Aminomethyl-1,4-dioxane.—A modified procedure of Amundsen and Nelson[4] was used; 7.6 g. (0.2 mole) of lithium aluminum hydride was crushed under dry ether and refluxed with stirring in 400 ml. of dry ether for two hours. After cooling the mixture to 0°, 22.6 g. (0.2 mole) of cyano-1,4-dioxane in 40 ml. of dry ether was added dropwise over 0.5 hour. After an additional 0.5 hour, 8 ml. of water was added, then 6 ml. of 6 *N* sodium hydroxide, and finally 28 ml. of water. The ether solution was decanted into a fluted filter, the residual salts refluxed briefly with two 100-ml. portions of ether, and the combined ether solution dried over anhydrous sodium sulfate. Removal of the ether and fractionation of the residual oil under reduced pressure gave 9.9 g. (42%) of a colorless water-soluble liquid with a strong ammonia odor, boiling at 84° (18 mm.), n^{20}_{D} 1.4660, d^{20}_{4} 1.0798.

Anal. Calcd. for $C_5H_{11}O_2N$: C, 51.26; H, 9.45; *MR*, 29.80. Found: C, 51.03; H, 9.78; *MR*, 30.02.

The product reacted with benzenesulfonyl chloride (Hinsberg test), giving N-(dioxanylmethyl)-benzenesulfonamide. The amide melted at 77–78° and crystallized as needles from alcohol.

Anal. Calcd. for $C_{11}H_{15}O_4NS$: N, 5.45. Found: N, 5.39.

N-(Dioxanylmethyl)-4-aminobenzenesulfonamide.—19.8 g. (0.085 mole) of *p*-acetamidobenzenesulfonyl chloride was added slowly to a solution of 9.9 g. (0.085 mole) of aminomethyl-1,4-dioxane in 13.6 g. (0.17 mole) of anhydrous pyridine. The mixture, heated at 100° for one hour and then poured into 85 ml. of water acidified with hydrochloric acid, gave 18.6 g. of crude product melting at 72–73° after crystallization from water. The material was refluxed for 1.5 hours with 100 ml. of 2 *N* sodium hydroxide, filtered, and the filtrate neutralized with concentrated hydrochloric acid. Upon cooling, the oil gave a yellow solid which was crystallized from 500 ml. of hot water containing decolorizing charcoal. The product, separating as fine white flakes, weighed 10 g. (43%), melted at 98–101° (but not to a clear liquid) and decomposed at 205°.

Anal. Calcd. for $C_{11}H_{16}O_4N_2S$: C, 48.53; H, 5.93; S, 11.77. Found: C, 48.60; H, 6.07; S, 11.82.

---

[4] L. H. Amundsen and L. S. Nelson, This Journal, **73**, 242 (1951).

DEPARTMENT OF CHEMISTRY
WHEATON COLLEGE
WHEATON, ILLINOIS

Synthesis of 2-Methyl-5-*t*-butylacylbenzenes

BY E. EARL ROYALS AND RAJ NANDAN PRASAD[1]

RECEIVED SEPTEMBER 20, 1954

During the course of the present investigation, it was shown by Taylor and Watts[2] that direct Friedel-Crafts acetylation of *p*-*t*-butyltoluene leads to a rearranged product, probably 2-methyl-4-*t*-butylacetophenone. This has been confirmed in our own experience, and we have demonstrated that the use of a low reaction temperature does not prevent the rearrangement. Acetylation of *p*-*t*-butyltoluene with acetyl chloride and aluminum chloride in carbon disulfide at −20 to −30° led to the formation of an acyl derivative in 57% yield. This acyl derivative gave a semicarbazone melting at 197°, while the semicarbazone of 2-methyl-5-*t*-butylacetophenone (prepared as described below) melts at 183°; a mixture of the two semicarbazones melted at 156–160°. Taylor and Watts also report[2] a melting point of 197° for the semicarbazone of their acetyl derivative of *p*-*t*-butyltoluene. Hence, other methods were investigated for the synthesis of pure 2-methyl-5-*t*-butylacylbenzenes.

Chloromethylation of *t*-butylbenzene gave *p*-*t*-butylbenzyl chloride in 70% yield. Reaction of the Grignard reagent from *p*-*t*-butylbenzyl chloride with acetic anhydride gave[3] 2-methyl-5-*t*-butylacetophenone in 19% yield. This product gave a semicarbazone, m.p. 183°, which did not depress the m.p. of the semicarbazone of authentic 2-methyl-5-*t*-butylacetophenone prepared as described below; it did, however, markedly depress the m.p. of the semicarbazone of the product of direct actylation of *p*-*t*-butyltoluene. The reaction of *p*-*t*-butylbenzylmagnesium chloride with acetic anhydride also led to the formation of 12% of a second unidentified ketone, m.p. of semicarbazone 144–145°, and a small amount of 1,2-di-(*p*-*t*-butylphenyl)-ethane, m.p. 149°. This latter product was produced in 57% yield by coupling *p*-*t*-butylbenzylmagnesium chloride in the presence of silver bromide according to the procedure of Gardner and Borgstrom.[4]

Bromination of *p*-*t*-butyltoluene in the presence of iodine as catalyst gave 2-methyl-5-*t*-butylbromobenzene in 73% yield.[2] Carbonation of the Grignard reagent of this halide gave 2-methyl-5-*t*-butylbenzoic acid, m.p. 98°.[5] Reaction of 2-methyl-5-*t*-butylphenylmagnesium bromide with acetic anhydride at −35 to −50° according to the procedure of Newman and Booth[6] gave 2-methyl-5-*t*-butylacetophenone in 36% yield. The structure of this product was proved by hypohalite oxidation to the known[5] 2-methyl-5-*t*-butylbenzoic acid, m.p. 98°; the ketone gave a semicarbazone, m.p. 183°, identical with that of the product of reaction of *p*-*t*-butylbenzylmagnesium chloride with acetic anhydride. A more satisfactory and convenient procedure for the preparation of 2-methyl-5-*t*-butylacetophenone proved to be the organocadmium procedure of Gilman and Nelson.[7] 2-Methyl-5-*t*-butylphenylmagnesium bromide was converted to the corresponding organocadmium reagent and caused to react with the appropriate acyl halide to give the series of 2-methyl-5-*t*-butylacylbenzenes reported in Table I.

Experimental[8]

Chloromethylation of *t*-Butylbenzene.[9]—*t*-Butylbenzene, 134 g. (1 mole), was mixed with 120 g. of formalin, 36 g. of concd. hydrochloric acid, 68 g. (0.5 mole) of anhydrous zinc chloride and 10 g. of trioxymethylene. Dry hydrogen chloride was bubbled into the mixture with stirring; a temp. of 75–82° was maintained during a reaction period of 27 hours. The reaction mixture was poured into 500 ml. of ice-water, the organic layer was separated, and the aqueous layer extracted five times with 50-ml. portions of ether. The ether extracts and organic layer were combined and washed successively with cold water, 5% aqueous sodium carbonate solution, and again with cold water. The ethereal solution was dried over anhydrous sodium sulfate, the ether was distilled off, and the residue was distilled to give

---

[1] Abstracted from a thesis presented by R. N. Prasad to the Graduate Faculty of Emory University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1954.

[2] E. P. Taylor and G. E. Watts, *J. Chem. Soc.*, 1123 (1952).

[3] Compare P. R. Austin and J. R. Johnson, This Journal, **54**, 647 (1932) for similar reactions of benzylmagnesium chloride.

[4] J. H. Gardner and P. Borgstrom, *ibid.*, **51**, 3375 (1929).

[5] Taylor and Watts, ref. 2, report 101° as the m.p. of this acid; we were unable to raise our m.p. by repeated crystallizations.

[6] M. S. Newman and H. T. Booth, Jr., This Journal, **67**, 154 (1945).

[7] H. Gilman and J. F. Nelson, *Rec. trav. chim.*, **55**, 518 (1936).

[8] M.p.'s were determined in capillary tubes and are uncorrected.

[9] *Cf.*, A. Levy and C. Darzens, *Compt. rend.*, **199**, 1426 (1934); R. Berg, *Roczniki Chem.*, **14**, 1249 (1934); G. S. Skinner, J. A. Gladner and R. F. Heitmiller, This Journal, **73**, 2230 (1951).

TABLE I

SYNTHESIS OF 2-METHYL-5-*tert*-BUTYLACYLBENZENES BY REACTION OF DI-(2-METHYL-5-*t*-BUTYLPHENYL)-CADMIUM WITH ACYL CHLORIDES

Acyl group	Yield of product[a]	B.p. °C.	B.p. Mm.	$n^{24}\mathrm{D}$	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Acetyl[b]	40	140	18	1.5127	82.06	82.00	9.53	9.47
Propionyl[c]	37	148	18	1.5080	82.30	82.21	9.87	9.69
Isobutyryl[d]	68	103	2.4	1.5009	82.51	82.17	10.16	9.91
Pivaloyl[d]	52	122–123	3	1.4934	82.70	82.73	10.41	10.11

[a] Calcd. on the basis of acyl halide used. [b] M.p. of semicarbazone, 183°. *Anal.* Calcd. for $C_{14}H_{21}N_3O$: C, 67.98; H, 8.56; N, 16.99. Found: C, 67.91; H, 8.42; N, 17.00. [c] M.p. of semicarbazone, 146.5–147°. *Anal.* Calcd. for $C_{15}H_{23}N_3O$: N, 16.08. Found: N, 16.05. [d] These ketones failed to give crystalline semicarbazones.

90 g. of *p-t*-butylbenzyl chloride, b.p. 110–115° (6–7 mm.). Taking into account 40 g. of recovered *t*-butylbenzene, the yield of *p-t*-butylbenzyl chloride was 70%. The reaction was repeated seven times, and the combined product was carefully distilled through a 3-ft. column packed with glass helices to give pure *p-t*-butylbenzyl chloride, b.p. 88–89° (3 mm.) (reported 119–121° (16.5 mm.)[9c]), $n^{24}\mathrm{D}$ 1.5194. Oxidation of a sample of this material with concd. nitric acid gave *p-t*-butylbenzoic acid, m.p. 164°.[10]

p-t-**Butyltoluene** was prepared by the method of Verley[11] and the combined product of several runs was fractionally distilled through a 1.2 g. × 90 cm. Todd column packed with Podbielniak "Heli-Pak" to give pure *p-t*-butyltoluene, b.p. 106° (55 mm.), $n^{20}\mathrm{D}$ 1.4919. Oxidation of a sample of this material with concd. nitric acid gave *p-t*-butylbenzoic acid, m.p. 164°.[10]

Acetylation of *p-t*-Butyltoluene.—This reaction was carried out essentially as described by Taylor and Watts,[2] except that a reaction temperature of −8 to −5° was used. The major product obtained was probably 2-methyl-4-*t*-butylacetophenone, b.p. 90° (1 mm.), $n^{25}\mathrm{D}$ 1.5191, m.p. of semicarbazone, 197°.

Bromination of *p-t*-Butyltoluene.—This bromination was effected essentially as described by Taylor and Watts.[2] 2-Methyl-5-*t*-butylbromobenzene, b.p. 97–98° (4 mm.), $n^{25}\mathrm{D}$ 1.5323, was obtained in 73% yield.

Reaction of *p-t*-Butylbenzylmagnesium Chloride with Acetic Anhydride.—*p-t*-Butylbenzyl chloride, 91 g. (0.5 mole), in 300 ml. of dry ether was added dropwise during four hours to 12.2 g. (0.5 mole) of magnesium turnings in 100 ml. of dry ether. The reaction was carried out under nitrogen. The reaction mixture was stirred for three hours under reflux, and allowed to stand overnight. The resulting Grignard solution was pumped under nitrogen to a separatory funnel and added during two hours to a stirred solution of 153 g. (1.5 moles) of acetic anhydride in 200 ml. of dry ether. Stirring was continued for four hours under reflux. The reaction mixture was treated with ice-cold dilute hydrochloric acid; the organic layer was separated, washed successively with water, 10% aqueous sodium bicarbonate, 10% aqueous sodium carbonate, water, and finally dried over anhydrous potassium sulfate. The ether was removed, and the product fractionally distilled through a Todd column with monel spiral packing. In addition to 7 g. of *p-t*-butyltoluene, two reaction products were isolated: (a) 18 g., b.p. 92–95° (2.2 mm.), $n^{24}\mathrm{D}$ 1.5115; (b) 11 g., b.p. 97° (2.2 mm.), $n^{24}\mathrm{D}$ 1.5048. Fraction (a) gave a semicarbazone, m.p. 183°. A mixed m.p. with the semicarbazone of 2-methyl-5-*t*-butylacetophenone was 183°, while that with the semicarbazone of 2-methyl-4-*t*-butylacetophenone was 155–160°. *Anal.* Calcd. for $C_{13}H_{21}N_3O$: C, 67.98; H, 8.56; N, 16.99. Found: C, 67.91; H, 8.42; N, 17.00.

Fraction (b) gave a semicarbazone, m.p. 144–145°. A mixed m.p. with the semicarbazone of fraction (a) was 125–130°. This ketone has not been identified.

A solid residue from the above fractional distillation, 15 g., after two crystallizations from acetone gave 1,2-di-(*p-t*-butylphenyl)-ethane, m.p. and mixed m.p. with an authentic sample, 149°.

Preparation of 1,2-Di-(*p-t*-butylphenyl)-ethane.—This compound was prepared according to the procedure of Gardner and Borgstrom.[4] The product was obtained in 57% yield, m.p. 149°. *Anal.* Calcd. for $C_{22}H_{30}$: C, 89.73; H, 10.27. Found: C, 89.92; H, 10.11.

Reaction of 2-Methyl-5-*t*-butylphenylmagnesium Bromide with Acetic Anhydride.—A Grignard reagent was prepared in the usual manner from 113.5 g. (0.5 mole) of 2-methyl-5-*t*-butylbromobenzene and 12.2 g. (0.5 mole) of magnesium turnings in 300 ml. of dry ether. Sixty ml. of this solution was dropped over an excess of Dry Ice. Hydrolysis of the resulting complex gave 17 g. (88%) of crude 2-methyl-5-*t*-butylbenzoic acid. Two crystallizations from aqueous alcohol gave 9.6 g. of the acid melting sharply at 98°. This m.p. could not be raised by recrystallization.[5]

The remainder of the Grignard solution was caused to react with acetic anhydride according to the procedure of Newman and Booth.[6] The temperature of the reaction mixture was difficult to control, and rose from −50 to −35° before addition of the Grignard solution was complete. Distillation of the product gave 40 g. (53%) of 2-methyl-5-*t*-butylacetophenone, b.p. 110–115° (7 mm.). Redistillation through a Todd column with monel spiral packing gave 26.8 g. of the ketone, b.p. 135° (13 mm.), $n^{25}\mathrm{D}$ 1.5124. This ketone gave a semicarbazone, m.p. 182–183°.

Synthesis of 2-Methyl-5-*t*-butylacylbenzenes by the Organocadmium Procedure.[7]—The following preparation of 2-methyl-5-*t*-butylacetophenone is typical.

To the Grignard reagent, prepared as usual from 113.5 g. (0.5 mole) of 2-methyl-5-*t*-butylbromobenzene and 12.2 g. (0.5 mole) of magnesium turnings in 260 ml. of dry ether, was added 49.6 g. (0.27 mole) of anhydrous cadmium chloride at a temperature below 13° during a period of 45 minutes. The ether was distilled off and replaced by 200 ml. of dry benzene. The temperature was slowly raised to 80°, at which time a Gilman test was faintly positive. The reaction mixture was cooled to 20°, and a solution of 36 g. (0.46 mole) of acetyl chloride in 150 ml. of dry benzene was added during 45 minutes. The reaction mixture was slowly heated to reflux and maintained at that temperature for one hour and 40 minutes. The reaction mixture was worked up as directed by DeBenneville.[7] Distillation of the product gave 34.8 g. of 2-methyl-5-*t*-butylacetophenone having the properties recorded in Table I.

The other 2-methyl-5-*t*-butylacylbenzenes reported in Table I were similarly prepared by use of the appropriate acid chloride.

DEPARTMENT OF CHEMISTRY
EMORY UNIVERSITY
EMORY UNIVERSITY, GEORGIA

---

[10] Reported, K. T. Serijan, H. F. Hipsher and L. C. Gibbons, THIS JOURNAL, **71**, 873 (1949), m.p., 165.0–165.6°; m.p. of *m-t*-butylbenzoic acid, 127.0–127.6°.

[11] A. Verley, *Bull. soc. chim.*, [3] **19**, 67 (1898).

Synthesis of β-Methylcinnamaldehyde

BY E. EARL ROYALS AND E. R. COVINGTON

RECEIVED OCTOBER 16, 1954

The similarity of β-methylcinnamaldehyde to citral in molecular weight and certain structural features suggested that it might possibly possess a lemon-like odor. Consequently, we undertook to prepare the compound in sufficient quantity to permit purification and determination of its organoleptic properties. A synthesis of β-methylcinnamaldehyde was first reported by Rupe and Geisler[1] by Rupe rearrangement of methylphenylethy-

---

[1] H. Rupe and L. Geisler, *Helv. Chim. Acta*, **11**, 656 (1928).