Chlorination. II. Free Radical *vs.* Hell–Volhard–Zelinsky Chlorination of Cyclohexanecarboxylic Acid

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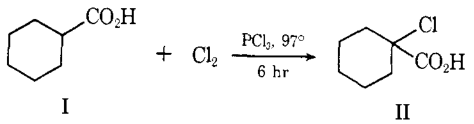
Abstract: Treatment of cyclohexanecarboxylic acid with chlorine at temperatures below *ca.* 100° gives comparatively nonselective chlorination, even in the dark or in the presence of phosphorus halides. In the range 100–150°, there is a competition between nearly random and selective α-chlorination in the presence of phosphorus halides, and at 170°, the product is almost exclusively the α-chloro acid when as little as 0.6 mol % of PCl_3 is present. At higher temperatures formation of considerable unsaturated acid is observed. It is suggested that a free-radical mechanism is operating at low temperatures, yielding, at higher temperatures, to the Hell–Volhard–Zelinsky reaction, which presumably involves addition of chlorine to an enol and leads to the α-chloro acid. At still higher temperatures the α-chloro acid undergoes elimination of HCl to form the unsaturated acid.

The carboxyl function is capable of exerting directive effects on chlorination reactions in aliphatic systems in a number of ways, depending on whether the reaction in question is free radical in nature or not.[2] If free-radical conditions pervade, polar or resonance stabilization effects may influence the position of attack by the hydrogen-abstracting species, depending on its reactivity.[3,4]

If free-radical conditions do not control, yet another directive effect giving α-chlorination (presumably by way of an enol[5]) may be exhibited by the carboxyl function. It was the purpose of this study to determine the conditions which dictate whether radical or nonradical chlorination of aliphatic acids will be preponderant.

Treatment of aliphatic carboxylic acids containing at least one α-hydrogen with bromine or chlorine in the presence of a phosphorus halide or precursor thereof is the classical method of preparation of α-halo acids known as the Hell–Volhard–Zelinsky (HVZ) reaction.[5,6] Although the method has been regarded as being preparatively useful for both α-bromo and α-chloro acids, practical applications in the case of the simple aliphatic acids have been confined largely to the bromo derivatives with only a few exceptions.[7,8] The method has been reported to be unsatisfactory for the preparation of 1-chlorocyclobutanecarboxylic acid.[9]

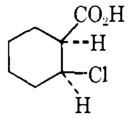
The synthesis of 1-chlorocyclohexanecarboxylic acid (II) in 70–75% yield by chlorination of I over 6 hr at 97° in the presence of catalytic amounts (3 wt %) of PCl_3 has been reported by Jason and Fields.[8] In comparison, chlorination of I at 25° over 11 hr in the absence of PCl_3 reportedly gave a 77% yield of randomly substituted monochlorocyclohexanecarboxylic acids,[8] but details are lacking and no other attempted direct chlorination of I has been reported.[10]



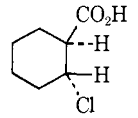
I II

Results

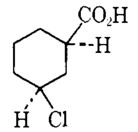
In our hands, a number of attempts to chlorinate I at 100° under conditions described by Jason and Fields[8] gave a maximum of 17% yield of II. The other products of the reaction were found to consist of the other six monochlorocyclohexanecarboxylic acids, III–VIII,[2] and a relatively large amount (10–20%) of more highly chlorinated acids, plus some esters and/or lactonic materials.



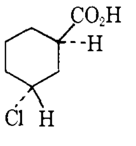
III, *cis*-2



IV, *trans*-2



V, *cis*-3



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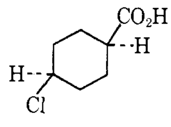
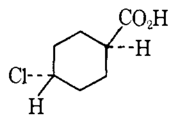


VII, *cis*-4



VIII, *trans*-4

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[1] To whom correspondence should be addressed.

[2] See paper I in this series: J. C. Little, Y.-L. C. Tong, and J. P. Heeschen, *J. Am. Chem. Soc.*, **91**, 7090 (1969).

[3] G. A. Russell, *Tetrahedron*, **8**, 101 (1960).

[4] G. A. Russell, A. Ito, and R. Konaka, *J. Am. Chem. Soc.*, **88**, 2988 (1963).

[5] H. B. Watson, *Chem. Rev.*, 7, 173 (1930).

[6] (a) A. R. Surrey, "Name Reactions in Organic Chemistry," 2nd ed, Academic Press, New York, N. Y., 1961, p 129; (b) R. C. Fuson, "Reactions of Organic Compounds," John Wiley & Sons, Inc., New York, N. Y., 1962, p 36.

[7] (a) G. Reutenauer, *Bull. Mens. ITERG*, 32 (1947); *Chem. Abstr.*, **42**, 1879*a* (1948); (b) G. Reutenauer, M. Lecomte, and M. Regent, *Bull. Mens. ITERG*, 32 (1948); *Chem. Abstr.*, **42**, 3321*c* (1948); (c) W. Griehl, W. J. Schulze, and H. Furst, *Ber.*, **91**, 1165 (1958); (d) J. A. Sonia and C. E. Lisman, U. S. Patent 2,595,899 (1952); *Chem. Abstr.*, **47**, 1183*f* (1953); (e) J. A. Sonia and E. H. Scremin, U. S. Patent 2,674,620 (1954); *Chem. Abstr.*, **49**, 5510*b* (1955), (f) S. L. Bass and W. L. Burlew, U. S. Patent 1,993,713 (1935); *Chem. Abstr.*, **29**, 2550 (1935); (g) S. L. Bass, U. S. Patent 2,010,685 (1935); *Chem. Abstr.*, **29**, 6608 (1935); (h) H. F. Brust and H. O. Senkbeil, U. S. Patent 2,809,992 (1957); British Patent 752,761 (1956); *Chem. Abstr.*, **51**, 9674*i* (1957); (i) A. Hrubesch and B. Schlictung, German Patent 835,888 (1953); *Chem. Abstr.*, **47**, 11227*f* (1953); (j) see also H. H. Guest and C. M. Goddard, Jr., *J. Am. Chem. Soc.*, **66**, 2074 (1944).

[8] E. F. Jason and E. K. Fields, U. S. Patent 3,052,716 (1962); Belgian Patent 596,687 (1961); British Patent 966,544 (1964); *Chem. Abstr.*, 61, 13199*a* (1964).

[9] W. A. Nevill, D. S. Frank, and R. D. Trepka, *J. Org. Chem.*, 27, 422 (1962).

[10] J. von Braun, F. Jostes, and W. Münch [*Ann.*, **453**, 128 (1927)] have prepared II by reaction of PCl_5 with the N,N-diethylamide of I, followed by hydrolysis of the resulting iminodichloride.

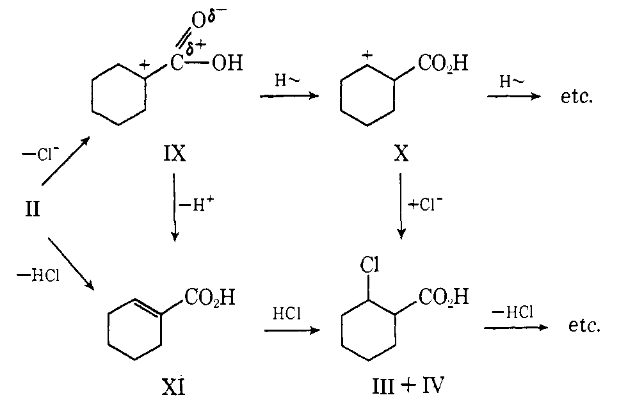
The product distribution was essentially unaltered when the chlorination was carried out in the dark rather than in the presence of incident light, and when freshly distilled I and PCl_3 were used. Employment of smaller amounts (1%) of PCl_3 gave lower yields of II (*ca.* 7%), and irradiation with a Pyrex-filtered GE sunlamp resulted in a product containing less than 5% II. We are forced to conclude from these experiments that some very subtle factors are perhaps playing a role, thus preventing us from repeating the earlier results.[11]

The question then arose as to whether the observed product distribution is the result of (a) free-radical chlorination which could be relatively nonselective in nature, (b) initial HVZ chlorination in the α position followed by rearrangement to an equilibrium mixture, or (c) competititon between free-radical and classical HVZ reactions.

Some support can be found for each of the above alternatives. Free-radical chlorination of aliphatic acids to give relatively nonspecific isomer distributions is well known.[2,12] This explanation for the formation of all possible monochloro acids (II–VIII) is therefore quite plausible, assuming that there is a thermally initiated reaction of fairly long chain length to account for the reaction which takes place in the absence of light. The relatively high percentages of α-chlorinated material (17%) might not be expected by analogy with similar studies, which show that abstraction of hydrogen adjacent to an electron-withdrawing group by the electrophilic chlorine radical is unfavorable.[4,12,13] However, photochlorination of I at 80° (1 *M* in chlorobenzene) in the absence of PCl_3 gave mixtures containing up to 11% II with distribution of the other monochloro acids very similar to that obtained at 100° without solvent in the presence of PCl_3. The effects of PCl_3 concentration on the yield of II at 100° gives some indication that possibly alternative (c) (competition between radical and HVZ chlorination) is operating: when only 1% PCl_3 was used the yield of II dropped to 7%.

Support for alternative (b) could be found in the observed thermal instability of the product mixture: attempted distillation gave copious evolution of HCl even after the solution had been thoroughly degassed and/or washed with water. Moreover, redistillation of a material which had been washed and then twice distilled (with continual HCl release), gave similar results, indicating that the instability was probably a property of the chloro acid mixture itself, rather than due to the catalytic action of some phosphorus residues, etc.[14]

If HCl elimination proceeds by way of the carbonium ion IX, rearrangement to, *e.g.*, X, might be anticipated, since the positive charge in IX is directly adjacent to the carbonyl dipole and is thus destabilized. Alternately, a concerted elimination of HCl to form XI followed by 1,4 addition of HCl has the same net effect of rearrangement of II → III + IV. Further rearrangements to form other isomers could proceed in a similar manner. A direct analogy for this type of rearrangement can be drawn from the observation that treatment of 1-hydroxycyclohexanecarboxylic acid with HBr leads to 4-bromocyclohexanecarboxylic acid.[15] Similar rearrangements have been reported.[16,17]



Vaughan,[18] on the other hand, has reported that addition of hydrogen chloride to XI under conditions similar to those used during our chlorination studies (acetic acid, dry HCl, 100–110°) proceeds to give at least 66% III with the remainder assumed to be IV. We have repeated this work[2] and found the product distribution listed in Table I, as determined by esterification of the crude reaction mixture and glpc analysis. Although the reaction is not as clean-cut as originally postulated,[18] nevertheless it is significant that the preponderant product of the reaction is III rather than the more random distribution which we have found during the chlorination of I. These results indicate that, although there is some tendency for the chloro acids to rearrange, the bulk of the products observed are the result of some other process and are probably the primary products of the reaction.

Table I. Chlorocyclohexanecarboxylic Acids Resulting from HCl Addition to XI at 100°[a,b]

Isomer	Product, %
II (1-)	0
III (*cis*-2-)	80
IV (*trans*-2-)	5
V (*cis*-3-)	0
VI (*trans*-3-)	8
VII (*cis*-4-)	4
VIII (*trans*-4-)	3

[a] See ref 2. [b] See ref 18.

Some additional evidence that the mixture of acids obtained at 100° was indeed the primary reaction product was provided by subjecting a sample of III to actual chlorination conditions; chlorine was passed through a mixture of III, I, and PCl_3 in chlorobenzene at 90°.

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(11) In studies carried out in our laboratory some time subsequent to those described herein (using a different source of starting materials or different acids), erratic results in the form of lower selectivity to the α-chloro acids have occasionally been obtained. We are currently examining the HVZ chlorination of these acids in considerable detail and hope to clarify some of the inconsistencies.

(12) See, for example, (a) C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York, N. Y., 1957, p 364; (b) H. Singh and J. M. Tedder, *J. Chem. Soc., B*, 605 (1966); (c) M. S. Kharasch and H. C. Brown, *J. Am. Chem. Soc.*, **61**, 2142, 3432 (1939); **62**, 925 (1940).

(13) G. A. Russell and A. Ito, *ibid.*, **85**, 2983 (1963).

(14) Conversion of the crude chlorinated acids to their methyl esters was somewhat more successful and eventually a monochloro ester fraction which was stable to distillation was isolated.[2]

(15) H. T. Bucherer and K. Dohlern, *J. Prakt. Chem.*, **140**, 251 (1934).

(16) See ref 6b, pp 173–174.

(17) D. S. Noyce, H. I. Weingarten, and L. J. Dolby, *J. Org. Chem.*, 26, 2101 (1961).

(18) W. R. Vaughan, R. L. Craven, R. Q. Little, Jr., and A. C. Schoenthaler, *J. Am. Chem. Soc.*, 77, 1594 (1955).

Table II. Chlorination of Cyclohexanecarboxylic Acid

Example	Temp, °C	Solvent (concn of I)	Catalyst	Conversion of I, %	Time, hr	Analysis of chlorinated fraction[a]							
						II	III	IV	V	VI	VII	VIII	"Highers"
1	40	C_6H_5Cl (1 *M*)	*hν*	*Ca.* 15	4.0	4	9	9	24	24	18	12	
2	77–86	C_6H_5Cl (2 *M*)	3% PCl_3	64	7.0	3	(6)	2	24	27	17	(12)	8
3	80	C_6H_5Cl (1 *M*)	*hν*	*Ca.* 15	4.0	11	8	10	22	23	15	11	
4	97–100	None	1% PCl_3	84	7.1	7	(6)	5	23	22	8	(10)	20
5	97–101	None	3% PCl_3	71	7.1	17	(7)	9	18	18	9	(11)	12
6[b]	90–101[c]	None	3% PCl_3	72	8.5	17	(6)	4	17	17	10	(8)	21
7[b]	140 ± 2	None	0.6% PCl_3	76	4.7	25	(5)	9	16	16	5	(7)	18
8[b]	150 ± 2	None	0.6% PCl_3	91	4.4	87	(1)	2	2	3	2	(1)	3
9[b]	165 ± 2	None	0.6% PCl_3	90	3.8	97	2.8%						0.6
10[b]	170 ± 2	None	0.6% PCl_3	93	4.9	99	(0.1)	0.2	0.3	0.3	0.1	(0.1)	0.4
11[b]	170 ± 2	None	1% PCl_3	94	4.6	99	(0.1)	0.2	0.1	0.3	0.0	(0.1)	0.4
12[b]	170 ± 2	None	None	76	4.4	29	(5)	8	12	16	7	(7)	18
13[b]	180 ± 2	None	1% PCl_3	77	7.1	96[d]	(0.1)	0.1	0.2	0.4	0.1	(0.1)	1
14[b]	190 ± 2	None	0.6% PCl_3	73	4.1	91[e]	2.7%						2
15[b]	195 ± 2	None	1% PCl_3	47	7.1	67[f]	(1)	3	3	2	1	(1)	7

[a] Values in parentheses are estimated. [b] Run in the dark. [c] Temperature reached 135° briefly at one point. [d] 2% XI also formed. [e] *Ca.* 4% XI also formed. [f] 15% XI also formed.

After about 2 hr, the mixture was analyzed by esterification followed by glpc.[2] At least 87% of the original III survived the treatment after suitable correction (see Experimental Section) for the additional material which probably was formed by chlorination of I.

We conclude from these observations that at least the bulk of the products from the chlorination of I are the result of kinetic control, with only a small amount of secondary reaction products being formed under the conditions employed. Hence, alternative b can be ruled out, and it appears that the chlorination of I at temperatures of 70–100° proceeds largely by a nearly random process which is most likely free radical in nature.

To gain further information regarding possible competition between radical and HVZ chlorination (alternative c above), we have made a brief study of the effect of temperature and presence or absence of PCl_3 on the isomer distribution. The results are summarized in Table II. Chlorination at 40° of a 1 *M* solution of I in chlorobenzene gave a product mixture containing only 4% II, with increasing substitution at positions further removed from the carboxyl group as might be expected from consideration of probable polar effects of the carboxyl[2,12] during free-radical chlorination. Similar isomer distributions were found when the chlorination was carried out at 80° in chlorobenzene, with the exception that a slightly higher proportion of II was found. This latter result may be due either to a competing reaction as suggested above, or else to a solvent-complex effect, which we will discuss in a subsequent paper.[19] Chlorination in the presence of 4% PCl_3 at 68–77° gave a smaller amount of the HVZ product, II. At 100° the II is produced apparently somewhat in proportion to the PCl_3 present, as mentioned above.

Increasing the temperature of the reaction above 100°, however, had a startling effect on the proportion of II which was formed: at 170°, yields as high as 98–99% II were formed at 93–94% conversion of I in the presence of a catalytic amount of PCl_3.[11] The reaction was carried out in the dark without solvent and resulted in formation of less than 1% of the other monochloro acids III–VIII and about 0.5% products whose methyl esters had higher glpc retention times.[2,20] Increasing the temperature beyond 170° gave selective chlorination at the 1 position, but dehydrohalogenation to XI took place, presumably followed or accompanied by other solvolysis reactions to give lactones, esters, or rearranged monochloro acids (III–VIII), or by addition of chlorine, as evidenced by an increase again in products other than II (*cf.* example 15, Table II).

The catalytic effect of the PCl_3 on the formation of the α-chloro acid is demonstrated by examples 10–12 (Table II). In the absence of PCl_3, only 29% II was formed, with an almost random distribution of other products. As little as 0.6% PCl_3 was effective in producing a nearly quantitative yield of 1-chlorocyclohexanecarboxylic acid.[21]

Thus it appears from these preliminary experiments that chlorination of cyclohexanecarboxylic acid in the presence of PCl_3 is markedly dependent upon temperature. At temperatures less than 100°, a comparatively random chlorination, which is most likely free radical in nature, is occurring. At temperatures of *ca.* 100–150°, there is apparently a competition between a free-radical mechanism and a mechanism which gives a specific chlorination at the 1 position. This latter mechanism is probably operating almost exclusively at temperatures greater than about 150°. However, dehydrochlorination and subsequent formation of other products becomes important at temperatures greater than about 190°, limiting the preparatively useful chlorination temperatures to 150–190° in this system.

A plot of several examples from Table II illustrates these conclusions in Figure 1. Although the data are only approximately comparable because of different catalyst concentrations, etc., the dramatic changeover from one mechanism to the other, particularly near

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(19) J. C. Little, Y.-L. C. Tong, and T. E. Zurawic, manuscript in preparation. See E. S. Huyser in "Advances in Free Radical Chemistry," Vol. I, G. H. Williams, Ed., Academic Press, New York, N. Y., 1965, pp 99–101.

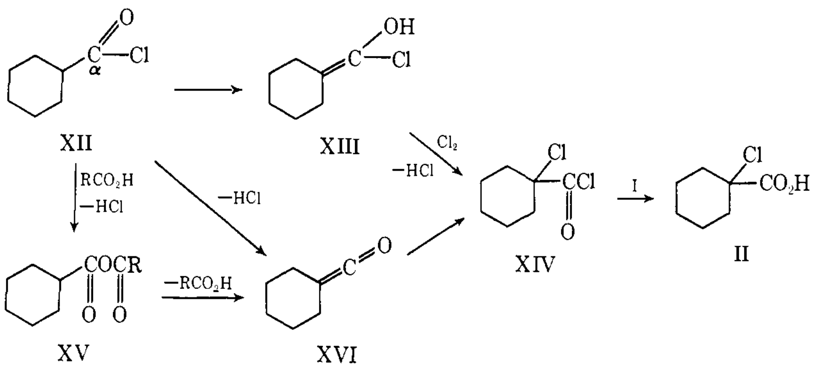
(20) About 95% of the product acids could be flash distilled indicating that no more than 5% was nonvolatile and hence not detectable by glpc. In view of the instability of these compounds to heating, undoubtedly some of the distillation residue resulted from this source, and therefore the actual composition of the reaction mixture was probably very close to the values shown in Table II.

(21) Use of 0.3% PCl_3 gave an 80% yield of II under the conditions of examples 10–12 (Table II). Increasing the amount of PCl_3 to 1.5–2.0% had little effect on the primary product distribution. A small amount (*ca.* 2%) of dehydrohalogenation of II to form XI accompanied by color formation was observed at the higher concentrations.

140–150°, is readily seen. The equally striking effect of the instability of the α-chloro acid II is seen near 190–200°. For the preparation of II, the ideal balance between these two extremes appears near 170°, and we have confirmed this with a number of runs on various scales.[11]

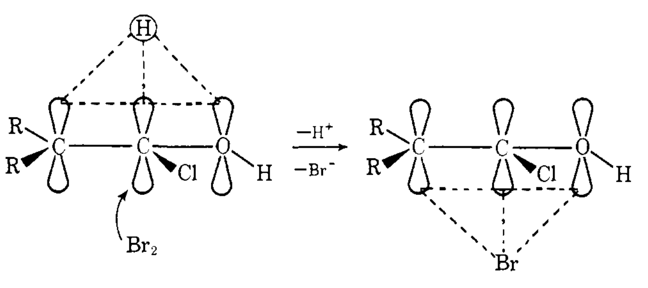
Discussion

Figure 1 demonstrates quite clearly the remarkable changes in product distribution which take place during the chlorination of I in the presence of PCl_3. Particularly striking is the change over the relatively narrow temperature range of 140–150°. It seems logical that these variations in product distribution reflect temperature effects on at least two competing chlorination mechanisms. The free-radical mechanism appears to explain quite adequately the distributions observed below 140°, and the most reasonable choice of mechanisms to give exclusively α-chlorination would be one involving formation of a double bond between C_1 and C_α, (*e.g.*, enolization[5]) followed by addition of chlorine. Direct chlorination of the acid I *via* its enol can probably be ruled out because it does not explain the catalytic activity of the PCl_3 or the presumed thence-derived acid chloride, XII. At least three other possibilities have been suggested, however. Watson[5] postulated that chlorination of aliphatic carboxylic acids in the presence of PCl_3 (Hell–Volhard–Zelinsky reaction[6]) proceeds through enolization of the acid chloride followed by rate-determining addition of chloride to the enol (such as XIII). It has also been proposed[22] that the acid chloride undergoes elimination of HCl to form a ketene (such as XVI) in the HVZ reaction.



Addition of chlorine would then yield XIV. An alternate route to the ketene might be by way of the anhydride XV.

Kwart and Scalzi[23] have proposed that bromination of cyclohexanecarbonyl chlorides in $SOCl_2$ proceeds by



XVII XVIII

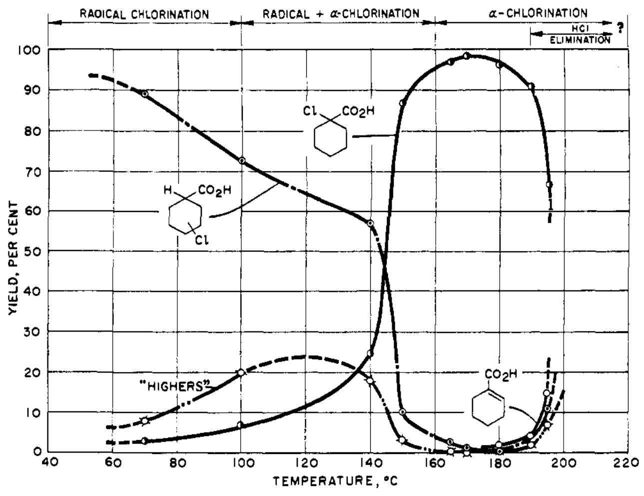


Figure 1. Chlorination of cyclohexanecarboxylic acid in presence of PCl_3, showing the effect of temperature on product distribution.

way of attack by halogen on the protonated acid chloride (*cf.* XVII → XVIII) in order to account for a lack of evidence supporting rapid preenolization, but still accommodate dependency of the rate upon halogen concentration[23,24] and other factors. Support for this proposal has been offered by Turner and Kubler.[25] The applicability of this picture to our system, of course, remains to be demonstrated, since the medium is different, and also differences between HVZ bromination and chlorination have already been noted.[5]

Regardless of the actual mechanism of the selective α-chlorination reaction, if we assume that this mechanism and the radical path are the only two operating in the system under present study, it is possible to estimate from the data in Table II the relative amounts of the products resulting from each. Examples 1 and 3 undoubtedly typify the results of radical chlorination at low conversion, and it can be seen that the amount of the 1-chloro isomer (II) is small (4–11%) in comparison to the total amount of the other monochloro acids (III–VIII). At 100° and at higher conversions without solvent the amount of II is again small (7%) in comparison to the total of III–VIII (58%), even though PCl_3 is present. It seems reasonable to assume that all of the II formed as the result of radical chlorination in this case also, and in general, the amount of 1-chlorocyclohexanecarboxylic acid (II) produced by the *radical* mechanism is about 10% of the total of the other chloro

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[22] A. Kronstein, *Ber.*, **54B**, 1 (1921); *Chem. Abstr.*, **15**, 1882 (1921).

[23] H. Kwart and F. V. Scalzi, *J. Am. Chem. Soc.*, **86**, 5496 (1964).

[24] C. Cicero and D. Mathews, *J. Phys. Chem.*, **68**, 469 (1964).

[25] J. A. Turner and D. G. Kubler, *Furman Univ. Bull., Furman Studies*, 12, 45 (1965); *Chem. Abstr.*, **63**, 12988*g* (1965).

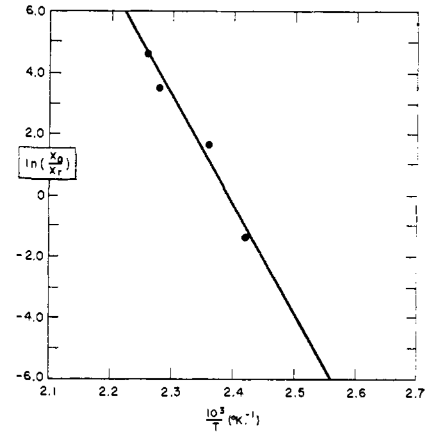

Figure 2. Temperature relationship of the ratio of the mole fraction of specific α-chlorination products with those formed by a free radical path chlorination of cyclohexanecarboxylic acid in the presence of PCl_3. Data are from examples 7–10, Table III.

acids, III–VIII, which are formed, ignoring the more highly chlorinated material. The balance of the II may thus be assumed to arise by way of the mechanism involving *specific α-chlorination*, and inspection of the ratios will allow approximation of the product distribution resulting from the two mechanisms.

Application of this reasoning to examples 7–10 of Table II, which were all carried out without solvent in the dark in the presence of 0.6% PCl_3, yields the data shown in Table III, where X_a = mole fraction of the monochloro acids derived from the specific α-chlorination mechanism, and X_r = mole fraction resulting from the radical mechanism.

Table III. Products Derived from Enolic *vs.* Radical Chlorination in the Presence of PCl_3

Example	Temp, °C	II, %	III–VIII, %	X_a	X_r
4	97–100	7	93	0	1.0
7	140 ± 2	25	58	0.20	0.80
8	150 ± 2	87	11	0.86	0.14
9	165 ± 2	97	2.8	0.97	0.03
10	170 ± 2	99	1.1	0.99	0.01

The data of Table III can be related, interestingly enough, by a plot of ln (X_a/X_r) *vs.* $1/T$. As Figure 2 indicates, a fairly good fit can be obtained for a straight line having a slope of −34,000° and an intercept of 145°. These numbers are obviously far too large to represent differences between the activation parameters of two simple, single-step competing reactions, since $\Delta\Delta H^{\ddagger}$ would have to be of the order of 68 kcal/mol and $\Delta\Delta S^{\ddagger}$ about 160 eu. It therefore seems logical that if this evaluation of the data has real meaning, then the observed differences in activation parameters reflect a high effective activation enthalpy and entropy for the specific α-chlorination mechanism. The latter values actually probably represent the sum of the thermodynamic quantities for several prior equilibria in addition to those of the actual rate-determining step. All of the mechanisms which have so far been postulated for the specific α-chlorination reaction[5,22,23] involve a number of such prior equilibria, and other mechanisms would probably be equally complex. The reaction path involving ketene formation,[22] in addition, would also involve a rate-controlling step which undoubtedly has a high $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ itself.

Regardless of the theoretical implications, the data summarized in Figure 2 appear to be useful in predicting product distributions, at least under the conditions given.

In summary, we have demonstrated a remarkable effect of temperature on the directive abilities of the carboxyl group (or derivative thereof) during chlorination in the presence of PCl_3. At low temperatures, a radical chain process appears to be operating, while high temperatures favor substitution at the α position, probably preceded by addition of chlorine to the double bond of an enol. This reversal contrasts with the normal observation that low temperatures favor addition while higher temperatures favor a radical substitution path, as in the case of chlorination of aromatic hydrocarbons.[26] We are continuing study of both of these reaction paths.

Experimental Section

Chlorination of Cyclohexanecarboxylic Acid (I). The chlorinations summarized in Table II were carried out essentially as described previously[2] except for examples 1 and 3 which were run as 1 *M* solutions in dry chlorobenzene in the absence of PCl_3 and irradiated by a 275-W GE sunlamp. Example 2 was carried out by adding the solvent chlorobenzene and acid (2 *M*) and drying the system by azeotropic distillation prior to adding the PCl_3. Example 6 was conducted in a blackout hood, and examples 7–15 were carried out in a flask shielded from incident light to minimize photoinitiation. There was occasionally observed an "induction period" in some of the preliminary studies using PCl_3 catalyst in chlorobenzene: the yellow color of chlorine built up during the first 45–90 min of addition before a sudden exothermic reaction, release of HCl, and disappearance of color followed by smooth, rapid uptake of chlorine took place. Preliminary efforts to alter this induction period by degassing, irradiation, or addition of chloride ion (as triethylbenzylammonium chloride) were without success. No such induction period was observed in later runs made without solvent.

Samples of the crude reaction mixture were esterified with BF_3–methanol or diazomethane and then analyzed by glpc as previously described.[2]

Stability of *cis*-2-Chlorocyclohexanecarboxylic Acid (III) under Chlorination Conditions. A total of 0.7 g (0.01 mole) of chlorine was passed slowly through a mixture of 6.5 g (0.04 mole) of III, 1.28 g (0.01 mole) of I, 0.1 g of PCl_3, and 50 ml of dry chlorobenzene at 90°. The reaction mixture was stirred for another 30 min and then cooled and sparged with nitrogen to remove HCl and unreacted chlorine. The total elapsed reaction time was about 2 hr. After washing with water, the mixture was dried over $MgSO_4$ and concentrated *in vacuo* to yield 8.3 g of acid which solidified upon cooling. The mixture was then treated with 50 ml of BF_3–methanol reagent[2,27] at reflux for 20 min and then concentrated *in vacuo*. The residue was extracted with benzene and the benzene solution was dried ($MgSO_4$) and concentrated *in vacuo* to yield the crude methyl esters. Distillation yielded a fraction, bp 60–73.5° (17 mm), wt 0.54 g, which consisted mostly of methyl cyclohexanecarboxylate (glpc); an intermediate fraction, bp 73.5–106.5° (17 mm), wt 0.26 g, and found to be about 50% methylcyclohexanecarboxylate and 50% methyl *cis*-2-chlorocyclohexanecarboxylate; and an additional fraction, bp 105–107° (17 mm), wt 6.46 g, which was found (glpc) to contain about 0.15 g of methyl cyclohexanecarboxylate, 6.20 g of methyl *cis*-2-chlorocyclohexanecarboxylate, and small amounts of other methyl monochlorocyclohexanecarboxylates. Thus, of the 0.04 mole of II which was charged to the reaction mixture, at least 0.035 mole survived, making the assumption that, of the 0.0056 mole of the I which was not recovered and is presumed to have been either chlorinated, lost during the work-up, or otherwise undetected by the analytical procedure used, no more than 0.001 mole was converted to III.

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The Photorearrangement of Benzonorbornadiene

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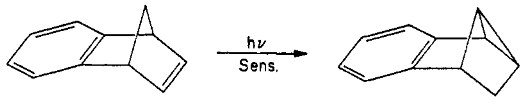
Abstract: The triplet sensitized rearrangement of benzonorbornadiene (1,4-dihydro-1,4-methanonaphthalene) has been studied in detail. Through labeling experiments, evidence is obtained for an intermediate diradical which resembles a partially closed quadricyclane ring. The quantum yield for the reaction is 0.5 with the T_1 state of benzonorbornadiene estimated to be 70 kcal. No fluorescence was detected from benzonorbornadiene and evidence is presented which points to a facile rearrangement during direct irradiation which differs from the triplet-state reaction.

The photochemistry of the bicyclo[2.2.1]hepta-2,5-diene ring has been explored extensively. The hydrocarbon has been studied in solution[2] and in the vapor phase,[3] and recently 7-oxo derivatives[4] and 7-aza derivatives[5] have been investigated. The primary photoprocess in solution is isomerization to the tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane ring (quadricyclane). The details of this isomerization, however, are poorly understood.

For instance, the isomerization is effected by direct irradiation[2a,4,6] or by sensitization.[2b,6d,7] The quantum yield has not been reported in any of these cases and the excited states involved (*i.e.*, the triplet, first excited singlet, vibrationally excited ground state, or some combination thereof) have not been assigned.[8] The ring closure is often depicted as a concerted process although there is no experimental evidence on the point and different excited states could have different pathways.

The work on benzonorbornadiene was initiated to study the effect of incorporating one of the bicycloheptadiene double bonds in an aromatic ring. *A priori*, the primary products could be a quadricyclane, methylnaphthalenes,[9] or benzyne and cyclopentadiene if reactions analogous to norbornadiene take place. Also, based on absorption spectra and by analogy to barrelene and benzobarrelene,[10] benzonorbornadiene should have E_{S_1} lower than and E_{T_1} higher than, norbornadiene. This should enhance intersystem crossing[11] and increase the triplet concentration on direct irradiation of benzonorbornadiene relative to norbornadiene.

When the rearrangement of benzonorbornadiene **1** gave **2** instead of the expected products,[13] the mechanism of the rearrangement was investigated further.



1 2

Results

Prolonged periods of direct irradiation did not appear to give any **2**, while acetophenone sensitization gave good conversion. The need for a triplet sensitizer was also established for the diacetoxy derivative,[13] and three mechanisms were postulated to explain the results (Scheme I).

Precedence can be found for each. Intermediate **3** resembles the proposed intermediate for hydride reduc-

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[8] Roquitte[3] concluded from studying the direct irradiation of norbornadiene in the vapor phase and in ether solution that cyclopentadiene and acetylene ($\Phi \approx 0.45$ in vapor and $\Phi = 0.12$ in ether) probably are formed from a higher vibrational level of the first excited singlet state while the origin of toluene ($\Phi = 0.042$ in both media) is unknown. No quadricyclane was detected. It seems reasonable to assume that quadricyclane forms in the vapor phase but because of excess vibrational energy, which is lost in solution, isomerizes back to norbornadiene. The lack of quadricyclane formation in ether is puzzling.[2]

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