Prominent in the infrared spectrum was the strong N=N stretch typical of diazirines at 1575 cm^{-1}. The ultraviolet spectrum consisted of a shoulder at λ 342 mμ (ϵ 1710) as well as the aromatic ring absorptions at λ_{max} 224 mμ (ϵ_{max} 11,300) and λ_{max} 217 mμ (ϵ_{max} 9710). The proton spectrum showed only the diazirine proton as a singlet at τ 7.87 and the A_2B_2 quartet similar in shape and position to that of *p*-chloronitrobenzene.

The sensitivity on the drop-weight tester was 50% fires at 2 in. (RDX = 10 in.). *Anal.* Calcd for $C_7H_5N_3O_2$: C, 51.50; H, 3.67; N, 25.8. Found: C, 51.26; H, 3.41; N, 25.63.

Reaction of Benzaldehyde *t*-Octylimine and Difluoramine. Preparation of N^1-α-Fluorobenzylidine-N^2-*t*-octylhydrazine. Into a stirred solution of 4.34 g (0.02 mole) of benzaldehyde *t*-octylimine in 25 ml of CCl_4 contained in a 110-ml evacuated U tube was admitted 448 ml (0.02 mole) of HNF_2. The solution was stirred at 0° for 30 min and then allowed to warm to room temperature for an additional 30 min.

The volatile contents were removed by pumping briefly through cold traps at −80, −126, and −196°. The remainder of the CCl_4 solution was shaken briefly with 10 ml of H_2O and the layers were separated. An aliquot of the CCl_4 solution was evaporated to the nonvolatile residue and physical measurements were obtained on the product, identified as N^1-α-fluorobenzylidene-N^2-*t*-octylhydrazine.

The F^{19} spectrum was a sharp singlet at ϕ +85.2. The proton spectrum consisted of the typical *t*-octyl pattern at τ 9.10, 8.83, and 8.55 in the area ratio 9:6:2. The N–H resonance was observed as a broad band centered at τ 4.82. The aromatic protons were split into the typical aromatic 3:2 pattern at τ 3.00 and 2.50.

The approximate boiling point was 100° (1 mm). To the bulk of the CCl_4 solution was added dropwise 3 ml of concentrated HCl. A white solid formed immediately, filtered off, and washed with anhydrous ether. The yield of dried product was 3.55 g, 62% of theory, of N^1-α-fluorobenzylidene-N^2-*t*-octylhydrazinium hydrochloride. The sample sublimed, mp 115° dec. The F^{19} spectrum was a sharp singlet at ϕ +42.0. *Anal.* Calcd for $C_{15}H_{24}N_2ClF$: C, 62.90; H, 8.40; N, 9.78; F, 6.64; Cl, 12.40. Found: C, 62.55; H, 9.00; N, 9.75; F, 6.30; Cl, 11.70.

Reaction of Benzaldehyde *t*-Butylimine and Difluoramine in Acetic Anhydride. Preparation of N-Acetyl-N^1-benzoyl-N-*t*-butylhydrazine. Into a solution of 1.61 g (0.01 mole) of benzaldehyde *t*-butylimine dissolved in 10 ml of acetic anhydride was allowed to expand 300 cc of HNF_2. The reaction was stirred at ambient temperature for 2 hr. The volatile contents were removed under vacuum until a solid residue remained. The residue was washed with 30 ml of cold ether. From the 1.1 g (47% of theory) of white solid residue was obtained 0.8 g of crystalline material, mp 135–137°.

The infrared spectrum was characterized by absorption at 3300 cm^{-1} (amide N–H), at 1675 cm^{-1} (acetyl carbonyl, CH_3CON), and at 1640 cm^{-1} (benzoyl carbonyl, C_6H_5CON.) The infrared evidence points to the formation of N-acetyl-N^1-benzoyl-N-*t*-butylhydrazine rather than the unrearranged acetoxybenzylidene hydrazone because the ester acetoxy group should absorb at a higher wavenumber.

The proton nmr spectrum, run in $CDCl_3$, consisted of a sharp single peak at τ 8.55 due to the methyl group adjacent to the carbonyl and the aromatic 3:2 pattern at τ 2.63 and 2.15. The single amide proton was observed at τ −0.9. *Anal.* Calcd for $C_{13}H_{18}N_2O_2$: C, 66.67; H, 7.69; N, 11.90. Found: C, 66.73; H, 7.90; N, 11.89.

Acknowledgment. This work was carried out under the sponsorship of the U. S. Army Missile Command, Redstone Arsenal, Alabama, under Contract Number DA-01-021 AMC-11536 (Z).

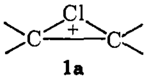
Polar Additions to Olefins. II. The Chlorination of Di-*t*-butylethylene[1]

Robert C. Fahey

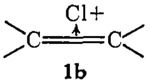
Contribution from the Department of Chemistry, University of California, San Diego, La Jolla, California 92038. *Received May 25, 1966*

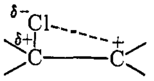
Abstract: The polar chlorination of *cis*-di-*t*-butylethylene in carbon tetrachloride gives *dl*-3,4-dichloro-2,2,5,5-tetramethylhexane (**3**) without concurrent formation of rearranged products. Chlorination of *trans*-di-*t*-butylethylene leads to *meso*-3,4-dichloro-2,2,5,5-tetramethylhexane (**4**) along with the rearranged product (**5b**) resulting from a stereospecific shift of a methyl group. These results show that both dichloride formation and rearrangement occur directly from a bridged chloronium ion. The *trans* stereospecificity of addition (>99.5%) to the *cis*-olefin, which is destabilized relative to the *trans* isomer by 9.3 kcal, indicates that substantial stabilization toward rotational isomerism is present in the intermediate chloronium ion as a result of the chlorine bridging.

The formation of chlorine-bridged cations or chloronium ions (**1**) is a marginal phenomenon as is shown by the nonstereospecific addition of chlorine to arylalkenes[2] as compared with stereospecific *trans* addition to symmetrical dialkyl olefins.[3] The lack of significant rate acceleration by a neighboring chlorine atom in solvolysis reactions[4] has been taken as evidence that the driving force for the formation of chlorine-bridged ions is small. In view of this weak driving force for chlorine bridging, two questions are of interest with respect to the intermediate formed in the chlorination of linear alkenes. First, is the cation a symmetrically bridged chloronium ion (**1**)[5] or does it have an unsymmetrical structure (**2**) of the type considered by de la Mare[6] in which electrostatic interactions between the carbonium carbon and the chlorine atom prevent


1a

or


1b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[1] Supported by National Science Foundation Grants GP-2647 and GP-5852.

[2] R. C. Fahey and C. Schubert, *J. Am. Chem. Soc.*, **87**, 5172 (1965), and references therein.

[3] (a) H. J. Lucas and C. W. Gould, *ibid.*, **63**, 2541 (1941); (b) M. L. Poutsma, *ibid.*, **87**, 2161 (1965); (c) M. L. Poutsma, *ibid.*, **87**, 2172 (1965).

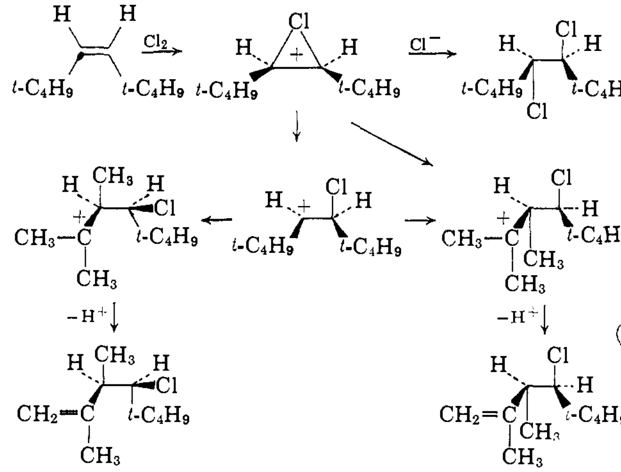
[4] E. Grunwald, *ibid.*, **73**, 5458 (1951); S. Winstein, E. Grunwald, and L. L. Ingraham, *ibid.*, **70**, 821 (1948).

[5] The alternative formulation for the chloronium ion (**1a**) as a π-complex (**1b**) has been proposed by Dewar: M. J. S. Dewar, *Bull. Soc. Chim. France*, **18**, C71 (1951).

[6] P. B. D. de la Mare in "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp 93–95.

rotation about the intervening bond? Second, does structural rearrangement accompanying chlorine addition to *t*-butylethylene[7] occur directly from a bridged ion, or from a classical ion formed concurrent with or from a bridged species?

A study of the stereochemistry of chlorination of *cis*- and *trans*-di-*t*-butylethylene was undertaken in an attempt to answer these questions. Steric repulsion between the *t*-butyl groups destabilizes the *cis* isomer by 9.3 kcal relative to the *trans* form.[8] Such steric repulsion would be retained or increased upon formation of a symmetrically bridged intermediate, but could be relieved by rotation in an open carbonium ion. Thus, if the stabilization from chlorine bridging does not offset the steric strain, isomerization should occur and stereospecific *trans* addition would not be expected. If rearrangement occurs from an open carbonium ion, rearrangement should lead to two isomers corresponding to methyl migration to either side of the carbonium carbon plane. However, if a stable, symmetrically bridged chloronium ion is involved, addition should take place *trans* and rearrangement should yield a single product resulting from methyl migration *trans* to the chlorine bridge.

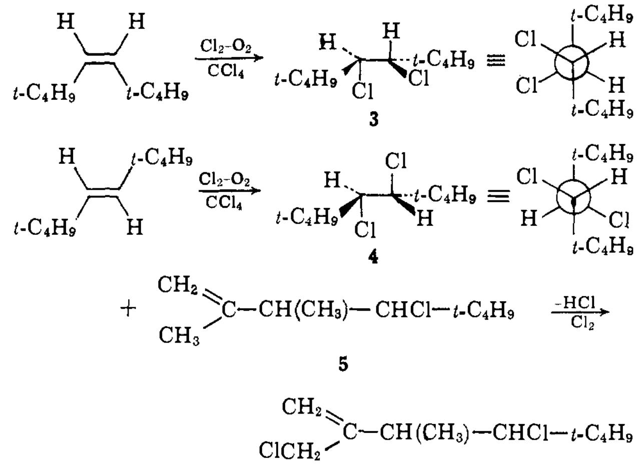


(1)

A previous study of chlorine addition to *trans*-di-*t*-butylethylene in the presence of antimony pentachloride yielded only rearranged dichloride.[9] Considering Poutsma's results with *t*-butylethylene, it was expected that, in the absence of antimony pentachloride, less rearrangement would occur and rearranged chloro olefin, rather than dichloride, would be the product.

Results

Chlorine additions were carried out in carbon tetrachloride under oxygen to inhibit radical reaction. Contrary to expectations, the *cis* olefin yielded a single dichloride (**3**) from direct addition of chlorine without rearrangement. Chlorination of *trans*-di-*t*-butylethylene initially yielded dichloride (**4**) and chloro olefin (**5**), the latter being converted to the dichloro olefin (**6**) in the later stages of the addition when the starting olefin was nearly fully consumed. Pure samples of the products were isolated by preparatory vpc and the structures were assigned on the basis of their elemental analyses and their nmr spectra. The dichlorides **3** and **4** are shown to be *dl*- and *meso*-3,4-dichloro-2,2,5,5-tetramethylhexane, respectively, on the basis of the magnitude of their vicinal H–H coupling constants.



3

4

CH_2=C(CH_3)–CH(CH_3)–CHCl–*t*-C_4H_9

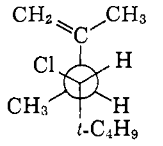
5

CH_2=C(CH_2Cl)–CH(CH_3)–CHCl–*t*-C_4H_9

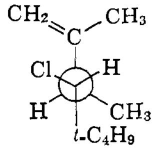
6

The *t*-butyl groups must assume a nearly *trans* relationship, and the vicinal H–H coupling in **4** should be larger than that in **3** on the basis of the known variation of vicinal coupling constants with H–C–C–H dihedral angle.[10] Of course, this coupling is not observed in the main proton lines, since the two protons are equivalent, but is observed as a doublet splitting in the ^{13}C–H satellite lines. The observed values are 0.8 and 5.2 cps for **3** and **4**, respectively.

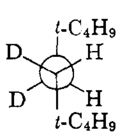
The configuration of **5** and **6** may also be inferred from the observed vicinal coupling constants, although the argument is somewhat more tenuous since both isomers of these materials were not obtained. For 4-chloro-2,3,5,5-tetramethylhex-1-ene (**5**) the possible structures are **5a** and **5b**. The expected H–H vicinal coupling constants for these compounds may be estimated from the values found for **3**, **4**, and *dl*-2,2,5,5-tetramethylhexane-3,4-d_2 (**7**). Vicinal coupling constants are affected by the dihedral angle and by the electronegativity of substituents on the carbon atom.[10] Thus, the observed coupling for **7**, 4.2 cps,[11] is considerably larger than for **3**. The main decrease in the coupling constants for **3** and **4** is undoubtedly due to the electronegativity effect of the chlorine atoms. The chloro, methyl, and isopropenyl substituents should exert nearly the same effect in **5a** and **5b** as the two chlorines in **3** and **4**, so that, with respect to electronegativity effects, **5a** and **5b** should exhibit the same couplings as **3** and **4**, respectively. In **7**, the H–C–C–H angle must be locked near 60°, whereas in **3** and **5a** some angular deviation from 60 toward 90° is possible and may contribute to a decrease in the coupling. While such angular deviation might be somewhat different in **5a** than in **3**, a substantial change in the



5a



5b



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[7] M. L. Poutsma, *J. Am. Chem. Soc.*, **87**, 4285 (1965).

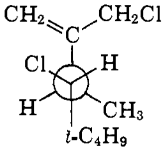
[8] R. B. Turner, D. E. Nettleton, and M. Pevelman, *ibid.*, **80**, 1430 (1958).

[9] W. H. Puterbaugh and M. S. Newman, *ibid.*, **81**, 1611 (1959).

[10] A. A. Bothner-By, in "Advances in Magnetic Resonance," Vol. 1, J. S. Waugh, Ed., Academic Press, Inc., New York, N. Y., 1965, p 201.

[11] R. C. Fahey and G. C. Graham, unpublished results.

coupling is not expected. The H-C-C-H angle in **4** must be 180°, while in **5b** this angle could deviate owing to the different steric requirements of the groups present, and a smaller H-C-C-H coupling would be expected. The observed coupling for **5**, 3.6 cps, is thus consistent with structure **5b** and larger than that expected for **5a**. Since no expected mechanism would lead stereospecifically to compound **5a**, assignment of the product as **5b** is also consistent with the finding of only a single isomer of the rearranged product. The secondary product, 4-chloro-2-chloromethyl-3,5,5-trimethylhex-1-ene (**6**), with an observed vicinal coupling of 3.7 cps, is, by an analogous argument, assigned structure **6a**.

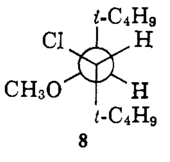


6a

In experiments with purified olefin ($\geqslant$99.5% purity), it was shown that dichloride formation is stereospecific and *trans* with less than 0.5% of isomeric dichloride being formed. Moreover, addition to the *cis*-olefin gives less than 0.5% of rearranged product. The primary product composition in the chlorination of the *trans*-di-*t*-butylethylene is 54% **4** and 46% **5b** and remains constant from 20 to 80% reaction, after which formation of compound **6a** is observed.

From competition experiments with starting olefin ratios of *cis*/*trans* = 1.3 and 8.8, it was shown that the relative rate ratio, k_{trans}/k_{cis}, has the value 2.7.

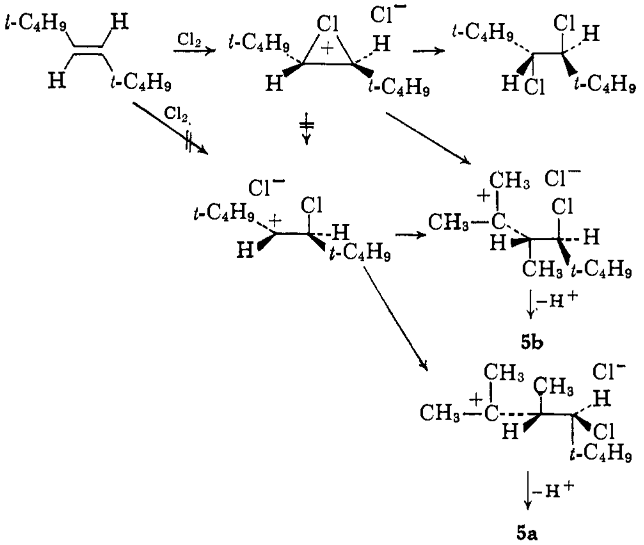
One chlorination experiment with *cis*-di-*t*-butylethylene was carried out in methanol. From nmr and vpc analyses of the product mixture, it was estimated that **3** and **8** are formed in equal amounts, the configuration of **8** being assigned on the basis of the observed vicinal H-H coupling constant (1.3 cps). Rearranged material constituted $\leqslant$ 1% of the total product.



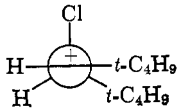
8

Discussion

The stereospecificity of addition and of rearrangement in the chlorination of *trans*-di-*t*-butylethylene strongly implies that a bridged intermediate is the immediate precursor of both the dichloride and the rearranged carbonium ion, and that little or none of the open ion, which would not be expected to undergo stereospecific rearrangement, is formed. The effect of alkyl substitution on the rate of olefin chlorination indicates that at the transition state positive charge is present at both olefinic carbon atoms,[7] as expected if **1** is the initially formed intermediate. The slower rate of chlorination of *cis*-di-*t*-butylethylene than of the *trans* isomer is consistent with the formation of a transition state leading to a bridged intermediate, since the bridged ion should show increased steric interaction between the *t*-butyl groups over that obtaining in the ground state.



The *trans* stereospecificity of the addition to the *cis*-olefin provides a striking demonstration of the isomerizational stability of the intermediate ion. Even in the more polar solvent, methanol, where the intermediate ion should have a greater opportunity to isomerize, stereospecific *trans* addition is obtained. This result allows a semiquantitative lower limit to be placed on the stability derived from bridging in the intermediate ion. Consider the limiting case of an open ion in which no interaction takes place between the chlorine and the neighboring carbonium carbon (**9**) and the case of the symmetrical chloronium ion (**10**). The energy of the chlorine interaction with the carbonium carbon must offset the steric repulsion of the *t*-butyl groups or free rotation will occur. In **10** the steric repulsion must be greater than the 9.3 kcal present in the starting olefin. In **9** it is probably about the same as in the *cis*-olefin, since, although the groups are no longer completely eclipsed, one carbon is now sp^3 rather than sp^2 hybridized and the corresponding decrease from 120 to 109° in the bond angle brings the *t*-butyl groups closer together. Thus, a rough lower limit of 9 kcal can be placed on the rotational stabilization derived from chlorine bridging. This is quite consistent with the symmetrically bridged formulation of the intermediate (**1**). It does not rule out an unsymmetrical ion (**2**), but does place a definite requirement on the energy of the interaction symbolized by the dashed line.



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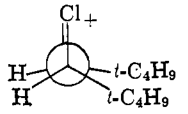

10

Experimental Section

Materials. *cis*-Di-*t*-butylethylene was prepared according to the procedure described by Hennion and Banigan[12] and was converted to *trans*-di-*t*-butylethylene by irradiation for 2 hr under a General Electric sun lamp in the presence of a trace of iodine. Preparatory vpc purification (20 ft × $^3/_8$ in. 30% SE-52 on a Chromosorb P column at 140° and 150 cc/min helium flow) of the crude olefins gave materials of 99.5% purity (by vpc analysis). Carbon tetrachloride and methanol were B. and A. Reagent Grade.

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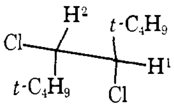
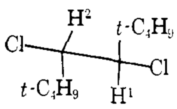
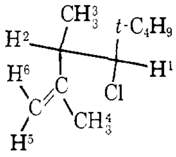
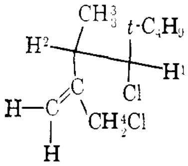
[12] G. F. Hennion and T. F. Banigan, *J. Am. Chem. Soc.*, **68**, 1202 (1946).

Chlorine gas was obtained from the Matheson Company and passed through a sulfuric acid trap prior to use.

***dl*-3,4-Dichloro-2,2,5,5-tetramethylhexane (3).** A 1:1 mixture of chlorine and oxygen was passed into a solution of 0.8 g of *cis*-di-*t*-butylethylene in carbon tetrachloride with stirring at 0° over a period of 6 min, after which nmr and vpc analyses indicated that all of the olefin had reacted. Evaporation of the solvent left 1.3 g of white solid which was purified by preparatory vpc (4 ft × 3/8 in. 30% polypropylene glycol on Chromosorb P at 160°; helium flow, 150 cc/min; retention time, 21–29 min). The purified product, mp 53–54°, was used to obtain the nmr data reported in Table I.

Table I. Nmr Data[a]

Compound	τ	Multiplicity	Rel. area
 **3**	6.06	singlet	1
	8.92		9
	^{13}C–H satellite[b]	$J_{^{13}C-H} = 143$	
		$J_{H^1H^2} = 0.8$	
 **4**	5.96	singlet	1
	8.83	singlet	9
	^{13}C–H satellite[c]	$J_{^{13}C-H} = 150$	
		$J_{H^1H^2} = 5.2$	
 **5b**	5.2–5.4	multiplet (H^5, H^6)[d]	2
	6.32	doublet (H^1), $J = 3.6$	1
	7.16	quartet of doublets (H^2), $J = 7.0, 3.6$	1
	8.18	doublet of doublets (H^4), $J = 0.7, 1.4$[d]	3 3
	8.80	doublet (H^3), $J = 7.0$	3
	8.94	singlet (t-C_4H_9)	9
 **6a**	4.73	narrow multiplet (H^5, H^6)	2
	5.85	(H^4)	2
	6.28	doublet (H^1,H^2), $J = 3.7$	1
	7.00	quartet of doublets (H^2), $J = 7.0, 3.7$	3
	8.70	doublet (H^3), $J = 7.0$	3
	8.93	singlet (t-C_4H_9)	9

[a] Spectra were measured on 15% solutions in carbon tetrachloride using a Varian HR-60 spectrometer and were calibrated by the sideband technique. Values of τ are accurate to ±0.02 and coupling constants, J (cps), to ±0.1. [b] Measured on a saturated solution in carbon tetrachloride. [c] Measured on a 35% solution in carbon tetrachloride. [d] In spin decoupling experiments, saturation of the resonance at τ 5.2–5.4 caused the τ 8.18 multiplet to collapse to a singlet. When the τ 8.18 resonance was saturated, the multiplet at τ 5.2–5.4 collapsed to an AB pattern (τ_A 5.20, τ_B 5.92, J_{AB} = 2.2).

Chlorination of *trans*-Di-*t*-butylethylene. A solution of 0.6 g of *trans*-olefin in carbon tetrachloride was stirred in the dark at 0° and a 1:1 mixture of chlorine and oxygen passed into the solution. After 15 min vpc analysis showed that little starting olefin remained and three major products had formed. The crude reaction mixture was purified by vpc (3 ft × 3/8 in. 30% polypropylene glycol on Chromosorb P at 90–150°; helium flow 150 cc/min) and the three major components were collected. 4-Chloro-2,3,5,5-tetramethyl-1-hexene (**5b**) had a retention time of 42–46 min.

Anal. Calcd for $C_{10}H_{19}Cl$: C, 68.75; H, 10.96; Cl, 20.29. Found: C, 68.39; H, 10.67; Cl, 19.81.

meso-3,4-Dichloro-2,2,5,5-tetramethylhexane (**4**) had a retention time of 56–62 min.

Anal. Calcd for $C_{10}H_{20}Cl_2$: C, 56.88; H, 9.55; Cl, 32.73. Found: C, 57.14; H, 9.42; Cl, 32.58.

4-Chloro-2-chloromethyl-3,5,5-trimethylhex-1-ene (**6a**) had a retention time of 78–85 min.

Anal. Calcd for $C_{10}H_{18}Cl_2$: C, 57.42; H, 8.67; Cl, 33.90. Found: C, 57.28; H, 8.47; Cl, 33.39.

All three purified compounds are liquids. Their nmr spectra are given in Table I.

Chlorination of *cis*-Di-*t*-butylethylene in Methanol. A 1:1 mixture of chlorine and oxygen was passed through a solution of 0.35 g of *cis*-olefin in 5 ml of methanol at 0° for 10 min. The reaction mixture was worked up in water with two pentane extractions. The combined pentane layers were dried over anhydrous potassium carbonate and the pentane was evaporated leaving 0.4 g of crude product. This material was analyzed by vpc and by nmr, showing that about 20% of unreacted olefin remained. In addition to peaks for olefin, dichloride **3**, and a trace of methanol, the nmr spectrum (20% v/v in carbon tetrachloride) showed peaks at τ 6.32, d (doublet), J = 1.3 cps, A (area) = 1; τ 6.54, s (singlet), A = 3; τ 6.99, d, J = 1.3 cps, A = 1; τ 8.96, s, A = 9; τ 9.05, s, A = 9.

If this material is compound **8**, then, from the relative line intensities, it is estimated that **3** and **8** are formed in approximately equal amounts. The two compounds were only marginally separable on a variety of vpc columns so that a pure sample of **8** could not be isolated. No prominent peaks were observed on vpc at retention times between that of the olefin and that of the dichloride, allowing an estimate that ≤1% of rearranged chloroolefin was formed.

Quantitative Chlorinations. In a typical run, 0.1 g of olefin in 10 ml of carbon tetrachloride was placed in a reaction flask immersed in an ice bath and fitted with magnetic stirrer, thermometer, drying tube, and gas inlet stopcock. Light was excluded, the solution stirred, and a mixture of chlorine (flow *ca.* 0.5 cc/min) and dry air (100 cc/min) passed over the solution. Samples were withdrawn at intervals and analyzed directly by vpc. With *cis*-olefin the only major product peak was that for dichloride **3**, but four minor peaks comprising 0.2, 0.8, 0.1, and 0.1% of the total product were detected after 90% conversion. The product compositions observed on addition to the *trans* isomer are given in Table II. The vpc analyses showed no interconversion of olefins under the reaction conditions.

Table II. Chlorination Products of *trans*-Di-*t*-butylethylene

	Product composition				
Time,[a] min	% **3**	% **4**	% **5b**	% **6a**	% other products
12	. . .	60 ± 5	40 ± 5	. . .	. . .
20	. . .	56 ± 2	44 ± 2	. . .	. . .
30	. . .	54	46	. . .	. . .
40	. . .	56	44	. . .	. . .
50	<1	54	46	<1	<1
60	<1	54	46	<0.5	<1
68	<1	53	47	<0.5	<1
80	<1	53	47	<0.5	<1
95	<0.5	53	47	<0.5	<0.5
110	<0.5	54	45	0.6	<0.5
130	<0.5	54	36	8	2
150	<0.3	56	0	37	7[b]

[a] From start of chlorine–air flow over reaction. [b] Four components: two at shorter retention time than **6a**, 1.4 and 2.4%; two at longer retention time than **6a**, 1.0 and 2.4%.

Relative rates were measured on olefin mixtures; with a *cis*/*trans* starting olefin ratio of 1.30, k_{trans}/k_{cis} = 2.7 ± 0.1 based on seven determinations between 10 and 95% reaction of *trans*-olefin. For an initial *cis*/*trans* ratio of 8.8, five determinations between 10 and 85% conversion of *trans*-olefin yielded k_{trans}/k_{cis} = 2.7 ± 0.2.

Vpc Procedure. An Aerograph Model 202 chromatograph with thermal conductivity detectors was used for all analytical measurements. For the quantitative studies, a 10 ft × 1/8 in. 3% polypropylene glycol on Chromosorb G column was employed with a 30 cc/min helium flow. In a typical analysis, the temperature was programmed from 50 to 150° at 2.5° per min. Retention times (min) were: *trans*-di-*t*-butylethylene, 3.5; *cis*-di-*t*-butylethylene, 6.5; **5b**, 19.5; **4**, 28; **3**, 31; **6a**, 37. Peak areas were measured with a disk integrator attached to the recorder, and the correspondence between peak area ratios and mole ratios was established with known mixtures.

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