solution was filtered and treated with dry acetylene under a pressure of 10 cm. of mercury.[10] The precipitate of acetylide was collected on a fluted filter and after washing three times with 10 ml. of alcohol crystallized twice from *n*-propanol. The filtrate from the reaction mixture on standing lost acetylene and, due to the decomposition of the monoalkylmercuri acetylide, deposited more of the bis compound.

Analysis of Compounds.—Decyl mercury bromide was analyzed according to the method of White.[11] Calcd. for $C_{10}H_{21}HgBr$: Hg, 47.56. Found: Hg, 47.40. The acetylides were decomposed by White's process[11] and the mercury determined by the volumetric procedure of Rupp.[12] Results are listed in Table I.

Summary

1. Decyl mercury bromide and four new bisalkylmercury acetylides have been prepared and their melting points reported.

2. *n*-Propanol has been found to be a suitable medium from which to crystallize members of the bisalkylmercury acetylide series.

3. The melting point curves of the dialkynyl mercurys and the bisalkylmercury acetylides are very similar and lie approximately 29° apart.

4. The values for the melting points of the alkyl mercury bromides as high as the decyl member have been determined on pure samples. The melting point curve shows a small but regular alternation.

5. A simplified procedure for the preparation of straight chain alcohols has been reported.

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(10) Vaughn, *ibid.*, **9**, 528 (1932).

(11) White, THIS JOURNAL, **42**, 2359 (1920).

(12) Rupp, *Chem.-Ztg.*, **32**, 1077 (1908).

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Preparation of *tert*-Butylacetic Acid and its Derivatives

BY AUGUST H. HOMEYER[1] WITH FRANK C. WHITMORE AND
V. H. WALLINGFORD

This study was undertaken because of our interest in compounds containing the neopentyl group.[2]

No significant information is available on the preparation, properties or derivatives of *tert*-butylacetic acid. Although it has been reported[3] several

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(1) Mallinckrodt Research Fellow.

(2) Whitmore and co-workers, THIS JOURNAL, 1932–1933.

(3) (a) Delacre [*Bull. sci. acad. roy. Belg.*, 7–41 (1906); *Chem. Zentr.*, I, 1233 (1906); *J. Chem. Soc.*, **90** [I], 476 (1906)] by oxidation of 3,3-dimethylbutanol-1; (b) Ozanne and Marvel [THIS JOURNAL, **52**, 5270 (1930)], by ozonolysis of 2-bromo-4,4-dimethylpentene-1; (c) McCubbin and Adkins, [*ibid.*, **52**, 2549 (1930)] by oxidation of 4,4-dimethylpentanone-2. (d) McCubbin [*ibid.*, **53**, 357 (1931)] by oxidation of dineopentyl ketone. (e) Whitmore and Church, [*ibid.*, **54**, 3710 (1932)] by ozonolysis of 2,4,4-trimethylpentene-1; (f) Favorsky and Opel [*J. Russ. Phys.-Chem. Soc.*, **50**, 34–80 (1918); *Chem. Abstracts*, **18**, 2498 (1924)] by oxidation of *tert*-butylallene; (g) Favorsky and Morew [*J. Russ. Phys.-Chem. Soc.*, **50**, 571–581 (1918); *Chem. Abstracts*, **18**, 2496 (1924); *Chem. Zentr.*, III, 998 (1923)] by oxidation of *tert*-butylacetylene.

times, its formation resulted from reactions unsuited for its preparation in quantity and high purity, and only two derivatives[4] have been prepared from it. Difficulty in its synthesis arises from the failure[5] of *tert*-butyl halides to react satisfactorily with the sodium derivatives of malonic or acetoacetic esters and the non-availability and non-reactivity of neopentyl halides.[6]

tert-Butylacetic acid is readily prepared in 80–90% yield by degradation of 4,4-dimethylpentanone-2 with sodium hypobromite. Since the ketone may enolize in two ways, it is surprising that halogenation is limited to the methyl group.[7] This fact suggests that the hydrogen atoms of the neopentyl group are closely held.

Although *tert*-butylacetic acid contains a neopentyl group it shows no abnormalities in its reactions. Ethyl *tert*-butylacetate yields the amide by ammonolysis in contrast to ethyl trimethylacetate[8] which does not undergo this reaction. The Hofmann rearrangement[9] of *tert*-butylacetamide gives neopentylamine. Neopentyl cyanide is obtained from the amide by action of phosphorus oxychloride.

Since the bromination of acids and acyl halides takes place through enolization[10] followed by addition, no rearrangement would be expected to occur. The bromination of *tert*-butylacetic acid and its acid chloride yields the corresponding α-bromo compounds. No rearranged products were found. α-Bromo-*tert*-butylacetic acid has been reported as having been prepared from a compound believed to be α-bromo-*tert*-butylmalonic acid.[11] The product melted at 57° whereas α-bromo-*tert*-butylacetic acid prepared by the present method melts at 72–73°. Attempts by Richard[12] to prepare α-halogenated acids from α-hydroxy-*tert*-butylacetic acid and its esters by the action of phosphorus halides failed, probably due to the formation of stable esters of phosphorus acids.

The replacement of the bromine of α-bromo-*tert*-butylacetamide by hydrogen through the action of zinc and acetic acid gave *tert*-butylacetamide quantitatively.[13]

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(4) The *p*-bromophenacyl ester, m. p. 81–81.5°; Ref. 3b. The amide, m. p. 132°; Refs. 3c, d, e.

(5) Unpublished work of W. R. Trent of this Laboratory. Also, *tert*-butylmagnesium chloride does not react satisfactorily with ethylene oxide to give 3,3-dimethylbutanol-1, which might be oxidized to the corresponding acid. Abderhalden and Rossner obtained some *tert*-butylmalonic ester by the reaction of *tert*-butyl bromide with sodiomalonic ester at room temperature, *Z. physiol. Chem.*, **163**, 177 (1927).

(6) Whitmore and Fleming, THIS JOURNAL, **54**, 3460 (1932); **55**, 4161 (1933).

(7) *Cf.* Hurd and Thomas, *ibid.*, **55**, 1646 (1933).

(8) The statement made by Bannow in a note to a paper by E. Fischer and Dilthey [*Ber.*, **35**, 856 (1902)] that ethyl trimethylacetate does not yield the amide when heated with alcoholic ammonia has been confirmed in this Laboratory.

(9) Whitmore and Homeyer, THIS JOURNAL, **54**, 3435 (1932).

(10) Watson, *Chem. Rev.*, **7**, 173–201 (1930).

(11) Abderhalden and Rossner, *Z. physiol. Chem.*, **163**, 177 (1927).

(12) Richard, *Ann. chim. phys.*, [8] **21**, 402 (1910).

(13) *Cf.* Bougault [*ibid.*, [9] **5**, 341 (1916)] who prepared α,α-dibromo-*tert*-butylacetamide by an indirect method and reduced it to *tert*-butylacetamide with zinc and acetic acid.

Experimental

4,4-Dimethylpentanone-2.—This material was prepared by W. R. Trent from diisobutylene by oxidation with sodium dichromate and sulfuric acid;[14] b. p. 124–125° (733 mm.); n^{20}_{D} 1.4028.

tert-**Butylacetic Acid.**—One kg. of finely crushed ice and a solution of 525 g. of sodium hydroxide in 2 liters of ice water were placed in a 5-liter 3-necked flask fitted with a mercury-sealed stirrer, thermometer and dropping funnel. The flask was cooled in a large bath of ice and salt water. Two hundred forty cc. of bromine (4.75 moles) was added from the dropping funnel during one hour to the stirred sodium hydroxide solution. As soon as the sodium hypobromite solution had been prepared, 171 g. of 4,4-dimethylpentanone-2 was added during about ten minutes. The solution was stirred for fourteen hours; then the mixture was steam distilled. Stirring was continued during distillation to prevent bumping. The distillate amounted to about 600 cc. of water and 175 g. of a mixture of bromoform and carbon tetrabromide. The residue from the steam distillation was acidified by addition of 600 cc. of concentrated sulfuric acid (excess) from the dropping funnel, the delivery tube of which dipped below the surface of the stirred liquid. The *tert*-butylacetic acid was steam distilled; the distillate amounted to about 1100 cc. The oil layer was separated (weight 151 g.) and the aqueous layer was extracted with 200 cc. of ether. After evaporating the ether the extracted material amounted to 17 g. and was added to the main portion. The product was dried and purified by distillation at reduced pressure through a 70 × 1 cm. indented column of the total condensation, adjustable take-off type.[15] The yield was 155 g. of *tert*-butylacetic acid or 89% of the theoretical. Its properties[16] are: b. p. 96° (26 mm.); 183.0–183.3° (739 mm.) (Cottrell); m. p. 6–7°; n^{20}_{D} 1.4096; d^{20}_{4} 0.9124; M.R. found (Lorentz–Lorenz formula): 31.48; calcd. (Eisenlohr values): 31.46.

The sodium salt crystallized in plates from alcohol on dilution with ether. *Anal.* Calcd. for $C_6H_{11}O_2Na$: Na, 16.65. Found: Na, 16.59.

The calcium salt is not very soluble in either hot or cold water. *Anal.* Calcd. for $C_{12}H_{22}O_4Ca$: Ca, 14.82. Found: Ca, 14.81.

tert-**Butylacetyl chloride** was prepared by means of thionyl chloride in 93% yield; b. p. 79–81° (150 mm.); n^{20}_{D} 1.422; d^{20}_{4} 0.968; M.R. found: 35.2, calcd. 34.8.

tert-**Butylacetamide** was obtained in 82% yield from the acid chloride and aqueous ammonia below 10°. *tert*-Butylacetamide crystallized in large colorless plates on the addition of petroleum ether to its solution in ethyl acetate, m. p. 132°.

Five cc. of ethyl *tert*-butylacetate sealed in a tube with 20 cc. of absolute alcohol saturated with ammonia at 0° yielded no amide after standing at room temperature for five months. Four grams of the original ester separated from the ammoniacal solution when it was diluted with water. Five cc. of ethyl *tert*-butylacetate sealed in a tube with 10 cc. of concentrated aqueous ammonia showed no signs of reaction after standing at room temperature for four months. Heating at 100° for twenty-three hours caused no change but after heating at 150–170° for ten days the ester layer had disappeared completely and 1.1 g. of *tert*-butylacetamide, m. p. 131–131.5°, and about 2 cc. of *tert*-butylacetic acid were isolated.

A tube containing 5 cc. of ethyl trimethylacetate and 20 cc. of absolute alcohol saturated with ammonia at 0° was kept at room temperature for five months and then

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(14) See Butlerow, *Ann.*, **189**, 46–83 (1877). Some of the earlier batches of ketone were made by ozonolysis of 2,4,4-trimethylpentene-1; *cf.* Ref. 3e.

(15) Whitmore and Lux, THIS JOURNAL, **54**, 3451 (1932).

(16) The boiling points given in the literature (Ref. 3) for *tert*-butylacetic acid vary from 175 to 190° and the freezing point according to Delacre (Ref. 3a) is −11°. The values given in "International Critical Tables," Vol. I, p. 203, b. p. 190°, m. p. −11°, appear to be based on Delacre's work.

was heated at 100° for seventeen hours. The product yielded 4 g. of the original ester but no amide was detected. In a similar experiment the tube was heated at 190° for sixty hours. A crystalline mass was obtained which disappeared completely when 10 cc. of water was added. Further dilution gave 3 g. of the original ester but no amide could be isolated. In a third experiment with ethyl trimethylacetate and methyl alcoholic ammonia the tube was heated at 200° for twenty-four hours. The crystalline mass was filtered off before adding water. It quickly evaporated from the suction filter. No amide could be detected.

tert-**Butylacetdiethylamide** was obtained in 79% yield as a viscous oil, b. p. 69° (3 mm.); n^{20}_{D} 1.4438.

tert-**Butylacetanilide** separated from ethyl acetate and petroleum ether as yellow crystals, m. p. 130°. It was decolorized by boiling its alcoholic solution with bone char and crystallized on diluting with water in small needles, m. p. 131°. *tert*-Butylacetanilide did not darken after keeping for six months. When mixed with *tert*-butylacetamide, m. p. 132°, the melting point was depressed to 100–105°.

tert-**Butylacetonitrile.**—Fifty-eight grams of *tert*-butylacetamide was made into a paste with 100 cc. of dry benzene and warmed on the steam-bath for twelve hours with 45 g. of phosphorus oxychloride. The liquid was decanted from the sludge, washed with water, with sodium bicarbonate solution and again with water and fractionated through a 30 × 1 cm. indented column. The yield of neopentyl cyanide was 44 g. or 90%; b. p. 135–136.4° (737 mm.); m. p. 32.5°.

Esters of *tert*-**Butylacetic Acid.**—*tert*-Butylacetyl chloride was added slowly to the pure alcohols. After warming on the steam-bath for a short time the product was washed with water, sodium bicarbonate solution, dried and fractionated. The yields were practically quantitative.

PROPERTIES OF *tert*-BUTYLACETATES

	B. p., °C. (mm.)	n^{20}_{D}	d^{20}_{4}	MR (obs.)	MR (calcd.)
Methyl	126.5 (739)[a]	1.3981	0.8710	36.06	36.06
Ethyl	144.5–144.7 (739)	1.4010	.8604	40.70	40.68
n-Propyl	92 (65)	1.4067	.8585	45.32	45.30
n-Butyl	91 (30)	1.4118	.8568	49.97	49.92
Benzyl[b]	146–148 (26)	1.4842			
Bornyl[b]	115–117 (5)	1.4615			
Menthyl[b]	114–115 (4–4.5)	1.4500			

[a] Cottrell b. p. [b] The yield of the last three esters was only 72–76%.

Vinyl Diacetonealkamine *tert*-**Butylacetate Hydrochloride.**—Nine grams of *tert*-butylacetyl chloride and 8.5 g. of vinyl diacetonealkamine hydrochloride were heated together at 100° for two hours, at 140° for two hours more and finally at 150–160° for three hours. Hydrogen chloride was evolved and the mixture became fluid. The product was dissolved in 40 cc. of water. After making strongly alkaline with sodium hydroxide the free ester was extracted with ether, dried over potassium carbonate and the hydrochloride was precipitated by saturating the solution with hydrogen chloride. Nine grams of vinyl diacetonealkamine *tert*-butylacetate hydrochloride was obtained as a white crystalline powder, m. p. *ca.* 210° with decomposition.

α-**Bromo**-*tert*-**Butylacetic Acid.**—Forty-five grams of dry *tert*-butylacetic acid, 24 cc. of dry bromine and 2 cc. phosphorus trichloride in a flask connected to a reflux condenser were warmed at 60–70° for three hours and finally at 100° for one hour. The product solidified on cooling. It was distilled from a Claisen flask, an ordinary distilling flask cooled by a stream of water being used as a receiver in which the product solidified. The fraction distilling at 102–109° (2 mm.) weighed 61 g., 81%; m. p. 72–73°.

Anal. Calcd. for $C_6H_{11}O_2Br$: Br, 40.98. Found: Br, 40.34.

Attempts to isolate salts of this acid failed.

α-Bromo-*tert*-butylacetyl Bromide.—Thirty-five grams of dry *tert*-butylacetic acid and 3.9 g. of red phosphorus were treated in a flask fitted with a reflux condenser with 35 cc. of dry bromine added dropwise. The mixture was shaken at frequent intervals. After adding all the bromine the reaction mixture was warmed on the steam-bath for one and one-half hours. The crude product was decanted into a Claisen flask and distilled. The bromide was obtained as a fuming liquid, b. p. 82° (18 mm.).

α-Bromo-*tert*-butylacetamide.—Thirty grams of the bromo acid bromide was added dropwise to 75 cc. of concentrated aqueous ammonia cooled in ice and stirred. The amide was filtered off and recrystallized from ethyl acetate. α-Bromo-*tert*-butylacetamide, m. p. 138°; yield 16 g. or 71%.

Anal. Calcd. for $C_6H_{12}OBrN$: Br, 41.19. Found: Br, 40.87.

Five grams of the bromoamide was dissolved in a solution of 15 cc. of acetic acid and 7 cc. of water. Four grams of 30-mesh zinc was added and the mixture was warmed on the steam-bath for two hours. Thirty cc. of warm water was added to dissolve the amide and the solution was filtered. The amide was extracted with two 40-cc. portions of ether. Evaporation yielded 2.9 g. of *tert*-butylacetamide (97% yield) which melted at 129° before recrystallization. After crystallizing from ethyl acetate by diluting with petroleum ether it melted at 131° and showed no depression when mixed with a known sample of *tert*-butylacetamide.

α-Bromo-*tert*-butylacetdiethylamide was prepared in 72% yield from the bromide: b. p. 106–109° (5 mm.); m. p. 35–37°.

Anal. Calcd. for $C_{10}H_{20}OBr_2N$: Br, 31.96. Found: Br, 31.34.

α-Bromo-*tert*-butylacetyl chloride was prepared in 92% yield from *tert*-butylacetyl chloride; b. p. 93–97° (37 mm.). The amide prepared from this product was identical with that obtained from the bromo-acid bromide.

α-Bromo-*tert*-butylacetyl Urea.—Ten grams of urea crystals and 13 g. ot α-bromo-*tert*-butylacetyl chloride were mixed and warmed on the steam-bath for a few minutes. After keeping at room temperature for twenty-four hours, the reaction mixture was warmed to 100° for one hour. The product was washed with water and dilute sodium bicarbonate solution, and the residue was recrystallized from ethyl acetate. α-Bromo-*tert*-butylacetyl urea melts at 188.5°; yield 10 g. or 70%.

Anal. Calcd. for $C_7H_{13}O_2BrN_2$: Br, 33.72. Found: Br, 33.70.

Ethyl α-bromo-*tert*-butylacetate was obtained in 75% yield from α-bromo-*tert*-butylacetyl chloride; b. p. 93° (23 mm.); n^{20}_{D} 1.4510.

Anal. Calcd. for $C_8H_{15}O_2Br$: Br, 35.83. Found: Br, 36.43.

Menthyl α-Bromo-*tert*-butylacetate.—Twenty-three grams of α-bromo-*tert*-butylacetyl chloride was added to 17 g. of Mallinckrodt menthol, U. S. P. After warming on the steam-bath it was washed and distilled from a Claisen flask at reduced pressure, b. p. 148–150° (4 mm.); n^{20}_{D} 1.4753.

Anal. Calcd. for $C_{16}H_{29}O_2Br$: Br, 23.99; found, 25.48.

Bornyl α-bromo-*tert*-butylacetate; b. p. 148–153° (4–5 mm.); n^{20}_{D} 1.4876.

Benzyl α-bromo-*tert*-butylacetate; b. p. 145–147°(4.5 mm.); n^{20}_{D} 1.5160. Some benzyl chloride was also formed.

Summary

tert-Butylacetic acid has been prepared in good yield and high purity from 4,4-dimethylpentanone-2 and sodium hypobromite. Many of its

derivatives have been prepared and characterized. Bromination of the acid or its chloride yielded the corresponding α-bromo compounds. Several derivatives of α-bromo-*tert*-butylacetic acid have been prepared. No rearranged products were observed.

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The Chloro Derivatives of *m*-Cresol

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This study had as its objective a survey of those chloro derivatives of *m*-cresol in which the chlorine atoms are ortho or para to the hydroxyl group. Information concerning these compounds is meager and often contradictory.

2-Chloro-*m*-cresol.—Gibson[2] describes 2-chloro-*m*-cresol, prepared from its methyl ether, as massive, ill-defined, transparent crystals melting at 55–56°. When prepared from 2-nitro-*m*-cresol or from *m*-cresol by chlorination of the disulfonic acid, it formed clusters of fragile tetragonal crystals which melted at 49–50°.

The 2-nitro-*m*-cresol was prepared from *m*-cresol by nitration in fuming sulfuric acid[3] and reduced to the corresponding amino compound by means of sodium hydrosulfite. Forty-four grams of 2-amino-*m*-cresol yielded, upon diazotization and treatment with cuprous chloride (using the technique developed by Marvel and McElvain for the preparation of *o*- and *p*-chlorotoluene[4]), 32 g. of 2-chloro-*m*-cresol boiling at 198–199°.

Anal. Calcd. for C_7H_7OCl: Cl, 24.91. Found: Cl, 24.77.

The clorination of *m*-cresol in fuming sulfuric acid was effected by a method similar to the one used for the preparation of 2-nitro-*m*-cresol[3] except that, in the place of nitric acid, one mole equivalent of chlorine[5] was passed into the acid solution. Chlorine was not readily absorbed. After hydrolysis at 200°, the resulting oil which separated from the distillate was fractionated five times. It gave a small fraction boiling at 198–199° and a larger fraction at 199–205° which consisted mostly of the unreacted *m*-cresol. The 198–199° fraction was set in the ice box and seeded with 2-chloro-*m*-cresol prepared from 2-nitro-*m*-cresol. The crystals that separated out from the oil were suction filtered and recrystallized from petroleum ether.

Chlorination of the disulfonic acid of *m*-cresol (prepared by sulfonation with concd. sulfuric acid) in the presence of five moles of sodium hydroxide and subsequent hydrolysis in acid solution at 200° gave 2-chloro-*m*-cresol and a fraction boiling at 235–245° which consisted of 2,6-dichloro-*m*-cresol to be described later.

4-Chloro-*m*-cresol.—The preparation of 4-chloro-*m*-cresol from *m*-cresol by direct chlorination in the vapor state,[6] or in solution,[2,7] or by

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[1] Presented in partial fulfilment of the requirements for the Ph.D. degree.

[2] Gibson, *J. Chem. Soc.*, 1424–1428 (1926).

[3] Hodgson and Beard, *J. Chem. Soc.*, **127**, 498 (1925).

[4] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1923, Vol. III, p. 33.

[5] Houben, "Die Methoden der organischen Chemie," Vol. III, p. 799.

[6] Biedermann, *Ber.*, **6**, 325 (1873).

[7] Kalle and Co., German Patents 90,847, 93,694.