Di-*t*-butylcyclopropenone and Substituted Di-*t*-butylcyclopropenyl Cations

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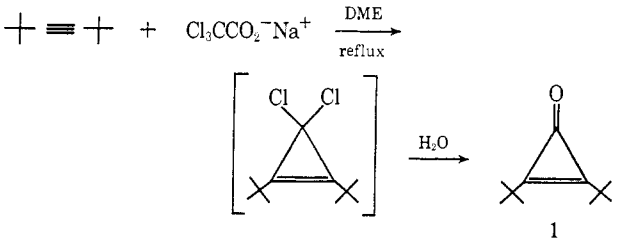
Abstract: Di-*t*-butylcyclopropenone (**1**) has been synthesized and its chemistry investigated. Pyrolysis or photolysis afforded di-*t*-butylacetylene. Condensation of **1** with malononitrile and ethyl cyanoacetate generated the triafulvenes **2** and **3**, respectively. Substituted di-*t*-butylcyclopropenyl cations **5** including the tri-*t*-butylcyclopropenyl cation (**5a**) have been prepared *via* the reaction of **1** with organolithium reagents. The pK_{R^+} values of these cations have been determined by potentiometric titration and are discussed. Some reactions of cation **5a** are described.

Our interest in the effects of *t*-butyl substitution on the stability and chemistry of cyclopropenones and cyclopropenyl cations motivated our investigation of synthetic routes to these systems. The present paper describes the results of our studies.[1]

Synthesis of Di-*t*-butylcyclopropenone. Di-*t*-butylcyclopropenone (**1**) was first prepared in our laboratory by the reaction of sodium trichloroacetate with di-*t*-butylacetylene in dimethoxyethane at reflux followed by aqueous hydrolysis.[2,3] However, the extremely poor yield[4] coupled with the relative difficulty in preparing di-*t*-butylacetylene[5] made an alternative pathway necessary. A better approach to **1** involves a modified



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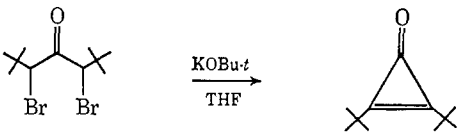
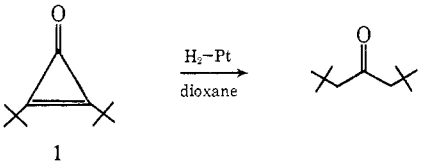
Favorskii reaction of α,α'-dibromodineopentyl ketone with potassium *t*-butoxide in tetrahydrofuran at room temperature.[6] This reaction can be conveniently monitored by infrared spectroscopy by observing the appearance and gradual increase in intensity of the characteristic bands of **1** in the 1800- and 1600-cm^{-1} regions (*vide infra*) at the expense of the doublet band of the starting dibromo ketone in the 1700-cm^{-1} region. Compound **1** was isolated in 35–40% yield as a white low melting crystalline solid which can be easily purified by sublimation at reduced pressure.



1, 35–40%

The spectral properties of **1** are in complete accord with the assigned structure. In the infrared **1** (CCl_4) exhibits characteristic bands at 1875 (m), 1855 (s), 1820 (s), and 1640 (s) cm^{-1}.[2c,d,3] In addition to strong end absorption, **1** (95% EtOH) shows an n → π * absorption band at 260 mμ (log ε 1.66). The corresponding n → π * transition of di-*n*-propylcyclopropenone (95% EtOH) was observed at 252 mμ (log ε 1.72).[3a,b,7] The nmr spectrum of **1** ($CDCl_3$) gives only the expected sharp singlet at δ 1.34. As anticipated, the mass spectrum of **1** with exception of the molecular ion peak at *m/e* 166 is very similar to that of di-*t*-butylacetylene.

Reactions of Di-*t*-butylcyclopropenone. Catalytic hydrogenation of **1** (Pt, dioxane) at atmospheric pressure afforded dineopentyl ketone.[2c,d,8]



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Photolysis of a 3% solution of **1** in ether at 2537 Å (n → π * excitation) resulted in decarbonylation with the formation of di-*t*-butylacetylene.[9] Pyrolysis[2c,d] of **1** in a sealed tube under reduced pressure at 320–327° afforded the same result. This reaction which is apparently general might serve as a convenient synthetic route

(1) For a preliminary communication of some of these results see J. Ciabattoni and E. C. Nathan, III, *J. Amer. Chem. Soc.*, 90, 4495 (1968).

(2) This carbenoid pathway was first described by Vol'pin and later by Breslow: (a) M. E. Vol'pin, Yu. D. Koreshkov, and D. N. Kursanov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 560 (1959); (b) D. N. Kursanov, M. E. Vol'pin, and Yu. D. Koreshkov, *J. Gen. Chem. USSR*, 30, 2855 (1960); (c) R. Breslow, T. Eicher, A. Krebs, R. A. Peterson, and J. Posner, *J. Amer. Chem. Soc.*, 87, 1320 (1965); (d) R. Breslow, L. J. Altman, A. Krebs, E. Mohacsi, I. Murata, R. A. Peterson, and J. Posner, *ibid.*, 87, 1326 (1965); (e) R. Breslow and L. J. Altman, *ibid.*, 88, 504 (1966); (f) parent cyclopropenone has also been synthesized: R. Breslow and G. Ryan, *ibid.*, 89, 3073 (1967).

(3) For reviews of cyclopropenone chemistry see (a) A. Krebs, *Angew. Chem. Intern. Ed. Engl.*, 4, 10 (1965); (b) G. L. Closs, *Advan. Alicyclic Chem.*, 1, 53 (1966).

(4) The major product of this reaction has been tentatively assigned as 4,4-dichloro-2,3-di-*t*-butylcyclobutenone on the basis of its spectral data. See ref 2d for an analogy.

(5) (a) G. F. Hennion and T. F. Banigan, Jr., *J. Amer. Chem. Soc.*, 68, 1202 (1946); (b) W. H. Puterbaugh and M. S. Newman, *ibid.*, 81, 1611 (1959).

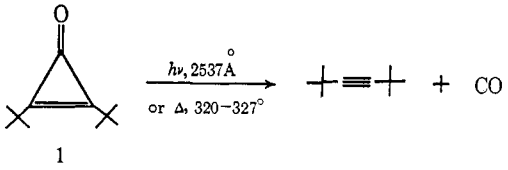
(6) (a) The method employed was essentially that of Breslow: see ref 2c, d, and R. Breslow, J. Posner, and A. Krebs, *ibid.*, 85, 234 (1963); see also N. J. McCorkindale, R. A. Raphael, W. T. Scott, and B. Zwanenburg, *Chem. Commun.*, 133 (1966); (b) Professor F. D. Greene and J. F. Pazos have kindly informed us that they have prepared **1** by the same pathway.

(7) For a discussion of the ultraviolet absorption spectra of dialkylcyclopropenones see ref 2d and A. Krebs and B. Schrader, *Justus Liebigs Ann. Chem.*, 709, 46 (1967).

(8) The catalytic reduction of *trans*-2,3-di-*t*-butylcyclopropanone with platinum in dioxane likewise afforded dineopentyl ketone. J. F. Pazos and F. D. Greene, *J. Amer. Chem. Soc.*, 89, 1030 (1967).

(9) Similarly, the photolysis of diphenylcyclopropenone affords diphenylacetylene: T. D. Roberts, Ph.D. Thesis, Ohio State University, 1967; *Dissertation Abstr.*, 29, 3657-B (1968).

to some relatively inaccessible branched dialkylacetylenes.



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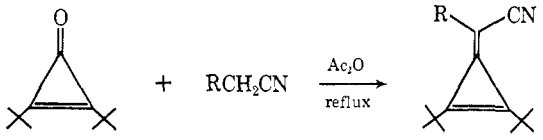
The stability of **1** to base is noteworthy. Treatment of **1** with a solution of 25% aqueous sodium hydroxide at reflux for 2 hr resulted in its recovery in 86% yield (after sublimation). Di-*n*-propylcyclopropenone, on the other hand, was completely destroyed under identical conditions. The carbonyl carbon of **1** is not seriously hindered to attack by nucleophiles. Perhaps the stability of **1** is due to the fact that ring opening would result in steric compression of the *t*-butyl groups since a *cis*-di-*t*-butylethylene derivative is generated.

Condensation of **1** with malononitrile or ethyl cyanoacetate in refluxing acetic anhydride in the presence of a trace of β-alanine afforded the white crystalline triafulvene derivatives **2** and **3**, respectively.[10,11] The infrared and ultraviolet data of **2** and **3** compare favorably



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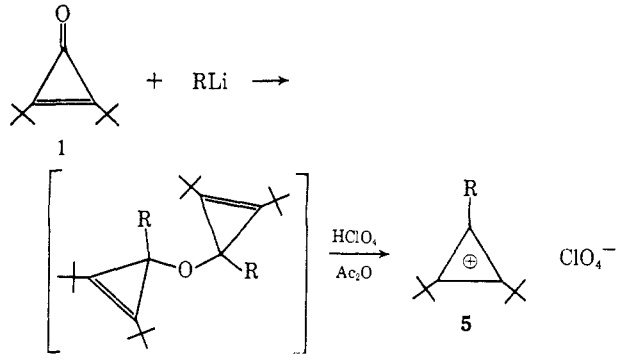
2, R = CN
3, R = CO_2Et

with that reported previously for a similar aliphatic triafulvene.[10c] In the infrared (KBr) **2** exhibited characteristic bands at 2205 (s), 2190 (s), and 1850 (s) cm^{-1} while the corresponding bands of **3** were observed at 2195 (s) and 1850 (s) cm^{-1} with additional carbonyl absorption at 1685 (s) cm^{-1}. The ultraviolet spectra (CH_3CN) of **2** and **3** consisted of a single symmetrical maximum at 245 mμ (log ε 4.33) and 255 mμ (log ε 4.37), respectively. The nmr spectrum ($CDCl_3$) of **2** exhibited only a sharp singlet at δ 1.43. The corresponding *t*-butyl resonance of **3** occurred at δ 1.47. In addition, **3** showed the expected pattern for the ethyl group with exception of the high-field line of the methyl triplet which is obscured by the *t*-butyl signal.

Synthesis of Substituted Di-*t*-butylcyclopropenyl Cations. Cyclopropenones may suffer nucleophilic addition to the carbonyl group or to the carbon–carbon double bond (conjugate addition). It was anticipated that conjugate addition to **1** would be difficult due to the hindered nature of the C_2 and C_3 atoms which possess neopentyl character. Accordingly, we have found that the reaction of **1** with a variety of organolithium reagents[12] affords after appropriate work-up the corresponding substituted di-*t*-butylcyclopropenyl cations **5**.[13] The addition of a benzene solution of **1** to a slight excess of lithium reagent at room temperature under nitrogen followed by hydrolysis with saturated aqueous KH_2PO_4 at 0° affords an oil, probably the biscyclopropenyl ether **4**, which in all cases exhibited the characteristic cyclopropene absorption in the infrared at 1820–1825 cm^{-1}.[3b,14] Subsequent treatment of an ethereal solution of **4** with a 10% solution of perchloric acid in acetic anhydride at 0° results in the immediate precipitation of **5** as a white solid. Recrystallization from either acetone or acetone–ether gave analytically pure cations in relatively good yield. Tri-*t*-butylcyclopropenyl perchlorate (**5d**), like tri-*n*-propylcyclopropenyl perchlorate, can be recrystallized from water unchanged.



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4

5

a, R = CH_3
b, R = $CH_3(CH_2)_3$
c, R = $CH_3CH_2CHCH_3$
d, R = $(CH_3)_3C$
e, R = C_6H_5

A summary of the nmr data which clearly establishes the structures of these cations is presented in Table I.

Table I

Cation	% yield[a]	Mp, °C	Nmr[c]	pK_{R^+} ± 0.1[e]
5a	51	134–135	2.98 (3 H, s) 1.51 (18 H, s)	6.4
5b	34	138–138.5	3.33 (2 H, t) 1.6–2.2 (4 H, m) 1.51 (18 H, s) 0.98 (3 H, t)	6.5
5c	41	235–245 dec[b]	3.54 (1 H, sxt) 1.7–2.2 (2 H, m) 1.55 (18 H, s) 1.50 (3 H, d)[d] 1.03 (3 H, t)	6.5
5d	58	248–250 dec[b]	1.58 (27 H, s)	6.5
5e	52	202–204 dec[b]	8.20–8.45 (2 H, m) 7.67–8.10 (3 H, m) 1.65 (18 H, s)	4.9

[a] Reactions were usually run on a 1.5–9-mmol scale. [b] Decomposition temperature depends on rate of heating. [c] In parts per million relative to internal TMS; compounds were run in $CDCl_3$, **5e** was run in CD_3CN; s = singlet, d = doublet, t = triplet, m = multiplet, sxt = sextet. [d] Methyl doublet is partially hidden under the *t*-butyl signal. [e] Determined by potentiometric titration in 50% aqueous acetonitrile; values represent an average of duplicate runs.

Of particular importance are the unique low-field absorptions for the methyl, methylene, and methinyl protons on the carbon atom directly bonded to the three-

(10) (a) S. Andreades, *J. Amer. Chem. Soc.*, 87, 3941 (1965); (b) E. D. Bergmann and I. Agranat, *ibid.*, 86, 3587 (1964); (c) A. S. Kende and P. T. Izzo, *ibid.*, 86, 3587 (1964).

(11) For reviews of triafulvene chemistry see (a) E. D. Bergmann, *Chem. Rev.*, 68, 41 (1968); (b) A. S. Kende, *Trans. N. Y. Acad. Sci.*, 28, 981 (1966); see also ref 3a and 3b.

(12) The organolithium compounds were purchased from Foote Mineral Co., Exton, Pa., or Alfa Inorganics, Inc., Beverly, Mass.

(13) For reviews on cyclopropenyl cations see I. A. D'yakonov and R. R. Kostikov, *Russ. Chem. Rev.*, 36, 557 (1967), as well as ref 3a and 3b.

(14) (a) R. Breslow and H. W. Chang, *J. Amer. Chem. Soc.*, 83, 2367 (1961); (b) R. Breslow, J. Lockhart, and H. W. Chang, *ibid.*, 83, 2375 (1961).

membered ring of cations **5a**, **5b**, and **5c**, respectively.[15] The low-field absorption for the phenyl protons in cation **5e**, particularly the *ortho* hydrogens, should also be noted. In all cases the expected downfield shift of the *t*-butyl resonance relative to the cyclopropenone **1** is observed. The sharp singlet of tri-*t*-butylcyclopropenyl cation **5d** at δ 1.58 ($CDCl_3$) remained unchanged with no significant line broadening at $-60°$. All cations exhibited a characteristic band at 1420–1430 cm^{-1} in addition to strong broad absorption of the perchlorate ion at 1090 cm^{-1} in the infrared.[15a] Phenyldi-*t*-butylcyclopropenyl perchlorate (**5e**), in contrast to cations **5a–d**, exhibited a band of medium intensity at 1835 cm^{-1}. The trialkylcyclopropenyl cations **5a–d**, like di-*t*-butylcyclopropenone (**1**), did not show a maximum for the $\pi \rightarrow \pi^*$ transition in the ultraviolet region above 220 mμ in agreement with simple Hückel theory. The energy required for a $\pi \rightarrow \pi^*$ transition in these cations (3β) is predicted to be much greater than that required for ethylene (2β).[3a,b] The phenyl-substituted cation **5e**, however, showed a band in acetonitrile at 264 mμ (log ϵ 4.29).

It should be emphasized here that the reaction of cyclopropenones with organolithium reagents does *not* provide a general synthesis of substituted cyclopropenyl cations. This is apparently true for Grignard reagents also.[2c] For example, we have found that the reaction of phenyllithium with diphenylcyclopropenone affords products arising from *conjugate* addition.[16] This is in direct contrast to phenylmagnesium bromide which gives the triphenylcyclopropenyl cation under the appropriate work-up conditions.[2c] Furthermore, the reaction of *t*-butyllithium with di-*n*-propylcyclopropenone failed to yield the *t*-butyldi-*n*-propylcyclopropenyl cation in our hands. Our initial attempts to prepare the vinyldi-*t*-butyl- and benzhydryldi-*t*-butylcyclopropenyl cations by reaction of **1** with vinyl- and benzhydryllithium, respectively, have also failed.

pK_{R^+} Studies. The effect of substituents on the stability of cyclopropenyl cations has been investigated primarily by measurement of the pK_{R^+} values for the carbonium ion–carbinol equilibrium. By this method Breslow has clearly demonstrated that the relative ability of substituents to stabilize the cyclopropenyl cation is given by the order alkyl > phenyl > hydrogen.[15a] However, nothing is known regarding the relative influence of methyl, primary, secondary, and tertiary alkyl substituents on the pK_{R^+} values.[17]

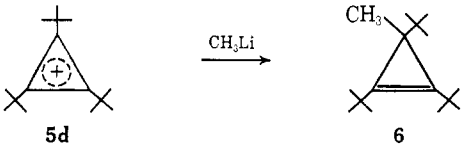
The apparent pK_{R^+} values given in Table I for cations **5a–e** were determined by potentiometric titration (glass–calomel electrodes) in 50% aqueous acetonitrile with 0.104 *N* NaOH. The procedure employed was identical with that described by Breslow for the tri-*n*-propylcyclopropenyl cation.[15a] In all cases classical titration curves were obtained whose midpoints were taken as the p*K*'s. The reversibility of all titration curves was demonstrated by back-titration with 0.10 *N* HCl.

The destabilizing effect of a phenyl substituent relative to an alkyl substituent has been demonstrated previously and is clearly evident here in the p*K* of **5e** relative to the p*K*'s of cations **5a–d**. The p*K* of phenyldi-*t*-butylcyclopropenyl cation **5e** is 1.6 units lower than the p*K*'s of the three tributylcyclopropenyl cations **5b–d**. In comparison, the p*K* of the triphenylcyclopropenyl cation is 1.0 unit lower than the propyldiphenylcyclopropenyl cation.[15a] However, in the latter case both covalent carbinols have a stilbene system. The larger p*K* difference in the former case may reflect phenyl stabilization of the carbinol of **5e** assuming of course that a styrene system would be generated.[15a]

Using the pK_{R^+} value as a criterion of stability, the cations **5a–d** are somewhat less stable than the tri-*n*-propylcyclopropenyl cation.[18] The reasons for this are not clear since the inductive electron-releasing ability of alkyl groups apparently increases in the following order: methyl < ethyl < isopropyl < *t*-butyl.[19,20] Thus, it was expected that *t*-butyl would be more effective than *n*-propyl in stabilizing cyclopropenyl cations; hyperconjugation is probably unimportant here.[15a] On the other hand, solvation of charge would be more difficult in the hindered *t*-butyl substituted cations relative to the tri-*n*-propylcyclopropenyl cation and may be playing a significant role.

With the limited data at hand, an evaluation of the relative influence of inductive, steric, and solvation[14] effects on the p*K*'s of these trialkylcyclopropenyl cations is not possible.[21]

Reactions of the Tri-*t*-butylcyclopropenyl Cation. The reaction of a suspension of tri-*t*-butylcyclopropenyl perchlorate (**5d**) in benzene with methyllithium afforded 3-methyl-1,2,3-tri-*t*-butylcyclopropene (**6**). The infrared spectrum reveals the weak but characteristic band of covalent cyclopropenes at 1820 cm^{-1} (CCl_4).[3b] In the nmr ($CDCl_3$) the three expected singlets at δ 1.18, 1.10, and 0.89 with the integral ratios 18:3:9, respectively, were observed. The mass spectrum of **6** does not reveal a molecular ion peak at *m/e* 222 (M) but exhibits peaks at *m/e* 207 (M − 15) and *m/e* 165 (M − 57) for the tri-*t*-butyl- and methyldi-*t*-butylcyclopropenyl cations, respectively. It is interesting to note that the peak at *m/e* 165 (base peak) is much more intense than the *m/e* 207 peak with loss of a *t*-butyl radical being much preferred over loss of a methyl radical from the molecular ion.[22]



5d **6**

(15) (a) R. Breslow, H. Höver, and H. W. Chang, *J. Amer. Chem. Soc.*, 84, 3168 (1962); (b) D. G. Farnum, G. Mehta, and R. G. Silberman, *ibid.*, **89**, 5048 (1967).

(16) J. Ciabattoni, P. J. Kocienski, and G. Melloni, submitted for publication.

(17) The trimethylcyclopropenyl cation has been synthesized but its pK_{R^+} has not yet been reported. G. L. Closs and V. N. M. Rao *J. Amer. Chem. Soc.*, **88**, 4116 (1966); G. L. Closs, W. A. Böll, H. Heyn, and V. Dev, *ibid.*, **90**, 173 (1968). The parent cyclopropenyl cation has also been prepared; see ref 15b and R. Breslow, J. T. Groves, and G. Ryan, *ibid.*, **89**, 5048 (1967).

(18) The reported pK_{R^+} of the tri-*n*-propylcyclopropenyl cation is 7.2. We have observed a value of 7.0 under the previously described conditions; see ref 15a.

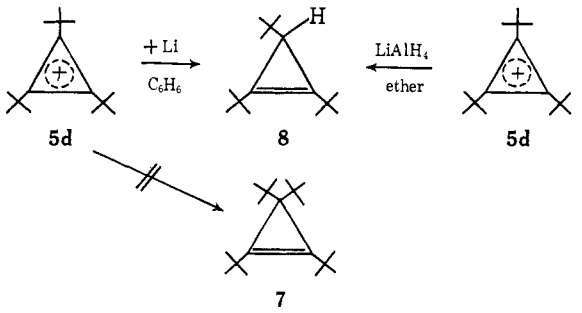
(19) M. J. S. Dewar, "Hyperconjugation," Ronald Press Co., New York, N. Y., 1962.

(20) W. M. Schubert, R. B. Murphy, and J. Robins, *Tetrahedron*, **17**, 199 (1962).

(21) For a good discussion of carbonium ions see D. Bethell and V. Gold, "Carbonium Ions," Academic Press Inc., New York, N. Y., 1967.

(22) The mass spectrometry of the triphenylcyclopropenyl cation has been studied: M. A. Battiste and B. Halton, *Chem. Commun.*, 1368 (1968).

It was of interest to attempt the synthesis of the extremely hindered tetra-*t*-butylcyclopropene (**7**) *via* the reaction of **5d** with *t*-butyllithium in benzene. However, only reduction with the formation of 1,2,3-tri-*t*-butylcyclopropene (**8**) and presumably isobutylene was observed. Lithium aluminum hydride reduction of **5d** afforded the same substituted cyclopropene.



The presence of a cyclopropene was confirmed by the weak absorption in the infrared (CCl_4) at 1835 cm^{-1}.[3b] The nmr spectrum ($CDCl_3$) exhibited three singlets at δ 1.37, 1.16, and 0.82 with integral ratios 1:18:9, respectively. In the mass spectrum peaks of weak intensity at *m/e* 208 (M) and 207 (M − 1) and a very intense base peak at *m/e* 151 (M − 57) were observed due to the molecular ion and the tri-*t*-butyl- and di-*t*-butylcyclopropenyl cations, respectively. Again, loss of a *t*-butyl radical is much more favored over loss of a hydrogen radical from the molecular ion.

Further interesting aspects of the chemistry of di-*t*-butylcyclopropenone and the derived cyclopropenyl cations are currently being investigated.

Experimental Section

Melting points were taken on a Kofler micro heating stage; all melting and boiling points are uncorrected. Infrared and ultraviolet spectra were obtained with a Perkin-Elmer Model 337 spectrophotometer and a Cary Model 14 recording spectrophotometer, respectively. All nmr spectra were recorded with a Varian A-60A spectrometer. Chemical shifts are reported in parts per million (ppm) from TMS as internal standard with the number in parentheses indicating the number of protons causing the signal. The letter following indicates the multiplicity of the signal: s, singlet; d, doublet; t, triplet; q, quartet; sxt, sextet; and m, multiplet. Unless otherwise indicated all spectra were obtained in deuteriochloroform. Mass spectra were obtained with a Hitachi RMU-6D mass spectrometer. Analyses were performed by Midwest Microlab, Inc., Indianapolis, Ind., and Galbraith Laboratories, Inc., Knoxville, Tenn.

Materials. Reagent grade benzene, ether, tetrahydrofuran, and dimethoxyethane were refluxed over lithium aluminum hydride and distilled prior to use. Reagent grade *p*-dioxane was purified by distillation from sodium metal; chloroform was purified as described by Fieser;[23] acetonitrile was purified utilizing the procedure of Walden and Birr.[24] Neopentyl chloride was purchased from K and K Laboratories, Inc.; *t*-butylacetyl chloride was obtained from the Aldrich Chemical Co., Inc. Both reagents were distilled prior to use. Reagent grade acetic anhydride (Baker Chemical Co.) was distilled and stored under nitrogen prior to use. Reagent grade perchloric acid (70% by weight) was also obtained from Baker Chemical Co., and used without further purification. Solutions of *t*-butyl-, *sec*-butyl-, and *n*-butyllithium were purchased from Foote Mineral Co.; solutions of methyl- and phenyllithium were obtained from Alfa Inorganics, Inc. Potassium *t*-butoxide was obtained from the MSA Research Corporation and used without further purification.

Di-*t*-butylacetylene. The synthetic scheme described by Hennion[5a] and Newman[5b] was adopted. The intermediate pinacolone dichloride was prepared as described by Bartlett.[25] Di-*t*-butylacetylene was obtained as a colorless liquid, bp 117–118°, after two fractional distillations on a 24-in. Teflon annular spinning-band column; nmr spectrum: 1.18 (18 H, s); mass spectrum: *m/e* 138, 123, 95, 81, and 67.

Di-*t*-butylcyclopropenone (1) from Di-*t*-butylacetylene.[2d] A suspension of 4.77 g (0.0345 mol) of di-*t*-butylacetylene and 8.46 g (0.0456 mol) of sodium trichloroacetate in 25 ml of anhydrous dimethoxyethane was heated at reflux under nitrogen for 2 hr. Hydrolysis and extraction with methylene chloride afforded a viscous oil exhibiting infrared absorption at 1800–1850 and 1640 cm^{-1} after vacuum distillation (bp 73° (0.12 mm)). The crude product was diluted with 50 ml of methylene chloride and extracted with five 5-ml portions of 65% aqueous sulfuric acid. Neutralization of the acid layer and extraction with four 25-ml portions of ether afforded crystalline **1** (33 mg, 0.6%), mp 61–61.5° after solvent removal and sublimation (25° (0.05 mm)); infrared spectrum: $\nu_{max}^{CCl_4}$ (cm^{-1}) 2980 (s), 2945 (m), 2920 (m), 2880 (m), 1875 (m), 1855 (s), 1820 (s), 1640 (s), 1485 (m), 1465 (m), and 1375 (m); ultraviolet spectrum: λ_{max}^{EtOH} 260 mμ (log ϵ 1.66); mass spectrum; *m/e* 166, 138, 123, 95, 81, and 67; nmr spectrum: 1.34 (18 H, s).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.47; H, 10.91. Found: C, 79.45; H, 10.82.

The methylene chloride layer above was concentrated and the residual oil subjected to two vacuum distillations (bp 70–80° (0.07 mm)) to yield 0.110 g of a colorless liquid tentatively identified as 4,4-dichloro-2,3-di-*t*-butylcyclobutenone;[2d] infrared spectrum $\nu_{max}^{CCl_4}$ (cm^{-1}) 2970 (s), 2910 (m), 2870 (m), 1800 (s, sh), 1785 (s), 1630 (w), 1605 (w), 1570 (m), 1485 (m), 1465 (m), 1400 (w), and 1365 (m); ultraviolet spectrum: λ_{max}^{EtOH} 227 mμ (log ϵ 3.87), 307 mμ (log ϵ 2.12); mass spectrum: *m/e* 248, 250, and 252; nmr spectrum: 1.33 (9 H, s), 1.55 (9 H, s).

Di-*t*-butylcyclopropenone (1) from Dineopentyl Ketone. The entrainment modification[26] of the procedure described by Whitmore[27] was utilized to prepare neopentylmagnesium chloride. Reaction was effected by dropwise addition of a solution of 40.2 g (0.220 mol) of freshly distilled 1,2-dibromoethane in 50 ml of anhydrous ether to 200 ml of a stirred ethereal solution of 18.8 g (0.212 mol) of neopentyl chloride over 13.0 g (0.530 g-atom) of magnesium turnings. Addition took place over 10 hr while the reaction mixture was gently refluxed with external heating. The solution of neopentylmagnesium chloride was then transferred under nitrogen to a constant pressure addition funnel and added dropwise over 6.5 hr to a stirred solution of 20.1 g (0.150 mol) of *t*-butylacetyl chloride in 100 ml of ether. The resulting suspension was stirred an additional 8 hr at reflux and the crude reaction product worked up with concentrated aqueous hydrochloric acid in usual fashion. Vacuum distillation (bp 75–79° (20 mm)) afforded 21.7 g (85%) of dineopentyl ketone; infrared spectrum: $\nu_{max}^{CCl_4}$ (cm^{-1}) 2950 (s), 2900 (s), 2865 (s), 1715 (s), 1480 (s), 1470 (s), 1370 (s), and 1355 (s); nmr spectrum: 1.03 (18 H, s), 2.29 (4 H, s).

A solution of 46.8 g (0.293 mol) of bromine in 100 ml of purified chloroform was added to a solution of 21.6 g (0.126 mol) of dineopentyl ketone in 250 ml of chloroform over 4 hr. The solution was allowed to stand overnight. Removal of solvent and vacuum distillation (bp 75–90° (1.0 mm)) afforded 38.3 g (93%) of α,α'-dibromodineopentyl ketone as a crystalline solid, mp 70–71°, infrared spectrum: $\nu_{max}^{CCl_4}$ (cm^{-1}) 2960 (s), 2935 (m), 2910 (m), 2870 (m), 1740 (s), 1720 (m), 1715 (m), 1485 (s), 1475 (s), 1400 (m), 1375 (s), and 1340 (s); nmr spectrum: 1.18 (18 H, s), 4.42 (2 H, s).

Anal. Calcd for $C_{11}H_{20}Br_2O$: C, 40.27; H, 6.14; Br, 48.71. Found: C, 40.24; H, 6.07; Br, 48.68.

A solution of 13.3 g (0.041 mol) of the above dibromo ketone in 200 ml of anhydrous tetrahydrofuran was treated with 10.4 g (0.093 mol) of potassium *t*-butoxide over 1 hr. The progress of the reaction was monitored by infrared spectroscopy which indicated that the 1740-cm^{-1} band of the substrate had been quantitatively destroyed after stirring the reaction mixture an additional hour. The crude product was diluted with 300 ml of methylene chloride and washed with two 100-ml portions of 5% hydrochloric acid. The methylene chloride layer was extracted with five 25-ml portions

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of 65% (v/v) sulfuric acid and the resulting acid layer neutralized with sodium carbonate to pH ~10. The neutral aqueous phase was extracted with ether and afforded, after solvent removal, a crystalline solid. Sublimation (25° (0.75 mm)) yielded 2.44 g (36%) of di-*t*-butylcyclopropenone (**1**) identical with an authentic sample prepared as described above from di-*t*-butylacetylene.

Catalytic Hydrogenation of 1. To a prereduced suspension of 22.5 mg of platinum oxide in 3 ml of anhydrous dioxane was added a solution of 0.114 g (0.684 mmol) of **1** in 1 ml of dioxane. Stirring the resulting suspension for 4.5 hr at room temperature under 1 atm resulted in the smooth uptake of 2 mol of hydrogen. Removal of dioxane afforded dineopentyl ketone identical with an authentic sample prepared as described above; nmr spectrum: 1.03 (18 H, s), 2.29 (4 H, s).

Decarbonylation of 1. Di-*t*-butylcyclopropenone (**1**) (50 mg, 0.302 mmol) was sealed in a Pyrex ampoule under vacuum (0.1 mm) and immersed in a Wood's metal bath at 320–327° for 4 hr. The tube was removed and the nmr spectrum of the contents was identical with that of authentic di-*t*-butylacetylene.

A 3% solution (w/v) of **1** in anhydrous ether was photolyzed at 2537 Å in a quartz uv cell using six General Electric G25T8 mercury lamps. The consumption of substrate was monitored by glpc (15% carbowax on Chromosorb P, 6-ft column, 183°). After 4 hr a single peak was observed whose retention time corresponded exactly with that of authentic di-*t*-butylacetylene (column temperature 70°). The nmr spectrum of the photolysate after solvent removal established the product to be di-*t*-butylacetylene.

Condensation of 1 with Ethyl Cyanoacetate. A solution of 0.421 g (2.54 mmol) of **1**, 0.294 g (2.60 mmol) of ethyl cyanoacetate and a catalytic amount of β-alanine[10a] in 12 ml of freshly distilled acetic anhydride was refluxed for 43.5 hr. Removal of solvent on a rotary evaporator afforded a crystalline solid which was recrystallized twice from cyclohexane to yield 0.277 g (42%) of 1,2-di-*t*-butyl-3-(cyanocarbethoxymethylene)cyclopropene, mp 122–123°; infrared spectrum: ν_{max}^{KBr} (cm^{-1}) 2965 (s), 2870 (w), 2195 (s), 1850 (m), 1685 (s), 1505 (s), 1485 (s), 1460 (s), 1365 (s), 1270 (vs), 1230 (s), 1190 (s), 1165 (s), 1155 (s), 1085 (vs), and 775 (s); ultraviolet spectrum: $\lambda_{max}^{CH_3CN}$ 255 mμ (log ε 4.37); nmr spectrum: 1.32 (3 H, partially hidden t), 1.47 (18 H, s), 4.26 (2 H, q).

Anal. Calcd for $C_{16}H_{23}NO_2$: C, 73.53; H, 8.87; N, 5.36. Found: C, 73.20; H, 8.84; N, 5.29.

Condensation of 1 with Malononitrile. Di-*t*-butylcyclopropenone (0.501 g, 3.01 mmol) and malononitrile (0.225 g, 3.40 mmol) were condensed as described above for ethyl cyanoacetate. After reflux for 6.5 hr the solvent was removed to afford a crystalline solid (236 mg, 37%). Two recrystallizations from ether yielded 1,2-di-*t*-butyl-3-(dicyanomethylene)cyclopropene, mp 182–182.5°; infrared spectrum: ν_{max}^{KBr} (cm^{-1}) 2975 (s), 2205 (s), 2190 (s), 1850 (m), 1500 (s), 1480 (m), 1460 (m), 1365 (m), 1230 (m), and 1170 (m); ultraviolet spectrum: $\lambda_{max}^{CH_3CN}$ 245 mμ (log ε 4.33); nmr spectrum: 1.43 (18 H, s).

Anal. Calcd for $C_{14}H_{18}N_2$: C, 78.46; H, 8.47; N, 13.07. Found: C, 78.62; H, 8.72; N, 13.21.

Reaction of 1 with *t*-Butyllithium. *t*-Butyllithium (7.70 mmol) was added to 10 ml of anhydrous benzene under nitrogen at room temperature. To this stirred organolithium solution was added a solution of 0.972 g (5.85 mmol) of ketone **1** in 3 ml of anhydrous benzene. The ketone was added dropwise over 2 min and the resulting solution stirred for 0.5 hr. The crude product was then hydrolyzed by injection into 100 ml of saturated, aqueous potassium dihydrogen phosphate at 0°. The organic product was extracted with two 50-ml portions of ether and dried over anhydrous magnesium sulfate. Solvent removal afforded a viscous oil which showed characteristic cyclopropene absorption at 1825 cm^{-1} presumably due to bis(tri-*t*-butylcyclopropenyl) ether (**4d**).

The oil was subsequently diluted with 35 ml of anhydrous ether without purification and transferred to a round-bottomed flask under nitrogen. The solution was cooled in an ice bath to 0° and 2.0 ml of a freshly prepared solution of 10% perchloric acid in acetic anhydride was added dropwise over 1 min with stirring. An immediate precipitate (1.08 g, 52%) formed which was collected by vacuum filtration and washed with additional anhydrous ether. Recrystallization from acetone afforded analytically pure tri-*t*-butylcyclopropenyl perchlorate (**5d**) as white needles, mp 248–250° (dec); infrared spectrum: ν_{max}^{KBr} (cm^{-1}) 2980 (s), 1485 (s), 1465 (m), 1425 (m), 1370 (s), 1225 (s), 1197 (m), 1090 (vs), and 625 (s); nmr spectrum: 1.58 (27 H, s).

Anal. Calcd for $C_{15}H_{27}ClO_4$: C, 58.73; H, 8.87; Cl, 11.56. Found: C, 58.65; H, 8.74; Cl, 11.54.

In identical fashion the substituted di-*t*-butylcyclopropenyl cations described below were prepared.

Reaction of 1 with *sec*-Butyllithium. Addition of ketone **1** to a benzene solution of *sec*-butyllithium followed by hydrolysis and work-up afforded 0.397 g (41%) of cation **5c** upon treatment with 10% perchloric acid–acetic anhydride. Recrystallization from acetone–ether afforded analytical material, mp 235–245° dec; infrared spectrum: ν_{max}^{KBr} (cm^{-1}) 2980 (s), 1485 (s), 1465 (s), 1425 (m), 1375 (s), 1223 (s), 1204 (m), 1090 (vs), and 625 (s); nmr spectrum 1.03 (3 H, t), 1.50 (3 H, partially hidden d), 1.55 (18 H, s), 1.7–2.2 (2 H, m), 3.54 (1 H, sxt).

Anal. Calcd for $C_{15}H_{27}ClO_4$: C, 58.73; H, 8.87; Cl, 11.56. Found: C, 58.92; H, 8.82, Cl, 11.47.

Reaction of 1 with *n*-Butyllithium. Recrystallization of the crude product (0.314 g, 34%) from acetone–ether afforded cation **5b**, mp 138–138.5° dec; infrared spectrum: ν_{max}^{KBr} (cm^{-1}) 2980 (s), 1490 (s), 1470 (s), 1440 (m), 1430 (m), 1370 (s), 1221 (s), 1202 (s), 1090 (vs), and 625 (s); nmr spectrum: 0.98 (3 H, t), 1.51 (18 H, s), 1.6–2.2 (4 H, m), 3.33 (2 H, t).

Anal. Calcd for $C_{15}H_{27}ClO_4$: C, 58.73; H, 8.87; Cl, 11.56. Found: C, 58.55; H, 9.09; Cl, 11.32.

Reaction of 1 with Methyllithium. Recrystallization of the crude product (0.407 g, 51%) from acetone–ether afforded cation **5a**, mp 134–135°; infrared spectrum: ν_{max}^{KBr} (cm^{-1}) 2980 (s), 1490 (s), 1470 (m), 1430 (m), 1375 (m), 1370 (m), 1230 (m), 1090 (vs), and 625 (s); nmr spectrum: 1.51 (18 H, s), 2.98 (3 H, s).

Anal. Calcd for $C_{12}H_{21}ClO_4$: C, 54.44; H, 8.00; Cl, 13.39. Found: C, 54.51; H, 8.05; Cl, 13.21.

Reaction of 1 with Phenyllithium. The crude product (0.521 g, 52%) was recrystallized from acetone to yield analytically pure **5e**, mp 202–204° dec; infrared spectrum: ν_{max}^{KBr} (cm^{-1}) 2970 (s), 1835 (m), 1595 (s), 1500 (s), 1480 (s), 1475 (s), 1465 (s), 1450 (m), 1420 (s), 1390 (s), 1370 (s), 1300 (w), 1225 (s), 1198 (m), 1090 (vs), 777 (s), 684 (s), and 624 (s); ultraviolet spectrum: $\lambda_{max}^{CH_3CN}$ 264 mμ (log ε 4.29); nmr spectrum: (CD_3CN) 1.65 (18 H, s), 7.67–8.10 (3 H, m), 8.20–8.45 (2 H, m).

Anal. Calcd for $C_{17}H_{23}ClO_4$: C, 62.48; H, 7.09; Cl, 10.85. Found: C, 62.24; H, 7.06; Cl, 10.68.

pK_{R^+} Studies. The pK_{R^+} values of cations **5a–e** were measured duplicating the potentiometric procedure developed by Breslow[15a] for the tri-*n*-propylcyclopropenyl cation. In each case a solution of 0.040 mequiv of the appropriate cation was prepared in 20 ml of purified acetonitrile. To the acetonitrile solution was added 20 ml of a premixed solution prepared by carefully neutralizing equivalent amounts of 0.10 *M* sodium hydroxide and 0.10 *N* hydrochloric acid. The stirred, aqueous acetonitrile solutions were then titrated with 0.05 ml portions of 0.104 *N* sodium hydroxide and the pH of the solutions measured after addition of each aliquot with a Colemane Model 39 pH meter equipped with glass–calomel electrodes. As the equivalence point was approached 0.0250-ml aliquots were added to define better the shape of the titration curves. In each case the aliquots were delivered with a biopipet[28] to ensure reproducibility. Classical titration curves were obtained whose midpoints were taken as the p*K*'s; reported values represent averages of duplicate runs which did not differ by more than 0.1 p*K* unit. The tri-*n*-propylcyclopropenyl cation was included as a calibration of method.[15a] The reversibility of the equilibrium was experimentally demonstrated in all cases by rapid back titration of the solutions with aqueous 0.10 *N* hydrochloric acid; pK_{R^+} values: tri-*n*-propylcyclopropenyl perchlorate, 7.0;[18] **5d**, 6.5; **5c**, 6.5; **5b**, 6.5; **5a**, 6.4; **5e**, 4.9.

Reaction of the Tri-*t*-butylcyclopropenyl Cation 5d with Methyllithium. A suspension of 0.104 g (0.340 mmol) of tri-*t*-butylcyclopropenyl perchlorate in 25 ml of anhydrous benzene under nitrogen was treated with 0.86 mmol of methyllithium. The solution was stirred 0.5 hr, cooled in an ice bath, and hydrolyzed by dropwise addition of H_2O at 0°. The crude reaction product was filtered, diluted with two 25-ml portions of ether and dried over magnesium sulfate. Removal of ether afforded an oil which was distilled in a Kragen tube (oil bath temperature 80–120° (8 mm)) to yield 3-methyl-1,2,3-tri-*t*-butylcyclopropene (**6**); infrared spectrum: $\nu_{max}^{CCl_4}$ (cm^{-1}) 2960 (s), 2900 (m), 2865 (m), 1820 (w), 1475 (m), 1460 (m), 1390 (m), 1365 (m), and 1360 (m); mass spectrum: *m/e* 207, 165; nmr spectrum: 0.89 (9 H, s), 1.10 (3 H, s), 1.18 (18 H, s).

Anal. Calcd for $C_{16}H_{30}$: C, 86.40; H, 13.60. Found: C, 86.37; H, 13.51.

Reaction of Cation 5d with Lithium Aluminum Hydride. A suspension of 0.261 g (0.850 mmol) of tri-*t*-butylcyclopropenyl per-

(28) Available from Schwartz Bioresearch, Orangeburg, N. Y.

chlorate in 25 ml of anhydrous ether was treated with a solution of 0.0368 g (0.965 mmol) of lithium aluminum hydride in 10 ml of ether. The reaction was stirred 0.5 hr under nitrogen at room temperature, cooled in an ice bath, and hydrolyzed by dropwise addition of water. The crude reaction product was filtered, diluted with two 25-ml portions of ether, and dried over magnesium sulfate. Removal of ether afforded a viscous oil which was subjected to Kragen tube distillation (oil bath temperature 80–120° (8 mm)). The product was identified as 1,2,3-tri-*t*-butylcyclopropene (**8**) from the following data: infrared spectrum: $\nu_{max}^{CCl_4}$ (cm^{-1}) 2960 (s), 2900 (m), 2865 (m), 1835 (w), 1475 (m), 1465 (m), 1395 (m), 1365 (m), 1355 (w), and 1275 (w); mass spectrum: *m/e* 208, 207, and 151; nmr spectrum: 0.82 (9 H, s), 1.16 (18 H, s) 1.37, (1 H, s). An acceptable analysis could not be obtained for this compound.[15a]

Anal. Calcd for $C_{15}H_{28}$: C, 86.46; H, 13.54. Found: C, 85.66; H, 13.57.

Reaction of Cation 5d with *t*-Butyllithium. A suspension of 0.0962 g (0.314 mmol) of tri-*t*-butylcyclopropenyl perchlorate in 25 ml of anhydrous benzene was prepared under nitrogen and quenched by dropwise addition of 0.706 mmol of *t*-butyllithium. The resulting solution was stirred 0.5 hr and worked up as previously described. Kragen tube distillation of the crude product afforded 1,2,3-tri-*t*-butylcyclopropene (**8**) identical with an authentic sample prepared as described above from the reaction of **5d** with lithium aluminum hydride.

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The Syntheses of the (−)-α- and (+)-β-*cis*-Bergamotenes[1]

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Abstract: Syntheses of (−)-α-*cis*-bergamotene (**2**) and (+)-β-*cis*-bergamotene (**3**) from (−)-β-pinene are described. The isomer **2** was shown to be identical with a sesquiterpene hydrocarbon isolated from oils of opopponax (*Commiphora erythraea* var. *glabrescens* Engler) and black pepper (*Piper nigrum* L.). The isomer **3** was found to be different from an isolate of Indian valerian oil (Valeriana wallichi) which has been assigned this structure.

The structure **1** has been proposed for a sesquiterpene hydrocarbon, which was isolated from bergamot oil by Sorm and coworkers, and given the name bergamotene.[2] This structural assignment was apparently based solely on the infrared spectrum[3] and has never been fully substantiated, although the nmr spectrum of the compound agrees with structure **1** and was used to suggest the *trans* stereochemistry of attachment of the side chain as shown.[4,5] This compound, now called α-*trans*-bergamotene in analogy to the structure of α-pinene, has been more recently detected in a number of other essential oils.[6] Muller and Jennings[7] reported its occurrence in black pepper accompanied by an unknown sesquiterpene hydrocarbon to which they assigned the α-*cis*-bergamotene structure **2**. The same compound was isolated from oil of opopanax by Wenninger.[8]

More recently, Bhattacharyya, *et al.*, isolated a hydrocarbon from Indian valerian oil, to which they assigned the β-*cis*-bergamotene structure **3**. While the chemical evidence cited[9] is in very good accord with the gross structure **3**, the *cis* stereochemistry was suggested on the basis of a comparison of the nmr spectrum with that of β-pinene. Even though the chemical shift of the quaternary methyl group in **3** fell midway between the values for the two quarternary methyl groups in β-pinene, the authors used this in conjunction with a conformational argument to favor the *cis* stereochemistry. However, comparison of this value with the reported chemical shifts of the quaternary methyl groups in copaene (**4**)[10] and mustakone (**5**),[11] suggested to us that, in fact, β-bergamotene possessed the *trans* structure. We felt that an unambiguous synthesis would be necessary to settle this question and that of the structure of α-*cis*-bergamotene. In this paper we describe the stereospecific synthesis of (−)-α-*cis*-bergamotene (**2**) and (+)-β-*cis*-bergamotene (**3**).

Synthesis of compounds of the *cis*-bergamotene structure would, in the most direct approach, involve substitution on the *cis*-quaternary methyl group in the pinane

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