil. None of these workers described any large ring compounds, but, since the extracts apparently were not saponified except possibly by Yost, these carbinols may have been overlooked, especially if present, as seems to be the case with 98% of the large ring compounds of the muskrat, as non-volatile esters. The results of saponification experiments described in this note indicate that no large ring carbinols or ketones are present in beaver scent glands. To be sure, the neutral, unsaponifiable fraction yielded a small amount of a viscous yellow oil on distillation with about the correct boiling point of a musk carbinol or ketone, but this oil had the composition $C_{11}H_{18}O_2$ and had a spicy odor, quite unlike musk. On oxidation with chromic acid, the oil gave a product with a cedar-like odor, with, however, no reminiscence of musk.

The acid fraction yielded benzoic acid, various phenolic substances, small amounts of anisic acid,⁵ and in addition an amorphous acid, insoluble in benzene and ether, tentatively called

(1) Stevens and Erickson, *THIS JOURNAL*, **64**, 144 (1942).

(2) Walbaum and Rosental, *J. prakt. Chem.*, **117**, 225 (1927).

(3) St. Pfau, *Perfumery and Essent. Oil Record*, **18**, 205 (1927).

(4) Yost, *C. A.*, **25**, 4131 (1932).

(5) I am indebted to Professor Werner Bergmann for help in the identification of the anisic acid.

castoric acid. Oddly there seemed to be few long chain fatty acids present. This fact coupled with the absence of musk bodies is in sharp contrast to the abundance of fatty acids in the glands of the musk-deer, the civet cat and the muskrat.

Experimental Part

Dried beaver castors (113 g., Fritsche Bros.) were sliced and extracted with ether, and insoluble tarry material was extracted with acetone (1.9 g. of yellow-brown crystalline material which separated from the acetone was not investigated). The solvents were removed from the combined extracts, the dark colored tarry residue (70 g.) was saponified with boiling 10% ethanolic potassium hydroxide, and the neutral products were separated from the acidic. The neutral, red oil (6.3 g.) yielded, after three fractional distillations, 1.5 ml. of a viscous, yellow, unsaturated (rapid bromine absorption from acetic acid) oil, b. p. 147–155° (1 mm.) with a spicy odor. *Anal.* Calcd. for $C_{11}H_{18}O_2$: C, 72.5; H, 9.9. Found: C, 72.4; H, 9.9. An oil (36.2 g.) similarly prepared from 913 g. of glands (Firmenich & Co.), yielded, after separation of a considerable amount of cholesterol, a distillate, b. p. 86–195° (10–1 mm.), which, combined with similar fractions, was distilled through an efficient column. No pure product was obtained in the range 111–146° (1 mm.) (both boiling point and viscosity increased gradually). The fraction, b. p. 132–141° (1 mm.), had a fine spicy odor, did not react with 2,4-dinitrophenylhydrazine, and on oxidation with chromic acid, gave a product with a strong cedar, but no musk, odor.

The alkaline solution from the saponification was acidified, the precipitated black-red oil extracted with ether, the ether extracted with sodium bicarbonate,⁶ the alkaline solution acidified, the liberated acids extracted with ether, and, after removal of the solvent, steam-distilled, yielding 21.5 g. of benzoic acid. The non-volatile residue was dissolved in a large excess of hot sodium carbonate, the cooled solution, after saturation with carbon dioxide, was filtered, and the acidified filtrate deposited a dark-colored precipitate which, centrifuged from benzene twice, yielded 36 g. of air-dried castoric acid as a light chocolate powder, insoluble in ether and benzene, but soluble in methanol.

The aqueous solution separated from the castoric acid was extracted with chloroform, the organic solvent removed, the residue steam-distilled, and the cooled aqueous solution of the non-volatile products deposited crystals which after treatment with norite and crystallization from benzene yielded anisic acid, m. p. 178–180° (a mixture with an authentic sample, m. p. 180–181°, melted at 178–180.5°).

(6) The separations were made difficult by the deposition of tars. There was however no troublesome frothing of any of the alkaline solutions, indicating the absence of any long chain fatty acids.

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NEW HAVEN, CONN. RECEIVED OCTOBER 15, 1943

Preparation of Malononitrile

BY ALEXANDER R. SURREY

Malononitrile can be prepared by the dehydration of cyanoacetamide with phosphorus pentachloride, by the fusion of the dry materials.¹ This method is not satisfactory for the preparation of large quantities of malononitrile inasmuch as very careful manipulation is needed to prevent the violent decomposition of the product during or before its distillation. The following more convenient method has now been perfected.

(1) Corson, Scott and Vose, "Organic Syntheses," **10**, 66 (1930).