4-(β-Diethylaminoethylamino)-phenyl 4-Nitrophenyl Sulfoxide Hydrochloride.—A solution of 3 g. of the base (I) in 50 ml. of glacial acetic acid and 1.5 ml. of 30% hydrogen peroxide was allowed to stand for twenty-four hours and was then heated on a steam-bath for thirty minutes. The reaction mixture was made alkaline with sodium hydroxide and extracted with ether. After drying and removing the ether, the residual oil was dissolved in absolute alcohol and treated with alcoholic hydrogen chloride; dry ether was then added to turbidity. On standing in the refrigerator an orange powder separated; yield, 1.7 g. After several recrystallizations from alcohol–ether, a product melting at 157–159° was obtained.

Anal. Calcd. for $C_{18}H_{24}N_3O_3ClS$: N, 10.56; Cl, 8.93. Found: N, 10.58, 10.34; Cl, 8.90, 9.06.

4-(β-Diethylaminoethylamino)-phenyl 4-Nitrophenyl Sulfone (II).—Sixty grams of β-diethylaminoethyl chloride and 28 g. of 4-nitrophenyl 4-aminophenyl sulfone was heated with stirring in 150 ml. of nitrobenzene at 120–130° for eight hours. The nitrobenzene was removed by steam distillation and the residue was made alkaline with sodium hydroxide and extracted with ether. The ether was dried and removed by distillation. The thick oily residue solidified on standing; yield 13.5 g. (35%). After several recrystallizations from alcohol, the sulfone was obtained in the form of light-yellow needles melting at 109°.

Anal. Calcd. for $C_{18}H_{23}N_3O_4S$: N, 11.14. Found: N, 11.18.

4-(β-Diethylaminoethylamino)-phenyl 4-Nitrophenyl Sulfone Hydrochloride.—A solution of II in ether was treated with alcoholic hydrogen chloride. The yellow solid which precipitated was recrystallized from absolute alcohol giving a product which melted at 190–192°.

Anal. Calcd. for $C_{18}H_{24}N_3O_4ClS$: N, 10.16; Cl, 8.58. Found: N, 10.42; Cl, 8.4.

RESEARCH LABORATORIES OF
WINTHROP CHEMICAL COMPANY, INC.
RENSSELAER, NEW YORK RECEIVED NOVEMBER 11, 1944

The Phenylhydrazone Hydrochloride and Some Substituted Phenylhydrazones of *d*-3-Methylcyclopentanone

BY G. H. STEMPEL, JR., W. O. FORSHEY, JR., AND GERSON S. SCHAFFEL

A survey of the literature has revealed that no phenylhydrazone of 3-methylcyclopentanone has been reported. It was therefore with some surprise that a white, crystalline precipitate was observed to form in a polarimeter tube in which the rate of the reaction of *d*-3-methylcyclopentanone with phenylhydrazine, in the presence of excess phenylhydrazine hydrochloride, was being studied by the method of Orning and Stempel.[1] Upon examination the precipitate proved to be the hydrochloride of *d*-3-methylcyclopentanone phenylhydrazone, the positive ion necessary for its formation resulting from the removal of a proton from the phenylhydrazonium ion by the phenylhydrazone. Attempts to prepare the phenylhydrazone itself from the salt were unsuccessful since the phenylhydrazone appears to be too unstable to handle, decomposing spontaneously and rapidly to give a tarry liquid. The hydrochloride is moderately stable when kept in contact with dilute hydrochloric acid solution, but decomposes slowly when dry.

A number of substituted phenylhydrazines were allowed to react with *d*-3-methylcyclopentanone, including the *p*-methoxy-, *p*-bromo-, *p*-nitro- and 2,4-dinitrophenylhydrazines. Of these only the *p*-nitro- and 2,4-dinitrophenylhydrazines yielded stable hydrazones.

Experimental

***d*-3-Methylcyclopentanone.**—This compound was prepared from *d*-pulegone by the following steps: (1) hydrolysis of *d*-pulegone to *d*-3-methylcyclohexanone by the method of Wallach[2]; (2) oxidation of the *d*-3-methylcyclohexanone to *d*-β-methyladipic acid by the method of Hartman[3]; and (3) cyclization of *d*-β-methyladipic acid, recrystallized several times from petroleum ether, to *d*-3-methylcyclopentanone by distilling with barium hydroxide according to the method of Thorpe and Kon.[4] The *d*-3-methylcyclopentanone prepared in this way had the following properties: b. p. 145° corrected to 760 mm., $[\alpha]^{27}_{\mathrm{D}}$ 153.28°, $[\alpha]^{27}_{5461}$ 190.98°, n^{27}_{D} 1.4282. The rotation of this preparation agrees well with that reported by Godchot, *et al.*,[5] for a sample prepared by cyclizing β-methyladipic acid with acetic anhydride: $[\alpha]^{20}_{\mathrm{D}}$ 152.84°, $[\alpha]^{20}_{5461}$ 188.88°, which in turn is considerably higher than rotations, $[\alpha]_{\mathrm{D}}$, reported by Zelinsky[6] (135.9°), Wallach[7] (132.96°), and Richaud[5] (130.09°). Godchot[5] reported that the *d*-3-methylcyclopentanone formed by cyclization of his *d*-β-methyladipic acid by distilling with barium carbonate, instead of acetic anhydride, had a rotation of only 146.30°, indicating that partial racemization had occurred during the cyclization. It appears that no racemization took place during the cyclization using barium hydroxide reported here.

***d*-3-Methylcyclopentanone Phenylhydrazone Hydrochloride.**—To a mixture of 1 ml. (approx. 0.01 mole) each of phenylhydrazine and *d*-3-methylcyclopentanone was added 1–2 drops of glacial acetic acid. The mixture was kept at or below room temperature by cooling. After five to ten minutes 5 ml. of 1:10 hydrochloric acid was added, followed by enough 95% alcohol (5–10 ml.) to bring about complete miscibility. Then 10 ml. of ether and 2 ml. of concentrated hydrochloric acid were added. When the solution was allowed to evaporate at room temperature, glistening white needles of the hydrochloride separated. The product was then filtered off, washed quickly with alcohol, then ether, and dried in a vacuum desiccator. It had no definite melting point, rapid decomposition beginning at 35–40°. The yield varied from 0.5 to 0.7 g. in different runs.

Anal. Calcd. for $C_{12}H_{17}N_2Cl$: C, 64.13; H, 7.63. Found: C, 64.21; H, 7.48.

The hydrochloride decomposed rapidly enough when dry so that all weighings for analyses had to be made in sealed tubes. The salt-like nature of the hydrochloride was shown by its instantaneous reaction in aqueous solution with silver nitrate to precipitate silver chloride and by the determination of its neutral equivalent by titration with standard sodium hydroxide. Calcd.: neutral equivalent, 224.74. Found: neut. equiv., 226 and 227.

Substituted Phenylhydrazones of *d*-3-Methylcyclopentanone.—The *p*-nitrophenylhydrazone, yellow needle, melting at 155°, and the 2,4-dinitrophenylhydrazones orange needles melting at 144.5–145.5°, were prepared by the methods given by Shriner and Fuson.[8] The melting

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(1) Orning and Stempel, *J. Org. Chem.*, **4**, 410 (1939).

(2) Wallach, *Ber.*, **28**, 1965 (1895).

(3) W. W. Hartman, "Organic Syntheses," Coll. Vol. I, 2nd Edition, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 19, Note 1.

(4) Thorpe and Kon, *ibid.*, p. 192.

(5) Godchot, Cauquil and Calas, *Bull. soc. chim.*, [5] **6**, 1357 (1939).

(6) Zelinsky, *Ber.*, **35**, 2489 (1902).

(7) Wallach, *ibid.*, **29**, 2965 (1896).

(8) Shriner and Fuson, "Identification of Organic Compounds," 2nd edition, John Wiley and Sons, Inc., New York, N. Y., 1940, pp. 142–143.

point of the *p*-nitrophenylhydrazone was depressed by the addition of pure *p*-nitrophenylhydrazine, m. p. 157°.

Anal. Calcd. for the *p*-nitrophenylhydrazone, $C_{12}H_{15}N_3O_2$: C, 61.78; H, 6.49. Found: C, 61.76; H, 6.48. Calcd. for the 2,4-dinitrophenylhydrazone, $C_{12}H_{14}N_4O_4$: C, 51.79; H, 5.07. Found: C, 51.82; H, 4.81.

Attempts to prepare the *p*-methoxy- and *p*-bromophenylhydrazones by similar methods were not successful.

The authors are indebted to Miss Joy Swan for some of the analyses.

DEPARTMENT OF CHEMISTRY
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RECEIVED NOVEMBER 24, 1944

Condensation of Chloromaleic Anhydride with Substituted Propenylbenzenes

BY MARTIN E. SYNERHOLM

The condensation of maleic anhydride with isosafrole to form 6,7-methylene-dioxy-3-methyl-1,2,3,4,-tetrahydronaphthalene-1,2-dicarboxylic acid anhydride has been reported by Hudson and Robinson.[1] They similarly condensed isosafrole with ethyl acetylenedicarboxylate, obtaining the corresponding 3,4-dihydronaphthalene derivative as the acid anhydride, m. p. 178°.

The latter compound has now been shown to form when chloromaleic anhydride is heated in xylene with isosafrole. Analogous compounds formed when chloromaleic anhydride was condensed with isoeugenol and 2-ethoxy-4-propenylphenol.

Experimental.—The procedures were similar for the three cases. Thirteen grams of chloromaleic anhydride, 15 g. of the propenyl compound, and 50 ml. of xylene were refluxed for six hours. The color turned to a bright red and hydrogen chloride was eliminated during the reaction. On cooling, the products crystallized from the xylene. The yields and properties are tabulated.

DERIVATIVES OF 3-METHYL-3,4-DIHYDRONAPHTHALENE-1,2-DICARBOXYLIC ACID ANHYDRIDE

Derivative	Yield, g.	Solvent	M. p., °C.	Formula	Analyses,[2] % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
6,7-Methylenedioxy	10	Benzene	176–177	$C_{14}H_{10}O_5$	65.1	65.0	3.91	3.95
6-Methoxy-7-hydroxy	9	Xylene	225–226	$C_{14}H_{12}O_5$	64.7	65.0	4.65	4.69
6-Ethoxy-7-hydroxy	6	Toluene	192–196	$C_{15}H_{14}O_5$	65.7	65.6	5.14	5.07

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(1) Hudson and Robinson, *J. Chem. Soc.*, 715 (1941).

(2) Analyses by Elisabeth Heber-Smith.

BOYCE THOMPSON INSTITUTE FOR PLANT RESEARCH, INC.
YONKERS 3, NEW YORK

RECEIVED NOVEMBER 7, 1944

COMMUNICATIONS TO THE EDITOR

TRIFLUOROACETIC ACID AS A CONDENSING AGENT

Sir:

I wish to report the use of trifluoroacetic acid as an agent for the condensation of acetic anhydride with anisole to produce *p*-methoxyacetophenone. The reaction proceeds well (63%, or 91% if allowance is made for recovered anisole) at moderate temperatures (60–70°). Trifluoroacetic acid has several advantages over other reagents commonly employed for such condensations: there is no demethylation of anisole or the product; there is little if any heat of reaction so that all reagents may be mixed at one time; no stirring is required; no corrosive gases are used or formed; the trifluoroacetic acid may be recovered.

Procedure.—On mixing 15 g. of anisole, 14.8 g. of anhydrous trifluoroacetic acid, and 27 g. of acetic anhydride, heat (of mixing) was evolved and a pink color was produced. On warming to 60–70° the color deepened into cherry red. After six hours at 60–70° the mixture was poured into water. The acids were removed by shaking with water and the organic layer was extracted with alkali, but no phenol or *p*-hydroxyacetophenone was found. On vacuum distillation there were isolated 4.7 g. (31%) of anisole and 13.1 g. (63%) of *p*-methoxyacetophenone, b. p. 134–137 at 15–16 mm. This material crystallized and melted over the range 30–36°. The crude semicarbazone formed in 76% yield melted at 193–195°. On recrystallization it melted at 195.6–197.0° cor. These facts indicate that almost pure para derivative was produced.[1] The mixed melting point with purified semicarbazone from commercial *p*-methoxyacetophenone (Eastman Kodak Co.) was not depressed. In a similar experiment, except that the reaction was carried out at 110–125°, a much smaller yield of ketone was obtained as tars were formed.

I have also used trichloroacetic acid[2] in a similar manner, but it is less desirable than trifluoro-

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(1) Wahl and Silberzweig, *Bull. soc. chim.*, [4] **11**, 69 (1912), give 36°, 197°, of 138–139° as melting points of ketone and semicarbazone and boiling point of ketone at 15 mm.

(2) Unger, *Ann.*, **504**, 269 (1933).