icals have, in fact, been photolytically generated from secondary amines in strongly acidic media.[16] Paralelling our present results, spontaneous production of aminium radicals from protonated chloramines *under mild conditions* was observed,[15] and subsequent fast addition to unsaturated hydrocarbons. If ordinary aliphatic aminium radicals are generated in weakly basic, neutral, or weakly acidic aqueous media, we have found,[17] rapid loss of α protons occurs with subsequent oxidative dealkylation. Hence, the characteristic reactions of aminium ions near neutrality are different from those in strongly acidic media.

Experimental Section

Water and triethylenediamine perchlorate were purified as previously described.[1] Aqueous hypochlorous acid solutions were prepared by the procedure of Higuchi and Hasegawa.[18] The mononitrate salt was prepared analogously to the perchlorate salt, and recrystallized thrice from ethanol. It was transferred to stoppered containers in a drybox prior to weighing due to its hygroscopicity. Other salts and buffers used were of the purities previously described.[1]

For determination of hypochlorous acid, stock solutions were diluted and analyzed spectrophotometrically in the presence of excess iodide ion, as previously described,[2] using the molar absorptivity reported by Awtrey and Connick.[19]

Stopped-flow kinetics were obtained in the apparatus of ref 1, employing procedures used there. Hypochlorous acid solutions of known concentration were mixed in the apparatus 1:1 with known concentrations of triethylenediamine in buffered salt solutions to give final ionic strengths after mixing of 0.2. The chlorammonium species was observed at 357 nm and the cation radical[1] was followed at 465 nm.

Registry No.—II, 35666-89-8; IV, 35666-90-1.

(16) W. C. Danen and R. C. Rickard, *J. Amer. Chem. Soc.*, **94**, 3254 (1972).
(17) L. A. Hull, G. T. Davis, D. H. Rosenblatt, H. K. R. Williams, and R. C. Weglein, *ibid.*, **89**, 1163 (1967).
(18) T. Higuchi and J. Hasegawa, *J. Phys. Chem.*, **69**, 796 (1965).
(19) A. D. Awtrey and R. E. Connick, *J. Amer. Chem. Soc.*, **73**, 1842 (1951).

Steric Crowding in Organic Chemistry. VI. Reactivity of Tri-*tert*-butylethylene and Related Compounds[1]

G. J. ABRUSCATO AND T. T. TIDWELL*

Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208

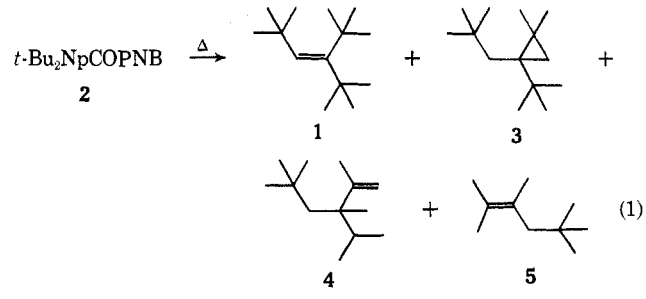
Received July 13, 1972

Pyrolysis of di-*tert*-butylneopentylcarbinyl *p*-nitrobenzoate (**2**) or benzoate (**7**) gives tri-*tert*-butylethylene (**1**), 1-*tert*-butyl-1-neopentyl-2,2-dimethylcyclopropane (**3**), and 2,3,5,5-tetramethyl-3-*tert*-butyl-1-hexene (**4**). A pathway to these products involving initial formation of an ion pair is proposed. Hydrogenation and bromination of **1** are relatively slow, presumably due to steric shielding of the double bond. Ozonation of **1** leads to cleavage of the double bond without formation of an epoxide. Hydroboration of **1** is slow and after oxidation with alkaline hydrogen peroxide gives 4-*tert*-butyl-2,2,5,5-tetramethyl-3-hexanone (**9**), *trans*-2,3-di-*tert*-butyl-4,4-dimethyltetrahydrofuran (**10**), and the expected 4-*tert*-butyl-2,2,5,5-tetramethyl-3-hexanol (**11**). Oxidation of the hydroboration product with *m*-chloroperbenzoic acid yields **10** and **11'** but none of **9**. It is proposed that **9** arises from a free-radical oxidation route which competes with the retarded normal ionic oxidation by alkaline hydrogen peroxide but not with the faster ionic oxidation by *m*-chloroperbenzoic acid, while **10** is derived from cyclization of the initially formed borane to give a boron heterocycle **13** which leads to **10** on oxidation. Reaction of di-*tert*-butylacetyl chloride with *tert*-butyllithium leads to the formation of 9,11,tri-*tert*-butylcarbinol, 4-*tert*-butyl-4-hydroxy-2,2,5,5-tetramethyl-3-hexanone (**19**), 3,6-di-*tert*-butyl-5-hydroxy-2,2,7,7-tetramethyl-4-octanone (**20**), and 3,6-di-*tert*-butyl-2,2,7,7-tetramethyl-4,5-octadione (**21**). A mechanism involving radical and radical anion intermediates is proposed for this transformation.

There is a continuing intense interest in the influence of steric strain on the properties of olefins.[2b,3] These studies have involved olefins that are strained by their incorporation in rings[3a-c,e] and those strained by the presence of bulky substituents.[2b,4]

As part of a study of the effects of extreme steric crowding on the physical and chemical properties of organic compounds, tri-*tert*-butylethylene (**1**) has been prepared in this laboratory. Its synthesis has been described,[2b,4] as well as some aspects of its chemical reactivity[4] and studies of the effect of crowding on the Raman,[4] ultraviolet,[2b] and ^{13}C nmr[2c] spectra of olefins. This report contains a description of a number of chemical reactions of **1** and some related compounds which are potential precursors to a compound which is an as yet unrealized synthetic goal in this laboratory: tetra-*tert*-butylethylene. The unusual course taken in some of these reactions illustrates the remarkable influence of extreme steric crowding in affecting chemical reactivity.

Preparation of Tri-*tert*-butylethylene (1).—This synthesis was accomplished by the pyrolysis of di-*tert*-



(1)

* Address correspondence to Department of Chemistry, University of Toronto, Scarborough College, West Hill, Ontario, Canada.

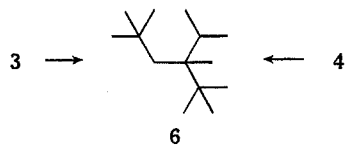
(1) Acknowledgment is made to the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. Part V, ref 2a; part IV, ref 2b; part VII, ref 2c.

(2) (a) G. J. Abruscato and T. T. Tidwell, *J. Amer. Chem. Soc.*, **94**, 672 (1972); (b) G. J. Abruscato, R. G. Binder, and T. T. Tidwell, *J. Org. Chem.*, **37**, 1787 (1972); (c) G. J. Abruscato, P. D. Ellis, and T. T. Tidwell, *Chem. Commun.*, 988 (1972).

(3) (a) C. C. Levin and R. Hoffmann, *J. Amer. Chem. Soc.*, **94**, 3446 (1972); (b) G. L. Buchanan and G. Jamieson, *Tetrahedron*, **28**, 1123, 1129 (1972); (c) W. L. Mock, *Tetrahedron Lett.*, 475 (1972); (d) L. Radom, J. A. Pople, and W. L. Mock, *ibid.*, 479 (1972); (e) R. Keese and E.-P. Krebs, *Angew. Chem., Int. Ed. Engl.*, **11**, 518 (1972).

(4) G. J. Abruscato and T. T. Tidwell, *J. Amer. Chem. Soc.*, **92**, 4125 (1970).

butylneopentylcarbinyl *p*-nitrobenzoate (2), which gave **1**, the cyclopropane **3**, the rearranged olefin **4**, and the fragmentation product **5** in isolated yields after gas chromatographic separation of 26, 10, 13, and about 1%, respectively. Compounds **3** and **4** were characterized by their spectral properties, analyses, and hydrogenation to the same product: methylisopropyl-*tert*-butylneopentylmethane (**6**). Compound **5** was identified by its spectral properties and its reported[5] formation as a by-product in the dehydration of di-*tert*-butylneopentylcarbinol.

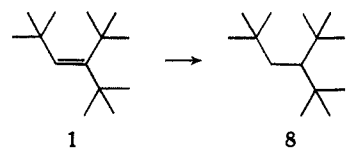


The hydrogenolysis of the cyclopropane **3** to **6** proceeded with some difficulty. Thus, no reaction was observed on treatment of **3** with PtO_2 in glacial acetic acid at 95° and 55 psi of hydrogen, or with Raney nickel in methanol at 110° and 1700 psi of hydrogen. Reaction at 25° and 60 psi of hydrogen with PtO_2 in acetic acid containing perchloric acid gave 90% starting material and 10% **6**. Compound **3** was shown to be stable to the reaction conditions including the perchloric acid but excluding the hydrogen.

The preparation of *p*-nitrobenzoate **2**, the precursor of **1**, by the published procedure[6] has been reported[5c] to involve "great difficulty" and in our hands gives variable yields in the range of 20–50%. The corresponding benzoate, di-*tert*-butylneopentylcarbinyl benzoate (**7**), was prepared by the use of the more soluble benzoyl chloride in 47% yield, and this reaction appeared to be more reproducible than the synthesis of the *p*-nitro derivative. Ester **7** was less reactive than **2**, but on pyrolysis at 225° and atmospheric pressure gave a 41% yield of purified **1**, as well as **3**–**5** and an additional product tentatively identified as 4-*tert*-butyl-2,6,6-trimethyl-2-heptene, presumably derived from acid-catalyzed ring opening of **3**. It has also been reported[5] that dehydration of di-*tert*-butylneopentylcarbinol by various techniques gives zero to good yields of **1**.

The formation of products of rearrangement and fragmentation in the pyrolyses of **2** and **7** suggests that these reactions proceed by ion pairs of carbonium ions and benzoate anions, as opposed to concerted elimination pathways. The formation of **1**, **3**, and **4** in the solvolysis of **2** supports this hypothesis. Formation of cyclopropane **3** as a product from a reaction involving a tertiary carbonium ion is most unusual. To our knowledge the only other reported examples of such processes involve deaminations of polycyclic amines,[7] although protonated cyclopropane intermediates have been invoked in rearrangements of tertiary cations in strong acids.[8,9] Since our initial publication[4] dehydrations of alcohols have also been observed[5b] to give rise to **3** and related cyclopropanes.

Hydrogenation of 1.—Treatment of **1** with 60 psi of hydrogen over PtO_2 in glacial acetic acid gave a product containing 20% unreacted **1** and 80% of the saturated hydrocarbon 3-*tert*-butyl-2,2,5,5-tetramethylhexane (**8**).



Under similar conditions **4** was completely hydrogenated to **6**, suggesting some steric inhibition to hydrogenation in the crowded **1**. This phenomenon has been observed previously for 1,1-dineopentylethylene[10] and hexaisopropenylbenzene.[11]

Bromination.—Addition of bromine to **1** in CCl_4 in the dark at 25° resulted in rapid but not instantaneous decoloration of the bromine and evolution of acidic vapor. The nmr spectrum of the reaction product showed a large number of signals in regions ascribable to the protons of aliphatic bromides and rearranged olefins. The product was not characterized further. Apparently addition–elimination and rearrangement pathways for the reaction were predominating, as would be expected for the crowded structure. Such reactions apparently occur in the bromination of 1,1-dineopentylethylene,[10] hexaisopropenylbenzene,[11] and α,o,o,p-tetramethylstyrene.[12a] Qualitatively **1** did not decolorize bromine as fast as did cyclohexene, showing that there was a steric barrier to the initial electrophilic attack. Quantitative rate studies for bromination of **1** confirm the low reactivity of this olefin.[12b]

Ozonolysis.—The reaction of **1** with ozone proceeded normally and gave as the only observed products di-*tert*-butyl ketone and pivalaldehyde (eq 2). Thus, **1**

$$\underset{\mathbf{1}}{t\text{-BuCH=C-}t\text{-Bu}_2} \xrightarrow[2.\ (MeO)_3P]{1.\ O_3} t\text{-BuCH=O} + t\text{-Bu}_2\text{C=O} \quad (2)$$

differs from hexaisopropylbenzene, which does not react with ozone,[11] and various other crowded olefins which give epoxides on ozonation.[13] The possibility remains that an intermediate epoxide may have been destroyed by excess ozone or trimethyl phosphite.

Hydroboration.—The reaction of **1** with diborane proceeded slowly so that relatively long reaction times were needed to avoid the recovery of substantial amounts of starting material. Hydroboration of **1** with *in situ* generation of diborane, followed by oxidation with alkaline hydrogen peroxide, gave 35% 4-*tert*-butyl-2,2,5,5-tetramethyl-3-hexanone (**9**), 32% *trans*-2,3-di-*tert*-butyl-4,4-dimethyltetrahydrofuran (**10**), and

(5) (a) J. E. Dubois, J. S. Lomas, and D. S. Sagatys, *Tetrahedron Lett.*, 1349 (1971); (b) J. S. Lomas, D. S. Sagatys, and J.-E. Dubois, *ibid.*, 165 (1972); (c) *ibid.*, 599 (1971).

(6) P. D. Bartlett and T. T. Tidwell, *J. Amer. Chem. Soc.*, **90**, 4421 (1968).

(7) W. G. Dauben and P. Laug, *Tetrahedron*, **20**, 1259 (1964).

(8) G. M. Kramer, *J. Amer. Chem. Soc.*, **92**, 4344 (1970); (b) M. Saunders and P. Vogel, *ibid.*, **93**, 2559, 2561 (1971).

(9) An additional example of cyclopropane formation from a tertiary carbonium ion has been observed in the solvolysis of phenyl di-*tert*-butylcarbinyl *p*-nitrobenzoate: H. Tanida and H. Matsumura, *ibid.*, in press.

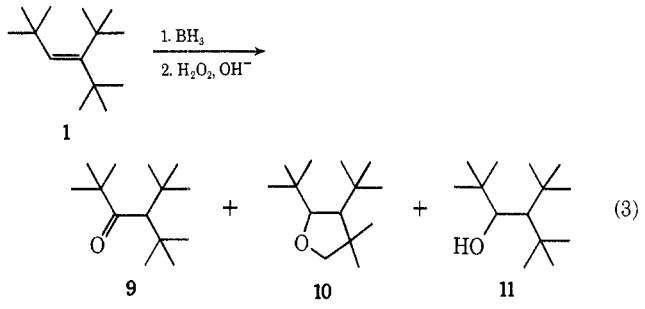
(10) P. D. Bartlett, G. L. Fraser, and R. B. Woodward, *J. Amer. Chem. Soc.*, **63**, 495 (1941).

(11) E. M. Arnett, J. M. Bollinger, and J. C. Sanda, *ibid.*, **87**, 2050 (1965).

(12) (a) E. S. Huyser and L. Kim, *J. Org. Chem.*, **33**, 1243 (1968); (b) J.-É. Dubois and M. Loïzos, *C. R. Acad. Sci., Ser. C.*, **274**, 1130 (1972).

(13) (a) P. D. Bartlett and M. Stiles, *J. Amer. Chem. Soc.*, **77**, 2806 (1955); (b) P. S. Bailey, J. W. Ward, and R. E. Hornish, *ibid.*, **93**, 3552 (1971).

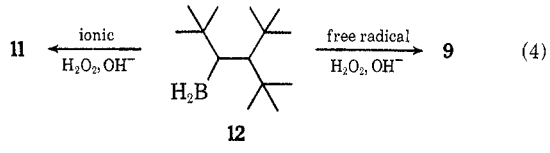
21% 4-*tert*-butyl-2,2,5,5-tetramethyl-3-hexanol (**11**) (eq 3). Ketone **9** and alcohol **11** were identified by their



(3)

spectral properties, the oxidation of **11** to **9** with chromic acid, and the independent synthesis of **9** and **11** by the reaction of di-*tert*-butylacetyl chloride with *tert*-butyllithium (*vide infra*).[14] The nmr spectrum of **11** is unique in that the geminal *tert*-butyl groups are diastereotopic and nonequivalent in the nmr. To our knowledge **11** and compound **20** (*vide infra*) are the only examples of compounds with *tert*-butyl groups rendered nonequivalent by a neighboring asymmetric atom. The tetrahydrofuran **10** was identified on the basis of its spectral properties and elemental analysis, and tentatively assigned the trans arrangement of the *tert*-butyls on the basis of steric considerations. The spin-spin coupling between the 2,3 hydrogens in **10** is 5 Hz, which is consistent with but not definitive for the trans geometry.[15]

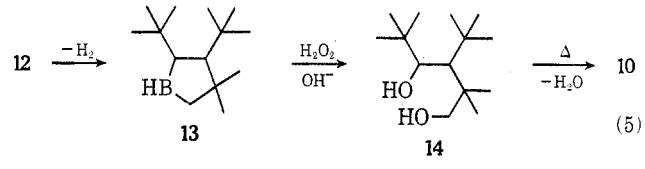
Ketone **9** is probably formed by a free-radical reaction of borane **12**. It has been proposed[16] that radical reactions of boranes in basic solutions of hydrogen peroxide may become important when the normal ionic oxidations are made less favorable, as may be the case with the highly crowded **12**. Confirmatory evidence for this hypothesis was obtained by the reaction of **12** with the more effective oxidizing agent *m*-



(4)

chloroperbenzoic acid,[17] which gave a mixture of products including the normal alcohol **11** but no ketone.

The presumed route for the formation of the tetrahydrofuran **10** involves cyclization of **12** to borane **13**, which on oxidation either forms **10** directly or forms the diol **14** which cyclizes during the work-up (eq 5). The



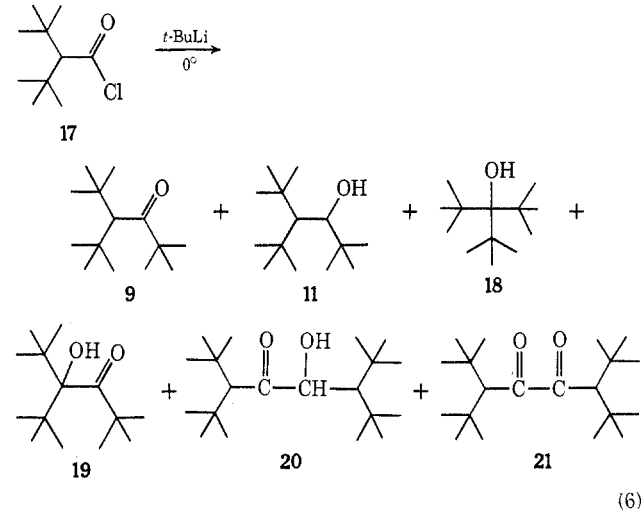
(5)

cyclization of alkylboranes is a well-known phenomenon, particularly in sterically crowded molecules.[18] Cyclic boranes yield diols on oxidation in some cases[18a,b] and cyclic ethers in others,[18c] but it may be that the latter examples involving vigorous oxidation proceed through diols, inasmuch as the crowded 3,3,4,4-tetramethylheptane-2,5-diol is known[19] to cyclize to a tetrahydrofuran at 100°.

An attempt was made to isolate the boranes formed in the reaction by omitting the oxidation step, but the only materials isolated were alcohols and carbonyl compounds of unknown structure, apparently formed by air oxidation of the boranes.

Reaction of Ethyl and Methyl Di-*tert*-butylacetates with *tert*-Butyllithium.—In an attempt to develop an alternative synthesis of the tri-*t*-butylethane skeleton the reactions of ethyl di-*tert*-butylacetate (**15**) and methyl di-*tert*-butylacetate (**16**) with *tert*-butyllithium were examined. Either of these esters with 1 equiv of *tert*-butyllithium gave di-*tert*-butylacetic acid and unreacted starting material as the only observed products. The reaction of the esters at the alkyl group presumably reflects the low reactivity of the carbonyl group due to steric hindrance, so that cleavage reactions similar to those observed between ethers and alkyllithiums[20] predominate. The cleavage of hindered esters by *tert*-butyllithium has been observed previously.[21]

Reaction of Di-*tert*-butylacetyl Chloride (17) with *tert*-Butyllithium.—Addition of *tert*-butyllithium to **17** in pentane at 0° led after work-up to the isolation of 79% of starting material (obtained as the acid after base hydrolysis) and the surprising array of products shown in eq 6. The yields of **9**, **11**, **18**, **19**, **20**, and **21** were 2, 9.5, 1, 3.6, 5%, and trace (impure), respectively.



(6)

Compounds **9** and **11** were identified by comparison with samples prepared in this work, and tri-*tert*-butylcarbinol (**18**) was identical with material prepared by

(14) Ketone **9** has been independently prepared but the only reported characterization was the carbonyl stretching frequency: J.-É. Dubois and M. Boussu, *C. R. Acad. Sci., Ser. C*, **268**, 1603 (1969).

(15) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, New York, N. Y., 1969, p 287.

(16) D. J. Pasto, S. K. Arora, and J. Chow, *Tetrahedron*, **25**, 1571 (1969).

(17) The oxidation of organoboranes with peracids has been examined previously: (a) J. R. Johnson and M. G. Van Campen, Jr., *J. Amer. Chem. Soc.*, **60**, 121 (1938); (b) G. Wilke and P. Heimbach, *Justus Liebegs Ann. Chem.*, **652**, 7 (1962).

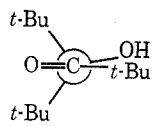
(18) (a) T. J. Logan and T. J. Flautt, *J. Amer. Chem. Soc.*, **82**, 3446 (1960); (b) H. C. Brown, K. J. Murray, H. Müller, and G. Zweifel, *ibid.*, **88**, 1443 (1966); (c) P. F. Winternitz and A. A. Carotti, *ibid.*, **82**, 2430 (1960).

(19) M. F. Ansell, W. J. Hickenbottom, and P. G. Holton, *J. Chem. Soc.*, 349 (1955).

(20) G. E. Coates and K. Wade, "Organometallic Compounds," Vol. 1, 3rd ed, Methuen and Co., London, 1967, Chapter 1.

(21) (a) E. P. Kaplan, S. V. Zakharova, and A. D. Petrov, *Zh. Obshch. Khim.*, **33**, 2103 (1963); *J. Gen. Chem. USSR*, **33**, 2048 (1963); (b) A. D. Petrov, E. P. Kaplan, and M. Kurash, *Zh. Obshch. Khim.*, **32**, 19 (1962); *J. Gen. Chem. USSR*, **32**, 20 (1962).

the known route.[13a] The ketol 4-*tert*-butyl-4-hydroxy-2,2,5,5-tetramethyl-3-hexanone (**19**) was identified by its elemental analysis, infrared spectrum (OH at 3632 and C=O at 1687 cm^{-1}), nmr spectrum (two *tert*-butyls at δ 1.10 and one at 1.23, and the OH at 1.79), and independent preparation from pivalil (**22**) and *tert*-butyllithium. The intramolecular hydrogen bond generally observed[22] in α-hydroxy ketones was absent in the case of **19**, presumably due to the prevalence of the conformation shown.



19

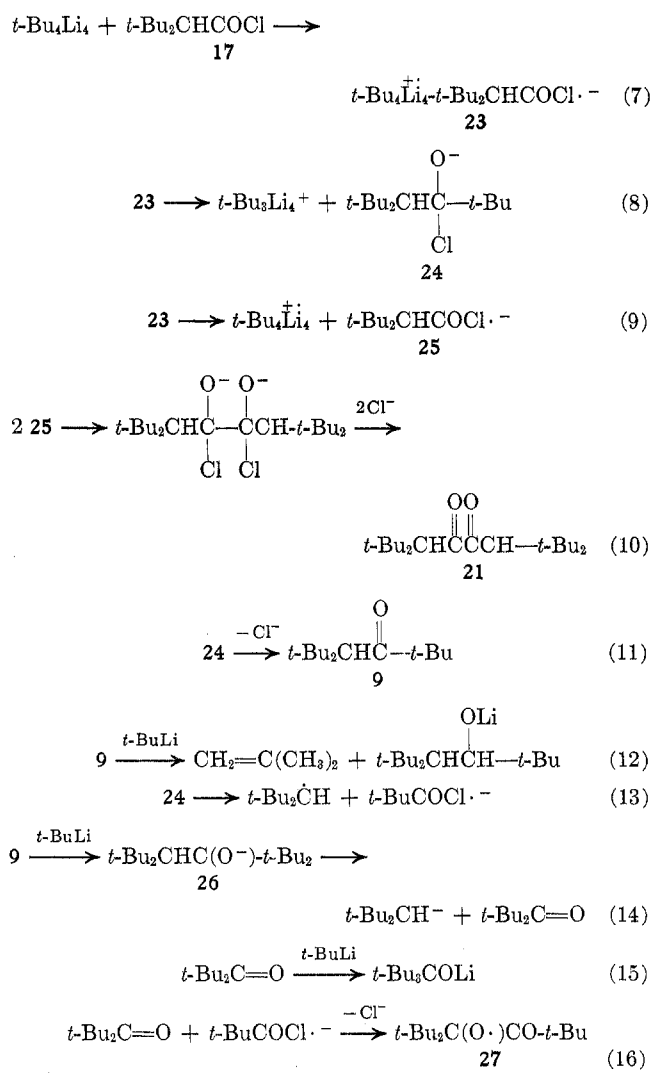
3,6-Di-*tert*-butyl-5-hydroxy-2,2,7,7-tetramethyl-4-octanone (**20**) and 3,6-di-*tert*-butyl-2,2,7,7-tetramethyl-4,5-octadione (**21**)[23] (the latter compound was obtained pure in another reaction, *vide infra*) were characterized by their elemental analyses and spectral properties. The nmr spectrum of **20** showed three *tert*-butyl absorptions, indicating magnetic nonequivalence of the two diastereotopic *tert*-butyls at C-6.

Another experiment at −70° with addition of 17 to excess *tert*-butyllithium eliminated the presence of starting material in the product and gave **9**, **11**, **18**, **20**, and **21** in isolated yields of 3.5, 9, 4, 20, and 10%, respectively. Ketol **19** was not observed.

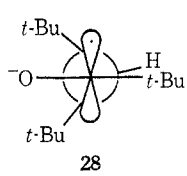
The mechanism shown in Scheme I is proposed to account for these results, although many of these steps are speculative and reasonable alternatives can be written. *tert*-Butyllithium in alkane solutions is known to exist as tetramers,[24] and the electron-transfer process shown in eq 7–9 has been proposed as a significant reaction pathway for alkyllithiums.[25] The acyloin condensation[26] is known to occur with acid chlorides, and eq 10 suggests a plausible route to diketone **21**, which could undergo reduction by *tert*-butyllithium to form the acyloin **20**. There has been a previous report[21b] of acyloin condensation of ethyl benzoate induced by isopropyl- or *tert*-butyllithium, although the mechanism proposed[21b] involved the intervention of free lithium metal, which was presumably not present in the commercial *tert*-butyllithium in pentane utilized in this work. The diketone **21** has been obtained from the reaction of **17** with ethylmagnesium bromide and copper catalysts.[23] A radical mechanism was proposed[23] for the latter reaction, but the absence of products analogous to **18** and **19** shows that it is only superficially related to that shown in eq 6.

The formation of di-*tert*-butylmethyl radical or anion (eq 13, 14) would lead to the presence of di-*tert*-butylmethane in the product. Based on this prediction, a search was made of the volatile portion of the reaction mixture, and the presence of this compound was confirmed by isolation and comparison with an authentic specimen. The absence of **19** from the reaction product when **17** was added to *tert*-butyllithium is in accord with this mechanism, as the di-*tert*-butyl ketone formed would be rapidly consumed by the excess *tert*-butyllithium.

Scheme I
Reaction of Di-*tert*-butylacetyl Chloride (**17**) with *tert*-Butyllithium



Radical Anion of 4-*tert*-Butyl-2,2,5,5-tetramethyl-3-hexanone (9).—A sample of **9** was provided to Professor G. A. Russell and coworkers, who measured the esr spectrum of ketyl **28** formed from reduction of **9** with potassium in dimethoxyethane. The hyperfine splittings of the α hydrogen and the carbonyl carbon were $A_{\alpha}^{H} < 1.8$ and $A_{CO}^{C} = 34$ G, respectively.[27] The small magnitude of the former value supports the importance of the conformation shown, which is similar to the conformation proposed for the ketol **19**.



28

(22) L. Joris and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **90**, 4599 (1968).

(23) Dione **21** has been prepared independently but the full characterization has not been reported: J.-E. Dubois and M. Boussu, *Tetrahedron Lett.*, 2523 (1970).

(24) H. L. Lewis and T. L. Brown, *J. Amer. Chem. Soc.*, **92**, 4664 (1970).

(25) C. G. Screttas and J. F. Eastham, *ibid.*, **88**, 5668 (1966).

(26) S. M. McElvain, *Org. React.*, **4**, 256 (1948).

(27) G. A. Russell, D. F. Lawson, H. L. Malkus, and P. R. Whittle, *J. Chem. Phys.*, **54**, 2164 (1971).

Experimental Section

Elemental analyses were performed by Galbraith Laboratories or the Bernhardt Microanalytisches Laboratorium. Melting points and boiling points are uncorrected. Infrared spectra were run on Perkin-Elmer 257 or 337 grating spectrophotomers. Nmr spectra were run on a Varian A-60 or XL-100 spectrometer in carbon tetrachloride solution with tetramethylsilane as an internal standard. Mass spectra were obtained using a Perkin-Elmer Hitachi RMU instrument. Vapor phase chromatography was carried out using Varian Aerograph 90-P3 and 1820-1 instruments and the following columns: SE-52 (10 ft × 0.375 in., 30% SE-52 on Chromosorb W), FFAP-1 (20 ft × 0.375 in., 30% FFAP on Chromosorb W), FFAP-2 (10 ft × 0.375 in., 30% FFAP on Chromosorb W), QF-1 (10 ft × 0.375 in., 30% QF 1 on Chromosorb W), Carbowax (10 ft × 0.375 in., 30% Carbowax 20M on Chromosorb W) (all used on 90-P3), SE-30 (10 ft × 0.375 in., 30% SE-30 on Chromosorb W), and DEGS (10 ft × 0.375 in., 30% DEGS on Chromosorb W) (last two used on 1820-1).

Tri-*tert*-butylethylene (1).—The preparation and physical properties of this compound have been described.[2b,4] The first fraction from the vpc separation (SE-52, 165°, 100 ml/min He) of the product from pyrolysis of 15.5 g (0.0428 mol) of di-*tert*-butylneopentylcarbinyl *p*-nitrobenzoate (2) appeared to be a trace of **1,2,2-trimethyl-1-neopentylethylene** (5):[5] nmr (CCl_4) δ 0.99 (s, 9, *t*-Bu), 1.64 (s, 9, 3 Me), and 1.98 (s, 2, CH_2Bu); mass spectrum (70 eV) molecular ion *m/e* 140. The second vpc fraction consisted of 2.22 g (26%) of 1, and the third fraction was separated by vpc (FFAP-1, 80°, 75 ml/min He) into two components. The first component, retention time 4 hr, was 0.84 g (10%) of **1-*tert*-butyl-1-neopentyl-2,2-dimethylcyclopropane** (3): ir (CCl_4) 3060 cm^{-1} (cyclopropyl CH); near-ir[28] (CCl_4) 6115 cm^{-1} (cyclopropyl overtone); nmr (CCl_4) δ 0.65 (s, 2, CH_2 of cyclopropyl), 1.00 (s, 9, *t*-Bu), 1.02 (s, 9, *t*-Bu), 1.12 (s, 3, Me), 1.38 (s, 3, Me), and 1.60 and 1.74 (center peaks of an AB quartet of diastereotopic CH_2 of the neopentyl, J = 16 Hz); mass spectrum (70 eV) molecular ion *m/e* 196.

Anal. Calcd for $C_{14}H_{28}$ (196.38): C, 85.63; H, 14.37. Found: C, 85.00; H, 14.95.

The second component, retention time 4.5 hr, was 1.09 g (13%) of **3-*tert*-butyl-2,3,5,5-tetramethyl-1-hexene**[6] (4): ir (CCl_4) 1625 cm^{-1} (C=C); nmr (CCl_4) δ 0.90 (s, 9, *t*-Bu), 0.99 (s, 9, *t*-Bu), 1.15 (s, 3, saturated Me), 1.20 and 1.45 (center peaks of an AB quartet of the diastereotopic CH_2 of the neopentyl, J = 15 Hz), 1.82 (d, 3, vinyl Me, J = 2 Hz), 4.79 (d, 1, vinyl H, J = 2 Hz), and 4.95 (m, 1, vinyl H, J = 2 Hz); mass spectrum (70 eV) molecular ion *m/e* 196.

Anal. Calcd for $C_{14}H_{28}$ (196.38): 85.63; H, 14.37. Found: C, 85.16; H, 14.71.

Hydrogenolysis of 3.—Cyclopropane 3 (85 mg, 0.4 mmol) was treated with 60 psi of hydrogen and 86 mg of PtO_2 in 10 ml of glacial acetic acid containing one drop of 70% perchloric acid for 23 hr at 25°. The mixture was filtered and the filtrate was made basic with KOH solution and extracted with pentane. The pentane was washed with saturated NaCl, dried (Drierite), concentrated, and separated by vpc (FFAP-1, 125°, 80 ml/min He) into two components. The major component was unreacted 3 (90%). The second component was 10% of **4-*tert*-butyl-2,2,4,5-tetramethylhexane** (6): nmr (CCl_4) δ 0.92 (s, 9, *t*-Bu), 1.02 (s, 9, *t*-Bu), 1.01 (d, 6, $CHMe_2$, J = 8 Hz), 1.11 (s, 3, Me), 1.43 (q, 2, diastereotopic CH_2, J = 18 Hz), and 2.08 (septet, 1, $HCMe_2$, J = 8 Hz).

Anal. Calcd for $C_{14}H_{30}$ (198.40): C, 84.76; H, 15.24. Found: C, 84.90; H, 15.08.

Repetition of the experiment in the absence of hydrogen gave only unreacted 3. Hydrogenation of 4 under similar conditions but without perchloric acid gave only 6.

Di-*tert*-butylneopentylcarbinyl benzoate (7) was prepared according to the procedure for the *p*-nitrobenzoate 2, with benzoyl chloride in pentane being added to the lithium salt of di-*tert*-butylneopentylcarbinol in pentane. Fractional crystallization from pentane gave 47% of 7: mp 64–68°; nmr (CCl_4) δ 1.10 (s, 9, *t*-Bu), 1.30 (s, 18, 2 *t*-Bu), 2.42 (s, 2, CH_2), and 7.3–7.9 (m, 5, aromatic).

Pyrolysis of 7.—Benzoate 7 (16 g, 0.49 mol) was heated slowly to 225° in a glass tube with an outlet to a Dry Ice trap at atmospheric pressure. The tube was cooled and rinsed with pentane, and the solid benzoic acid was filtered off. The filtrate was separated by vpc (SE-52, 135°, 75 ml/min He) into five fractions: 0.16 g (0.25%) of the material tentatively identified as 5 (*vide supra*), 0.5 g (5%) of material tentatively identified as 4-*tert*-butyl-2,6,6-trimethyl-2-heptene (presumably derived from 3), nmr (CCl_4) δ 0.80 (s, 9, *t*-Bu), 0.82 (s, 9, *t*-Bu), 1.23 (m, 2, CH_2), 1.59 (d, 3, Me, J = 2 Hz), 1.67 (d, 3, Me, J = 2 Hz), 1.96 (m, 1, HC-*t*-Bu), and 4.89 (d, 1, vinyl H, J = 10 Hz), 0.4 g of an unidentified olefin, 3.94 g (41%) of 1, and a mixed fraction. This last fraction was separated by vpc (DEGS, 80°, 50 ml/min He) into 0.63 g (7%) of 3 and 2.37 g (25%) of 4.

Solvolysis of 2.—A solution of 208 mg (0.5 mmol) of 2 in 100 ml of 60% aqueous dioxane was put into a constant temperature bath at 55° for 25 hr. The dioxane solution was diluted with water and extracted with pentane. The pentane extract was washed with saturated NaCl, dried (Drierite), and concentrated. Separation by vpc (FFAP-1, 110°, 75 ml/min He) afforded 10% of 1, 5% of 3, 5% of an unidentified olefin, and 80% of 4.

Hydrogenation of 1.—A mixture of 138 mg (0.73 mmol) of 1 and 39 mg of PtO_2 in 20 ml of glacial HOAc was shaken for 11 hr in a Parr hydrogenation apparatus at a pressure of 60 psi of hydrogen. The mixture was filtered and the filtrate was diluted with water and extracted with pentane. The pentane extract was washed with saturated Na_2CO_3 and NaCl, dried (Drierite), and concentrated. Separation of the residue by vpc (Carbowax, 130°, 75 ml/min He) afforded 88% of unreacted 1 and 12% of material assigned the structure **3-*tert*-butyl-2,2,5,5-tetramethylhexane** (8): nmr (CCl_4) δ 0.93 (s, 9, *t*-Bu), 1.01 (s, 18, 2 *t*-Bu), and 1.2–1.5 (undefined, overlapping multiplets due to $-CH_2$ and $-CH$).

Anal. Calcd for $C_{14}H_{30}$ (198.40): C, 84.76; H, 15.24. Found: C, 85.01; H, 14.97.

Hydrogenation of 183 mg (0.935 mmol) of 1 with 145 mg of PtO_2 in 10 ml of acetic acid for 24 hr at 60 psi of hydrogen gave after vpc separation a 50% recovery of material consisting of 20% unreacted 1 and 80% 8. These were the conditions under which 4 underwent complete hydrogenation.

Ozonolysis of 3.—A solution of the olefin (186 mg, 0.95 mmol) in 50 ml of dry CH_2Cl_2 was put into a glass tube fitted with a fritted bubbler extending to its bottom. Ozone (generated by a Welsbach ozonator) was bubbled into the solution at −70°. A trap containing 2% aqueous KI was placed to receive the effluent gases from the reaction tube, and after 15 min began showing evidence of an excess of ozone by turning slightly yellow. After another 15 min, the KI solution was colored a dark orange. The bubbling was continued for an additional 15 min to ensure complete reaction. The reaction mixture was transferred to a flask and stirred overnight with 50 ml of trimethyl phosphite. After removal of the CH_2Cl_2 by distillation, the solution was analyzed by vpc (QF-1, 125°, 75 ml/min He) and found to contain pivalaldehyde and di-*tert*-butyl ketone by comparison of their retention times with those of authentic material; no starting material was observed. The solution was made basic with aqueous NaOH to hydrolyze the trimethyl phosphite and was extracted with pentane. The pentane extract was washed with water and saturated NaCl, dried (Drierite), and concentrated. Separation by vpc (QF-1, 100°, 75 ml/min He) of the residue yielded a small amount of pivalaldehyde and 50 mg (37%) of di-*tert*-butyl ketone. There was not a sufficient amount of the aldehyde to obtain definitive spectral data, but it was enough to yield a DNPH derivative melting at 204–209° (lit.[29] mp 209°). The identity of the ketone was confirmed by ir and nmr spectral comparison with that of authentic material.

Bromination of 1.—The olefin (72.4 mg, 0.37 mmol) in 1 ml of CCl_4 was put into a flask and wrapped with aluminum foil to keep out light, and 2 ml of a 0.172 M solution of bromine in CCl_4 was added slowly in the dark. During the addition acidic vapors, assumed to be HBr, were evolved. An nmr spectrum of the reaction mixture, after the disappearance of the bromine color, showed a multitude of peaks at δ 1.5–2 ppm presumably due to $BrCCH_3$ and/or vinyl methyl groups; at δ 3–4 ppm due to BrCH and/or $BrCH_2$; and at δ 5–6 ppm due to vinyl protons other than the vinyl hydrogen of the starting material.

Hydroboration–Oxidation of 1.[30]—A 100-ml flask, equipped with a magnetic stirrer and an addition funnel and protected

(28) Determined with a Cary 14 ultraviolet–visible spectrophotometer.

(29) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "Systematic Identification of Organic Compounds," 5th ed, Wiley, New York, N. Y., 1965, p 320.

(30) G. Zweifel and H. C. Brown, *Org. React.*, **13**, 1 (1963).

from outside moisture with a drying tube, was charged with 1.08 g (5.5 mmol) of 1 and 0.68 g (18 mmol) or $NaBH_4$ in 3 ml of anhydrous THF. The flask was immersed in an ice bath and 3.46 g (24.3 mmol) of $BF_3 \cdot OEt_2$ in 5 ml of anhydrous THF was added over 35 min with stirring. The mixture was stirred at 0° for 2.5 hr and then at 25° for 18 hr. The excess hydride was decomposed with water and the solution was made basic with 5 ml of 3 *N* NaOH. The mixture was heated to 40–50° and 5 ml of 30% H_2O_2 was added dropwise with stirring. The reaction mixture was then stirred at 25° for 9 hr, saturated with NaCl, and extracted with ether. The ethereal extract was dried (Drierite), concentrated, and separated into four fractions by vpc (SE-30, 200°, 75 ml/min He). The first fraction consisted of a trace amount of unreacted starting material. The second amounted to 0.375 g (35%) of **4-*tert*-butyl-2,2,5,5-tetramethyl-3-hexanone (9)**:[14] ir (CCl_4) 1688 cm^{-1} (lit.[14] ir 1688.4 cm^{-1}); nmr (CCl_4) δ 1.07 (s, 18 2 *t*-Bu), 1.18 (s, 9, *t*-Bu), and 2.89 (s, 1, HCC=O).

Anal. Calcd for $C_{14}H_{28}O$ (212.38): C, 79.18; H, 13.29. Found: C, 79.06; H, 13.25.

The third fraction was 0.369 g (32%) of **trans-2,3-di-*tert*-butyl-4,4-dimethyltetrahydrofuran (10)**: nmr (CCl_4) δ 0.97 (s, 9, *t*-Bu), 1.04 (s, 9, *t*-Bu), 1.12 (s, 3, Me), 1.23 (s, 3, Me), 1.55 (d, 1, HCCO, J = 5 Hz), 3.31 (s, 2, CH_2), and 3.59 (d, 1, HCO, J = 5 Hz).

Anal. Calcd for $C_{14}H_{28}O$ (212.38): C, 79.18; H, 13.29. Found: C, 78.98; H, 13.07.

The last fraction, 0.249 g (21%), was identified as **4-*tert*-butyl-2,2,5-5-tetramethyl-3-hexanol (11)**: ir (CCl_4) 3630 cm^{-1} (OH); nmr (CCl_4) δ 0.97, 1.08, and 1.15 (each s, 9, *t*-Bu), 1.41 (s, 1, OH), 1.43 (broad s, 1, HCCOH), and 3.75 (broad s, 1, HCOH).

Anal. Calcd for $C_{14}H_{30}O$ (214.39): C, 78.43; H, 14.10. Found: C, 78.21; H, 13.93.

Oxidation of **11** with chromic acid in acetone gave **9**, but treatment of **11** under the oxidative work-up conditions of the hydroboration above gave only recovered alcohol.

Hydroboration of **1** in diglyme with external generation of diborane by the published procedure[30] but a reaction period of 8 hr gave after oxidation **9** and **10** in the ratio of 3:2 as the only products.

Hydroboration of **1** in THF for 4 hr followed by the addition of excess *m*-chloroperbenzoic acid in chloroform and stirring for 2 hr gave after treatment with base and extraction a product which contained unreacted **1**, several unidentified compounds, and **10** and **11** in the ratio of 1:4. No ketonic products were observed in the infrared spectrum of the crude reaction mixture or in any of the components isolated by vpc.

Reaction of Pivalil (22) with *tert*-Butyllithium.—*tert*-Butyllithium (31.1 mmol, obtained as a 1.6 *M* solution in pentane from the Foote Mineral Co.) was placed in a 100-ml flask and immersed in a Dry Ice–isopropyl alcohol bath. Pure **22** (0.9 g, 5.3 mmol) in 1 ml of anhydrous pentane was added dropwise over 3 min at −70° with stirring under an atmosphere of helium. The reaction was stirred at −70° for 1 hr, allowed to warm slowly to 25°, and then stirred for an additional 30 min. The reaction mixture was cooled to −60° and water was added to stop reaction. After extraction with pentane, the pentane was washed with saturated NaCl, dried (Drierite), concentrated, and separated by vpc (SE 30, 175°, 75 ml/min He) into four components. The first was 40% of unreacted **22**, then next was 40% of pivaloin, the third was about 5% of an unidentified alcohol, and the last was about 15% of 4-*tert*-butyl-4-hydroxy-2,2,5,5-tetramethyl-3-hexanone (**19**): mp 112–116°; ir (CCl_4) 3632 (OH) and 1687 cm^{-1} (C=O); nmr (CCl_4) δ 1.10 (s, 18, 2 *t*-Bu), 1.23 (s, 9, *t*-Bu), and 1.79 (s, 1, OH).

Anal. Calcd for $C_{14}H_{28}O_2$ (228.38): C, 73.63; H, 12.36. Found: C, 73.70; H, 12.19.

Addition of *tert*-Butyllithium to Ethyl Di-*tert*-butylacetate (15).—*tert*-Butyllithium (100 ml, 0.125 mol) was added dropwise over 1 hr to 24.5 g (0.122 mol) of **15** [prepared from di-*tert*-butylacetyl chloride (**17**)[31] and ethanol] in 25 ml of anhydrous pentane with stirring under helium. The reaction was refluxed for 30 min and then decomposed with ice and concentrated H_2SO_4. The pentane layer was separated, washed with saturated solutions of Na_2CO_3 and NaCl, dried (Drierite), concentrated, and distilled at reduced pressure to give 14 g (57%) of unreacted **15**.

Acidification of the basic Na_2CO_3 wash yielded 7.5 g (36%) of di-*tert*-butylacetic acid.[31] No other products were detected upon analysis of the recovered ester and the residue from the distillation by vpc.

Addition of *tert*-Butyllithium to Methyl Di-*tert*-butylacetate (16).—*tert*-Butyllithium (55 ml, 0.068 mol) was added over 1 hr to a solution of 12.5 g (0.067 mol) of **16** [prepared from di-*tert*-butylacetyl chloride (**17**)[31] and methanol] in 25 ml of anhydrous pentane while stirring under helium. The solution was refluxed for 15 min and worked up as in the preceding example to give 1.2 g (9.5%) of unreacted starting material and 10.3 g (90%) of di-*tert*-butylacetic acid.

Addition of *tert*-Butyllithium to Di-*tert*-butylacetyl Chloride (17).—*tert*-Butyllithium (30 ml, 0.038 mol) was added dropwise at 0° over 30 min to a solution of 7 g (0.037 mol) of **17**[31] in 15 ml of anhydrous pentane with stirring and with helium flowing through the system. The reaction was refluxed for 30 min and then decomposed onto ice. The pentane layer was separated, washed with aqueous NaOH and saturated NaCl, dried (Drierite), concentrated, and refrigerated to yield 0.6 g of an impure solid after filtration. This solid was separated by fractional sublimation into 0.3 g (3.6%) of 4-*tert*-butyl-4 hydroxy-2,2,5,5-tetramethyl-3-hexanone (**19**) and 0.3 g (5%) of **3,6-di-*tert*-butyl-5-hydroxy-2,2,7,7-tetramethyl-4-octanone (20)**: mp 163–167°; ir (CCl_4) 3480 (OH) and 1699 cm^{-1} (C=O); nmr (CCl_4) δ 1.07 (s, 18, 2 *t*-Bu), 1.15 (s, 9, *t*-Bu), 1.16 (s, 9, *t*-Bu), 1.95 (d, 1, HCCOH, J = 2 Hz), 2.58 (s, 1, HCC=O), 3.01 (d, 1, OH, J = 5 Hz), and 4.28 (d, 1, CHOH, J = 5 Hz, fine splitting, J = 2 Hz).

Anal. Calcd for $C_{20}H_{40}O_2$ (312.54); C, 76.86; H, 12.90. Found: C, 77.02; H, 13.00.

The filtrate from the crystallization above was separated by vpc (SE-52, 150°, 75 ml/min He) into five components. The first component, tri-*tert*-butylcarbinol (**18**),[13a] was estimated to be a 1% yield based on the relative peak height of the chromatogram. The second component was less than a 1% yield of an unidentified solid. The third component consisted of 0.16 g (*ca.* 2%) of **9**, and the fourth amounted so 0.75 g (9.5%) of **11**. The last component was a small amount of a yellow liquid, apparently impure **21** (*vide infra*).

Acidification of the basic NaOH wash yielded *ca.* 5 g (78%) of di-*tert*-butylacetic acid.

Addition of Di-*tert*-butylacetyl Chloride (17) to *tert*-Butyllithium.—A solution of 5 g (26.2 mmol) of **17** in 10 ml of anhydrous pentane was added dropwise over 15 min at −70° to 88 mmol of *tert*-butyllithium with stirring and with helium flowing through the system. The reaction was stirred for 30 min while the temperature of the Dry Ice–isopropyl alcohol bath, in which the reaction flask was immersed, rose to −20°. At this temperature, water was added to stop the reaction. The pentane layer was separated, washed with aqueous NaOH and saturated NaCl, dried (Drierite), concentrated, and refrigerated to yield 0.8 g (20%) of **20**. The filtrate gave up an additional orange, crystalline solid upon standing for several days. This solid was filtered off and after column chromatography on silica gel with pentane gave 0.4 g (10%) of a bright yellow solid identified as **3,6-di-*tert*-2,2,7,7-tetramethyl-4,5-octadione (21)**: mp 123–128°; ir (CCl_4) 1700 cm^{-1} (C=O); nmr (CCl_4) δ 1.02 (s, 36, 4 *t*-Bu), and 3.65 (s, 2, HC-*t*-Bu_2).

Anal. Calcd for $C_{20}H_{38}O_2$ (310.52): C, 77.36; H, 12.33. Found: C, 77.28; H, 12.26.

The mother liquor remaining after filtration of the above two solids was separated into three fractions by column chromatography on Woelm neutral alumina, eluting with pentane. Each fraction obtained was further purified by vpc (SE-52, 150°, 75 ml/min He) to give 0.2 g (4%) of **18**, 0.2 g (3.5%) of **9**, and 0.5 g (9%) of **11**. Acidification of the basic NaOH wash yielded about 0.1 g (2%) of di-*tert*-butylacetic acid.

Registry No.—**1**, 28923-90-2; **3**, 36146-53-9; **4**, 36146-54-0; **6**, 28923-92-4; **7**, 36146-56-2; **8**, 36191-47-6; **9**, 24534-83-6; **10**, 36138-82-6; **11**, 36146-58-4; **19**, 36146-59-5; **20**, 36146-60-8; **21**, 29679-00-3.

(31) M. S. Newman, A. Arkell, and T. Funkunaga, *J. Amer. Chem. Soc.*, **82**, 2498 (1960).