New Aspects of the Chlorination of Some Arylalkanes Using Phosphorus Halide Catalysts

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The effect of radical initiators such as light and peroxides on the rate and selectivity of arylalkane chlorination catalyzed by phosphorus pentachloride is shown. In contrast to earlier reports, chlorination of arylalkanes with phosphorus halide catalysts in the dark at 25 °C is found to be relatively slow and unselective, the results being similar to those obtained without a catalyst. Instead, when the chlorination is performed with phosphorus pentachloride in the presence of light or peroxides, efficient reaction rates and high substrate and positional selectivity are obtained. Even with such basic hydrocarbons as (α-chloroethyl)toluene, ring substitution is almost completely suppressed. With ethylbenzene, the α/β substitution ratio is much higher than when the reaction is catalyzed by light or PCl_5 alone (28–35 compared with 8–15). This catalytic system permits the highly selective synthesis of some valuable intermediates.

(α,α′-Dichloroethyl)benzene and (α-chloroethyl)benzyl chloride are valuable intermediates in the synthesis of α-chlorostyrene, phenylacetylene, and vinylbenzyl chloride by dehydrochlorination.[1,2]

For this reason, we wished to study the synthesis of (α-chloroethyl)benzene, (α,α′-dichloroethyl)benzene, and (α-chloroethyl)benzyl chloride by chlorination of ethylbenzene (EB), (α-chloroethyl)benzene (α-CEB), and (α-chloroethyl)-toluene (α-CET) (60:40 mixture of meta and para isomers) using a phosphorus pentachloride catalyst with the aim of improving reaction rates and selectivities.

Low-temperature chlorination of these substrates with light or peroxides as the initiator is relatively slow and quite unselective. Raising the temperature increases the rate of reaction, but is unfeasible because the dichlorinated products are termally unstable.

Free-radical chlorination of alkanes and arylalkanes with phosphorus chloride catalysts is well known and has been widely studied. For instance Fell and Kung[3] observed increased positional selectivity (RS_ps of up to 30) when alkanes were chlorinated in the presence of PCl_3 and peroxides at 80–100 °C. Wyman et al.[4] reported that PCl_5 itself is a chlorinating agent of alkanes and arylalkanes at temperatures as high as 100 °C, but they did not observe increased selectivity.

More recently, Olah et al.[5] studied the chlorination of alkanes and arylalkanes at room temperature with PCl_5 in the absence of radical initiators and concluded that this catalyst is excellent and highly selective for the side chain chlorination of arylalkanes: an unexpected result, as they noted, since phosphorus chlorides, as weak Lewis acids, are expected to be Friedel–Crafts chlorination catalysts.

We now wish to report that in the temperature range of 20 to 40 °C, phosphorus chlorides are efficient and selective catalysts for the side chain chlorination of arylalkanes only if used in the presence of radical initiators such as light or peroxides. In the dark they are quite poor and unselective; the ratio of side chain to ring chlorination, for instance, is no better than in the uncatalyzed reaction.

Results and Discussion

Experiments were performed in a glass vessel: hydrocarbons (0.3–0.4 mol), phosphorus pentachloride (0.0024 mol, 1 wt %), and room light or peroxides (0.0014 mol). Chlorine was bubbled into the reaction mixture at a constant rate (0.14–0.20 mol in 2 h).

Experiments in the absence of light were carried out in the same glass vessel wrapped in aluminum foil.

The phosphorus pentachloride concentration in our experiments was much lower than in Olah's (10 mol %); however, we obtained essentially the same results when the phosphorus pentachloride concentration was 5 wt % as when it was 1 wt %.

Tables I and II report the results of the chlorination of EB and α-CEB in the absence of catalysts and in the presence of different catalytic species. The improvement in rate and selectivity when phosphorus pentachloride is used in the presence of light or peroxides is clearly seen.

In the absence of radical initiators, it is a poor and unselective catalyst. For EB, chlorination is faster than in the uncatalyzed reaction, but the degree of ring chlorination is also greater, a result more in line with Lewis acid catalysis than is the almost exclusive side chain chlorination reported by Olah.[5] Instead, no ring substitution is detected for α-CEB, the chloroethyl group being a weaker electron donor than the ethyl group.

Thus, phosphorus pentachloride appears to be a more active and selective catalyst with the less reactive α-CEB than with the more basic EB (conversions and selectivities are compared with those in the uncatalyzed experiments).

In the presence of light or peroxides, rates are much faster (almost complete conversion of the chlorine) and the substrate and positional selectivities are greatly improved.

Ring chlorination of EB is almost completely suppressed, and the α/β substitution ratios for EB and α-CEB are much better than for chlorination in the presence of PCl_5 or light alone.

For EB (Tables III and IV; see paragraph at the end of the paper about supplementary material), α/β relative selectivities per hydrogen are as high as 28–35 at substrate conversions of 10–20%, compared with 8–15[5,6] for reactions with light or phosphorus pentachloride alone. At higher conversions (Figure 1 and Tables III and IV) the α/β relative selectivity for EB is further increased (up to 50). This could be attributed to misleading effects of side reactions, but a real change in selectivity with decreasing basicity of the medium cannot be ruled out, as will also be seen with α-CET. No such change is observed with the less basic α-CEB (Table V; see paragraph at the end of the paper about supplementary material). The α/β ratios for this substrate are of the same order of magnitude as for EB (~30), as if the chlorine influences the α- and β-hydrogens to the same degree.[7]

In competitive experiments with toluene and α-CEB (Table IX), relative selectivities per α-hydrogen of 1–1.1 were obtained ($K_T/K_{\alpha\text{-CEB}}$ = 2.9–3.4).

The toluene/ethylbenzene relative reactivity determined by Olah is 1:3.3.

Consequently, the reactivity of the α-hydrogen in α-CEB is decreased by about 70%; if the reactivity of EB is assumed

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Table I. Chlorination of Ethylbenzene with Different Catalysts (T = 30 °C)

products	light, mol % PhC_2H_5 converted		dark, mol % PhC_2H_5 converted		
	PCl_5 = 0%	PCl_5 = 1%	PCl_5 = 0%	PCl_5 = 1%	PCl_5 = 1% perox = 1%
$PhCHClCH_3$	81.6	92.1	68.5	55.0	95.0
$PhCH_2CH_2Cl$	8.9	3.2	5.6	8.1	3.0
$Ph(Cl)CH_2CH_3$	9.5	1.6	26.0	37.8	
$PhCCl_2CH_3$		0.5			0.5
$PhCHClCH_2Cl$		0.2			0.3
polychlorinated		2.4			1.0
% (converted Cl_2/fed Cl_2)	79.4	100	46.8	68.7	100
$PhCHClCH_3/PhCH_2CH_2Cl$	9.3 (13.9)[a]	29.0 (43.5)[a]	12.2 (18.3)[a]	6.8 (10.2)[a]	31.5 (47.2)[a]
molar ratio Cl_2 fed/EB	0.5000	0.5000	0.5000	0.5000	0.4545

[a] Values in parentheses are α/β statistically corrected ratios.

Table II. Chlorination of (α-Chloroethyl)benzene with Different Catalysts

products	room light, mol % α-CEB converted		dark, mol % α-CEB converted		
	PCl_5 = 0%	PCl_5 = 1%	PCl_5 = 0%	PCl_5 = 1%	PCl_5 = 1% perox = 1%
$PhCCl_2CH_3$	71.6	87.9	73.4	76.1	83.1
$PhCHClCH_2Cl$	7.7	9.0	3.0	9.3	8.6
$PhCCl{=}CH_2$	5.7		1.8	5.1	3.8
$PhCCl_2CH_2Cl$	7.5	3.1	5.1	3.3	4.5
$PhCCl_2CHCl_2$	7.5		16.6	6.2	
% (converted Cl_2/fed Cl_2)	41	97.0	37.2	65.7	99.3
% (aliphatic Cl_2/converted Cl_2)	100	100	100	100	100
% (aromatic Cl_2/converted Cl_2)					
$PhCCl_2CH_3/PhCHClCH_2Cl$	a	10.1	a	a	9.7
molar ratio Cl_2 fed/α-CEB	0.50	0.51	0.52	0.38	0.56

[a] Due to the presence of massive quantities of polychlorinated products, values of α/β ratios were not calculated.

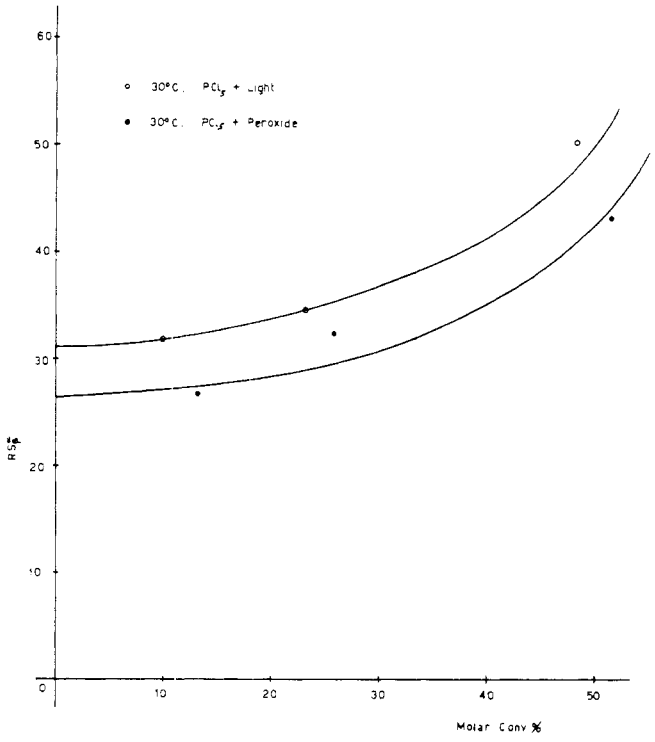


Figure 1. Variation of statistically corrected relative selectivity (RS_{β}^{α}) with molar conversion in the chlorination of EB.

to be 1, the reactivity of the α-hydrogen in α-CEB must be 0.3.

Haring and Knoll[8] found the following decreasing reactivities in the series toluene, benzyl chloride, benzal chloride: 1:0.2:0.04.

As Table VI clearly shows, temperatures higher than 40 °C are unsuitable because of extensive side reactions. The α/β relative selectivity is also enormously decreased, even if all of the side products are considered to be derived from (α-chloroethyl)- and (α,α′-dichloroethyl)benzenes.

The interesting characteristics of the PCl_5 + radical initiator system are further evidenced in the chlorination of α-CET (Tables VII and VIII; see paragraph at the end of the paper about supplementary material for Table VIII).

As Olah et al.[5] have observed, for aromatics more basic than toluene, as is the case for α-CET, ring substitution predominates in the presence of light, peroxides, or PCl_5 alone. The ionic character of the reaction medium is also indicated by extensive dehydrochlorination of the dichlorinated products.

Rates and selectivity are almost identical in the uncatalyzed reaction and that with PCl_5 alone. Olah[5] attributed this to deactivation of the phosphorus halide catalyst by formation of a strong complex with the aromatic π systems; thus, the catalyst does not coordinate with chlorine and uncatalyzed chlorination prevails.

With PCl_5 in the presence of light, however, the situation changes drastically from a chiefly ionic type chlorination to an almost radical one. In fact, ring chlorination is negligible and the rate is substantially increased.

The CH_2Cl/CCl_2CH_3 ratio is about 1.5 for substrate conversions below 30% and 2.5 at higher conversions. The latter value only approaches the value of 3 obtained in the competitive experiment with toluene and α-CEB. This result could be attributed to mutual interaction between the two substituents; it is assumed that reactivity is enhanced by electron-donating substituents and decreased by electron-withdrawing ones.[9]

The difference in selectivity at low and high conversions is

Table VI. Chlorination of α-(Chloroethyl)benzene at Different Temperatures (PCl_5 = 1%, Room Light)

temp, °C	% (Cl_2 conv/ Cl_2 fed)	molar ratio Cl_2 fed/α-CEB	product yields, mol % $PhCCl_2CH_3$	$PhCHClCH_2Cl$	$PhCCl{=}CH_2$	$PhCCl_2CH_2Cl$	$PhCCl_2CHCl_2$	$PhCCl_2CH_3$/ $PhCHClCH_2Cl$
30	89.3	0.4545	87.9	9.0		3.1		9.7
40	98.1	0.5263	89.0	8.8		2.2		10.1
60	70.8	0.4762	57.9	18.3	8.5	8.4	6.9	
80	95.7	0.5263	44.7	22.0	15.5	8.8	9.0	

Table VII. Chlorination of (α-Chloroethyl)toluene with Different Catalysts (T = 40 °C)

products	room light, mol % α-CET converted PCl_5 = 0%	PCl_5 = 1%	dark, mol % α-CET converted PCl_5 = 0%	PCl_5 = 1%	PCl_5 = 1% perox = 1%
$CH_2ClPhCHClCH_3$	50.2	70.6	27.5	36.6	67.6
$CHCl_2PhCHClCH_3$		2.3			3.3
$CH_3PhCCl_2CH_3$	30.9	22.3	39.0	38.9	17.5
$CH_3PhCHClCH_2Cl$	5.2	1.1			3.0
$CH_3PhCCl{=}CH_2$	13.8	0.7	33.5	24.5	3.1
$CH_3PhCCl_2CH_2Cl$		1.7			2.2
$CH_3PhCCl_2CHCl_2$		1.3			3.2
% (converted Cl_2/fed Cl_2)	77.9	98.5	75.0	83.6	98.6
% (aliphatic Cl_2/converted Cl_2)	24.8	97.6	19.1	21.4	98.0
% (aromatic Cl_2/converted Cl_2)	75.2	2.4	80.9	78.6	2.0
$CH_2ClPhCHClCH_3/CH_3PhCCl_2CH_3$	1.6	3.2	0.7	1.0	3.9
molar ratio Cl_2 fed/α-CET	0.4762	0.5556	0.4545	0.4926	0.5882

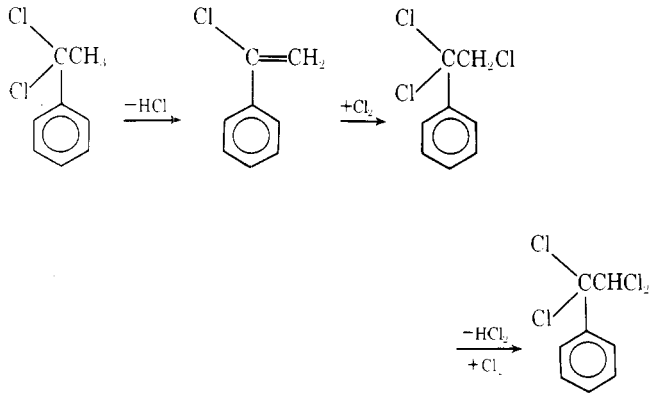
too great to be accounted for by side reactions alone. As in the case of EB, changing selectivity with decreasing basicity of the medium cannot be ruled out; thus, as PCl_5 ← aromatic complexes become weaker, the catalyst becomes more active in its effect to coordinate the chlorine.

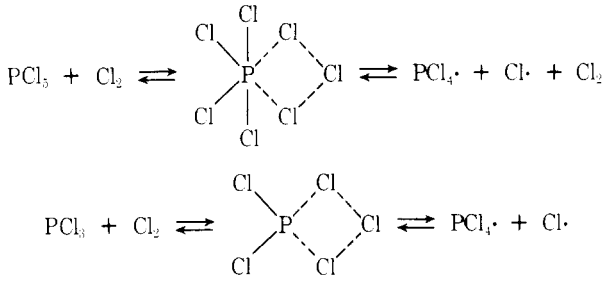
In the chlorination of substances containing an α-chloroethyl group, different amounts of side products such as chlorostyrene and (α,α′,β-trichloroethyl)- and (α,α′,β,β′-tetrachloroethyl)benzenes are formed, possibly according to the sequence shown in Scheme I, although consecutive polychlorination cannot be excluded.

Mechanism and Conclusions. The ability of phosphorus chlorides to catalyze chlorination of hydrocarbons has been widely established, but we believe that the effect of certain impurities on the course of the reaction has not been given sufficient consideration.[10] We have now shown that PCl_5 is a poor catalyst in the absence of light or peroxides, and we suspect that some researchers could have been misled by the accidental presence of one of these initiators in the reaction medium. In our experiments we used only freshly prepared substrates; thus, our results with PCl_5 alone could be explained by the absence of impurities.

In presenting a mechanism for catalysis in the absence of light and peroxides, Olah et al.[5] postulated the formation of complexes of chlorine with PCl_5 or PCl_3. In such a coordination complex chlorine acts as an electron acceptor and the Cl–Cl bond is weakened accordingly.

Scheme I





The ionic reactions were attributed to heterolytic cleavage of the complexed Cl_2, especially in polar solvents or with very basic substrates, and the increased selectivity to the PCl_4· radical, which exists either free or complexed with the aromatic systems,[3,5] in analogy with the π system → Cl· complex postulated in chlorination in the presence of aromatics.[11-13]

The promoting effect of light and peroxides is still unaccounted for, however.

The question of how these radical initiators promote such dramatic changes in the rates and selectivities of PCl_5-catalyzed chlorination is both fascinating and subtle. The unimolecular homolysis rate of diacyl peroxides at 30 °C is low. Induced decomposition of peroxides, a well-known phenomenon, may be involved. Radical initiators can be made more active by catalysts and promoters; these may cause the decomposition of the peroxy compounds to take place at a much lower temperature than usual.[14] But if (and how) this happens in our system, we are not able to say. A thorough mechanistic study was beyond the scope of this paper.

Experimental Section

All of the substrates used were of high purity (>99%): freshly produced commercial ethylbenzene (99.65% pure, containing only 0.18% toluene, 0.003% xylene, and 0.12% PON); (α-chloroethyl)benzene and (α-chloroethyl)toluene prepared in the laboratory by hydrochlorination of styrene and vinyltoluene (>99% pure); phosphorus pentachloride (high purity grade) used without further purification; phosphorus trichloride (Carlo Erba) distilled before use.

General Procedure for Chlorination. The hydrocarbons were added to PCl_5 in a magnetically stirred glass vessel. The vessel was

Table IX. Competitive Chlorination of Toluene and (α-Chloroethyl)benzene (PCl_5 1%, Room Light, T = 40 °C)

molar conv, %	product yields, mol %							$PhCH_2Cl/PhCCl_2CH_3$
	$PhCH_2Cl$	$PhCHCl_2$	$PhCCl_2CH_3$	$PhCHClCH_2Cl$	$PhCCl{=}CH_2$	$PhCCl_2CH_2Cl$	$PhCCl_2CHCl_2$	
12.5	74.6		25.4					2.9
32.6	73.6	2.4	21.2	2.8				3.47
52.7	70.1	4.2	21.7	1.8		0.7	1.5	2.2

Table X

	% wt	mol	retention time, s
ethylbenzene	53.0	0.290	318
(chlorophenyl)ethyl[a]	ND		527
(chlorophenyl)ethyl	ND		570
(α-chloroethyl)benzene	44.5	0.185	610
(β-chloroethyl)benzene	1.5	0.006	700
α,α′-dichloroethyl / α,β-dichloroethyl	0.3	0.001	
polychloro derivatives	0.6	0.002	

[a] Only two peaks. ND = not determined.

Table XI

substrate	mol	NMR, δ
α-CEB	0.167	4.95 (q, $CH_3CH(Cl)$–), 1.7 (d, $CH_3CH(Cl)$–)
α,α′-CEB	0.152	2.45 (s)
α,β-CEB	0.016	4.7 (–(Cl)$CHCH_2Cl$), 3.8 (–(Cl)-$CHCH_2Cl$)
α,α′,β-CEB	0.007	4.15 (s)
α,α′,β,β′-CEB	0.008	6.05s (s)

Table XII

products	mol	NMR, δ
α-CET	0.157	4.95 (q), 1.7 (d), 2.3 (s)
$CH_2ClPhCHClCH_3$	0.115	4.95 (q), 1.7 (d), 4.4 (s)
$CHCl_2PhCHClCH_3$	0.006	6.7 (d, $CHCl_2$), 4.95 (q), 1.7 (d)
$CH_3PhCCl_2CH_3$	0.030	2.45 (s), 2.3 (s)
$CH_3PhCHClCH_2Cl$	0.005	3.8 (m), 4.7 (m), 2.3 (s)
$CH_3PhCCl{=}CH_2$	0.005	5.4 (d, H_a), 5.65 (d, H_b), 2.3 (s)
$CH_3PhCCl_2CH_2Cl$	0.004	4.2 (s)
$CH_3PhCCl_2CHCl_2$	0.005	6.0 (s)

then placed in a water bath at the desired temperature and purged with nitrogen as it reached equilibrium. Dried chlorine (H_2SO_4) was bubbled in at a constant measured rate until the desired conversion was achieved. It was then discontinued, and the reaction mixture was washed with dilute aqueous ammonia until neutrality was obtained.

Apparatus for Chlorination. The chlorination apparatus consisted of a cylindrical (2 cm i.e.) magnetically stirred glass reactor equipped with a gas bubbler, thermometer, and venting tube. Samples were withdrawn with a syringe through a rubber septum. Chlorine was introduced from a cylinder through a manometric device, to keep the pressure constant, a flowmeter, and a drier. Gas chromatographic (GC) analyses were performed with a Carlo Erba Model G.I. chromatograph with a flame ionization detector. A glass capillary column (0.2 mm × 60 m) with OV 101 silicon grease as the stationary phase was used; the programmed column temperature was 60–140 °C, and the nitrogen pressure was 100 psia. Standardization was carried out with a known mixture of the pure components.

Only chlorination products of EB were analyzed by GC. Because of extensive hydrochlorination of the polychlorinated products, the chlorination products of α-CEB and α-CET were analyzed by NMR; the spectra were recorded on a JEOL C/60 HL spectrometer.

Ring substitution of EB was determined by GC. For α-CEB and α-CET, it was determined by substracting the side chain substituted chlorine from the total amount of reacted chlorine. Total chlorine either was taken to be the difference between the amount of chlorine introduced (from flowmeter) and the amount of unreacted chlorine (from iodometric titration of the off gas) or was ascertained by microcoulometric and chemical analyses of the neutralized product. Total side chain substituted chlorine was determined from the NMR spectra.

Chlorination of Ethylbenzene in the Presence of PCl_5 (1%) and Peroxide (T = 30 °C, Dark). Ethylbenzene (50 g, 0.471 mol), PCl_5 (0.5 g, 0.0024 mol), and decanoyl peroxide (0.5 g, 0.0014 mol) were placed in the reactor. Chlorine was fed in for 2 h at the rate of 7.5 g/h. No chlorine was detected in the off gas. After several washings and drying, 57.5 g of product was obtained. GC analysis is shown in Table X.

Chlorination of Ethylbenzene in the Presence of PCl_5 and the Absence of Light and Peroxides (T = 30 °C). EB (50 g, 0.471 mol) and PCl_5 (0.5 g) were placed in the glass reactor wrapped in aluminum foil. Chlorine was fed in at the rate of 8 g/h for 2 h. Only 10 g of chlorine was converted. GC analysis of the reaction products: [product (mol), retention time (s)] EB (0.348), 318; (chlorophenyl)ethyl (0.028), 527; (chlorophenyl)ethyl (0.020), 570; α-CEB (0.067), 610; β-CEB (0.011), 700; α,α′- and α,β-CEB (0.002); polychlorinated (0.002).

Chlorination of (α-Chloroethyl)benzene in the Presence of PCl_5 and Peroxide in the Absence of Light (T = 30 °C). α-CEB (49 g, 0.39 mol), PCl_5 (0.5 g), and decanoyl peroxide (0.5 g) were placed in the darkened reactor. Chlorine was fed in at the rate of 7.3 g/h for 2 h. A total of 14.0 g of chlorine was converted. Analysis of the chlorine in the product gives 25.2% wt of chlorine. The number of moles of chlorine in the product from NMR analysis (Table XI) was 0.198 (14.1 g), a value that is in excellent accord with chemical analysis of chlorine in the product (14.11 g).

Chlorination of α-CEB in the Presence of PCl_5 and Room Light (T = 30 °C): α-CEB (50 g), PCl_5 (0.5 g), chlorine fed in for 2 h (11.6 g); Cl_2 converted = 11.0 g (0.155 mol). Cl_2 in the product from NMR analysis was 0.148 mol: [product (mol)] α-CEB (0.228), α,α′-CEB (0.113), α,β-CEB (0.012), α-chlorostyrene, α,α′,β-CEB (0.004), α,α′,β,β′-CEB (0.005).

Chlorination of (α-Chloroethyl)toluene (60:40 Meta/Para Mixture) in the Presence of PCl_5 (1%) and Decanoyl Peroxide (1%) (T = 40 °C): α-CET (50 g, 0.324 mol), PCl_5 (0.5 g), decanoyl peroxide (0.5 g), chlorine fed in for 2 h (14.0 g); Cl_2 converted was 13.8 g (0.194 mol). Cl_2 in the product from NMR analysis (Table XII) was 13.49 g (0.190 mol).

Preparation of α-CEB and α-CET. Styrene or vinyltoluene (1 mol) was saturated for 3 h with gaseous HCl (1.2 mol) at temperatures as low as −30 to −50 °C while stirring. The product was allowed to warm at room temperature and then was washed several times with H_2O to neutrality. After drying over Na_2SO_4, (α-chloroethyl)benzene and (α-chloroethyl)toluene were recovered by vacuum distillation. α-CEB: bp 68 °C (9 mmHg); NMR δ 4.95 (q), 1.7 (d). α-CET: bp 65 °C (3 mmHg); NMR δ 4.95 (q), 1.7 (d), 2.3 (s). Yields were better than 90%.

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Registry No.—$PhCHClCH_3$, 672-65-1; $PhCH_2CH_2Cl$, 622-24-2; $Ph(Cl)CH_2CH_3$, 1331-31-3; $PhCCl_2CH_3$, 3141-41-1; $PhCHClCH_2Cl$, 1074-11-9; $PhCCl{=}CH_2$, 618-34-8; $PhCCl_2CH_2Cl$, 19676-38-1; $PhCCl_2CHCl_2$, 19676-39-2; $PhCH_2Cl$, 100-44-7; $PhCHCl_2$, 98-87-3; toluene, 108-88-3; ethylbenzene, 100-41-4; styrene, 100-42-5; *m*-vinyltoluene, 100-80-1; *p*-vinyltoluene, 622-97-9; *m*-(α-chloroethyl)-α-chlorotoluene, 69440-14-8; *m*-(α-chloroethyl)-α,α-dichlorotoluene, 69440-15-9; *m*-(α,α-dichloroethyl)toluene, 16835-10-2; *m*-(α,β-dichloroethyl)toluene, 69440-16-0; *m*-(α-chlorovinyl)toluene, 69440-17-1; *m*-(α,α,β-trichloroethyl)toluene, 69440-18-2; *m*-(α,α,β,β-tetrachloroethyl)toluene, 69440-19-3; *m*-(α-chloroethyl)toluene, 19935-78-5; *p*-(α-chloroethyl)-α-chlorotoluene, 54789-30-9; *p*-(α-chloroethyl)-α,α-dichlorotoluene, 69440-20-6; *p*-(α,α-dichloroethyl)toluene, 65114-80-9; *p*-(α,β-dichloroethyl)toluene, 54789-31-0; *p*-(α-chlorovinyl)toluene, 42107-37-9; *p*-(α,α,β-trichloroethyl)toluene, 69440-21-7; *p*-(α,α,β,β-tetrachloroethyl)toluene, 69440-22-8; *p*-(α-chloroethyl)toluene, 2362-36-9.

Supplementary Material Available. Chlorination of ethylbenzene with 1% PCl_3 at 30 °C with room light (Table III) and 1% peroxide (Table IV) and (α-chloroethyl)benzene and (α-chloroethyl)-toluene with 1% PCl_5 at 40 °C with room light (Tables V and VIII) (2 pages). Ordering information is given on any current masthead page.

References and Notes

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$$\underset{1^a\ \ 3.8\ \ 3.8\ \ 1^a}{CH_3\text{–}CH_2\text{–}CH_2\text{–}CH_3} \qquad \underset{1^a\ \ 3.8\ \ 1.8\ \ 0.6}{CH_3\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}Cl}$$

[a] Arbitrary assumed value.

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(10) G. A. Olah and T. R. Hokswender, Jr., *J. Org. Chem.*, **38**, 3478 (1973), have acknowledged increased yields of anti-Markownikoff HBr addition, catalyzed by PBr_3, while using an olefin not previously purified of contained peroxides.
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Structure and Conformation of Heterocycles. 11.[1] *cis*- and *trans*-2,3-Difluoro-1,4-dioxane. Gauche and Anomeric Effects of Fluorine

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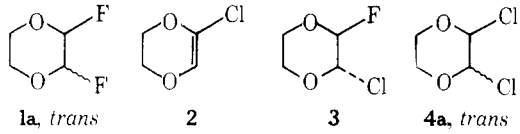
The title compounds were synthesized along with *trans*-2-fluoro-3-chloro-1,4-dioxane and conformationally analyzed using ^1H, ^{19}F, and ^{13}C NMR spectroscopic methods. The trans compound was concluded to occur in better than 96% as diaxial conformers. This is discussed in terms of the "anomeric effect" and "gauche effect" of fluorine.

We are currently investigating systems derived from 1,4-dioxanes, in particular such which bear polar substituents[1,2] and exhibit anomeric and related effects.[3] These effects have been for some time now the subject of intense experimental and theoretical probing.[3,4]

In this framework we undertook to examine the stereoisomeric 2,3-difluoro-1,4-dioxanes (**1**), a system which is of interest both for its reactivity as well as for its conformational features. For one, while the anomeric effect of fluorine was



1a, *trans* **b**, *cis* **2** **3** **4a**, *trans* **b**, *cis*

found and well studied in fluorinated carbohydrates,[5] it is otherwise poorly documented, and although it has been discussed in theoretical terms,[4] a somewhat controversial character emerges from some of these discussions as to the magnitude of this effect relative to other halogens.[4e]

As to the synthetic aspects of this study, the alleged preparation of **1**, without mentioning any configurational features, was cursorily mentioned in a literature procedure[6] which we found irreproducible in our hands. Furthermore, indiscriminate fluorination of 1,4-dioxane has been shown[7a] to give a plethora of highly fluorinated derivatives, but **1** was not isolated. We solved the synthetic problem by reacting *trans*-2,3-dichloro-1,4-dioxane (**4a**)[8] with the "naked" fluoride ion from KF and 18-crown-6 ether in acetonitrile.[9] A mixture of products was obtained containing both stereoisomers of **1**, 2-chloro-1,4-dioxene (**2**), and 2-fluoro-3-chloro-1,4-dioxane (**3**), all in variable amounts, the reaction being very temperature and concentration dependent. While we have not exhausted the study of the various reaction conditions, we were able to optimize the latter in order to obtain mostly **1a** (38%) and **1b** (55%), accompanied by some **2** (7%) but with complete absence of **3**, which appears to be an intermediate in the transformation. The starting material was completely consumed in all cases. The product mixture was readily resolved in GLC, and GC/MS measurements provided nice confirmation of the molecular structures and their fragmentation pattern.

The configurational as well as conformational assignments were made following the acquisition of extensive ^1H, ^{13}C, and ^{19}F NMR data as assembled in Table I, together with those of **4a** and **4b** for the sake of comparison. The latter stereoisomers have been analyzed in the past[10–12] (and our data are almost identical with the published ones), and their conformations are well established.[3c]

The first step toward an unequivocal assignment was made possible by the LAOCN 3[13] analysis of the AA′BB′ pattern of the $O\text{–}CH_2\text{–}CH_2\text{–}O$ moiety in **1a** (Figure 1 and Table I). The well-defined parameters and the resulting R value[20] of $J_{trans}/J_{cis} = 2.2$ (i.e., a dihedral angle of ca. 58.5°) indicate a noninverting chair conformation, in line with other substituted 1,4-dioxanes.[2,3c] While **1b** was not similarly analyzed by simulation, its $O\text{–}CH_2\text{–}CH_2\text{–}O$ spectrum (Figure 2) exhibits an unmistakably much narrower AA′BB′ pattern as compared to that of **1a** (a half-width ca. 20 vs. 80 Hz, respectively) as commonly encountered in the rapidly inverting cis-2,3-disubstituted dioxans vs. the fixed trans isomers.[1b,2] This configurational assignment was supported by the half-widths $w_{1/2}$ of the ^{19}F decoupled CHF signals in **1a** and **1b** which are 1.8

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