3-*p*-Anisyl-1-butanol.—3-*p*-Anisylbutanoic acid (15 g., 0.077 mole) was reduced with excess lithium aluminum hydride in ether. Distillation at reduced pressure gave 11 g. (79%) of 3-*p*-anisyl-1-butanol, b.p. 130° (3 mm.) (lit.[19] b.p. 158° (14 mm.)).

The *p*-bromobenzenesulfonate was recrystallized from ethanol–water; m.p. 72–73°.

Anal. Calcd. for $C_{17}H_{19}BrO_4S$: C, 51.13; H, 4.80. Found: C, 51.28; H, 4.88.

The N-phenylcarbamate of 3-*p*-anisyl-1-butanol[20] was recrystallized from ligroin, m.p. 56–57°.

Anal. Calcd. for $C_{18}H_{21}NO_3$: C, 72.21; H, 7.07. Found: C, 72.15; H, 7.04.

3-*p*-Anisyl-1-butene.—The crude 3-*p*-anisyl-1-butanol obtained by reduction of 50 g. (0.26 mole) of 3-*p*-anisylbutanoic acid with lithium aluminum hydride was acetylated by boiling under reflux with a slight excess of acetic anhydride in the presence of pyridine. Distillation under reduced pressure gave 46 g. (81% over-all) of 3-*p*-anisyl-1-butyl acetate, b.p. 132–134° (2.5 mm.). The ester was passed over glass helices heated at 525° using argon as a carrier gas. The pyrolysate was freed of acetic acid and distilled at reduced pressure to give 14.5 g. (40% based on unrecovered ester) of 3-*p*-anisyl-1-butene, b.p. 97° (9.5 mm.).

A sample of the olefin was hydrogenated in the presence of palladium–charcoal to **2-*p*-anisylbutane**, b.p. 100° (10 mm.).

Anal. Calcd. for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.54; H, 9.89.

3-*p*-Anisyl-2-butanol was prepared in 86% yield from 2-*p*-anisylpropanal and methylmagnesium iodide. The mixture of diastereoisomeric alcohols boiled at 102–104° (1 mm.) (lit.[5] b.p. 149° (14 mm.)).

***erythro*-3-*p*-Anisyl-2-butanol** was obtained from the diastereoisomeric mixture by recrystallization of the acid phthalate from benzene as reported by Winstein and Robinson.[5] Saponification of *erythro*-3-phenyl-2-butyl acid phthalate, m.p. 137–138° (lit.[5] m.p. 137–138°), gave, after distillation, *erythro*-3-phenyl-2-butanol, m.p. 60–61° (lit.[5] m.p. 60–61°).

The Reaction of 3-*p*-Anisyl-1-butylamine with Nitrous Acid.—A mixture of 28 g. (0.16 mole) of 3-*p*-anisyl-1-butylamine and 23 g. (0.33 g.f. wt.) of sodium nitrite in 125 ml. of glacial acetic acid was stirred at 2° for *ca.* 17 hours then at room temperature for *ca.* 25 hours and poured into a mixture of ice and water containing 100 g. of sodium hydroxide. The basic mixture was extracted four times with pentane and once with ether. The combined extracts were washed with dilute hydrochloric acid to remove unreacted amine (3% recovery), with dilute sodium carbonate solution, then with water, dried and evaporated. Partial distillation of the oily residue gave 1.15 g. of 3-*p*-anisyl-1-butene, b.p. 82° (5 mm.), which had a single peak in gas chromatography corresponding in retention time to that of authentic 3-*p*-anisyl-1-butene. The crude, undistilled acetate mixture was treated with excess lithium aluminum hydride and the alcohol mixture distilled to give 0.98 g. (9% total yield based on unrecovered amine) of 3-*p*-anisyl-1-butene, b.p. 105° (14 mm.); 6.63 g. (24%) of a mixture of diastereoisomeric 3-*p*-anisyl-2-butanols, infrared spectrum like that of a synthetic mixture of authentic *threo*- and *erythro*-3-*p*-anisyl-2-butanol, acid phthalate, m.p. 137–138°; and 11.5 g. (42%) of 3-*p*-anisyl-1-butanol, b.p. 153–154° (10 mm.), N-phenylcarbamate, m.p. 56–57°, infrared spectrum like that of authentic 3-*p*-anisyl-1-butanol except for a weak peak at 8.70 μ and a medium peak at 11.0 μ which indicate the presence of some 3-*p*-anisyl-2-butanol. Column holdup and pot residue amounted to *ca.* 3 g.

Preparation and Diazotization of 3-*p*-Anisyl-1-butylamine-3-^{14}C.—*p*-Methoxyacetophenone-7-^{14}C was obtained by the acylation[21] of anisole with acetyl-1-^{14}C chloride in carbon disulfide at 0° using anhydrous aluminum chloride as catalyst. Distillation at reduced pressure gave a 71% yield of *p*-methoxyacetophenone-7-^{14}C, b.p. 123–124° (7 mm.) (lit.[21] b.p. 139° (15 mm.)).

3-*p*-Anisyl-2-butenoic-3-^{14}C acid was obtained from 90 g. (0.60 mole, containing *ca.* 2 mcuries of ^{14}C-activity) of *p*-methoxyacetophenone-7-^{14}C by the procedure used for the inactive acid. Catalytic hydrogenation was carried out as reported for the inactive acid to give 82 g. (70% over-all) of 3-*p*-anisylbutanoic-3-^{14}C acid, b.p. 176–178° (5 mm.).

3-*p*-Anisylbutanoic-3-^{14}C acid (50 g., 0.26 mole) was converted into the corresponding amide by the procedure used for the inactive acid. 3-*p*-Anisylbutanamide-3-^{14}C was reduced with lithium aluminum hydride by the extraction procedure reported above. Inactive 3-*p*-anisyl-1-butylamine (19 g.) was added to act as a carrier and the product was distilled to give 42 g. (49% over-all) of 3-*p*-anisyl-1-butylamine-3-^{14}C, b.p. 99° (1.2 mm.).

3-*p*-Anisyl-1-butylamine-3-^{14}C was diazotized as reported for the inactive amine. Inactive 3-*p*-anisyl-1-butene (0.734 g.), *erythro*-3-*p*-anisyl-2-butanol (3.39 g.) and 3-*p*-anisyl-1-butanol (5.06 g.) were added to act as carriers, the mixture was treated with excess lithium aluminum hydride to convert acetates into the corresponding carbinols and the products were isolated by distillation. The 3-*p*-anisyl-1-butene-X-^{14}C product showed a single peak in gas chromatography and had an infrared spectrum identical with that of authentic 3-*p*-anisyl-1-butene after one redistillation. *erythro*-3-*p*-Anisyl-2-butanol-X-^{14}C, m.p. 60–61°, was obtained by recrystallization of the acid phthalate and saponification. 3-*p*-Anisyl-1-butanol-X^{14}-C was purified by recrystallization of the brosylate, m.p. 72–73°, followed by formolysis and saponification of the formate. Anisic-7-^{14}C acid, m.p. 184°, was obtained from a portion of each of the purified products by oxidation with excess potassium permanganate in refluxing 5% sodium hydroxide solution.

(19) A. Sosa, *Ann. chim.*, [11] **14**, 5 (1940).

(20) Sosa, ref. 19, reported obtaining an oil.

(21) C. R. Noller and R. Adams, THIS JOURNAL, **46**, 1889 (1924).

LEXINGTON, KY.

[CONTRIBUTION FROM THE MCPHERSON CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY, COLUMBUS 10, OHIO]

The Synthesis and Some Reactions of Di-*t*-butylacetic Acid and Di-*t*-butylketene[1]

BY MELVIN S. NEWMAN, ALFRED ARKELL[2] AND TADAMICHI FUKUNAGA[2]

RECEIVED OCTOBER 8, 1959

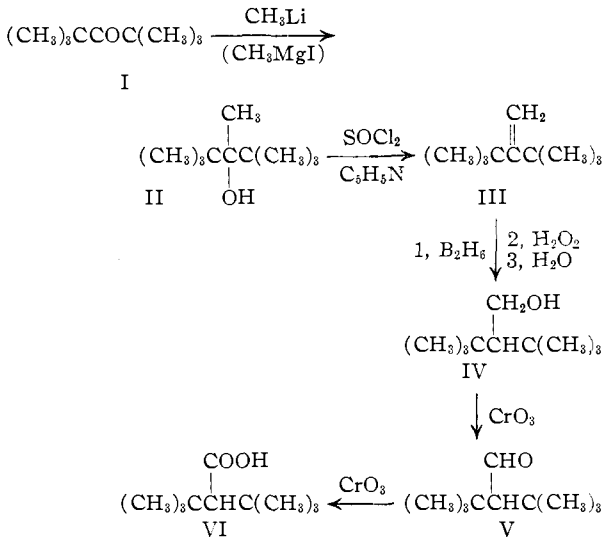
Di-*t*-butylacetic acid is prepared in good over-all yield from hexamethylacetone as shown in the chart, I → VI. On treatment of the acid chloride with sodium amide in liquid ammonia di-*t*-butylketene is formed. This ketene is stable and relatively unreactive compared to other known aliphatic ketenes. The possible intervention of di-*t*-butylketene in reactions of di-*t*-butylacetyl chloride raises the general question as to the importance of ketenes in reactions of acid chlorides having a hydrogen on the α-carbon.

In continuation of a program designed to develop methods for the synthesis of highly branched aliphatic compounds and to study the reactions thereof, we wished to prepare di-*t*-butylacetic acid. This compound was especially desired because it could be the parent of a series of highly hindered trisubstituted acetic acids. In this paper we re-

(1) This research was supported by the United States Air Force under contract No. AF 33 (616)-3412, monitored by the Aeronautical Research Laboratory, Wright Air Development Center.

(2) The material herein presented was taken from the Ph.D. theses of A. Arkell, 1958, and T. Fukunaga, 1959.

port the synthesis of di-*t*-butylacetic acid (VI) by the route outlined[3]

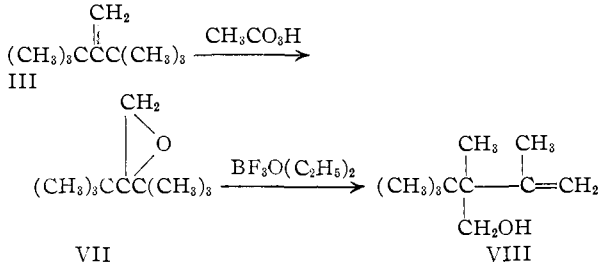


The reaction of hexamethylacetone I with methyllithium or methylmagnesium iodide afforded 2,2,3,4,4-pentamethyl-3-pentanol[4](II) in 71–75% yield and this was dehydrated to a mixture of olefins in 78% yield by means of thionyl chloride and pyridine.[5] Analysis by gas chromatography showed that about 90% of this mixture was 1,1-di-*t*-butylethylene(III) and 6% probably 2,3,3,4,4-pentamethyl-1-pentene although this structure was not rigorously proved. Other attempts at dehydration by means of 2-naphthalenesulfonic acid,[6] iodine[7] and phenyl isocyanate[8] were made, but these methods were abandoned after gas chromatographic analysis indicated that complex mixtures were at hand.

The olefin III was converted in 60–70% yields into 2,2-di-*t*-butylethanol (IV) by treatment with diborane (the intermediate alkyl boron was not purified) followed by oxidation with alkaline hydrogen peroxide and hydrolysis.[9] This method is thus shown to be applicable to olefins having moderate steric hindrance.

On careful oxidation of IV with chromium trioxide in aqueous acetic acid containing sulfuric acid it was possible to obtain di-*t*-butylacetaldehyde(V) in good yield. Under more vigorous treatment with the same oxidizing medium IV could be converted in 82% yield into di-*t*-butylacetic acid (VI). The structure of VI was confirmed by analysis and by n.m.r. spectroscopy.[10]

At one stage in this research attempts were made to oxidize 1,1-di-*t*-butylethylene(III) to its oxide VII and thence to di-*t*-butylacetaldehyde(V) by acid-catalyzed rearrangement. However, treatment of III with peracetic acid[11] afforded a complex mixture (at least five compounds) in which the desired VII was present in 30–50% yield. One attempt to convert VII to VI with chromic acid[12] discouraged this approach since only traces of VI were obtained. Finally a boron trifluoride etherate-catalyzed rearrangement of VII yielded a complex mixture of at least seven compounds, one of which was an unsaturated alcohol to which we tentatively assign the structure 2-*t*-butyl-2,3-dimethyl-3-buten-1-ol (VIII).[13] This appears to be the first reported case of acid catalyzed-rearrangement of an epoxide to form an unsaturated alcohol with rearranged carbon skeleton. The structure has not been rigorously established, but because we plan no further work this mention is made.



Certain reactions of VI and of its derivatives are of interest and are reported below. This phase of our study is not complete but is reported because of the interesting points raised. In appraising the facts, it should be pointed out that di-*t*-butylacetic acid has a *six number* of 18 and therefore should be quite resistant to reactions involving addition to the carbonyl group.[14]

On treatment of di-*t*-butylacetic acid (VI) with thionyl chloride at reflux a crude acid chloride was obtained which had a weak absorption band at 4.80 μ[15] in addition to the strong band at 5.57 μ characteristic for acid chloride carbonyl groups.[16] Since the acid chloride IX can be distilled at atmospheric pressure (b.p. 186°) without ketene formation, the possibility exists that the acid chloride may be formed, at least in part, by conversion of the starting acid (or an intermediate chlorosulfite thereof) to di-*t*-butylketene (X) followed by addition of hydrogen chloride to the latter. This possibility was checked by showing that di-*t*-butylketene (see below) adds hydrogen chloride rapidly to yield di-*t*-butylacetyl chloride. However, more work must

(3) See M. S. Newman and A. Arkell, *J. Org. Chem.*, **24**, 385 (1959), for an unsuccessful approach *via* synthesis of di-*t*-butylketene.

(4) F. C. Whitmore and K. C. Laughlin, THIS JOURNAL, **55**, 3732 (1933), report a m.p. of 42°.

(5) Compare F. C. Whitmore and F. A. Karnatz, *ibid.*, **60**, 2533 (1938), who obtained mainly 2-ethylbutyl chloride on similar treatment of 2-ethyl-1-butanol.

(6) Reference 4 above reports a 90% yield of crude III, but on rectification only 45% of III was obtained.

(7) F. C. Whitmore and K. C. Laughlin, THIS JOURNAL, **54**, 4012 (1932).

(8) Compare W. Oroshnik, G. Karmas and A. D. Mebane, *ibid.*, **74**, 295 (1952).

(9) H. C. Brown and B. C. Subba Rao, *ibid.*, **78**, 5694 (1956).

(10) We thank Dr. G. V. D. Tiers of the Minnesota Mining and Manufacturing Co., Minneapolis, Minn., for this study. He reports that the n.m.r. spectrum of VI leaves no doubt as to its purity and structure.

(11) Compare A. Byers and W. J. Hickinbottom, *J. Chem. Soc.*, 1328 (1948).

(12) See M. A. Davis and W. J. Hickinbottom, *ibid.*, 2205 (1958) and references therein for a discussion of the role of substituted ethylene oxides as intermediates in the oxidation of olefins with chromic acid.

(13) A small amount of VIII was also obtained in the above mentioned treatment of III with peracetic acid.

(14) M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 4, p. 206 ff.

(15) W. R. Harp, Jr., and R. S. Rasmussen, *J. Chem. Phys.*, **15**, 778 (1947), report a band at 4.64 μ and no absorption in the 5.5–6.0 μ region for ketene.

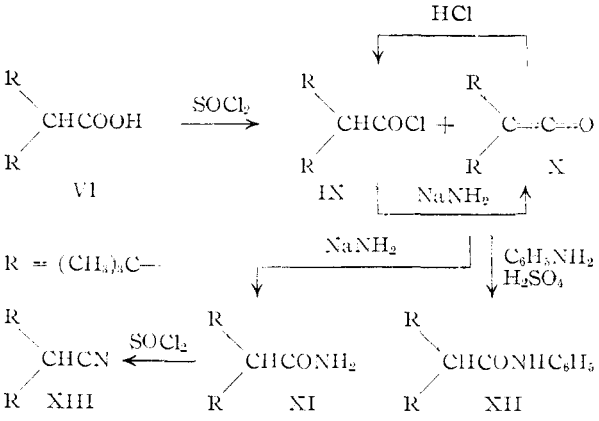
(16) L. V. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 125.

be done (and is under way) to show what fraction, if any, of di-*t*-butylacetyl chloride is formed *via* the ketene route.[17]

When a solution of di-*t*-butylacetyl chloride in ether was stirred with a suspension of sodium amide in liquid ammonia for one day there was obtained a small yield of di-*t*-butylacetamide (XI) but, surprisingly, a considerable amount (57%) of di-*t*-butylketene (X). The sodium amide was shown to be important since after six hours in pure dry liquid ammonia the acid chloride was not converted to ketene X or amide XI.[18] Preliminary experiments at higher temperatures show that other bases, such as pyridine, collidine and sodium triethylmethoxide, are capable of converting IX into X.

Di-*t*-butylketene (X) is the first aliphatic ketene which is stable as a monomer.[19] Actually it also is quite unreactive when compared with other ketenes. For example, it reacts slowly with water (in aqueous dioxane solution) unless catalyzed by acids or bases and can be recovered completely from liquid ammonia–ether after one day, even when ammonium chloride is added. However, the addition of sodium amide causes X to react slowly to yield di-*t*-butylacetamide (XI), which could readily be converted to di-*t*-butylacetonitrile (XIII) by heating with excess thionyl chloride.

Di-*t*-butylketene also failed to react with aniline after two hours at reflux in benzene but did form the anilide XII when sulfuric acid was added. Other reactions of di-*t*-butylketene X are being studied.



Experimental[20]

1,1-Di-*t*-butylethanol (II).—Hexamethylacetone I was prepared essentially as described[21] except that sodium amide was freshly prepared in liquid ammonia and the first alkylation of diisopropyl ketone was carried out in ether using methyl iodide. The second alkylation was effected in toluene. The over-all yield of hexamethylacetone, b.p. 145–151°, $n^{20}D$ 1.4215, was 52%. In a large-scale addition of methylmagnesium iodide (from 440 g. of methyl iodide) to hexamethylacetone, after refluxing for one hour, a crystal was noticed on the wall of the flask above the surface of the reaction mixture. The external heating was stopped and, on touching a piece of ice to the side of the flask near this crystal, crystallization of a large amount of some substance occurred rapidly and with sufficient evolution of heat to cause violent boiling. Hence in large runs this phenomenon must be anticipated in order to avoid a possibly serious accident. The desired 1,1-di-*t*-butylethanol,[22] b.p. 78–82° at 17 mm., m.p. of sublimed sample, 42.0–42.7°, was obtained in 71% yield. When methyllithium was used in place of methylmagnesium iodide the yield was slightly better (72–75%).

1,1-Di-*t*-butylethylene (III).—Thionyl chloride (131 g., purified by distillation from raw linseed oil) was added during 1.5 hours to a well stirred and ice-cooled solution of 131 g. of II in 400 ml. of pure dry pyridine. The temperature never exceeded 20° during the addition. The stirring was stopped and after several hours the liquid phases were forced through a filter onto 300 ml. of ice, leaving the pyridine hydrochloride behind. The product was taken into ether and treated in the usual way. The crude product was distilled from potassium hydroxide pellets (to remove an odoriferous sulfur compound) to yield III, b.p. 146–150°, $n^{20}D$ 1.4358–1.4363, in 77–78% yields. By gas chromatography this product was shown to consist of 90–92% of 1,1-di-*t*-butylethylene and about 6% of another olefin, probably 2,3,3,4,4-pentamethyl-1-pentene.

2,2-Di-*t*-butylethanol (IV).—To a solution of 9.5 g. (0.25 mole) of sodium borohydride in 250 ml. of purified diglyme,[9,23] were added 70 g. (0.50 mole) of III (of the purity above described) and then a solution of 11.2 g. (0.084 mole) of aluminum chloride in 50 ml. of diglyme. After stirring for one hour at 20–25° and 7 hours on the steam-bath most of the diglyme was removed under reduced pressure and the residue was treated with excess hydrochloric acid. The organic material, isolated by the usual procedure, weighed 73.8 g. To a solution of this in 100 ml. of alcohol containing 8 g. of sodium hydroxide was added 68 g. of 30% hydrogen peroxide at a rate sufficient to maintain gentle reflux. After one hour, 350 ml. of water was added and the organic product isolated in the usual manner (destroy excess peroxide with sodium bisulfite). On fractional distillation at 29 mm., 51.5 g. (65%) of IV, b.p. 105–110°, m.p. 52–54°, was obtained. The analytical sample, m.p. 54.0–55.0°, was obtained by recrystallization from low boiling petroleum ether (Skellysolve F) followed by sublimation.

Anal. Calcd. for $C_{10}H_{22}O$: C, 75.9; H, 14.0. Found[24]: C, 76.0, 76.1; H, 14.0, 14.0.

A mixture of 0.2 g. of pure IV, 0.5 g. of pure *p*-nitrobenzoyl chloride and 4 ml. of benzene was refluxed for 1 hour. Crystallization of the product from alcohol afforded 2,2-di-*t*-butylethyl *p*-nitrobenzoate as large colorless prisms, m.p. 78.8–79.4°.

Anal. Calcd. for $C_{17}H_{25}NO_4$: C, 66.4; H, 8.2; N, 4.6. Found: C, 66.3, 66.5; H, 8.1, 8.3; N, 4.6, 4.7.

Di-*t*-butylacetic Acid (VI).—To a stirred solution of 86.5 g. of IV in 270 ml. of sulfuric–acetic acid solution (made by adding 50 ml. of concd. sulfuric acid to 100 ml. of water and diluting to 500 ml. with acetic acid) was added 240 ml. of chromic acid solution (made by dissolving 125 g. of chromic oxide in 125 ml. of water and diluting to 500 ml. with acetic acid) during 1.5 hours. After standing overnight and heating on the steam-bath for one hour, 300 ml. of water was added and the organic product taken into ether–benzene. After the usual work-up 35.5 g. of crystalline acid was obtained. The neutral fraction on reoxidation in the same

(17) The fact that some optically active disubstituted acids have been converted to optically active acid chlorides does not rule out participation of the ketene mechanism unless the acid chloride is not partially racemic. To our knowledge, this point has not yet been rigorously demonstrated.

(18) The behavior of di-*t*-butylacetyl chloride with sodium amide in ammonia suggests that other acid chlorides may react *via* a ketene intermediate. Since these ketenes are in general much more reactive than di-*t*-butylketene (X), they would immediately combine with reagent to give the same product that would be obtained by a carbonyl-addition mechanism (or an ionization mechanism). The intervention of a ketene intermediate could be spotted by research with optically active acid halides or with those containing isotopic hydrogen on the α-carbon. We hope to study a few representative cases.

(19) E. H. Rodd, "The Chemistry of Carbon Compounds," Elsevier Publishing Co., Amsterdam, Holland, Vol. I, 1951, p. 527 ff.

(20) All melting points of pure compounds are corrected. The phrase "treated in the usual way" means that the ether–benzene solution of the desired product was washed with alkali and acid (as dictated by reagents or impurities present), with saturated sodium chloride solution and was then filtered by gravity through a layer of powdered anhydrous magnesium sulfate. Solvents were then removed by distillation.

(21) F. C. Whitmore and E. E. Stahly, THIS JOURNAL, **55**, 4153 (1933).

(22) J. B. Conant and A. H. Blatt, *ibid.*, **51**, 1230 (1929).

(23) H. C. Brown, E. J. Mead and B. C. Subba Rao, *ibid.*, **77**, 6209 (1955).

(24) All microanalyses by Galbraith Laboratories, Knoxville, Tenn.

way yielded 41.1 g. of acid, the total yield being 76.6 g. (82%) of VI, m.p. 72–74°. This product was quite pure and had an infrared spectrum identical to that of the purest sample, m.p. 80.5–81.5°, obtained by low temperature crystallization (−78°) from Skellysolve F, followed by vacuum sublimation.

Anal. Calcd. for $C_{10}H_{20}O_2$: C, 69.7; H, 11.7. Found: C, 69.6, 69.5; H, 11.6, 11.6.

A mixture of 8.6 g. of VI and excess pure thionyl chloride was refluxed for 1 hour after the initial vigorous reaction was over. Vacuum distillation afforded 9.2 g. (96%) of crude acid chloride IX as a colorless oil, b.p. 83–86° at 12 mm., infrared absorption at 4.8(w) and 5.57(s)μ.[16] This crude acid chloride (and other similar preparations) was used in further experiments and was not analyzed because of the presence of a small amount of di-t-butylketene (4.8 μ band).[15]

Di-t-butylketene (X).—To a suspension of sodium amide prepared from 1 g. of sodium and 50 ml. of ammonia was added a solution of 5 g. of di-t-butylacetyl chloride in 20 ml. of dry ether. After 24 hours 2.5 g. of ammonium chloride was slowly added. Dry ether was added and the ammonia removed by distillation. The ethereal solution was filtered from salts and on distillation afforded 2.3 g. (57%) of di-t-butylketene as a pale yellow oil, b.p. 74–76° at 47 mm. Redistillation yielded pure X, b.p. 73° at 45 mm., $n^{20}D$ 1.4370, infrared absorption at 4.80 μ, no absorption in the 5–6 μ region.[16]

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.9; H, 11.8. Found: C, 77.9, 77.9; H, 12.0, 12.1.

The residue from the original distillation yielded 1.3 g. (29%) of di-t-butylacetamide (XI), m.p. 109.5–110.2°, infrared absorption at 6.0 μ, on crystallization from aqueous ethanol and from benzene–Skellysolve B (petroleum ether, b.p. 65–70°).

When a solution of 9.5 g. of crude di-t-butylacetyl chloride in 30 ml. of ether was added to a stirred suspension of sodium amide (prepared from 3.5 g. of sodium in 125 ml. of liquid ammonia) and left for 18 hours there was obtained 6.9 g. (81%) of the amide XI.

Anal. Calcd. for $C_{10}H_{21}NO$: C, 70.1; H, 12.4; N, 8.2. Found: C, 70.1, 70.2; H, 12.4, 12.7; N, 8.2, 8.3.

When di-t-butylacetyl chloride, b.p. 186° at 750 mm., was treated with dry liquid ammonia in the absence of sodium amide no reaction had occurred after 6 hours and only the acid chloride was present. After 18 hours a mixture of ketene (4.8 μ), amide (6.0 μ) and acid chloride (5.6 μ) was present as shown by infrared analysis.

Infrared analysis of aliquots of a solution of di-t-butylketene(X) in liquid ammonia (containing slightly less than one equivalent of sodium amide) and dry ether after 3, 6, 9 and 12 hours showed that the intensity of the amide peak (6.0 μ) increased steadily at the expense of the ketene peak (4.8 μ), but even at the end ketene absorption was visible. The amide produced was identical to that described above prepared from di-t-butylacetyl chloride. In an experiment similar to the above except that no sodium amide was present, no amide band had appeared after 24 hours. After addition of powdered ammonium chloride and a further 19-hour reaction period still no conversion of X to di-t-butylacetamide had occurred.

After a solution of 0.5 g. of X, 1 g. of aniline and 5 ml. of benzene had been refluxed for 2 hours no anilide had been formed. Addition of 2 drops of concd. sulfuric acid caused a reaction and di-t-butylacetanilide(XII), m.p. 142.5–143.5°, was produced.

Anal. Calcd. for $C_{16}H_{25}NO$: C, 77.7; H, 10.2; N, 5.7. Found: C, 77.7; H, 10.2; N, 5.8.

On treatment of a small amount of X in benzene with dry hydrogen chloride immediate reaction to form the acid chloride (5.6 μ) occurred.

Di-t-butylacetaldehyde (V).—To a stirred solution of 7.9 g. of 2,2-di-t-butylethanol(IV) in 25 ml. of sulfuric–acetic acid solution (as used above for preparation of VI) held at 0–5° was added 14 ml. of chromic acid solution (as above) at a rate of 1 drop per second. There was immediate precipitation of green chromous oxide. During addition of the last 3.5 ml. the red color of chromium trioxide was noted. Heating for 10 minutes was needed to discharge this color. Extraction of the product with methylene chloride and the usual work-up yielded 4.6 g. (59%) of di-t-butylacetaldehyde, b.p. 56–60° at 4–6 mm., $n^{20}D$ 1.4390, from the neutral fraction and 1.2 g. (14%) of VI from the acid fraction.

Anal. Calcd. for $C_{10}H_{20}O$: C, 76.9; H, 12.9. Found: C, 77.0; H, 13.0.

The 2,4-dinitrophenylhydrazone, m.p. 171.5–172.5°, was prepared.[25]

Anal. Calcd. for $C_{16}H_{24}N_4O_4$: C, 57.1; H, 7.2; N, 16.7. Found: C, 57.0; H, 7.1; N, 16.8.

1,1-Di-t-butylethylene Oxide (VII).—A solution at 20° of 28.0 g. of 1,1-di-t-butylethylene(III) (about 90% pure as shown by gas phase chromatography) in 375 ml. of methylene chloride was treated during 15 minutes with 55.0 g. of 40% peracetic acid[26] containing 3.5 g. of sodium acetate. The temperature rose and was held between 20 and 30°. After standing overnight the organic product was isolated as usual and rectified. The oxide, b.p. near 180°, was obtained in about 40% yield and was purified by gas chromatography for analysis (infrared absorption at 8.15, 11.85 and 12.22 μ, epoxide regions[27]).

Anal. Calcd. for $C_{10}H_{20}O$: C, 76.9; H, 12.9. Found: C, 76.9; H, 13.0.

From a higher boiling fraction about 15–20% of an unsaturated alcohol VIII was obtained. Great difficulty in purification of this alcohol was experienced as excessive foaming interfered with distillation.

3-t-Butyl-2,3-dimethyl-1-buten-4-ol (VIII).—When one drop of boron fluoride etherate was added to 1.56 g. of VII heat was evolved. Gas phase chromatographic analysis of the reaction products showed that 40–60% of VIII was produced. An apparently homogeneous sample, m.p. 79.4–86.4°, was obtained. The presence of a primary alcohol function (broad absorption at 2.95 and 9.65 μ) and a terminal methylene group (11.22 μ) and an olefinic group (6.1 μ) were indicated by infrared absorption. One attempt to prepare a 3,5-dinitrobenzoate failed to yield a solid product.

Anal. Calcd. for $C_{10}H_{20}O$: C, 76.9; H, 12.9. Found: C, 76.7; H, 13.0.

The above compound was obtained as one of the products from the peracetic acid oxidation of III (above).

Di-t-butylacetonitrile (XIII).—A mixture of 6.9 g. of di-t-butylacetamide (XI), 50 ml. of benzene and 20 ml. of purified thionyl chloride was refluxed for 6 hours. After the usual work-up 4.6 g. (75%) of XIII, b.p. 76–78° at 10 mm., $n^{27}D$ 1.4368, was obtained.

Anal. Calcd. for $C_{10}H_{19}N$: C, 78.4; H, 12.5; N, 9.1. Found: C, 78.1, 78.2; H, 12.7, 12.8; N, 9.1, 9.3.

(25) G. D. Johnson, THIS JOURNAL, **73**, 5888 (1951).

(26) Titrated by the method of F. P. Greenspan and D. G. MacKellar, *Anal. Chem.*, **20**, 1061 (1948).

(27) Reference 16, p. 118.