(dried for 2 days *in vacuo* over calcium sulfate; 52 g, 0.6 mol), and dry dioxane (250 ml) were stirred at reflux for 13 hr. The mixture was cooled, poured into ice–water (300 ml), and extracted with pentane (4 × 75 ml). The pentane fractions were combined and washed with ice–water (2 × 100 ml), and the combined aqueous portions were extracted with pentane (1 × 75 ml). The organic phase and the other organic portions were combined, dried ($MgSO_4$), filtered, and concentrated at reduced pressure; the residue was distilled to give 21.8 g (78.6% from the diol) of product **23**, bp 57–61° (21 mm). The nmr spectrum ($CHCl_3$) showed a doublet at δ 1.74 (3 H, J = 6.8 Hz), a broad signal, 2.20 (1 H), and a symmetrical multiplet, 4.29 (1 H). Upon broad band deuterium irradiation, the signal at δ 2.20 became a doublet, J = 3.8 Hz; the signal at δ 4.29 became a quartet, J = 6.8 Hz, of doublets, J = 3.8 Hz.

(2-*r*-Methyl-*trans*-3,4,4-trideuteriocyclobutyl)triphenylphosphonium Bromide (24).[11,19] Sodium hydride (5.57 g, 0.232 mol, 9.80 g of 57% suspension in mineral oil) was washed with pentane (3 × 20 ml). Tetrahydrofuran (450 ml) and methyltriphenylphosphonium bromide (68.8 g, 0.193 mol, 70.3 g of 98% pure material) were added and the mixture was stirred 9 hr under a nitrogen atmosphere at 50–54°. Solid materials were allowed to settle and the orange supernatant was forced through a glass tube into an oxygen-free flask using nitrogen pressure. *threo*-1,3-Dibromobutane-*1,1,2-d*$_3$ (21.5 g, 0.0981 mol) from above was added dropwise while holding the temperature below 30°. The mixture was stirred 24 hr at 50–54°, allowed to cool, and filtered. Solvent was removed from the solid *in vacuo;* the material was recrystallized from water (69 ml) and dried *in vacuo* at 58° over calcium sulfate to give 18.3 g of product (45.5%), mp 233–250°.

1-(*Z*)-(1-Deuterioethylidene)-2-methyl-*trans*-3,4,4-trideuteriocyclobutane (16).[11] The phosphonium bromide **24** (18.3 g, 0.0442 mol), tetrahydrofuran (150 ml), and *n*-butyllithium (15.14% in hexane, 27.8 ml, 0.0530 mol) were stirred at room temperature for 1 hr under a nitrogen atmosphere. Acetaldehyde-*1-d*$_1$ (2.6 g, 0.057 mol) was added and the mixture was allowed to stir overnight. Ice–water (250 ml) and pentane (50 ml) were added; the aqueous layer and the solid residue were removed and washed with pentane (25 ml). The pentane fractions were combined and washed with ice–water (250 ml), at which point more solids precipitated. The aqueous layer and solid material were washed with pentane (25 ml), and all the pentane layers were combined and washed with ice–water (7 × 250 ml), dried ($MgSO_4$), filtered, and concentrated by spinning band distillation. A forerun (bp 84–94°, 0.292 g of the products, 45% pure by glpc) was taken followed by the main fraction (bp 94–98°, 1.358 g, 96% pure). After vacuum transfer, the pot residue consisted mainly of 1-ethylidene-2-methylcyclobutane products (1.058 g, 96% pure). The total yield was 2.43 g (55.0%) of a mixture of isomers (**16** and **25**) which could be separated by preparative glpc. With broad band deuterium irradiation the nmr spectrum of the longer retention time *Z* product **16** showed a doublet, J = 7.0 Hz, 1.19 (C(2) methyl); a doublet, J = 5.4 Hz, δ 1.41 (C(3) proton); a doublet, J = 1.5 Hz, δ 1.51 (vinylic methyl); and a quintet, J = 7.0 Hz, of quartets, J = 1.5 Hz, δ 3.01 (C(2)). A small amount (8.4%) of **19** with C(3) hydrogen trans to the methyl was present as indicated by the doublet, J = 8.9 Hz, δ 2.06.

Partial Resolution of 1-(*Z*)-(1-Deuterioethylidene)-2-methyl-*trans*-3,4,4-trideuteriocyclobutane.[16] Sodium borohydride (71.2 mg, 1.875 mmol), (−)-α-pinene ($[\alpha]^{23}$°D −47.6; 680 mg, 5.00 mmol), and diglyme (2.0 ml) were stirred under a nitrogen atmosphere. The temperature was lowered to 0° and boron trifluoride etherate (355 mg, 2.50 mmol) in diglyme (5.8 ml) was added dropwise over 10 min. After 4 hr at 0°, the olefin, **16** (522 mg, 5.22 mmol), was added. The reaction mixture was allowed to stand overnight. It was then diluted with ice–water (25 ml) and extracted with pentane (3 × 25 ml). The pentane layers were combined, washed with ice–water (3 × 25 ml), and dried ($MgSO_4$); the solution was filtered and concentrated by spinning band distillation. Vacuum transfer and preparative glpc of the pot residue gave 157 mg of product (60.3%), $[\alpha]^{27}_{222\text{nm}}$ −2040° (gas phase).

(19) *Cf.* E. L. Eliel, *J. Chem. Educ.*, **48**, 163 (1971).

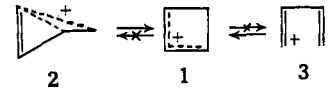
Solvolytic Rearrangement of 1,2,3-Tri-*tert*-butyl-3-dichloromethylcyclopropene and *cis*-3,4-Dichloro-1,2,3-tri-*tert*-butylcyclobutene[1]

Andrew E. Feiring[2] and Joseph Ciabattoni*

Contribution from the Metcalf Research Laboratories, Brown University, Providence, Rhode Island 02912. *Received March 2, 1973*

Abstract: Reaction of tri-*tert*-butylcyclopropenyl fluoroborate (**9**) with dichloromethyllithium at low temperature gave 1,2,3-tri-*tert*-butyl-3-dichloromethylcyclopropene (**6**). Compound **6** underwent facile isomerization to *cis*-3,4-dichloro-1,2,3-tri-*tert*-butylcyclobutene (**7**). Reduction of **7** with lithium aluminum hydride afforded 1,2,3-tri-*tert*-butylcyclobutene (**12**). Reaction of **7** with *tert*-butyllithium produced 1,2,3,4-tetra-*tert*-butylcyclobutene (**13**) and **12**. Tri-*tert*-butylcyclobutadieneiron tricarbonyl (**14**) was prepared by the reaction of diiron nonacarbonyl with **7**. Dichlorides **6** and **7** were found to undergo a novel solvolytic rearrangement in aqueous dioxane to 1,2-di-*tert*-butyl-3-pivaloylcyclopropene (**8**). Treatment of **8** with phosphorus pentachloride resulted in the formation of dichloride **7**. Kinetic data indicated that **6** is 28 times more reactive than **7** toward solvolysis. The results are consistent with an ionic mechanism involving cyclobutenyl cation **10** as a common intermediate.

The generation of carbonium ions within the framework of highly strained molecules is frequently accompanied by a complex series of σ bond rearrangements. Almost alone among small rings, the cyclobutenyl cation (**1**) normally shows little tendency to undergo such rearrangements. Indeed **1** should lie at the position of minimum energy with respect to its isomers such as the bicyclobutenium ion (unsaturated bicyclobutonium ion) **2** or vinyl cation **3**.



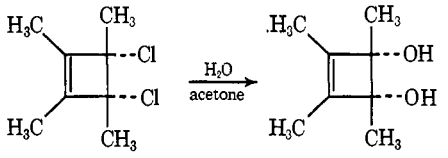
2 **1** **3**

The bicyclobutenium ion **2**, generated by the sol-

(1) For a preliminary communication, see J. Ciabattoni and A. E. Feiring, *J. Amer. Chem. Soc.*, **94**, 5113 (1972).

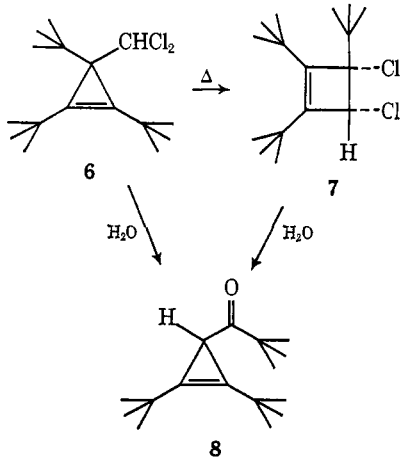
(2) Abstracted from the Ph.D. Thesis of A. E. Feiring, Brown University, 1973. National Science Foundation Graduate Trainee, 1970–1971.

volysis of cyclopropenylcarbinyl alcohol derivatives,[3-5] rearranges rapidly and irreversibly to the cyclobutenyl cation **1**. Although **2** can be trapped under conditions of rapidly collapsing ion-pair intermediates,[6] generally only products derived from **1** are observed. Similarly, the solvolysis of cyclobuten-3-yl derivatives affords products arising exclusively *via* the cyclobutenyl cation.[7] For example, the hydrolysis of *cis*-3,4-dichloro-1,2,3,4-tetramethylcyclobutene (**4**) in aqueous acetone afforded only the corresponding unrearranged cis diol **5**.[8,9]



4 **5**

In this account we wish to report on the syntheses and some properties of 1,2,3-tri-*tert*-butyl-3-dichloromethylcyclopropene (**6**) and *cis*-3,4-dichloro-1,2,3-tri-*tert*-butylcyclobutene (**7**). In particular, we report that the solvolysis of both **6** and **7** affords 1,2-di-*tert*-butyl-3-pivaloylcyclopropene (**8**) in high yield



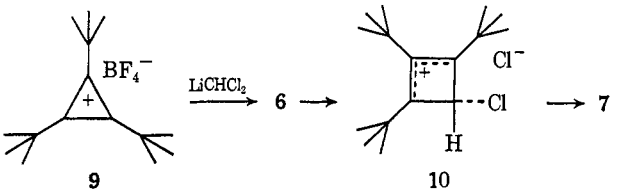
6 **7** **8**

and present evidence on the mechanisms of these novel rearrangements.

Results and Discussion

The preparation of **6** and **7** was based on a related synthesis of the corresponding trimethyl derivatives by Closs and Rao.[10] Addition of tri-*tert*-butylcyclopropenium fluoroborate (**9**)[11] to a cold (−65°) tetrahydrofuran solution of dichloromethyllithium (generated *in situ* from methylene chloride and *n*-butyllithium)[12] afforded 1,2,3-tri-*tert*-butyl-3-dichloromethylcyclopropene (**6**) as a waxy white crystalline solid in 93% yield (Scheme I). The infrared spectrum of **6**

Scheme I



9 **10**

(CCl_4) revealed the characteristic weak cyclopropene absorption at 1820 cm^{-1} (C=C) and the nmr spectrum (δ, $CDCl_3$) exhibited peaks at 1.02 (s, 9 H), 1.28 (s, 18 H), and 6.40 (s, 1 H). Further structural evidence was provided by the mass spectrum which showed peaks at *m/e* 292, 290, and 57.

Although stable for prolonged periods as a solid at room temperature, **6** was found to rearrange under a variety of conditions to the isomeric dichloride **7**. For preparative purposes, the most convenient procedure involved simple heating of **6** in an inert atmosphere for 5 hr at 150°. Two crystallizations of the resulting oil from methanol at low temperature afforded analytically pure **7** as a white crystalline solid, mp 38.0–38.5°, in 64% yield. Alternatively, the isomerization of **6** to **7** could be effected by preparative gas chromatography (5 ft, 15% SE-30 column at 180°, injection port temperature 200°), by allowing a deuteriochloroform solution of **6** to stand for 2 days at room temperature, or by dissolving **6** in liquid sulfur dioxide at −25°. In each case only one isomer was detected. The structure of **7** was fully supported by analytical and spectroscopic data. Elemental analysis and mass spectrometry established that the new compound was an isomer of the dichloromethylcyclopropene **6**. The nmr spectrum ($CDCl_3$) showed the presence of three nonequivalent *tert*-butyl groups at δ 1.13, 1.27, and 1.30 and a single proton at δ 4.92. The infrared spectrum of **7** showed a weak band at 1590 cm^{-1}, assigned to the C=C stretching mode. The stereochemistry of **7** was assigned as cis on the basis of its high dipole moment ($\mu = 3.5 \pm 0.2$ D).[9,13]

It is of interest to speculate on the mechanism of the isomerization. Since the mere dissolution of **6** in liquid SO_2 at low temperature results in the spontaneous generation of **7**, an ionic pathway is implicated. Ionization of cyclopropenylcarbinyl dichloride **6** would be expected to afford ultimately the cyclobutenyl cation intermediate **10**. Subsequent attack by chloride ion would afford the dichlorocyclobutene **7** (Scheme I). The stereoselective formation of *cis*-**7**, while surprising, has ample precedent.[8,9,14] For example, Katz and Gold found that quenching of the cyclobutenyl cation **11** with tetramethylammonium chloride gave exclusively the cis dichloride **4**.[14]

In addition to the above spectroscopic data, chem-

(3) (a) R. Breslow and M. Battiste, *ibid.*, **82**, 3626 (1960); (b) R. Breslow, J. Lockhart, and A. Small, *ibid.*, **84**, 2793 (1962); (c) R. Breslow in "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience, New York, N. Y., 1963.

(4) (a) R. Breslow, H. Bozimo, and P. Wolf, *Tetrahedron Lett.*, 2395 (1970); (b) P. F. Wolf, Ph.D. Thesis, Columbia University, 1964.

(5) W. J. Gensler, J. J. Langone, and M. B. Floyd, *J. Amer. Chem. Soc.*, **93**, 3828 (1971).

(6) A. E. Feiring and J. Ciabattoni, *J. Org. Chem.*, **37**, 3784 (1972).

(7) E. F. Kiefer and J. D. Roberts, *J. Amer. Chem. Soc.*, **84**, 784 (1962).

(8) M. P. Stevens, Ph.D. Thesis, Cornell University, 1961.

(9) R. Criegee, *Angew. Chem., Int. Ed. Engl.*, 1, 519 (1962).

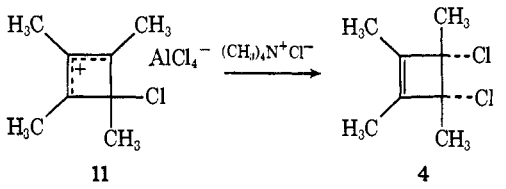
(10) G. L. Closs and V. N. M. Rao, *J. Amer. Chem. Soc.*, **88**, 4116 (1966).

(11) J. Ciabattoni, E. C. Nathan, A. E. Feiring, and P. J. Kocienski, *Org. Syn.*, in press.

(12) G. Kobrich and W. Drischel, *Angew. Chem., Int. Ed. Engl.*, **3**, 513 (1964). For a recent review of carbenoids and related organolithium compounds, see G. Kobrich, *ibid.*, **11**, 473 (1972).

(13) The dipole moment was determined by measurements on dilute solutions of **7** in hexane according to the method discussed in D. P. Shoemaker and C. W. Garland, "Experiments in Physical Chemistry," McGraw-Hill, New York, N. Y., 1967, pp 295-303. We are grateful to Dr. S. Cichanowski for this determination.

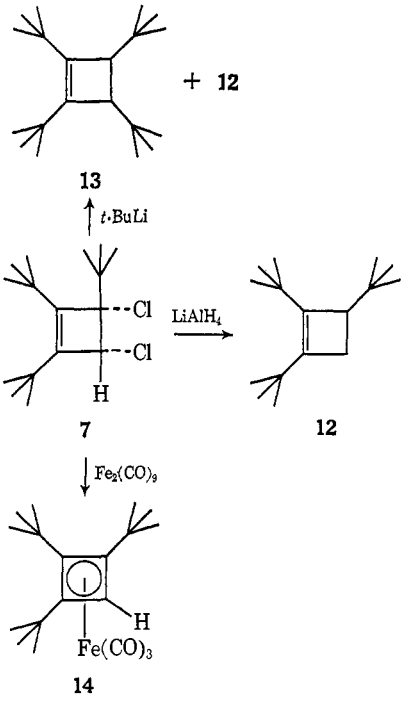
(14) T. J. Katz and E. H. Gold, *J. Amer. Chem. Soc.*, **86**, 1600 (1964).



11 4

ical evidence for the structure of 7 was obtained from its reactions with lithium aluminum hydride, *tert*-butyllithium, and diiron nonacarbonyl (Scheme II).

Scheme II



13 7 12 14

Reduction of 7 with lithium aluminum hydride in refluxing tetrahydrofuran (THF) afforded 1,2,3-tri-*tert*-butylcyclobutene (**12**) in 64% yield. The addition of 2 equiv of *tert*-butyllithium to a solution of 7 in pentane resulted in a vigorous exothermic reaction. Aqueous work-up of the reaction followed by column chromatography over silica gel afforded two hydrocarbons. The products were separated by preparative gas chromatography and identified as 1,2,3,4-tetra-*tert*-butylcyclobutene (**13**, 93%) and **12** (7%). Unfortunately, the spectroscopic data were not sufficient to permit an unambiguous assignment of the stereochemistry of **13**. An attempt to establish the stereochemistry of **13** by epoxidation failed since the compound proved to be inert to prolonged treatment with *m*-chloroperoxybenzoic acid. The mechanism of the reaction of 7 with *tert*-butyllithium merits some comment. The majority of reactions of alkyllithium reagents with alkyl halides yielding products of coupling and disproportionation have been shown to proceed *via* radical intermediates.[15] In the present case, each mole of dichloride reacted with 2 mol of alkyllithium with exclusively disproportionation occurring at the tertiary center and a mixture of coupling and disproportionation (with the former predominating) occurring at the secondary position. Steric factors are presumably responsible for the difference in behavior at the two sites. The coupling reaction at the secondary position is likely to occur in the direction which minimizes the steric interaction between the adjacent *tert*-butyl groups. This consideration suggests that **13** has the trans configuration.

Warming 7 with an excess of diiron nonacarbonyl in benzene, according to the procedure developed by Pettit,[16] followed by chromatography over alumina and sublimation under reduced pressure, produced tri-*tert*-butylcyclobutadieneiron tricarbonyl (**14**) as faint yellow crystals, mp 133–135°, in 29% yield. The structure of **14** was fully supported by analytical and spectroscopic data. The nmr spectrum (C_6D_6) showed three sharp singlets at δ 1.05 (18 H), 1.13 (9 H), and 3.90 (1 H), and the infrared spectrum (Nujol) showed the expected strong CO absorptions at 2030 and 1960 cm^{-1}.[17] The mass spectrum of **14**, in addition to exhibiting a strong parent ion at *m/e* 360, showed intense peaks at *m/e* 332, 304, and 276, representing a stepwise loss of the CO ligands.

The course of the above reactions has ample precedent in the chemistry of other 3,4-dihalocyclobutenes,[14,16–19] and the nature of the observed products serves to confirm the assignment of a cyclobutene structure to 7. Despite the presence of three bulky *tert*-butyl groups, the compound in the above cases appears to exhibit only normal reactivity. The hydrolysis of 7, however, afforded results in marked contrast to the expected.

The solvolysis of 7 in 20% aqueous dioxane containing 2 equiv of sodium bicarbonate afforded a clear oil which was shown to consist of two components by glpc analysis. The major component (93%) was collected by preparative glpc and identified as the known 1,2-di-*tert*-butyl-3-pivaloylcyclopropene (**8**) by comparison of its spectroscopic data with those reported by van Tamelen.[20] The minor component (7%), obtained as a yellow oil by preparative glpc, showed complex nmr absorption in the region δ 0.95–1.5 and was not characterized further. The kinetics of the solvolysis of 7 were examined under the same conditions by measuring the rate of disappearance of 7 by glpc. The hydrolysis was found to be a first-order process, and the calculated rate constants are presented in Table I; activation parameters are $\Delta H^{\pm}$ = 22.5 kcal/mol and $\Delta S^{\pm}$ (30°) = −7.8 eu. For comparison purposes, rate data for the solvolysis of

Table I. Solvolysis Rates

Compd	Solvent	Added salt (*M*)	Temp, °C	$k \times 10^4$ sec^{-1}
7[a]	20% aq dioxane	$NaHCO_3$(0.08)	65.2	3.55
7[a]	20% aq dioxane	$NaHCO_3$(0.08)	51.1	0.96
7[a]	20% aq dioxane	$NaHCO_3$(0.08)	29.8	0.071
4[b]	20% aq acetone		25.0	114.0

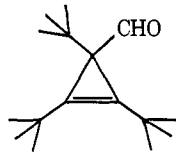
[a] This study; solutions were 0.04 *M* in substrate. [b] Reference 8; solutions were 0.015 *M*.

(15) H. R. Ward, *Accounts Chem. Res.*, 5, 18 (1972), and references contained therein.

(16) R. Pettit and J. Henery, *Org. Syn.*, 50, 21 (1970).
(17) L. Watts and R. Pettit, *Advan. Chem. Ser.*, No. 62, 549 (1966).
(18) K. Nicholas, L. S. Bray, R. E. Davis, and R. Pettit, *Chem. Commun.*, 608 (1971).
(19) M. Avram, D. Constantinescu, I. G. Dinulescu, and C. D. Nenitzescu, *Tetrahedron Lett.*, 5215 (1969).
(20) E. E. van Tamelen and T. H. Whitesides, *J. Amer. Chem. Soc.*, 93, 6129 (1971).

cis-3,4-dichloro-1,2,3,4-tetramethylcyclobutene (**4**)[8] under roughly comparable conditions[21] are also presented in Table I.

Similarly, the solvolysis of 1,2,3-tri-*tert*-butyl-3-dichloromethylcyclopropene (**6**) in 20% aqueous dioxane containing 2 equiv of sodium bicarbonate afforded the cyclopropenyl ketone **8** as the only observed product. The isomeric cyclopropenecarboxaldehyde **15**



15

could not be detected in the hydrolysis of **6** or **7**. The relative solvolysis rates of **6** and **7** were determined by observing the time required for a carefully measured amount of each substrate to exactly neutralize a known quantity of added base in 20% aqueous dioxane. The data are presented in Table II.

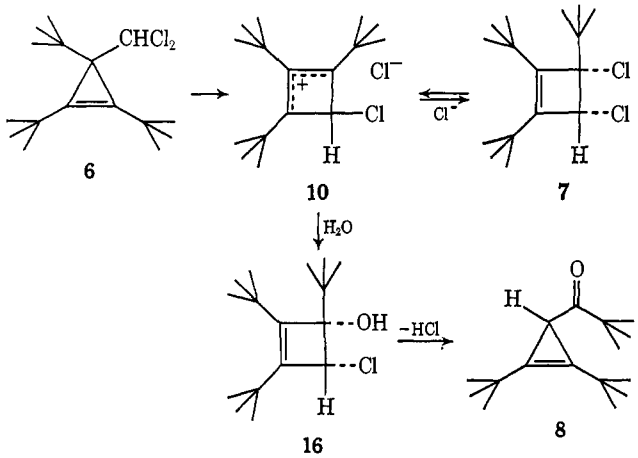
Table II. Solvolysis Rates of **6** and **7** in 20% Aqueous Dioxane at 40.6°

Compd	Neutralization time,[a] min	$k \times 10^4$ sec^{-1}	k_{rel}[b]
7	40.80	0.832	
7	39.90	0.841	1
6	1.46	23.0	
6	1.44	23.3	27.9

[a] Time required for 0.04 *M* substrate to neutralize 0.01457 *M* NaOH using phenolphthalein as an indicator. [b] Based on the average of the two runs for each substrate.

The results are consistent with an ionic process involving cyclobutenyl cation **10** as a common intermediate in the solvolysis of **6** and **7** (Scheme III).

Scheme III

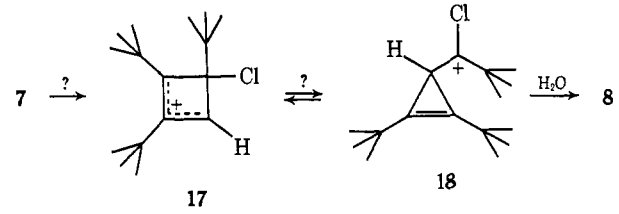


6 10 7 16 8

As mentioned earlier, **10** is also the probable intermediate in the isomerization of **6** to **7** under neat or inert solvent conditions. Reaction of **10** with water would afford the postulated chlorocyclobutenol **16** presumably as the cis isomer which could neither be isolated nor detected under the reaction conditions. Subsequent ionization of the secondary chloride of **16** with synchronous ring contraction provides the observed rearrangement product **8**.[22]

The data in Table I indicate that *cis*-3,4-dichloro-1,2,3,4-tetramethylcyclobutene (**4**) solvolyzes roughly 1500 times faster than *cis*-3,4-dichloro-1,2,3-tri-*tert*-butylcyclobutene (**7**).[8,21] This rate difference can be rationalized on the basis of steric hindrance to ionization in the case of **7** in which the reluctance of the third *tert*-butyl group to become eclipsed decreases the solvolysis rate of **7** relative to the unhindered **4**. On this basis it could also be argued that the secondary chloride may well be more reactive than the vicinal tertiary chloride of **7**. The difference in rate between **4** and **7** could then be ascribed to the fact that the former compound solvolyzes *via* ionization of a tertiary chloride whereas the latter *via* ionization of a secondary chloride. Accordingly, an alternative mechanism for the formation of **8** from **7** could involve cyclobutenyl cation intermediate **17** as shown in Scheme IV. Sub-

Scheme IV



sequent ring contraction of **17** to cyclopropenylcarbinyl cation **18** followed by attack of water would lead to **8**. This mechanism is unlikely for at least three reasons. First, the difference in rate between **4** and **7** might well be larger than that observed if ionization of the secondary chloride in **7** were the rate-determining step. For example, α,α-dimethylallyl chloride solvolyzes 14,000 times faster than α-methylallyl chloride.[23] Second, the solvolysis of the dichloromethylcyclopropene **6**, which also affords **8**, can give directly *via* ring expansion only the symmetrical cyclobutenyl cation **10**. The fact that **6** solvolyzes 28 times faster than **7** (Table II) excludes the latter compound as a possible intermediate in the solvolysis of the former. The third argument against the mechanism in Scheme IV concerns the apparent requirement of oxygen participation during the ring contraction, with carbonyl formation providing some of the driving force. Thus, treatment of the cyclopropenyl ketone **8** with PCl_5 effects the formation of cis dichloride **7**. The probable course of this reaction[24] is outlined in Scheme V. Ring expansion of intermediate **19** would afford **7** *via* cyclobutenyl cation **17**. The unrearranged dichloride **20** was not observed. The importance of oxygen participation is evidenced by the fact that **16** undergoes ring contraction to **8** whereas **17** suffers collapse by chloride ion to give the cyclobutene dichloride **7**. Furthermore, the dissolution of **6** and **7** in the highly ionizing liquid SO_2 under anhydrous conditions affords an nmr spectrum which in each case is consistent only with the presence of *cis*-dichlorocyclobutene **7**. It should be emphasized at this point that the mech-

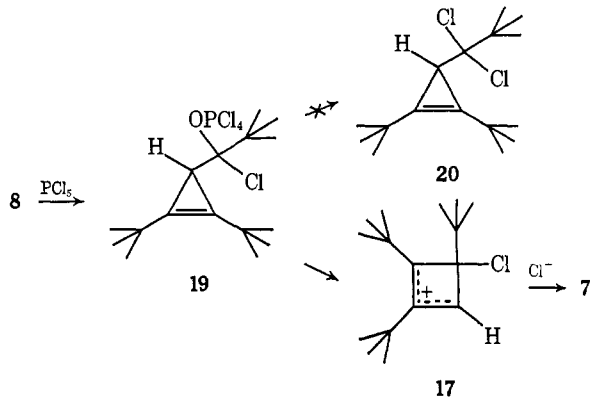
(21) The *Y* values for 20% aqueous dioxane and 20% aqueous acetone are −0.833 and −0.673, respectively: A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956).

(22) A similar electrolytic rearrangement of tri-*tert*-butylcyclobutenedicarboxylic acid to cyclopropenyl ketones was recently reported: G. Maier and F. Bosslet, *Tetrahedron Lett.*, 4483 (1972).

(23) C. A. Vernon, *J. Chem. Soc.*, 423 (1954).

(24) M. S. Newman and L. L. Wood, *J. Amer. Chem. Soc.*, **81**, 4300 (1959).

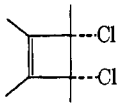
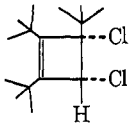
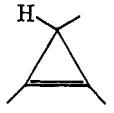
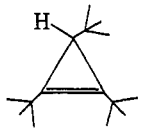
Scheme V



anism outlined in Scheme III provides for oxygen participation during the ring contraction. The alternative mechanism in Scheme IV requires carbonyl formation *after* the ring contraction.

The energy released by oxygen participation and carbonyl formation is not sufficient to effect the ring contraction of a cyclobutene to a cyclopropene. Since the solvolysis of less sterically hindered cyclobutene derivatives such as **4** does not produce cyclopropene products, it is clear that the *tert*-butyl groups are strongly influencing the course of the reaction. The source of the influence of the *tert*-butyl substituents is suggested by the data on C=C infrared stretching frequencies contained in Table III.

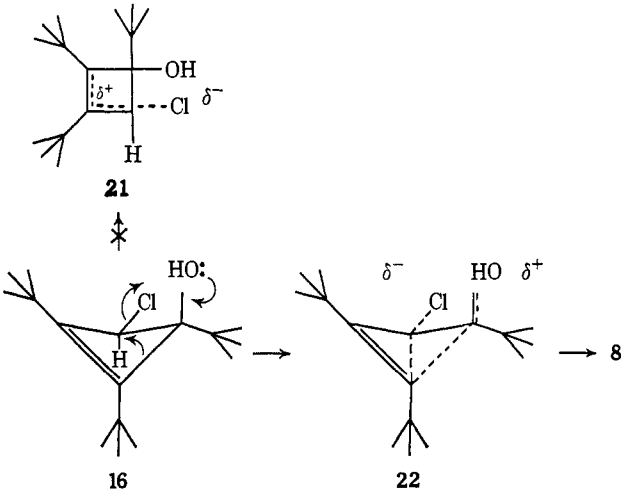
Table III. Double Bond Stretching Vibrations

Compd	$\nu_{C=C}$, cm^{-1}
	1684[a]
	1595[b]
	1880[c]
	1830[d]

[a] R. Criegee and G. Louis, *Chem. Ber.*, **90**, 417 (1957). [b] This study. [c] G. L. Closs, *Advan. Alicyclic Chem.*, **1**, 74 (1966). [d] J. Ciabattoni and E. C. Nathan, *J. Amer. Chem. Soc.*, **91**, 4766 (1969).

A likely consequence of the strain in highly crowded olefins is that the bulky substituents would either twist out of the plane or force an increase in the length of the double bond. In either case the π overlap would be disturbed giving a weaker bond, with the resultant lowering of the stretching frequency. Indeed, a decrease in stretching frequency has been shown to accompany increased crowding about a carbon–carbon double bond.[25] The data in Table III indicate that substitution of *tert*-butyl groups for methyl on a cyclopropene lowers the C=C stretching frequency by 50 cm^{-1}, whereas the same substitution on a cyclobutene decreases the frequency by about 90 cm^{-1}. This suggests that *tert*-butyl substitution has a somewhat greater adverse effect on the strain energy of a cyclobutene than on a cyclopropene. This is due to the fact that the bond angles would force the *tert*-butyl groups on the double bond to be closer together in the four-membered ring than in the three-membered ring. Alternatively, the ir effect could be ascribed to the much greater flexibility of the cyclobutene ring, which permits relief of eclipsed strain by ring puckering with concomitant twisting of the C=C bond.

It was pointed out earlier that part of the greater stability of a cyclobutenyl cation relative to a cyclopropenylcarbinyl cation (or its nonclassical representation, the bicyclobutenium ion **2**) is due to the much greater strain energy present in the latter species. In the present case, apparently the energy difference between these two species is somewhat decreased as a consequence of *tert*-butyl substitution. Thus, for ionization of the proposed chloro alcohol intermediate **16**, the transition state **22** resembling a bicyclobutenium



ion becomes more energetically accessible than the alternative transition state **21**. On the basis of the relative solvolysis rates of **4** and **7** (Table I), it is clear that **10** and therefore **21** are enormously destabilized (considering especially that **7** must be more strained than **4** initially) relative to **11**. The ir, kinetic, and product evidence taken together suggest that the three *tert*-butyl groups cause substantial puckering of the cyclobutenyl system. With the intervention of **22**, the participation of oxygen with carbonyl formation apparently drives the solvolysis of **16** entirely in the direction of cyclopropenyl ketone formation.[26]

Experimental Section

Melting points were obtained on a Kofler micro heating stage; all melting and boiling points are uncorrected. Infrared and ultraviolet spectra were recorded with a Perkin-Elmer Model 337 spectrophotometer and a Cary Model 14 recording spectrophotometer, respectively. All nmr spectra were run on a Varian A-60A instrument in the indicated solvents. Chemical shifts are reported in ppm from tetramethylsilane and the number in parentheses indicates the number of protons responsible for the signal. The

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

(26) We are grateful to a referee for his enlightening comments.

letter denotes the multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Mass spectra were obtained with an Hitachi RMU-6D instrument. Gas–liquid partition chromatography (glpc) analyses were obtained with a Hewlett-Packard Model 5750 instrument equipped with a thermal conductivity detector. Columns used were: a 3 ft × 0.25 in. column of 15% SE-30 on Chromosorb W (column A), and a 5 ft × 0.25 in. column of 15% SE-30 on Chromosorb W (column B). A helium carrier gas flow rate of 60 ml/min was used in all cases. Relative peak areas were measured by Disc integration and are not corrected for relative detector response. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn., or Meade Microanalytical Laboratory, Amherst, Mass.

Materials. Ethyl ether, tetrahydrofuran (THF), benzene, and hydrocarbon solvents were freshly distilled from $LiAlH_4$. Reagent grade anhydrous dioxane (B&A) and spectroquality methylene chloride (Eastman) were taken from freshly opened bottles and used directly. The following reagents were obtained from the indicated source and were used as received: *n*-butyllithium (Alfa), *tert*-butyllithium (Alfa), *m*-chloroperoxybenzoic acid (Aldrich, 85%), phosphorus pentachloride (MC&B), and sulfur dioxide (Merck). Column chromatography was performed using Baker 60–200 mesh silica gel or Woelm activity grade 1 alumina (neutral).

1,2,3-Tri-*tert*-butyl-3-dichloromethylcyclopropene (6). A flame-dried, 250-ml, round-bottom flask was charged with 2.72 g (32 mmol) of Eastman spectroquality methylene chloride and 160 ml of dry tetrahydrofuran. In an argon atmosphere, the solution was cooled to −65° with a Dry Ice–acetone bath and 13 ml (30 mmol) of 2.34 *M* *n*-butyllithium was added over 0.25 hr. The rate of addition was controlled so that the solution temperature did not rise above −60°. The resulting clear solution was stirred for an additional 10 min and 8.3 g (28 mmol) of tri-*tert*-butylcyclopropenium fluoroborate was added in one portion. After the mixture was stirred for 1.25 hr at −65°, the reaction was quenched by the addition of 10 ml of water. The resulting mixture, containing a thick white precipitate, was poured into 150 ml of hexane and 100 ml of water with vigorous stirring and filtered through a coarse sintered glass funnel. The layers were separated and the aqueous solution was extracted with 100 ml of hexane. The combined hexane layers were washed with 3 × 50 ml of H_2O and 1 × 50 ml of saturated aqueous NaCl and dried ($MgSO_4$). The hexane was removed *in vacuo* leaving a yellow oil. The oil was heated to 60° and evacuated to 0.1 mm to remove a volatile yellow impurity, leaving 7.6 g (93%) of product as a waxy white solid: ir (CCl_4) 2950 (s), 2900 (s), 2860 (s), 1820 (w), 1480 (s), 1460 (s), 1400 (w), 1370 (s), 1250 (m), 1190 (m), and 1050 (s) cm^{-1}; nmr (δ, $CDCl_3$) 1.02 (s, 9 H), 1.28 (s, 18 H), 6.40 (s, 1 H); mass spectrum *m/e* 292, 290, 57.

Rearrangement of 1,2,3-Tri-*tert*-butyl-3-dichloromethylcyclopropene (6) to *cis*-3,4-Dichloro-1,2,3-tri-*tert*-butylcyclobutene (7). A. A 50-ml, round-bottom flask containing 7.6 g (26 mmol) of **6** was evacuated to 0.1 mm and filled with argon several times. The flask was heated in a 150° oil bath for 5 hr. After the solution was cooled to room temperature, the resulting yellow oil was dissolved in 25 ml of absolute methanol and cooled in a Dry Ice–acetone bath. A viscous white oil formed rapidly. The mixture was removed from the bath and stirred vigorously until the oil crystallized, then cooled again until crystallization appeared complete. The crystals were filtered by suction, recrystallized from 20 ml of methanol as described above, and dried at 0.1 mm to give 4.9 g (64%) of **7** as a white powder: mp 38–38.5°; ir (CCl_4) 2970 (s), 2940 (s), 2900 (s), 1595 (w) 1470 (m), 1380 (m), 1360 (m) cm^{-1}; nmr (δ, $CDCl_3$) 1.13 (s, 9 H), 1.27 (s, 9 H), 1.30 (s, 9 H), 4.92 (s, 1 H); mass spectrum *m/e* 292, 290, 57.

Anal. Calcd for $C_{16}H_{28}Cl_2$: C, 65.97; H, 9.69. Found: C, 65.91; H, 9.61.

The dipole moment of **7** was determined to be 3.5 ± 0.2 D by measurements on dilute solutions of **7** in hexane.[13] *The dichlorocyclobutene is volatile and lachrymatory and may induce an allergic effect. Extreme caution should be used in its handling.*

B. A 60-mg sample of **6** was placed in an nmr tube. The tube was capped with a serum stopper pierced with two syringe needles. One of the needles was connected *via* a t-tube to an argon source and bubbler. The second needle was connected to a cylinder of sulfur dioxide. The nmr tube was cooled in a Dry Ice–acetone bath and *ca.* 0.6 ml of SO_2 was distilled in. The serum stopper was then rapidly replaced with a tight fitting standard nmr tube cap and the sample was stored at −25°. A 60-mg sample of **7**, prepared as in part A, was dissolved in liquid SO_2 in the same manner. The nmr spectra of both samples at −25°, taken within 10 min of sample preparation, were identical showing absorptions at δ 1.13 (s, 9 H), 1.30 (s, 9 H), 1.33 (s, 9 H), and 5.10 (s, 1 H). Both samples remained clear and colorless for several hours at −25°.

C. A 60-mg sample of **6** was dissolved in $CDCl_3$ in an nmr tube and the spectrum was scanned periodically. The spectra showed a gradual disappearance of the peaks of **6** with the appearance of the peaks assigned to **7**. The isomerization was essentially complete within 2 days at room temperature.

Reaction of *cis*-3,4-Dichloro-1,2,3-tri-*tert*-butylcyclobutene (7) with *tert*-Butyllithium. A flame-dried, 100-ml round-bottom flask was charged with 1.5 g (5.2 mmol) of **7** and 50 ml of pentane In an argon atmosphere, 6.5 ml (15 mmol) of 2.34 *M* *tert*-butyllithium in hexane was added over 15 min. The heat of reaction was sufficient to reflux the solution. After stirring at room temperature for 5 hr, the solution was poured into 50 ml of water. The layers were separated and the organic phase was washed with 1 × 50 ml of H_2O and 1 × 50 ml of saturated aqueous NaCl. After the solution was dried ($MgSO_4$), the solvent was removed *in vacuo* leaving 1.38 g of a faint yellow oil. The oil was chromatographed on 30 g of silica gel packed in hexane. Elution with 160 ml of hexane afforded 1.24 g of a clear oil. Glpc (column B, 200°) showed the presence of two components, both of which were collected by preparative glpc.

The minor component (7%, retention time = 4.5 min) was a colorless oil identified as 1,2,3-tri-*tert*-butylcyclobutene (**12**): ir (neat) 2960 (s), 2900 (s), 2860 (s), 1600 (vw), 1480 (m), 1390 (m), 1365 (m), and 1230 (s); nmr (δ, $CDCl_3$) 0.93 (s, 9 H), 1.10 (s, 9 H), 1.13 (s, 9 H), 1.85–2.43 (m, 3 H); mass spectrum *m/e* 222, 57.

Anal. Calcd for $C_{16}H_{30}$: C, 86.40; H, 13.60. Found: C, 86.61; H, 13.59.

The major component (93%, retention time = 15 min) was a white solid, mp 67–69°, identified as 1,2,3,4-tetra-*tert*-butylcyclobutene (**13**): ir (CCl_4) 2960 (s,) 2900 (s), 2880 (s), 1600 (s), 1460 (m), 1390 (m), 1360 (m), and 1220 (s) cm^{-1}; Raman 1599 (s); nmr (δ, $CDCl_3$) 0.95 (s, 18 H), 1.18 (s, 18 H), 2.17 (s, 2 H); mass spectrum *m/e* 278, 57; uv (λ^{EtOH}) 211 mμ (ϵ 7000).

Anal. Calcd for $C_{20}H_{38}$: C, 86.25; H, 13.75. Found: C, 86.42; H, 13.64.

Reaction of **7** (0.10 g, 0.34 mmol) in 10 ml of pentane with 0.15 ml (0.34 mmol) of *tert*-butyllithium in hexane as described above afforded a faint yellow oil after aqueous work-up. Glpc of the oil (column B, 200°) revealed that it contained a mixture of unreacted **7** plus the two hydrocarbons **12** and **13**.

Attempted Epoxidation of 1,2,3,4-Tetra-*tert*-butylcyclobutene (13). A solution of 0.278 g (1 mmol) of **13** and 0.204 g (1 mmol) of 85% *m*-chloroperoxybenzoic acid in 8 ml of methylene chloride was stirred under N_2 for 48 hr at room temperature. The solution was washed with 2 × 50 ml of 10% aqueous $NaHCO_3$ and 1 × 50 ml of H_2O. After the solution was dried ($MgSO_4$), evaporation of the methylene chloride *in vacuo* returned a white solid with an nmr spectrum identical with that of pure **13**.

Reaction of *cis*-3,4-Dichloro-1,2,3-tri-*tert*-butylcyclobutene (7) with $LiAlH_4$. A mixture of 0.65 g (2.2 mmol) of **7**, 0.154 g (4 mmol) of $LiAlH_4$, and 15 ml of tetrahydrofuran was refluxed for 30 hr. The excess hydride was decomposed by the dropwise addition of 10% aqueous NaOH. The white precipitate of inorganic salts was filtered off and washed with 10 ml of fresh THF. The combined filtrate and washing was poured into 70 ml of water and extracted with 3 × 10 ml of pentane. The pentane extracts were washed with 2 × 50 ml of H_2O and 1 × 50 ml of saturated aqueous NaCl and dried ($MgSO_4$). Concentration of the solution *in vacuo* returned 0.59 g of yellow oil. The oil was chromatographed on 15 g of silica gel packed in pentane. Elution with 60 ml of pentane, followed by evaporation of the solvent and molecular distillation of the residue (100° (120 mm)), afforded 0.31 g (64%) of 1,2,3-tri-*tert*-butylcyclobutene (**12**).

Purification of Diiron Nonacarbonyl.[27] Approximately 20 g of diiron nonacarbonyl (Pressure Chemical Corp.) was introduced into the top half of a pressure funnel equipped with a coarse sintered glass frit. It was washed successively with 2 × 50 ml of 25% aqueous HCl, 1 × 50 ml of H_2O, 2 × 50 ml of absolute ethanol, and 1 × 50 ml of dry ether. Each washing was accomplished by introducing the solvent, stirring the suspension for several minutes with a glass rod, and removing the solvent by pressure filtering with argon. A blanket of argon was maintained throughout the procedure. The solid was quickly transferred to a brown glass bottle and dried at 0.1 mm (room temperature) for 0.5 hr.

(27) E. H. Braye and W. Hubel, *Inorg. Syn.*, **8**, 178 (1966).

Tri-*tert*-butylcyclobutadieneiron Tricarbonyl (14).[16] A 250-ml, round-bottom flask was charged with 4.4 g (15 mmol) of 3,4-dichloro-1,2,3-tri-*tert*-butylcyclobutene (**7**) and 120 ml of dry benzene. The solution was heated in an argon atmosphere to 50–60° in an oil bath and 11.0 g (30 mmol) of freshly purified diiron nonacarbonyl was added in one portion. After 20 min the red color of the $Fe_3(CO)_9$ faded to a dirty green and an additional 5.5 g (15 mmol) of $Fe_2(CO)_9$ was added. The mixture was stirred at 50–60° for 1.5 hr, then cooled to room temperature and filtered through Celite. The Celite was washed with 100 ml of benzene and the filtrate and washings were combined. (*Caution! The solution contains a large quantity of volatile and toxic iron pentacarbonyl. It should be handled only in an efficient hood.*) The solution was concentrated *in vacuo* with heating to *ca.* 50° to a dark green oil. (The yellow liquid which collects in the rotary evaporator trap is a solution of iron pentacarbonyl in benzene. It should be carefully treated in the hood with a dilute solution of Br_2 in CCl_4 before disposal). The oil was taken up in a small volume of hexane and chromatographed on 120 g of alumina packed in hexane. Eluting with hexane, 10-ml fractions were taken; progress of the chromatography was monitored by glpc (column A, 200°). Fractions 9–17, containing a single component with a retention time of 12 min, were combined and concentrated to a yellow solid (2.0 g). Sublimation of the solid (80° (0.1 mm)) afforded 1.56 g (29%) of faint yellow crystals of **14**: mp 133–135°; ir (Nujol) 2030 (s), 1960 (s) cm^{-1}; nmr (δ, C_6D_6) 1.05 (s, 18 H), 1.13 (s, 9 H), 3.90 (s, 1 H); mass spectrum *m/e* 360, 332, 304, 276, 57.

Anal. Calcd for $C_{19}H_{28}FeO_3$: C, 63.34; H, 7.83; Fe, 15.50. Found: C, 63.15; H, 7.98; Fe, 15.26.

Fractions 6–8 were combined and concentrated to a colorless oil (0.5 g). Glpc of the oil showed the presence of two major components in approximately equal amounts. Both were collected by preparative glpc. The first component (retention time = 3.8 min) was a clear oil identified as 2,3,5-tri-*tert*-butylfuran:[20] ir (neat) 2960 (s), 2900 (s), 2860 (s), 1610 (m), 1460 (m), 1380 (m), 1360 (m), and 1250 (m) cm^{-1}; nmr (δ, $CDCl_3$) 1.23 (s, 9 H), 1.32 (s, 9 H), 1.38 (s, 9 H), 5.87 (s, 1 H); mass spectrum *m/e* 236, 221, 57. The second component was identified as 1,2,3-tri-*tert*-butylcyclobutene by comparison of its nmr spectrum with that of an authentic sample.

Solvolysis of *cis*-3,4-Dichloro-1,2,3-tri-*tert*-butylcyclobutene (7). A. **Product Studies.** A solution of 0.582 g (2 mmol) of **7**, 0.336 g (4 mmol) of anhydrous sodium bicarbonate, and 50 ml of 20% aqueous dioxane was heated in a 70° oil bath for 2.5 hr under nitrogen. The solution was poured into 100 ml of pentane and extracted with 2 × 50 ml of H_2O and 1 × 50 ml of saturated aqueous NaCl. After drying ($MgSO_4$), the pentane solution was concentrated *in vacuo* to afford 0.490 g of a clear oil. Glpc (column A, 190°) showed the presence of two components in a 93:7 ratio. The major component (retention time = 2 min) was obtained as a clear oil by preparative glpc and identified as 1,2-di-*tert*-butyl-3-pivaloylcyclopropene (**8**): ir (neat) 2960 (s), 2900 (s), 2860 (s), 1890 (w), 1680 (s), 1480 (s), 1470 (s), 1400 (m), 1370 (s), 1260 (m), 1220 (w), 1210 (w), 1190 (m), 1090 (s), 1020 (w), 990 (m) cm^{-1}; nmr (δ, $CDCl_3$) 1.13 (s, 18 H), 1.22 (s, 9 H), 2.70 (s, 1 H); mass spectrum *m/e* 236, 221, 151, 57. The minor component (retention time = 4 min) was obtained as a yellow oil by preparative glpc. It showed a complex absorption in the nmr in the region of 0.9–1.5 ppm and was not characterized further.

B. **Kinetics.** General procedure: 0.291 g (1 mmol) of **7** and 0.168 g of anhydrous sodium bicarbonate were carefully weighed into a 25-ml volumetric flask. The flask was filled to the mark with a solution of 20% aqueous dioxane which had been equilibrated at the appropriate solvolysis temperature. The flask was shaken briefly, then immersed in a constant-temperature bath. At appropriate intervals, 2-ml aliquots were withdrawn by pipet and quenched by draining into exactly 5 ml of pentane contained in a small separatory funnel. The pentane solution was washed with 1 × 5 ml of saturated aqueous NaCl, 1 × 5 ml of H_2O, and 1 × 5 ml of saturated aqueous NaCl. Exactly 40 μl of the pentane solution was analyzed by glpc (column A, 190°). The area of the peak corresponding to **7** (retention time = 12 min) was measured by Disc integration. Duplicate injections generally agreed to within 3%. Generally 5–7 aliquots were taken for each run to *ca.* 80% completion of the reaction. Throughout the course of the reaction only the glpc peaks due to **7** and the solvolysis products were observed (*i.e.*, no detectable intermediate was produced). Rate constants were calculated from the disappearance of **7** by a least-squares computer program. The calculated values are presented in Table I. Activation parameters were obtained from an Arrhenius plot of log k *vs.* $1/T$: $\Delta H^{\pm} = 22.5$ kcal/mol, $\Delta S^{\pm} = -7.8$ eu (30°).

Solvolysis of 1,2,3-Tri-*tert*-butyl-3-dichloromethylcyclopropene (6). A solution of 0.307 g (1 mmol) of **6**, 0.168 g (2 mmol) of sodium bicarbonate, and 25 ml of 20% aqueous dioxane was heated under N_2 to 60° for 20 hr. The solution was poured into 50 ml of pentane and extracted with 2 × 50 ml of H_2O and 1 × 50 ml of saturated aqueous NaCl. After drying ($MgSO_4$), the pentane solution was concentrated *in vacuo* to 0.238 g (96%) of colorless oil. The nmr and ir spectra of the oil were identical with those of a pure sample of 1,2-di-*tert*-butyl-3-pivaloylcyclopropene (**8**).

Relative Solvolysis Rates of 1,2,3-Tri-*tert*-butyl-3-dichloromethylcyclopropene (6) and *cis*-3,4-Dichloro-1,2,3-tri-*tert*-butylcyclobutene (7). The relative solvolysis rates were determined in 20% aqueous dioxane by measuring the time required for each to neutralize a known amount of added base. The solutions were initially 0.0400 M in substrate and 0.01457 M in NaOH. Thus, 58.2 mg of **7** or **6** was weighed into a 5-ml volumetric flask. *Ca.* 3.5 ml of dioxane, equilibrated at the solvolysis temperature, was added, followed by 2 drops of phenolphthalein solution. Then 1 ml of 0.07287 M aqueous NaOH solution, also equilibrated at the solvolysis temperature, was added by pipet and the flask was quickly filled to the appropriate mark with dioxane. The flask was shaken, then immersed in a constant-temperature bath at 40.6 ± 0.1°. The time interval from the addition of base to the disappearance of the pink phenolphthalein color was measured to 0.01 min. Duplicate runs were made for each compound.

Since each mole of substrate consumes 2 mol of base, the concentration, C_t, of substrate at the end point, t, was 0.0400 − 0.01457/2 = 0.03271 M. The solvolysis rate constants were calculated from the equation

$$2.303 \log (C_0/C_t) = kt$$

where C_0 is the initial concentration of substrate. The neutralization times, t, and the calculated rates are given in Table II.

The solutions of each substrate were combined and diluted with 30 ml of dioxane and 10 ml of the standard base solution. After remaining overnight in the constant-temperature bath, each solution was poured into 50 ml of pentane and worked up as usual. The nmr spectrum of the oil obtained in each case showed no significant peaks other than those assigned to 1,2-di-*tert*-butyl-3-pivaloylcyclopropene (**8**).

Reaction of 1,2-Di-*tert*-butyl-3-pivaloylcyclopropene (8) with Phosphorus Pentachloride. A small screw-cap vial was charged with 0.118 g (0.5 mmol) of **8** and 0.109 g (0.5 mmol) of PCl_5. A small stirring bar was added, the vial was capped, and the mixture was stirred overnight at room temperature. The material in the vial was taken up in 3 ml of hexane and washed with 2 × 3 ml of water. After the solution was dried ($MgSO_4$), the hexane was removed *in vacuo* leaving 0.133 g (92%) of a colorless oil. Glpc (column A, 190°) showed the presence of a single component with the retention time of *cis*-3,4-dichloro-1,2,3-tri-*tert*-butylcyclobutene (**7**). The nmr spectrum of the oil was identical with that of authentic pure cyclobutene **7**.

Acknowledgment. We are grateful to the Research Corporation for financial support of this research.