of the phenyl group it is not possible to comment on the chemical shifts found for this system other than to note that H_B absorbs at nearly the same field as the corresponding proton in the monoalkyl systems.

The shielding trend exhibited by the methine proton at C-9 is interesting, but puzzling. On the basis of the anisotropic shielding effect of the aryl rings one might expect this proton to be increasingly deshielded as its e' population increases; the observed tendency, however, is in the opposite direction. Furthermore, the e' populations of the 9-isopropyl and 9-*t*-butyl derivatives appear to be very similar but their H_M shieldings are not. Similar trends are found for the C-9 proton in the corresponding 9-alkylthioxanthene (Me, δ 3.97; Et, δ 3.81; *i*-Pr, δ 3.50; *t*-Bu, δ 3.79)[33] and 9-alkylacridine series,[34] as well as for the C-7 proton in the corresponding series of 1-*t*-butyl-7-alkyl-1,3,5-cycloheptatrienes (δ 3.26, 3.06, 2.82, and 3.23).[35] It seems reasonable to suggest that the effect is principally due to the alkyl groups.

(33) A. L. Ternay, Jr., and S. Evans, *Chem. Commun.*, 407 (1970).
(34) G. A. Taylor and S. A. Procter, *ibid.*, 1379 (1969).

Conclusions

These results, taken together, provide conclusive evidence that the alkyl groups in 9-ethyl- and 9-*t*-butyl-9,10-dihydroanthracene preferentially, if not exclusively, exist in the pseudoaxial orientation, contrary to the earlier claims of Nicholls and Szwarc[19] and Carruthers and Hall,[18] respectively. The same situation holds for the 9-isopropyl derivative while the 9-methyl and 9-phenyl substituted systems appear to exist as equilibrium mixtures of the two conformers but with predominantly pseudoaxial 9 substituents. Clearly, analogies between the chemical-shift differences in chair and boat forms of the six-membered ring are unwarranted especially if one contains unsaturated centers.

Also, these results support the proposed mechanism for the observed stereospecific *trans* reduction of 9,10-dialkylanthracenes, an essential feature of which was the concept that ethyl and larger groups would preferentially assume the pseudoaxial orientation.[22c]

(35) C. Cupas, personal communication.

Free-Radical Chlorination of Methyl Cyclohexanecarboxylates. I. Stereochemistry of the Chlorination Step

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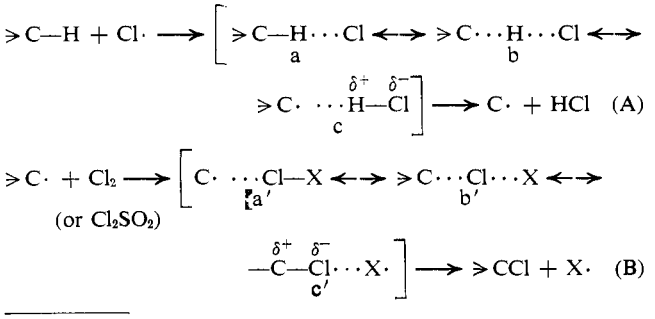
Abstract: The free-radical chlorination of methyl cyclohexanecarboxylate and its 4-methyl and 4-*t*-butyl derivatives by sulfuryl chloride shows a preference for *trans* attack at positions remote from the ester group. Even for the *trans*-4-*t*-butyl deriative, 3-chloro prefers to enter *trans* to the ester in spite of this position being *cis* to *t*-butyl as well as axial. It is proposed that this preferred *trans* orientation in the chlorination step results from polar interactions between the ester dipoles and the incipient dipole generated at the forming carbon chlorine bond in the transition state.

The investigations reported in this and the following paper were designed to add to knowledge of the two steps involved in free-radical chlorination. While a great deal of data is available,[2] while there is some considerable agreement that transition states for both reactions are reactant-like (a and a′), while electrical effects from contributions of c have been proposed to explain orienting effects of chlorination away from electronegative substituents,[3-6] the relative importance of steric factors in the two steps has not been clearly established.



A notable preference for *trans* or "anti" products (hereafter denoted "*trans* effect") has been observed in chlorinations of cyclic or acyclic systems suitable for observation of this phenomenon.[5c,d,7] This "*trans* effect" has alternately been explained either by steric interaction between the electronegative substituent and

(1) From the Ph.D. Dissertation of Charles D. Beard, University of Pennsylvania, 1968, and the M.S. thesis of Kenichi Akune, University of Pennsylvania, 1965.
(2) For reviews see (a) J. M. Tedder, *Quart. Rev. Chem. Soc.*, **14**, 336 (1960); (b) C. Walling, "Free Radicals in Solution," John Wiley & Sons, New York, N. Y., 1957, p 356 ff; (c) H. Singh and J. M. Tedder, *J. Chem. Soc., B*, 612 (1966); (d) J. Rouschand and A. Bruylants, *Bull. Soc. Chim. Belg.*, **76**, 50 (1967).
(3) C. C. Price and H. Morita, *J. Chem. Soc.*, **75** 3686 (1953).
(4) F. R. Mayo and C. Walling, *Chem. Rev.*, **46**, 191 (1950).
(5) (a) G. A. Russell, *J. Amer. Chem. Soc.*, **80**, 4997 (1958); (b) *Tetrahedron*, **8**, 101 (1960); (c) G. A. Russell and A. Ito, *J. Amer. Chem. Soc.*, **85**, 2983 (1963); (d) G. A. Russell and A. Ito, *ibid.*, **85**, 2988 (1963).
(6) E. M. Hodnett and P. S. Junega, *J. Org. Chem.*, **33**, 1233 (1968).
(7) (a) P. S. Fredericks and J. M. Tedder, *J. Chem. Soc.*, 3521 (1961); (b) W. A. Nevill, D. S. Frank, and R. D. Trepka, *J. Org. Chem.*, **27**, 422 (1962); (c) N. Colebourne and E. S. Stern, *J. Chem. Soc.*, 3599 (1965).

the incoming halogenating agent[7] or by electrostatic repulsions between substituent and the chlorinating species in the transition state,[5c,d] both of which favor maintenance of the maximum separation between electronegative species. The purpose of this paper is to report the results of a study of the chlorination of methyl cyclohexanecarboxylate and its 4-methyl and 4-*t*-butyl homologs, designed to provide further information on the origin of this "*trans* effect" in step B, *i.e.*, whether due to polar or steric perturbations or both. A second paper deals with the stereochemistry of hydrogen abstraction in step A.[8]

The six-membered ring is particularly suitable since its chemistry and conformation have been extensively studied and spectral data for this ring are somewhat easier to interpret than either larger or smaller ring systems.[9] Sulfuryl chloride was the chlorinating reagent of choice primarily for ease of operation. Although in some comparable studies, sulfuryl chloride has shown the same trends as photochlorination,[5d] very few comparisons are available for halides and esters.[2a,c] Accordingly, methyl *n*-pentanoate (II) and methyl *n*-hexanoate (III) were chlorinated with sulfuryl chloride and the results are summarized in Table I. The relative reactivities are adequately explained by assuming a deactivating polar effect, the magnitude of which decreases smoothly down the carbon chain, and the normal primary–secondary rate differences.

Table I. Chlorination of II and III[a-c]

	CH_3—	—CH_2—	—CH_2—	—CH_2—	—$COOCH_3$
	15.5	46.9	29.6	3.8	4.2
	0.35	1.58	1	0.13	0.14
CH_3—	—CH_2—	—CH_2—	—CH_2—	—CH_2—	—$COOCH_3$
10.7	33.8	30.8	21.6	3.2	2.1
0.33	1.46	1.41	1	0.15	0.10

[a] Results are expressed as per cent chlorination and as relative selectivities, defined as the ratios corrected to a per hydrogen basis with position 3 as standard. [b] Glpc retention times increased smoothly with increasing distance between chlorine and carbomethoxyl on a DEGS column. [c] Sulfuryl chloride in CCl_4 at 80° using dibenzoyl peroxide as initiator.

A similar direct comparison of our results with sulfuryl chloride (Figure 1) and those of Little with free-radical chlorination[10] indicates that these two chlorinating agents give very similar results also in the cyclohexane system.

Reference samples of methyl 1-chloro- (IV),[1] *cis*-2-chloro- (VI),[11] *trans*-2-chloro- (V),[11] *trans*-3-chloro- (VII),[12] and *trans*-4-chlorocyclohexanecarboxylate (IX)[12] were synthesized by the reported methods. The as yet unreported chloromethyl cyclohexanecarboxylate was prepared from cyclohexanecarbonyl chloride, paraformaldehyde and zinc chloride *via* the general method

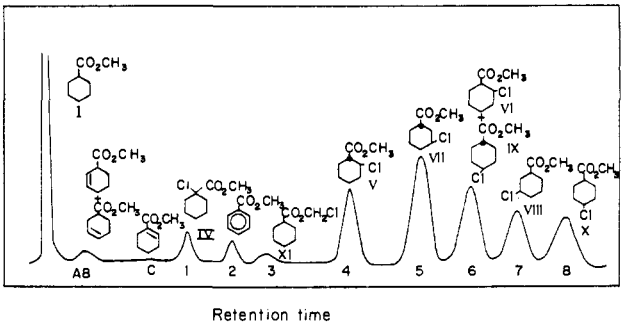


Figure 1. Glpc fractionation of chlorination products of methyl cyclohexanecarboxylate.

of Ulich and Adams.[13] Several attempted syntheses of methyl *cis*-3-chloro- (VIII) and *cis*-4-chlorocyclohexanecarboxylate (X) were unsuccessful and ultimately samples were collected by glpc from a large-scale chlorination and compared with the authentic compounds.[10c]

VI and IX had identical retention times on any of our columns, and thus glpc peak 6 (Figure 1) was collected and analyzed by nmr.[10] The ratio of the downfield hydrogens (>C*H*Cl) easily yielded the absolute concentrations of VI and IX. The early peaks (A–C) had retention times corresponding to methyl 2-, 3-, and 1-cyclohexenecarboxylates, respectively, and were probably the result of dehydrochlorination in the injection port of the gas chromatograph. Peak 2 was methyl benzoate sometimes present as a trace impurity in I. Samples of I purified by glpc failed to show this peak after chlorination but gave the same product distribution for the other compounds.

The nmr parameters and conformational equilibria for these chloro isomers have been thoroughly treated by Little, *et al.*[10] Our values for the important nmr parameters are summarized in Table II, together with

Table II. Nmr Chemical Shifts[a]

Compd[d]	δ($COOCH_3$), cps (ppm)	δ(>C*H*Cl), cps (ppm)	δ(*t*-butyl), cps (ppm)
I	214 (3.567)		
IV	224 (3.733)		
V	220 (3.667)	243 (4.050)	
VI	220 (3.667)	283 (4.717)	
VII	218 (3.633)	267 (4.450)	
VIII	217 (3.617)	229 (3.817)	
IX	218 (3.633)	234 (3.900)	
X	218 (3.633)	255 (4.250)	
XI		340 (5.667)[b]	
XII	215 (3.583)		51 (0.850)
XIII	220 (3.667)	240 (4.000)	53 (0.883)
XIV	217 (3.617)	275 (4.583)	58 (0.967)
XV	220 (3.667)	288 (4.800)	53 (0.883)
XVI	218 (3.633)	226 (3.767)	63 (1.050)
XVII	216 (3.600)	201 (3.350)[b]	56 (0.933)[c]
XVIII	217 (3.617)		50 (0.830)
XIX	220 (3.670)	203 (3.380)[b]	55 (0.920)[c]
XX	221 (3.680)	287 (4.791)	53 (0.891)
XXI	216 (3.600)		
XXII	220 (3.667)	241 (4.017)	
XXIII	219 (3.650)	283 (4.717)	
XXIV	217 (3.617)	257 (4.283)	
XXV	217 (3.617)	207 (3.450)	
XXVI	216 (3.600)	201 (3.350)[b]	

[a] Carbon tetrachloride as solvent with tetramethylsilane as internal standard at 60 MHz. [b] Equals two hydrogens. [c] Equals six hydrogens. [d] See Figures 1, 2, 3, and 4 for structures.

(8) C. C. Price and C. D. Beard, *J. Amer. Chem. Soc.*, **92**, 5921 (1970).

(9) (a) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, New York, N. Y., 1965, Chapter 2; (b) M. Hanack, "Conformation Theory," Academic Press, New York, N. Y., 1965, p 87.

(10) (a) J. C. Little, A. Sexton, Y. C. Tong, and T. E. Zurawic, *J. Amer. Chem. Soc.*, **91**, 7098 (1969); and (b) J. C. Little, Y. Tong, and J. P. Heeschen, *ibid.*, **91**, 7090 (1969); (c) we are indebted to Dr. Little for informing us of his results prior to publication and for supplying authentic samples of VI, VII, VIII, and X.

(11) W. R. Vaughn, R. L. Craven, R. L. Little, Jr., and A. C. Schoenthaler, *J. Amer. Chem. Soc.*, 77, 1594 (1955).

(12) D. S. Noyce and H. I. Weingarten, *ibid.*, **79**, 3093 (1957).

(13) L. H. Ulich and R. Adams, *ibid.*, **43**, 660 (1921).

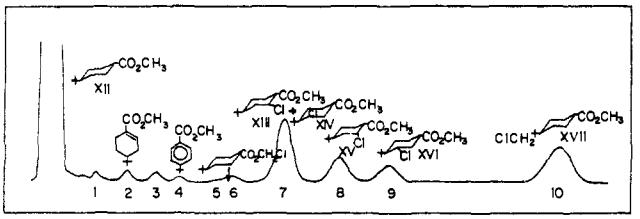


Figure 2. Glpc fractionation of chlorination products of methyl *trans*-4-*t*-butylcyclohexanecarboxylate.

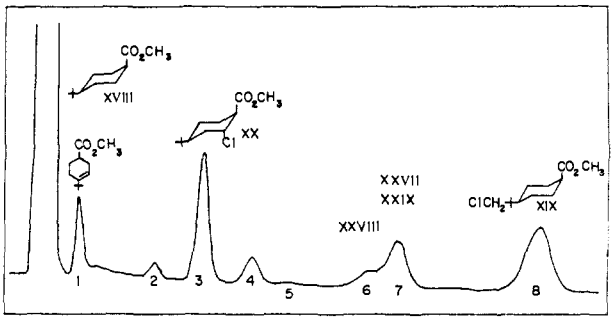


Figure 3. Glpc fractionation of chlorination products of methyl *cis*-4-*t*-butylcyclohexanecarboxylate.

the new compounds we have prepared. Little[10] has suggested that the chemical shifts of the hydrogen geminal to chlorine and the carbomethoxyl singlet constitute a reliable analytical method for further studies in analogous compounds.[10] This indeed conforms to our experience with the 4-methyl and 4-*t*-butyl homologs.

In addition to this nmr method of identification and analysis, the relative retention times on a DEGS column are indicative of configuration and position of substitution. The retention times for the acyclic chloro esters increase smoothly with increasing distance between substituents. Inspection of Figure 1 shows that while each *trans* isomer is eluted before its epimeric *cis* isomer, again retention times increase regularly with increasing separation of the substituents.

Since it was our desire to create a situation in which an electrically neutral group with large steric requirements directly opposed a much smaller polar group, methyl *trans*-4-*t*-butylcyclohexanecarboxylate (**XII**) was prepared and chlorinated. The various isomers (Figure 2) were isolated by glpc, and assigned structures in analogy to the chlorinated derivatives of I. Peaks 1–6 (Figure 2) were present in only trace quantities and their tentative identification is based on indirect evidence as follows. Peak 6 was absent in preliminary experiments involving chlorinations of *trans*-4-*t*-butylcyclohexanecarboxyl chloride followed by methanolysis before fractionation and it has a retention time expected for chloromethyl *trans*-4-*t*-butylcyclohexanecarboxylate. Peak 4 had ir and nmr spectra identical with authentic methyl 4-*t*-butylbenzoate. Peak 2 was assigned the structure of a dehydrochlorination product on the basis of enlargement of this peak following basic dehydrochlorination of the chlorination mixture. Peaks 1 and 3 are probably α-chlorination products based on strong ir bands at 1741 (C=O) and 1211 cm^{-1} (OCH_3) in 1, and 1741 (C=O), 1258 (OCH_3), and 1235 cm^{-1} (OCH_3) in 3.

Scrutiny of the data in Table II reveals that the chemical shift of *t*-butyl behaves similarly to $COOCH_3$, being deshielded by 3–5 cps when the ring is substituted with chlorine at position 3 as opposed to 2. Unfortunately **XIII** and **XIV** were not resolved on our columns, necessitating nmr analysis of glpc peak 7 as before. In general, decomposition on the gas chromatography column was not serious, but in this case occurred to the extent of 3–5%, as estimated from the amount of unsaturated ester peak. Of course, the dehydrochlorination is not random, but occurs primarily, if not exclusively, with compounds bearing an axial chlorine (**XIV**). Attempts to correct for this decomposition were of limited success due to irreproducibility and a possible error of 3% must be assumed for **XIV** and **XIII**.

Chemical proof, in addition to the spectral data, is furnished by treatment of the chlorination mixture with alcoholic potassium hydroxide at 80° *via* the method of of McGovern and Beroza.[14] Under these conditions, compounds with axial chlorine undergo dehydrochlorination whereas their equatorial counterparts are stable to the reaction conditions. Esterification with diazomethane followed by glpc analysis showed the essential absence of peak 8 and a proportionate decrease in peak 7 (axial chlorine). Peaks 9 and 10 remained intact as expected. These data strongly support the structure assignments.

If **XII** is a system in which the directive effects oppose each other, then methyl *cis*-4-*t*-butylcyclohexanecarboxylate (**XVIII**) should present the opposite situation, *i.e.*, the steric and polar effects should be additive. Unfortunately, chlorination of **XVIII** yielded products extremely difficult to separate and identify (Figure 3). The validity of the nmr method of identification is questionable when $COOCH_3$ is axial, since both downfield hydrogens and methyl ester chemical shifts may not follow the same shielding rules. In spite of these difficulties, several generalizations are clear. Peaks 2 and 4 (Figure 3) are identical in retention time and ir spectra with peaks 1 and 3 (Figure 2) and are probably α-chlorination products. Peak 8 (Figure 3) was readily identified as methyl *cis*-4-(chloro-*t*-butyl)cyclohexanecarboxylate (**XIX**) on the basis of the nmr spectrum. Peak 3 is tentatively designated methyl *trans*-2-chloro-*cis*-4-*t*-butylcyclohexanecarboxylate (**XX**) in analogy to VI and **XV** which have similar nmr spectra. We were unable either to separate or collect peaks 6 and 7 together without serious decomposition on the column. The nmr of the mixture did imply that three isomers were present probably the *trans*-3-chloro (**XXVII**), *cis*-2-chloro (**XXIX**), and *cis*-3-chloro (**XXVIII**) isomers. Presumably 1,3 interactions in **XXVIII** caused the downfield hydrogen chemical shifts in **XXVIII** and **XXIX** to be very similar.

It was also of interest to consider a system in which the polar and nonpolar groups were of similar steric "size," yet were effectively anchored in the desired diequatorial conformation. Methyl *trans*-4-methylcyclohexanecarboxylate (**XXI**) fulfilled these requirements and was chlorinated as before (Figure 4). Mass spectroscopy confirmed the monochloro formulation for

(14) T. P. McGovern and M. Beroza, *J. Org. Chem.*, 31, 1476 (1966).

peaks 7, 8, 9, and 10 (Figure 4) by showing molecular ion peaks at *m/e* 192, 190 in the approximate ratio of 1:3 paralleling the natural abundance of ^{35}Cl and ^{37}Cl.[15] Again nmr chemical shifts were as expected and allowed assignment of structure (Table II). Incomplete resolution of peaks 8 and 9 (Figure 4) required nmr analysis, again with considerable error due to decomposition on the column (3%). By careful glpc fractionation, peak 9 was isolated in pure form and identified as methyl *cis*-3-chloro-*trans*-4-methylcyclohexanecarboxylate (**XXV**). Peak 8 contained the *cis*-2-chloro (**XXIII**) and *trans*-3-chloro (**XXIV**) isomers. Peak 10 was methyl *trans*-4-chloromethylcyclohexanecarboxylate (**XXVI**).

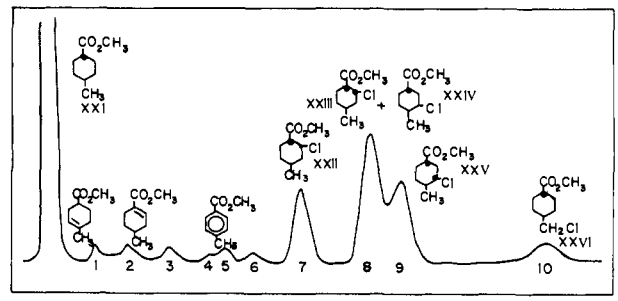


Figure 4. Glpc fractionation of chlorination products of methyl *trans*-4-methylcyclohexanecarboxylate.

Discussion

The distribution of chlorination products for I (Table III) is essentially in accord with predictions based on observations in related systems. A predominance of *trans* isomers is noted at positions 2 and 3, while position 4 shows no marked stereoselectivity, in agreement with similar observations at position 4 for chlorocyclohexane. Position 2 is much less reactive than 3 which in turn is less reactive than 4 as expected for a deactivating inductive effect which decreases with distance from $COOCH_3$. Of course these data give no clue as to the origin of the "*trans* effect."

Table III. Chlorination of I, XII, and XXI

Substance chlorinated	—Chlorination, %— Position 2	Position 3	—*trans*–*cis* ratio— Position 2	Position 3	Ratio of positions 3:2
I[a]	24.3	45.4	2.71	2.16	1.87
XXI[b,c]	33.6	53.5	1.30	2.13	1.69
XII[d]	32.9	27.1	1.30	1.35	0.82

[a] Position 4 showed 26% total chlorination, a *trans*/*cis* ratio of 1.04, and relative reactivity toward positions 2 and 3 of 2.15 and 1.15, respectively (per hydrogen basis). The results are only approximately the same as those reported for reaction of cyclohexanecarboxylic acid with chlorine.[10] [b] Corrected for decomposition on the glpc column. [c] 7.8% chlorination in the 4-methyl group (XXVI); reactivities relative to positions 2 and 3 of 0.31 and 0.19, respectively. [d] 32.4% chlorination in the 4-*t*-butyl group (XVII); reactivities relative to positions 2 and 3 of 0.44 and 0.53, respectively.

Hopefully, **XII** represents a system in which the electrically neutral *t*-butyl group possessing large steric requirements directly opposes the polar carbomethoxyl group of smaller steric "size." The observed *trans*/*cis* ratios are then an effective measure of the steric perturbations arising from *t*-butyl and the sum of steric and polar effects due to $COOCH_3$. The ratios of 1.30 and 1.35 indeed offer convincing evidence for significant polar interactions in the transition state since the chlorine prefers to enter *trans* to carbomethoxyl and *cis* to *t*-butyl. The preference for *trans* chlorination at both positions 2 and 3 argues against a contribution from product stability, since the *cis*-3-chlorine would be in the more stable equatorial position. It thus appears that the dominant factor directing chlorine to the *trans* orientation is preferred attack on the trigonal radical from the direction away from the polar ester group.

The opposed steric effects in **XII** should instead be additive in **XVIII**. The experimental difficulties have been pointed out, and tentative chlorination data (%) are as follows for the compounds given: **XX**, 31.0; **XXVII**, **XXVIII**, **XXIX**, 24.0; **XIX**, 34.3. Although a reasonable estimate of the concentration of **XXIX** is not available, undoubtedly it is small. Even if the larger glpc peak (7) were **XXIX**, which is probably not the case, the *trans*/*cis* ratio would still be >2, confirming the augmentation of steric effects as expected.

When the two groups more nearly approximate each other in steric "size," *e.g.*, methyl and $COOCH_3$ (**XXI**), an intermediate situation results (Table III). The *trans*–*cis* ratios of 1.30 and 2.13 once again support the concept of dominant orientation by polar interaction with the ester group.

In summary, we suggest polar interactions in the transition state (B) arising from c′ to be primarily responsible for the "*trans* effect" in this system, with steric factors playing a smaller role.

Most available evidence on the preferred conformation of aliphatic free radicals can be rationalized in terms of either a planar sp^2 or a rapidly equilibrating sp^3 arrangement.[16,17] An intermediate shallow pyramid with intermediate hybridization has also been suggested.[18] In any event, the stereochemistry of the radical in the present case is not apparent, although our arguments are not materially altered by assuming either a planar or rapidly interconverting tetrahedral radical.

This is depicted in the following representations of the transition states involved. For either 2- or 3-chlorination, the separation of the positive poles is essentially the same for either the *cis* or *trans* orientation, but the negative poles are considerably further separated (and therefore lower in energy) for the *trans* orientation.

Tertiary hydrogens are generally of the order of eight or nine times more reactive than primary hydrogens when sulfuryl chloride is used.[19,20] Therefore **XXX** should have been one of the most abundant chlorination products. Neither **XXX**a nor b could be detected either by gas chromatography or in the nmr spectra of the collected products. Although **XXX**a might be difficult to observe as an impurity in one of the other peaks (Figure 2), the hydrogen ratios are in close agree-

(15) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1967, p 431.

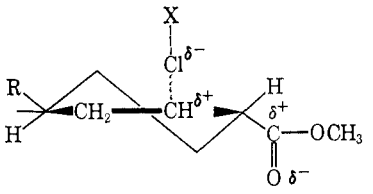
(16) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(17) M. Karplus and G. H. Fraenkel, *J. Chem. Phys.*, **35**, 1312 (1961).

(18) W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, p 30.

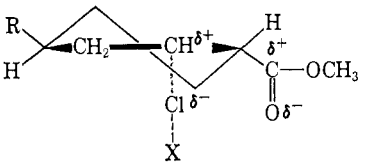
(19) G. A. Russell, *J. Amer. Chem. Soc.*, **80**, 4987 (1958).

(20) G. A. Russell, *ibid.*, **79**, 2997 (1957).

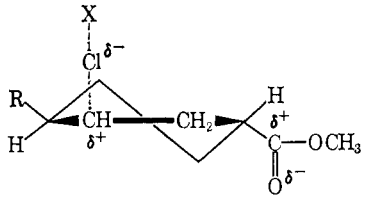


transition state for *trans*–2–chlorination

vs.

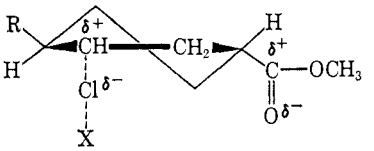


transition state for *cis*–2–chlorination

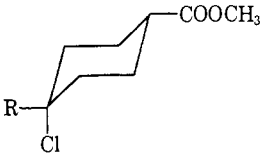


transition state for *trans*–3–chlorination

vs.



transition state for *cis*–3–chlorination



XXXa, R = *t*-butyl
b, R = CH_3

ment with theory, and offer some evidence against this idea. **XXX**b, however, should be easier to detect since the 4-methyl would be a singlet and found in the region 1.5–1.7 ppm in analogy to methyl 4-chloropentanoate which has a similar chemical shift for the terminal methyl group ($CH_3CHCl(CH_2)_2COOCH_3$). No trace of such a peak could be found and thus we conclude that **XXX** is formed only in small amounts, if at all. It is, of course, likely that **XXX**, if formed, would be more readily dehydrochlorinated, since the chlorine is tertiary, but only from **XVII** is there any significant increase in unsaturated ester formed (Figure 3). We have no satisfying explanation to offer for the low reactivity observed for the tertiary hydrogen, especially in view of the nonselective abstraction of equatorial and axial hydrogens.[8]

Experimental Section[21,22]

General. Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are uncorrected as are the boiling points. Infrared spectra were determined on a Perkin-Elmer 521 spectrophotometer and are expressed in cm^{-1}. Nmr spectra were measured on a Varian A-60A instrument as 15–20% solutions in carbon tetrachloride. Chemical shifts are reported in parts per million from tetramethylsilane as internal standard. Mass spectra were obtained on a Consolidated Electronics 21–130 cycloidal mass spectrograph.

n-Pentanoic, *n*-hexanoic, and cyclohexanecarboxylic acids were obtained from Eastman Organic Chemicals and esterified by the methanol–sulfuric acid technique. The methyl esters were homogeneous to glpc and had the following physical constants: methyl *n*-pentanoate (II), bp 126–127° (lit.[23] bp 127.3°); methyl *n*-hexanoate (III), bp 149–150° (lit.[23] bp 149.5°); and methyl cyclohexanecarboxylate (I), bp 182–184° (755 mm) (lit.[24] bp 183–184° (760 mm)).

Chlorination Procedure. All chlorinations were conducted using sulfuryl chloride as the chlorinating agent *via* a slight modification of the method of Brown and Ash.[25] Sulfuryl chloride was distilled prior to use and stored for short periods in a refrigerator wrapped with aluminum foil. Spectroquality carbon tetrachloride and dibenzoyl peroxide were used directly as received from Matheson Coleman and Bell.

In preliminary experiments[1] on chlorination[26] of cyclohexanecarbonyl chloride in carbon tetrachloride, followed by methanolysis and glpc fractionation, the same chlorinated products in approximately the same ratio as for direct chlorination of I (Figure 1) were observed. The only way we could duplicate the formation of α-chloro compound as the major product[27] was to omit the benzoyl peroxide catalyst.

In a typical chlorination, sulfuryl chloride, the substance to be chlorinated, carbon tetrachloride, and dibenzoyl peroxide were placed in a flask equipped with magnetic stirring, reflux condenser, and drying tube. The system was purged with dry nitrogen immersed in an oil bath and slowly heated to 70 ± 2°. A short period of induction was ordinarily observed followed by a rapid reaction with evolution of sulfur dioxide and hydrogen chloride. The reaction was usually completed in less than 2 hr. Variation of the period of heating had no effect on the product distribution. The reaction mixture was then poured into ice water and worked up as usual. The stability of the chloro isomers to the work-up conditions was established in all cases by direct glpc analysis of the reaction mixtures.

For analytical runs, a tenfold excess of material to be chlorinated was used and no polychlorination was observed. For preparative runs sulfuryl chloride and ester were used in the ratio of 1:3 leading to about 30% chlorination. Small amounts of polychlorinated substances were present but not identified.

Analytical Method. Isomeric chloro esters were analyzed by glpc on an F & M Model 700 dual column chromatograph with a thermal conductivity detector. Helium was used as the carrier gas at a flow rate of 60 ml/min at a tank pressure of 30 psi. An 8 ft × 0.25 in. stainless steel column packed with 20% diethylene glycol succinate on 60/80 Chromosorb W operating at temperatures of 130–170° was employed for all analyses.

Sensitivity factors or detector response ratios were determined with standard mixtures containing carefully weighed portions of the

(21) The phrase "worked up as usual" means that an etheral solution of the products was washed with dilute acid and/or alkali, water, and saturated salt solution followed by drying over anhydrous magnesium sulfate. The solvent was then removed on a rotary evaporator.

(22) Nmr, ir, and mass spectra of all products described herein including the monochloro derivatives of II and VI are available in the dissertation of Charles D. Beard, University of Pennsylvania, 1968.

(23) "Handbook of Chemistry and Physics," 41st ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1959–1960.

(24) H. Kwart and F. V. Scalzi, *J. Amer. Chem. Soc.*, **86**, 5496 (1964).

(25) H. C. Brown and A. B. Ash, *ibid.*, 77, 4019 (1955).

(26) Experiments on photobromination of cyclohexane-carbonyl chloride or bromine led to the α-bromo compound as the main product. The greater selectivity in bromination of these acyl halides is in accord with other reports of much greater selectivity for bromination (see P. S. Skell, Special Publication No. 19, The Chemical Society, London, 1964, p 131.

(27) C. C. Price and M. Schwarcz, *J. Amer. Chem. Soc.*, **62**, 2891 (1940).

appropriate chloro isomers. In each case, peak areas were in fact directly proportional to the mole ratios within experimental error (1%). Peak areas were determined by use of a Burrell Corp. planimeter as an average of three traces. The areas were checked by the method of peak height and width at half-height where possible. Preparative glpc separations were conducted on an Aerograph A-700 gas chromatograph using a 15 ft × 0.25 in. stainless steel column packed with 20% DEGS on 60–80 Chromosorb W. Decomposition of the chlorinated substances during glpc was a serious problem in early experiments. Careful control of the injection port temperature (≤175°) and a Pyrex insert greatly reduced decomposition. Treatment of the column with repeated injections of Silyl 8 column conditioner (Pierce Chemical Co.) essentially eliminated all decomposition.

Chloromethyl Cyclohexanecarboxylate (XI). Following the general procedure of Ulich and Adams,[13] 25 g (0.17 mol) of cyclohexanecarbonyl chloride was added dropwise to 5.13 g (0.17 mol) of paraformaldehyde with magnetic stirring over a period of 30 min. After addition of 30 mg of zinc chloride, the mixture was heated at 90° for 3 hr and then distilled directly through a small column giving 14.7 g (54%) of XI: bp 80–82° (5 mm); ir (CCl_4) 1760 (C=O), 745 (CCl), and 714 cm^{-1} (CCl); nmr (CCl_4) δ 5.67 (s, 2 H), 1.0–2.0 ppm (broad, 11 H).

Methyl *trans*-4-Methylcyclohexanecarboxylate (XXI). The procedure of Kwart and Scalzi[24] was followed with modification. Methyl *p*-toluate (60 g) was exhaustively hydrogenated in two batches each using 200 ml of acetic acid solvent and 4 g of 5% rhodium on aluminum at an initial pressure of 50 psi. After filtration of the catalyst and the normal work-up, glpc showed the products to be a mixture of 82% *cis* and 18% *trans* isomers. The mixture was refluxed 12 hr with 10% sodium methoxide in methanol. After cooling, the mixture was poured into dilute hydrochloric acid solution and worked up as usual. The mixture was now 20% *cis* and 80% *trans*. Distillation on an annular Teflon spinning band column gave XXI in 56% yield (>99% purity), bp 55–56° (2 mm). The remaining 44% could either be reprocessed or converted to the acid and purified by crystallization.[24] With patience very high yields of XXI could be obtained.

To verify that in fact the *trans* isomer was the one isolated by distillation, 2.0 g of the ester mixture (20% *cis*, 80% *trans*) was refluxed for 12 hr with aqueous 20% potassium hydroxide, followed by cooling and acidification. The solid *trans*-acid was collected and recrystallized from hexane, mp 112–113° (lit.[24] mp 113–113.5°). Treatment of this acid with ethereal diazomethane gave a compound identical with XXI in all respects.

Methyl *cis*-4-*t*-Butylcyclohexanecarboxylate (XVIII). *cis*-4-*t*-Butylcyclohexanecarboxylic acid was isolated *via* the ammonium salt as described[28] and crystallized from hexane, mp 116–118° (lit.[29,30] mp 117.5–118°). XVIII was prepared from the acid with ethereal diazomethane, bp 54–56° (0.5 mm) [lit.[31] bp 57–58° (0.7 mm)] and by glpc contained no trace of the *trans* isomer within the limits of the thermal conductivity detector.

Methyl *trans*-4-*t*-Butylcyclohexanecarboxylate (XII). *trans*-4-*t*-Butylcyclohexanecarboxylic acid was prepared by the method of Curtin, *et al.*,[32] mp 173–175° (lit.[28,29] mp 174–175°). XII was prepared from the acid with ethereal diazomethane, bp 67–69° (0.2 mm) [lit.[31] bp 65–66° (0.8 mm)] in 99% purity with 1% of XVIII as impurity.

Treatment of the Chlorination Products of XII with Methanolic Potassium Hydroxide. A typical reaction mixture of the monochloro isomers of XII (1.0 g) and 5 ml of 25% potassium hydroxide in methanol was refluxed for 10 hr. After removal of the precipitated potassium chloride, the solvent was removed *in vacuo*, and water was added to the residue. The alkaline layer was acidified with dilute sulfuric acid and then extracted with ether. The ether layer was dried over magnesium sulfate and then treated with ethereal diazomethane. The mixture was worked up as usual and the solvent evaporated prior to glpc analysis.

(28) H. H. Lau and H. Hart, *J. Amer. Chem. Soc.*, **81**, 4897 (1969).
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Free-Radical Chlorination of Methyl Cyclohexanecarboxylates. II. Stereochemistry of the Hydrogen-Abstraction Step

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Abstract: Catalytic hydrogenation of methyl perdeuteriobenzoate in acetic acid produced methyl cyclohexanecarboxylate with essentially all atoms *cis* to the ester deuterium. Similarly, catalytic addition of deuterium to methyl benzoate led to the analog with all atoms *trans* to the ester deuterium. Catalytic deuteration of methyl *p*-*t*-butylbenzoate also proceeded stereoselectively without significant exchange to give 78% methyl *cis*-4-*t*-butylcyclohexanecarboxylate-d_6. This product was epimerized by base, with exchange of the α-deuterium. Free-radical chlorination of these esters by sulfuryl chloride, followed by glpc separation of the monochloro isomers and determination of the H/D fraction on the chlorine-containing carbon, leads to the conclusion that the abstraction of hydrogen is governed by a normal H/D ratio of *ca.* 1.7 for free-radical chlorination but is unaffected by whether the hydrogen atom is *cis* or *trans* to the ester group or in an axial or equatorial position, *i.e.*, there is no significant stereoselectivity in the hydrogen-abstraction step.

Recently an explanation for the preferential formation of *trans* products (hereafter denoted "*trans* effect") in the free-radical chlorination of methyl cyclohexanecarboxylate and derivatives was proposed.[1] Electrostatic repulsions between the electronegative substituent and the chlorinating agent in the transition state for propagation step B were postulated as primarily responsible for the stereoselectivity. Steric repulsions were apparently small compared with polar interactions.[1]

$$R{-}H + X\cdot \longrightarrow R\cdot + HX \quad (A)$$

$$R\cdot + X_2 \longrightarrow RX + \cdot X \quad (B)$$

The "*trans* effect" is readily detected experimentally since it leads to a greater proportion of *trans* than of *cis* isomers. On the other hand, because of the

(1) C. C. Price, C. D. Beard, and K. Akune, *J. Amer. Chem. Soc.*, **92**, 5916 (1970).