rather easily prepared and isolated from readily accessible starting materials.

Experimental Section

Melting points were taken on a calibrated Fisher-Johns apparatus. Gas–liquid partition chromatographic analyses were performed using an Aerograph A-90P3 or A-700 equipped with an SE 30 column. Retention time data for one particular set of parameters are given in Table II. Tritium activity was measured using a Packard Tri-Carb spectrometer, Model 3324.[9]

TABLE II

CHARACTERISTIC RETENTION TIMES OF *t*-BUTYLBENZENES[a]

Compound	Retention time, min
t-Butylbenzene	1.1
1,3-Di-*t*-butylbenzene	2.7
1,4-Di-*t*-butylbenzene	3.2
1,3,5-Tri-*t*-butylbenzene	5.2

[a] A90-P3, SE 30, 6 ft × 0.25 in., 160°, 90 ml/min.

***t*-Butylbenzene-β-*t*.**—A solution of neophyl chloride[10] (21.7 g, 0.128 mole) and 50 ml of anhydrous ether was added in portions to a flask containing 3.05 g (0.126 g-atom) of magnesium turnings. After a 1-hr period of reflux and addition of an iodine crystal the reaction became self-sustaining and proceeded with almost complete consumption of magnesium. The resulting chilled solution of neophylmagnesium chloride was added dropwise to an ice-cold, magnetically stirred flask containing a mixture of 40 ml of anhydrous ether, 7 g of hydrogen chloride, and 1.0 g of tritium-labeled water (250 mcuries/ml) and allowed to stand with stirring for 24 hr. Hydrolysis was completed by addition of ordinary water. After phase separation, washing, and drying, the ethereal layer was concentrated by careful distillation to yield 17.9 g of yellow oil. Fractional distillation afforded 9.05 g, bp 65–67° (21 mm). Two 5-ml portions of unlabeled *t*-butylbenzene were added to the still pot and distilled in order to strip the remaining labeled material from the column. These fractions were combined yielding 18.6 g of *t*-butylbenzene-β-*t* with a specific activity of 1.00 × 10^6 cpm mmole^{-1}.

1,4-Di-*t*-butylbenzene-β-*t*.—A 100-ml flask equipped for magnetic stirring was charged with 25 ml (0.23 mole) of *t*-butyl chloride and 0.25 g of anhydrous ferric chloride. After the contents cooled to 0°, *t*-butylbenzene-β-*t* (10 ml, 0.064 mole) was added dropwise, and the resulting mixture was stirred for 1 hr at 0° and for 24 hr at room temperature. The dark red reaction mixture was hydrolyzed and extracted with 30 ml of cyclohexane. After washing of the cyclohexane layer with water and 2% sodium carbonate and drying over sodium sulfate, the solvent was removed by rotary evaporation yielding 12.5 g of crude crystalline product. Glpc indicated 96% purity, the remaining material being 1,3-di-*t*-butylbenzene (4%) and 1,3,5-tri-*t*-butylbenzene (2%). Two recrystallizations from absolute ethanol gave 8.4 g of product, mp 77–78° (lit.[11] mp 78°), specific activity 0.915 × 10^6 cpm mmole^{-1}.

1,3,5-Tri-*t*-butylbenzene-β-*t* from 1,4-Di-*t*-butylbenzene-β-*t*.—A 250-ml, round-bottom flask equipped with a Teflon paddle stirrer was charged with 1,4-di-*t*-butylbenzene-β-*t* (6.2 g, 32.6 mmoles) and *t*-butyl chloride (50 ml, 0.46 mole). The resulting solution was cooled to −10° with resultant precipitation of much hydrocarbon. Aluminum chloride (2.2 g, 16.5 mmoles) was added, and, with the temperature maintained between −10 and −5°, aliquots (*ca.* 10 ml) were rapidly withdrawn at specified times and quenched in ice and water. After hydrolysis of these, the organic layer was separated (pentane solvent), washed several times with water, and dried over sodium sulfate. Rotary evaporation of the solvent left partially crystalline residues which were subjected to glpc analysis. Following analysis, 1,3,5-tri-*t*-butylbenzene was isolated by repeated (four or more times) crystallization from methanol. After thorough drying, the tritium activity of weighed portions of each of the aliquots was determined. These data are summarized in Table I.

1,3,5-Tri-*t*-butylbenzene from *t*-Butylbenzene.—A 1-l., three-necked flask equipped with an efficient paddle stirrer, a low-temperature thermometer, and a solids-addition device was charged with *t*-butylbenzene (77.5 ml, 0.50 mole) and *t*-butyl chloride (500 ml, 4.6 moles). The solution was cooled to −40° with a Dry Ice–acetone bath, and anhydrous aluminum chloride (33 g, 0.25 mole) was added to the stirred solution in portions over a 10-min interval. Upon completion of addition the temperature was allowed to rise to between −15 and −10° and maintained with an ice–salt bath for a period of 2 hr. The bright yellow reaction mixture was then carefully poured into a 4-l. separatory funnel containing about 2 kg of crushed ice and water and the resulting mixture was agitated vigorously for about 10 min to complete hydrolysis. Following the separation of layers, the organic phase was washed well with water (three 300-ml portions) and dried over sodium sulfate. Distillation gave about 250 ml of unchanged *t*-butyl chloride, bp 50–52°. The remaining volatile material was removed by rotary evaporation, finally at 1 mm, to yield 120 g of partially crystalline product. The melted crystalline mass was transferred to a beaker thoroughly chilled in an ice–salt bath, suction filtered, and washed with two 75-ml portions of cold methanol (previously used to rinse vessels). A product (90 g, mp 65–70°) showing greater than 95% purity by glpc was obtained. Recrystallization from 150 ml of methanol gave 80 g, mp 72–74° (lit.[1] mp, 72.5–73°). Concentration and further recrystallization of the mother liquor gave an additional 10 g of product, mp 71–73°.

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[9] We are grateful to Dr. Joseph Gally, Pomona College, for generous allotments of instrument time.

[10] W. T. Smith and J. T. Sellas, *Org. Syn.*, **32**, 90 (1952).

[11] V. Ipatieff, B. Corson, and H. Pines, *J. Am. Chem. Soc.*, **58**, 919 (1936).

Reaction of Alkali Metal Diphenylmethides with Halo Acid Derivatives. Alkylation *vs.* Elimination

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Previously it was shown[2] that lithium enolates in ether react with lithium salts of halo acids to give carboxyalkylated ketones. In contrast, the potassium derivative of either anion failed to give alkylated products, and the sodium derivatives gave poor yields. It has now been found that sodium and potassium diphenylmethide in liquid ammonia react with salts of halo acids to give good yields of the alkylated acids. Thus, potassium diphenylmethide reacts with 3-bromopropionic acid to give 4,4-diphenylbutyric acid in 85% yield. One molecular equivalent of the base is consumed in neutralization of the carboxylic acid function. Sodium chloroacetate can similarly be used, without the consumption of the diphenylmethide in the neutralization step, to give 3,3-diphenylpropionic acid in 80% yield; however, attempts to prepare the sodium salt of 3-bromopropionic acid gave only polymeric material.

In contrast to the 3-bromopropionate anion, ethyl 3-bromopropionate underwent exclusively dehydrohalogenation to ethyl acrylate when treated with potas-

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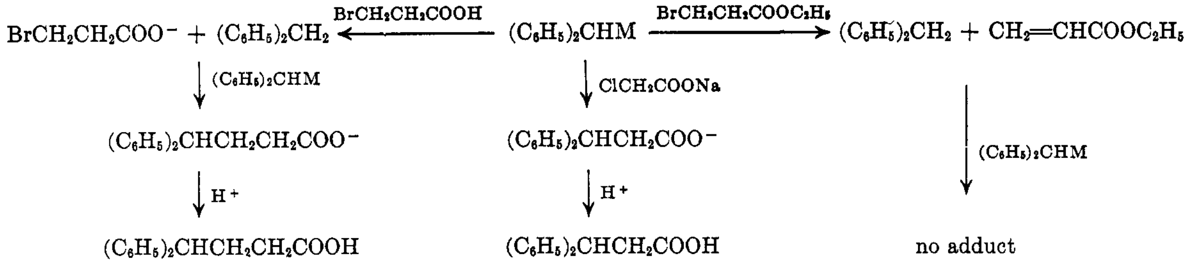
[2] W. H. Puterbaugh and R. L. Readshaw, *J. Am. Chem. Soc.*, **82**, 3635 (1960).

SCHEME I



sium diphenylmethide. Attempts to isolate an adduct of diphenylmethide and ethyl acrylate failed;[3] starting material was isolated when diphenylmethane and either an equivalent or a catalytic amount of potassium amide in liquid ammonia was treated with ethyl acrylate, using either direct or inverse neutralization.[4]

The alkylation of potassium diphenylmethide with the bromopropionate anion offers considerable advantage over the previous preparation of 4,4-diphenylbutyric acid derivatives by condensation of benzophenone with ethyl succinate[5] followed by decarboxylation and hydrogenation of the resulting itaconic acid derivative.[6] Thus, using the alkylation procedure, large quantities of the parent acid could be conveniently prepared in one step from commercially available materials. The synthesis of 3,3-diphenylpropionic acid from sodium or potassium diphenylmethide and commercial sodium chloroacetate offers some advantage over the alkylation of benzene with cinnamic acid, in that the product is more easily separated from starting materials, and further reaction, for example, cyclization to 3-phenyl-1-indanone, does not take place.[7] Scheme I summarizes these reactions.

Experimental Section

4,4-Diphenylbutyric Acid.—To a solution of 0.2 mole of potassium diphenylmethide[8] in 500 ml of liquid ammonia was added an ethereal solution of 15.3 g (0.1 mole) of bromopropionic acid. The orange color of the base was discharged by the last of the halo acid. The ammonia was evaporated and the residue was stirred with ether and water. The aqueous solution was separated, extracted with ether, and neutralized with hydrochloric acid. After recrystallization from ethanol there was obtained 21 g (85%) of 4,4-diphenylbutyric acid, mp 104°, undepressed by authentic 4,4-diphenylbutyric acid.[6] Evaporation of the ethereal solution gave, after distillation, 16 g of diphenylmethane. Repetition of the procedure as above, except using commercial sodium amide, afforded larger quantities of the acid in comparable yield.[9]

When ethyl acrylate was added to 1 molar equiv of potassium diphenylmethide in liquid ammonia, the orange color of the diphenylmethide ion was slowly discharged. After either direct or inverse[4] neutralization with ammonium chloride approximately 97% of the diphenylmethane was recovered, and a high-boiling ester fraction (ν 1750–1715 cm^{-1}) was obtained.

Addition of 1 molar equiv of ethyl 3-bromopropionate also decolorized an ammoniacal solution of potassium diphenylmethide; on work-up the acidic fraction yielded acrylic acid, identified by comparison of the index of refraction with that of an authentic sample (n^{20}D 1.4223), and the neutral fraction contained essentially all of the diphenylmethane (identified and analyzed by vapor phase chromatography).

3,3-Diphenylpropionic Acid.—To a solution of 0.1 mole of potassium diphenylmethide in 250 ml of liquid ammonia was added 11.7 g (0.1 mole) of solid sodium chloroacetate. The orange color of the base was discharged by the last of the salt. The ammonia was evaporated and the residue was dissolved in water. The aqueous solution was extracted with ether and acidified with hydrochloric acid. After recrystallization from aqueous ethanol there was obtained 18 g (80%) of 3,3-diphenylpropionic acid, mp 154°, undepressed by authentic 3,3-diphenylpropionic acid.

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(3) See M. T. Tetenbaum and C. R. Hauser, *J. Org. Chem.*, **23**, 229 (1958).

(4) P. J. Hamrick and C. R. Hauser, *J. Am. Chem. Soc.*, **81**, 2096 (1959).

(5) G. H. Daub and W. S. Johnson, *ibid.*, **72**, 501 (1950).

(6) S. Wawzonek and J. Kozikowski, *ibid.*, **76**, 1641 (1954).

(7) See C. F. Koelsch, H. Hochmann, and C. D. LeClaire, *ibid.*, **65**, 59 (1943).

(8) C. R. Hauser and P. J. Hamrick, *ibid.*, **79**, 3142 (1957).

(9) This experiment was performed by Eric Roskin.

Synthesis of Tetrakis(dimethylamino)ethylene

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Presented is a report of an alternate synthesis of tetrakis(dimethylamino)ethylene, $[(CH_3)_2N]_2C{=}C[N(CH_3)_2]_2$. This compound, interesting because of its chemiluminescence and its ability to form charge-transfer complexes, is generally prepared by the method of Pruett, *et al.*[1]

Tetrakis(dimethylamino)ethylene can be prepared in good yield by pyrolysis of the recently reported[2,3] tris(dimethylamino)methane, $HC[N(CH_3)_2]_3$. This method is analogous to the one reported by Winberg,

$$2HC[N(CH_3)_2]_3 \xrightarrow{\Delta} [(CH_3)_2N]_2C{=}C[N(CH_3)_2]_2 + 2HN(CH_3)_2$$

et al.,[4] in which $HCX(NR_2)_2$ is pyrolyzed to yield the corresponding tetraaminoethylene (X = OR, CN). The X in our example is $N(CH_3)_2$, thus avoiding the possibility of contamination due to substituent scrambling.[5] Other amino substituents can, of course, be used, those from volatile amines being of particular interest.

Experimental Section

Preparation of Tetrakis(dimethylamino)ethylene.—A 2.20-g (0.0152-mole) sample of tris(dimethylamino)methane was placed in a 10-ml, round-bottom flask equipped with a reflux condenser and the system was kept under a small pressure of dry nitrogen. The reaction flask was immersed in an oil bath and the reaction was kept at reflux by adjusting the temperature upward between 150 and 190° as the reaction proceeded. The appearance of product was monitored by taking nmr spectra of aliquots [τ 7.42 (s), benzene solvent, TMS internal standard]. The

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(1) R. L. Pruett, J. T. Barr, K. E. Rapp, C. T. Bahner, J. D. Gibson, and R. H. Lafferty, *J. Am. Chem. Soc.*, **72**, 3646 (1950).

(2) H. Weingarten and W. A. White, *ibid.*, **88**, 850 (1966).

(3) H. Brederick, F. Effenberger, and T. Brendle, *Angew. Chem.*, **78**, 147 (1966).

(4) H. E. Winberg, J. E. Carnahan, D. D. Coffman, and M. Brown, *J. Am. Chem. Soc.*, **87**, 2055 (1965).

(5) That substituent scrambling occurs in $HC(OCH_3)[N(CH_3)_2]_2$ was privately communicated to us by E. C. Taylor and R. Buntrock.