

References and Notes

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- (10) ^1H NMR spectra are essentially identical in CH_2Cl_2 and $\text{CHCl}_2\text{CHCl}_2$ as solvents.
- (11) An example which is likely to involve a 1,3 bond formation in a cyclobutenyl cation has been reported: E. J. Corey and W. H. Pirkle, *Tetrahedron Lett.*, 5255 (1967).
- (12) (a) In a preliminary report it was stated that migration of the AlCl_3 group should occur in equal probabilities by means of 1-2 as well as 1-3, shifts.^{1a} Repetition of the double resonance experiments and taking into account the differences in the T_1 relaxation times of methyl groups at sites a and b (see text) as well as the line-broadening measurements do unambiguously establish the nature of the migration process. (b) The authors are grateful to Dr. D. M. Lermal for suggesting this alternative mechanism: J. A. Ross, R. P. Seiders, and D. M. Lermal, *J. Am. Chem. Soc.*, **98**, 4325 (1976).
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- (18) Frequency separation between methyl resonances a + c and d in **3** and a and c in **1** is the same.
- (19) Especially the possibility that k_3 (migration along the seven-membered ring) might be an order of magnitude smaller than k_1 is interesting, in view of the observation that migration of the AlCl_3 group along the six-membered ring in **2a** occurs with a rate constant which is 2100 times smaller than k_1 (at 92 °C).
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Radical Brominations of Some Chloroalkanes. Evidence for Anchimeric Assistance by Neighboring Chlorine¹

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Abstract: In contrast to the rate-retarding effect of a chloro substituent on hydrogen abstraction at a secondary position by bromine atom, a chloro substituent facilitates the reaction at a vicinal tertiary position. This assistance by neighboring chlorine has been demonstrated by both intra- and intermolecular competitive radical brominations. For example, 1-chloro-2,3-dimethylbutane undergoes bromination (32 °C) at the 2 position about seven times faster than at the 3 position, and that rate enhancement is enough to make the overall rate for the substrate about 2.23 times that for 2,3-dimethylbutane. The dependence of the participation of neighboring halogen in the hydrogen abstraction reactions on the identity of the halogen and on the classification (primary, secondary, tertiary) of the reaction site is rationalized in terms of substantial polar contributions to the structure (and energy) of the radical transition states.

Enhancement of ionic substitution reactions by various neighboring groups has been extensively documented,³ and evidence for similar effects of neighboring bromine on radical reactions has been reported by various investigators.⁴ We report here selectivity and other kinetic data which reveal assistance by neighboring chlorine in hydrogen abstraction reactions.

In free-radical processes, a chloro substituent retards hydrogen abstraction at vicinal secondary positions relative to more remote ones; this effect has been taken to be a manifestation of normal electron withdrawal by halogen,^{5,6} and an effect other than retardation has required explanation. High vicinal selectivity in brominations of alkyl bromides, stereoselectivity, and 1,2 rearrangements of a bromo substituent during chlorinations of selected alkyl bromides have been rationalized in terms of bromine-bridged radicals.⁴ For a while, the vicinal selectivity was attributed, not to the kinetic effect

of neighboring bromine, as first suggested,⁶ but to a thermodynamic effect brought about by reversal of the hydrogen-abstraction reaction (i.e., $\text{R}\cdot + \text{HBr} \rightarrow \text{RH} + \text{Br}\cdot$).⁷ Extensive investigations by different research groups⁸ have set aside that challenge, however, and have shown that attack at a secondary position vicinal to a neighboring bromine is indeed kinetically favored over attack at more remote secondary positions during radical brominations.

Since a chloro substituent retards hydrogen abstraction at vicinal secondary positions relative to more remote ones, the kinetic assistance by a bromo substituent seems to require significant participation by neighboring bromine in the transition state, which presumably takes place because of the favorable energy associated with a bridged intermediate.

Kinetic assistance by neighboring bromine is now well documented,^{6,8} but reports of such assistance by neighboring chlorine are scanty.⁹ In addition to an early report of portions

Table I. Primary Products from the Bromination of 1-Chloro-2,3-dimethylbutane^a in Carbon Tetrachloride at 32 °C

Time, s	[2] ^b	[3] ^b	[2]:[3]
60	1.40	0.23	6.09
120	6.03	1.11	5.43
180	26.7	5.28	5.06 ^c
240	32.4	7.24	4.48
300	42.1	10.7	3.93
360	48.3	13.3	3.63
600	55.9	21.2	2.64 ^d
900	58.0	26.0	2.23
1200	64.5	29.3	2.20
1980	61.3	44.0	1.39 ^e
2880	39.7	27.8	1.43
4080	26.3	21.7	1.21
5280	17.8	15.4	1.16 ^f

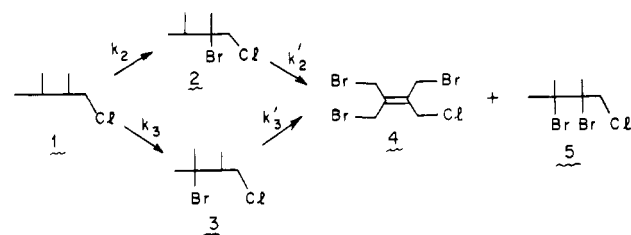
^a Initial concentration, 470 mM. ^b mM. ^c 0.6% reaction of 1. ^d 11.5% reaction of 1. ^e 51% reaction of 1. ^f 87% reaction of 1.

of this study,^{1a} two instances, both involving attack at tertiary positions, have been published. Radical bromination of *trans*-1-chloromethyl-4-methylcyclohexane occurs at the 1, not the 4, position,^{10a} an example of intramolecular competition. The relative rate of hydrogen abstraction by *tert*-butoxy radical from the tertiary site in isobutyl chloride (compared to an estimated rate for the corresponding reaction with isobutane) has been rationalized in terms of nearly balanced opposing effects (retardation by electron withdrawal, acceleration by anchimeric assistance) of the chloro substituent.^{10b} We present new evidence that firmly supports kinetic assistance at a tertiary position by neighboring chlorine during free-radical brominations. Our data also indicate that polar contributions are probably significant in the halogen-bridged radical transition states.

Results and Discussion

Reaction of 1-Chloro-2,3-dimethylbutane with Bromine.

1-Chloro-2,3-dimethylbutane (**1**) contains two tertiary positions, alike except for the relative position of substituent chlorine. The results of the bromination of **1** in carbon tetrachloride at 32 °C are summarized in Table I. Photoinitiated bromination of **1** produces initially 2-bromo-1-chloro-2,3-dimethylbutane (**2**) and 3-bromo-1-chloro-2,3-dimethylbutane (**3**). Both **2** and **3** react further with bromine under the reaction conditions to produce primarily 1-bromo-4-chloro-2,3-bis(bromomethyl)-2-butene (**4**), along with a small amount of 1-chloro-2,3-dibromo-2,3-dimethylbutane (**5**) (Scheme I). The

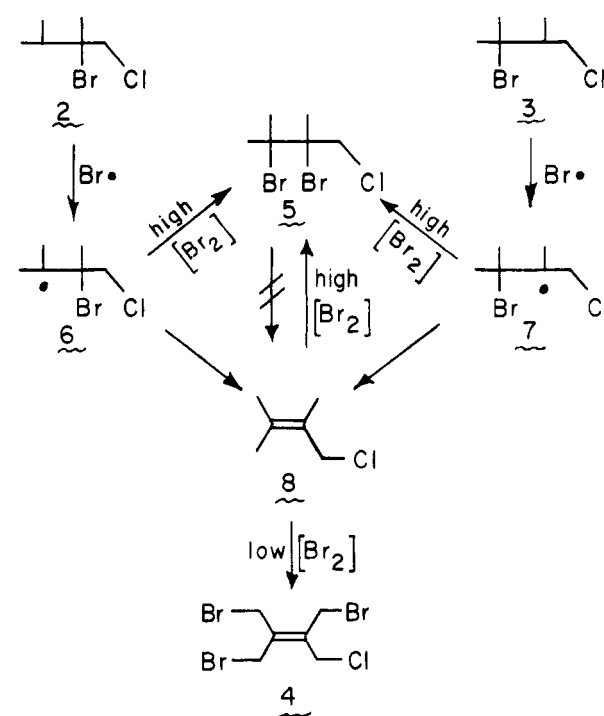
Scheme I


proportion of products **4** and **5** depends on the amount of bromine present in the reaction mixture. With a large amount of bromine present, **5** is produced exclusively and does not react further under the conditions employed. When only a small amount of unreacted bromine is maintained, the major product (80–95% of the product mixture) produced is the tetrahalide, **4**.

These reactions are photoinitiated. The NMR spectra of solutions of **1** or **2** and bromine in carbon tetrachloride which had been kept in the dark at about 29 °C for 1 h (equivalent

respectively to about 75 and 65% reaction with light) or much longer did not show any evidence of reaction products, even at greatly increased amplitude in the regions of absorption of the photoproducts.

Scheme II shows a possible pathway for the formation of **4**.

Scheme II


Bromine atom abstraction of the remaining tertiary hydrogen in **2** or **3** (probably assisted by neighboring bromine) produces a radical which could lose a bromine atom to produce alkene; **8**.¹¹ When a low concentration of bromine is maintained, **8** undergoes allylic bromination (product **4**) faster than bromine addition to the double bond (product **5**). We do not know whether high concentrations of bromine actually trap the intermediate radicals **6** and **7** or form **5** by addition to the double bond of **8**.¹²

The steps in Scheme I represented by k_2 and k_3 are composites of three reactions: hydrogen abstraction and its reverse and reaction of the intermediate radical with bromine. Earlier studies by two different groups of liquid-phase radical brominations of unbranched alkyl bromides have shown that reversal of the initial hydrogen-abstraction step⁷ is uncompetitive with bromine trapping; the proportions of isomeric dibromoalkanes from 1-bromobutane or from 1-bromoheptane were essentially unchanged over wide ranges of substrate: Br_2 ratios (10:1 to 1:100) and of extent of reaction.^{8f} That is, hydrogen bromide reversal played little or no role in the proportions of dibromoalkanes formed.

The equivalent conclusion is strongly indicated for the reactions of **1** with a small excess of bromine in carbon tetrachloride at 32 °C. Vicinal substitution is dominant even at less than 1% conversion, before much hydrogen bromide has been formed. (Even at high conversions, hydrogen bromide accumulation is unlikely because of its low solubility in carbon tetrachloride and the continuous sweep of the reaction mixture by a stream of nitrogen.) The system behaves as a pseudo-first order one: a very good linear plot of $\ln(1 - F)$, where F is the fraction of reaction, vs. time is obtained.¹³ This behavior is not only consistent with reaction sequences completely dominated kinetically by the hydrogen-abstraction steps but also unlikely with significant, selective reversal of those steps.

The ratio of intermediate products, **2**:**3**, decreases as the reaction proceeds, as is shown in Figure 1. Extrapolation of this

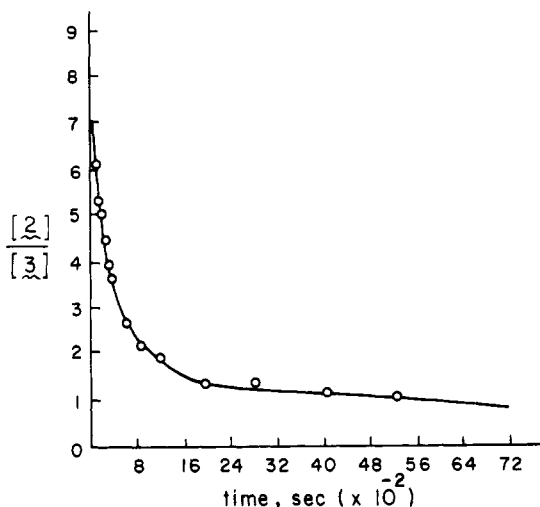


Figure 1. The ratio of 1,2- to 1,3-dihalide (vs. time) produced in the reaction of 1-chloro-2,3-dimethylbutane with bromine.

curve to zero time gives a value of approximately 7 for the initial 2:3 ratio, and this value can be taken as an approximation of the k_2/k_3 ratio.^{5a} Clearly then the 2 position in **1**, vicinal to chlorine, is approximately seven times more reactive than the more remote 3 position.¹³ This enhanced vicinal substitution contrasts with the reported retarding effect of vicinal chlorine on bromination at (nonequivalent) secondary positions.⁶ These kinetic data require significant participation by neighboring chlorine in the transition state for hydrogen abstraction at a tertiary position.

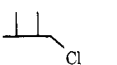
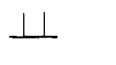
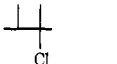
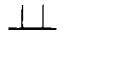
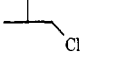
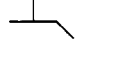
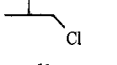
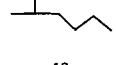
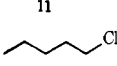
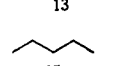
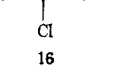
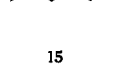
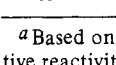
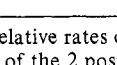
Reactions of 2-Bromo-1-chloro-2,3-dimethylbutane (2) and 3-Bromo-1-chloro-2,3-dimethylbutane (3) with Bromine. In order to determine whether both **2** and **3** are intermediates in the formation of **4** by the bromination of **1**, the isomeric dihalides were synthesized and subjected to the reaction conditions. Both compounds reacted under the bromination conditions employed to produce primarily **4** and a small amount of **5**.

Since competitive reactions are convenient for determining ratios of rate constants, a competitive bromination of **2** and **3** was run to determine their relative rates of reaction. Samples removed at different times were analyzed by gas chromatography¹⁴ to determine the ratio of reactants. The data for nine samples from two different reactions gave a k_2'/k_3' ratio of 3.4 ± 0.5 . The pseudo-first order kinetics of the separate reactions of **2** and **3** with bromine were also determined. The ratio of the experimental rate constants (nonlinear least squares; $k_2' = 2.55 \times 10^{-4} \text{ s}^{-1}$ and $k_3' = 6.16 \times 10^{-5} \text{ s}^{-1}$) is 4.1, a value nearly agreeing, within experimental error, with the competitive determination. The absolute values of k_2' and k_3' vary somewhat from determination to determination, probably because of slight variations in conditions. We are primarily concerned at present not with the absolute values of these rate constants but with their ratio, which shows that **2** reacts with bromine faster than does **3**. Since **2** reacts faster than **3** and its concentration in the mixture from **1** is always greater than that of **3**, it must be formed faster than **3** in the reaction of **1** with bromine.

Other Competitive Brominations. The results of the competitive photobromination of several alkane-alkyl chloride pairs are listed in Table II. These data indicate that the reaction of a tertiary site is accelerated by a neighboring chlorine, while the reaction at a secondary site is retarded.

1-Chloro-2,3-dimethylbutane (**1**) reacts 2.23 times faster with bromine than does 2,3-dimethylbutane (**9**). The rate enhancement at the position vicinal to chlorine was calculated by "correcting" the overall relative rate of **1** for the contribution from substitution at the 3 position (0.14 relative to 1.0 at

Table II. Relative Rates of Hydrogen Abstraction by Bromine Atoms

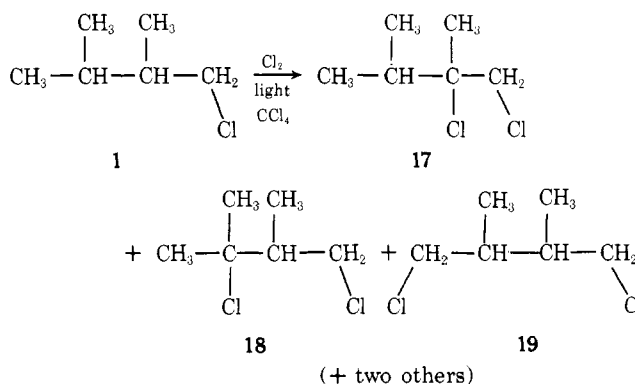
Reactants	Temp, °C	$(k_A/k_B)_{\text{obsd}}^a$	$(k_A/k_B)_{\text{per H}}$
A B			
 	32	2.23 ± 0.27	3.91 ± 0.47^b
 	32	2.20 ± 0.19	4.40 ± 0.38
 	19	3.61 ± 0.50	3.61 ± 0.50
 	19	4.94 ± 0.55	4.94 ± 0.55
 	32	5.04 ± 0.45	5.04 ± 0.45
 	26	0.39 ± 0.05	0.39 ± 0.05^c
 	26	1.11 ± 0.10^d	0.43 ± 0.05^e

^a Based on relative rates of disappearance of reactants. ^b The relative reactivity of the 2 position in **1**; see text. ^c Average for all secondary positions. ^d 3-Chloropentane reacts to give primarily geminal substitution; only 26% of the product results from vicinal substitution. ^e Relative reactivity of vicinal CH_2 in **16** to CH_2 in **15**.

the 2 position; $k_2/k_3 = 7$) and for the presence of two equivalent tertiary hydrogens in **9**. The rate at the 2 position in **1** relative to a tertiary hydrogen in **9**, therefore is $2.23 \times 1/1.14 \times 2 = 3.91$. Neighboring chlorine enhances the reactivity of the 2 position relative to the 3 position in **1** sufficiently to make the overall rate of **1** higher than that for **9**. This result is opposite to that expected for an electron-withdrawal effect alone (which is manifested at the 3 position in **1**; rate relative to one hydrogen in **9**, 0.55) and must be attributed to an anchimeric effect of the chloro substituent.

Quite similar rate enhancements are observed for the tertiary hydrogen in 2-chloro-2,3-dimethylbutane (**10**) relative to the one in **9** and for that in 1-chloro-2-methylpropane (**11**) relative to the one in 2-methylbutane (**12**)¹⁵ or in 2-methylhexane (**13**). This rate enhancement value of about 4 for a chloro substituent is substantial but considerably less than that reported^{8d} for a bromo substituent (factor of 27.3; 2-bromo-2,3-dimethylbutane vs. **9**). A chloro substituent is therefore not as effective in stabilizing the transition state for vicinal tertiary hydrogen abstraction as is a bromo substituent.

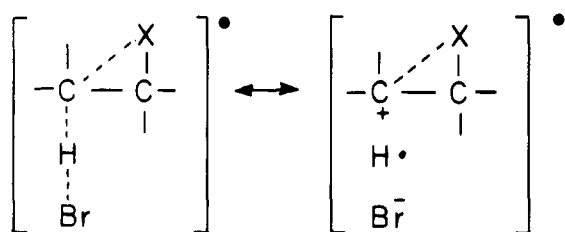
In comparison with these brominations, attack by chlorine atom shows much less preference for a tertiary position vicinal to a chloro substituent. Photoinitiated chlorination of **1** at 30–40 °C produces mainly **17**, **18**, and **19**, in relative amounts



of 3:4:5, respectively. The relative amounts of **18** and **19** are normal for isomeric tertiary (1 H) and primary (6 H) chlorination products. The significant difference in selectivity by bromine and chlorine is well known and is associated with the degree of C-H bond breaking in the transition state.⁵ The greater degree of C-H bond breaking with bromine attack allows a bridging contribution from neighboring halogen to become more significant than it is with chlorine attack. When the reactivity and selectivity of chlorine atom are altered by lowering the reaction temperature, however, some favorable kinetic contribution from a vicinal chloro substituent, even in chlorination, is indicated. A 4:3 ratio of products **17:18** was obtained by chlorination at -70°C (chloroform solvent). The selectivity of bromine atom for a position vicinal to a bromo substituent is also enhanced by lowering the reaction temperature.^{8a,b}

Neighboring chlorine does not enhance the abstraction of a vicinal secondary hydrogen by bromine atom. The overall relative reactivity of 1-chloropentane:pentane (**14:15**; Table II) is 0.39:1, and vicinal substitution is less extensive than substitution at the other secondary positions.⁶ 3-Chloropentane (**16**) reacts slightly faster with bromine than does pentane (**15**), but the principal product is 3-bromo-3-chloropentane, not 2-bromo-3-chloropentane. Favored substitution geminal to a chlorine in bromination reactions has been reported previously.^{6,16} When the contribution of the geminal substitution (74%) to the overall relative rate of bromination of **16** is subtracted, substitution vicinal to the chloro substituent is found to be retarded (relative rate per H, 0.43).

A bromo substituent is more effective in lowering the activation energy for vicinal hydrogen abstraction than is a chloro substituent, a result consistent with the smaller size and polarizability of the chloro substituent, which is therefore less able to interact with the developing radical center. The developing radical center itself makes a significant contribution, however, for chloro participation shows up only at a tertiary position and bromo participation shows up at both secondary and tertiary positions but not at a primary one. These comparisons of bromo and chloro substituents are conveniently and convincingly rationalized in terms of polar contributions to the radical transition states for hydrogen abstraction reactions (**20**).



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The electron-donor abilities of incipient alkyl radicals lie in the order tertiary > secondary > primary. As the transition state for hydrogen abstraction is being approached, the polar contribution—i.e., electron donation from the alkyl center to the attacking bromine atom—will become more important to the actual structure (and energy) of the transition state. Electron depletion at a secondary alkyl position, but not a primary one, is sufficient to lead to participation (bridging) and further lowering of the transition state energy by neighboring bromine, but only with a tertiary alkyl position is electron depletion sufficient for effective participation by the smaller, less polarizable neighboring chlorine. At both secondary and tertiary positions, the larger, more polarizable bromo substituent is a better neighboring participant than is the chloro substituent.¹⁷

Experimental Section

NMR data were obtained with a Varian Associates A-60A, HA-100, or Perkin-Elmer R12B spectrometer and are reported relative to internal tetramethylsilane. GC data were obtained with a Hewlett-Packard 700 gas chromatograph equipped with a hydrogen flame detector and a 10 ft \times $\frac{1}{8}$ in. aluminum column packed with Carbowax 20M on Chromosorb P. Elemental microanalyses were by R. Seab of these laboratories.

All alkyl halides and alkanes used as reagents were washed successively with concentrated sulfuric acid, water, saturated sodium bicarbonate solution, and water, dried over 4A molecular sieve, and distilled before use. Each reagent gave only one GC peak. Carbon tetrachloride was distilled and stored over 4A molecular sieve.

1-Chloro-2,3-dimethylbutane. During 3.5 h, ~ 0.2 molar equiv of chlorine was swept by a nitrogen stream into 2,3-dimethylbutane irradiated by a clear 150-W tungsten lamp placed 1 in. from the reaction flask. From the mixture, 1-chloro-2,3-dimethylbutane was isolated (10% yield) by distillation through a Teflon spinning band column: bp $122\text{--}124^{\circ}\text{C}$; $^1\text{H NMR}$ (CCl_4) δ 0.86 and 0.93 [pair of d, $J = 6.5$ Hz, 6, $(\text{CH}_3)_2\text{C}$], 0.96 (d, $J = 6.5$ Hz, 3, CH_3C), 1.7 (m, 2, CHCH), and 3.4 (m, 2, CH_2Cl).

A slower, but cleaner, continuous chlorination procedure based on a Soxhlet extractor was devised. In a 500-mL flask equipped with the Soxhlet extractor (without extraction thimble), 2,3-dimethylbutane was continually refluxed through the extractor while a dilute stream of chlorine in nitrogen was bubbled through the material in the extractor. During this addition the Soxhlet portion of the apparatus was irradiated with a clear, 150-W tungsten lamp situated 2 in. from the solution. Irradiation and chlorine addition were continued for 8 days. Unreacted starting material was removed by distillation under normal pressure, and the residue was distilled through a Teflon spinning band column to yield (12%) 1-chloro-2,3-dimethylbutane (**1**) bp $123.5\text{--}124^{\circ}\text{C}$. GC analysis showed that the product was obtained in greater than 99% purity.

Synthesis of 2-Bromo-1-chloro-2,3-dimethylbutane (2). Acid-catalyzed chlorination of 3-methyl-2-butanone²⁰ gave a 34% yield of **1-chloro-3-methyl-2-butanone**: bp $68\text{--}69^{\circ}\text{C}$ (33 mm); $^1\text{H NMR}$ (CCl_4) δ 1.15 [d, $J = 6.9$ Hz, 6, $(\text{CH}_3)_2\text{C}$], 2.95 (septet, $J = 6.9$ Hz, 1, Me_2CH), 4.15 (s, 2, CH_2Cl). The chloro ketone was converted, by treatment with methylmagnesium bromide in ether solution at dry ice temperature, to **1-chloro-2,3-dimethyl-2-butanol** in 38% yield: bp $33\text{--}34^{\circ}\text{C}$ (1 mm); n_D^{20} 1.4510 [lit.²¹ bp 45.6°C (3–5 mm), n_D^{20} 1.449]; $^1\text{H NMR}$ (CCl_4) δ 0.91 [pair of d, $J = 7$ Hz, 6, $(\text{CH}_3)_2\text{C}$], 1.12 (s, 3, CH_3CO), 1.8 (broad multiplet, 1, Me_2CH), 1.9 (s, variable with concentration, 1, OH), 3.51 (center spike of distorted, overlapping pair of d, $J = 13$ Hz, 2, CH_2Cl). Heating a stirred mixture of the chloro alcohol and concentrated hydrobromic acid at 100°C for 5 h led to the isolation (14% yield) of **2-bromo-1-chloro-2,3-dimethylbutane (2)**: bp $45\text{--}46^{\circ}\text{C}$ (15 mm); n_D^{20} 1.4842; $^1\text{H NMR}$ (CCl_4) δ 1.05 [pair of d, $J = 6.7$ Hz, 6, $(\text{CH}_3)_2\text{C}$], 1.84 (s, 3, CH_3CBr), 1.5 to 2.15 (broad multiplet, 1, Me_2CH), and 3.93 (pair of d, $J = 11.3$ Hz, 2, CH_2Cl). This NMR spectrum is virtually identical, except for the expected changes in chemical shift, with the published NMR spectrum of 1,2-dibromo-2,3-dimethylbutane.²²

Synthesis of 3-Bromo-1-chloro-2,3-dimethylbutane (3). Methyl 3-chloro-2-methylpropionate²³ was prepared by adding dry hydrogen chloride to methyl methacrylate at 60°C : bp $55\text{--}57^{\circ}\text{C}$ (15 mm); $^1\text{H NMR}$ (CCl_4) δ 1.25 (d, $J = 6.9$ Hz, 3, CH_3), 2.8 (m, 1, CHMe_2), 3.68 (s + m, 5, $\text{OCH}_3 + \text{CH}_2\text{Cl}$). The addition was slow; after 50 h, 68% of the methyl methacrylate was recovered and 21% of distilled product was isolated; after 30 days, the yield of product was about 75%. By reaction with methylmagnesium iodide in ethyl ether solution at 0°C , the chloro-substituted ester was converted to **4-chloro-2,3-dimethyl-2-butanol**: bp $45\text{--}48^{\circ}\text{C}$ (2.5 mm); n_D^{20} 1.5014; $^1\text{H NMR}$ (CCl_4) δ 1.06 (d, $J = 6.7$ Hz, 3, CH_3), 1.14 (s, 3, CH_3), 1.23 (s, 3, CH_3), 1.7 (bm, 1, Me_2CH), 2.8 (s, variable with concentration, 1, OH), 3.25 (dd, $J = 9.7$ and 10 Hz, 1, one of CH_2Cl), 3.85 (dd, $J = 3.3$ and 10 Hz, 1, other of CH_2Cl). From a mixture of the alcohol (0.15 mol), petroleum ether (250 mL), concentrated hydrobromic acid (30 mL), and hexamethylphosphoramide (5 mL) which had been stirred overnight at room temperature was isolated at 20% yield of **3-bromo-1-chloro-2,3-dimethylbutane (3)**: bp $45.5\text{--}47^{\circ}\text{C}$ (3.5 mm); $^1\text{H NMR}$ (CCl_4) δ 1.20 (d, $J = 6.7$ Hz, 3, CH_3), 1.75 and 1.85 [two s, 3 each, $(\text{CH}_3)_2\text{CBr}$], 1.5–2.2 (broad multiplet, 1, CCHCH), 3.30 (dd, $J = 9.3$ and 10 Hz, 1, one of CH_2Cl), and 3.93 (dd, $J = 3.3$ and 10.6

Hz, 1, other of CH_2Cl .) This NMR spectrum is virtually identical, except for the expected small changes in chemical shift, with the published NMR spectrum of 1,3-dichloro-2,3-dimethylbutane.²²

Brominations of Haloalkanes. General Procedure. A solution of alkyl halide in carbon tetrachloride (0.1–0.5 M) was placed in a flask equipped with a reflux condenser and a gas inlet tube. The reaction flask was irradiated with a clear, 150-W tungsten lamp situated 1 in. from the flask while a stream of nitrogen was directed onto the surface of liquid bromine and then into the alkyl halide solution until all of the bromine had been added. During the addition, the reaction mixture was stirred with an air-driven magnetic stirrer and cooled as necessary with a stream of air on the outside of the flask or with a cold finger condenser inserted into the solution. The light was then turned off, and the nitrogen allowed to bubble for another 30 min.

1-Chloro-2,3-dimethylbutane (1) in 25 mL of solution (0.470 M) was brominated according to the general procedure. Samples were removed at various times, quenched with 5% sodium thiosulfate solution, washed with saturated sodium bicarbonate and with water, dried over 4A molecular sieve, and analyzed by GC. The carbon tetrachloride served as an internal standard for the GC analysis. The data are summarized in Table I and Figure 1. In other experiments, concentration of the reaction mixture by distillation after all the bromine (0.25 molar equiv) had reacted led to the isolation of crystalline 1-bromo-2,3-bis(bromomethyl)-4-chloro-2-butene (**4**), in yields as high as 65% (based on bromine): mp 138–140 °C (crystallized from CCl_4 ; lit.²⁴ mp 136–138 °C); ^1H NMR (CCl_4) δ 4.15 (s, 6, CH_2Br) and 4.25 (s, 2, CH_2Cl). Anal. Calcd for $\text{C}_6\text{H}_8\text{Br}_3\text{Cl}$: C, 20.28; H, 2.27. Found: C, 20.10; H, 2.29. The mass spectrum corresponds to that published for **4**.²⁴

When the bromine was added all at once to a solution of **1** in carbon tetrachloride (about 0.5 M) rather than slowly in a nitrogen stream, the product was shown (by NMR analysis) to be largely **5** [^1H NMR (CCl_4) δ 2.02 (bs, 6, $(\text{CH}_3)_2\text{C}$), 2.09 (bs, 3, CH_3C), and 3.92–4.37 (AB q, $J = 12$ Hz, 2, CH_2Cl)]. When the reactant solution was 4 M in both **1** and bromine, **5** precipitated from the solution.

The dependence of the reaction on light was determined by use of a solution of **1** (10%) and bromine (several drops) in carbon tetrachloride in an NMR tube. After the solution had been kept in the dark at about 29 °C for 1 h and then for 16 h, the NMR spectra of it showed no absorptions for **2**, **3**, or **4**, even at greatly increased amplitude.

2-Bromo-1-chloro-2,3-dimethylbutane (2), 2.5 mmol and **3-bromo-1-chloro-2,3-dimethylbutane (3)**, 5 mmol were separately brominated according to the general procedure. With **3**, a strong bromine color persisted throughout the addition (1.25 mmol in 1 h), but with **2**, only a faint bromine color was maintained by faster addition (2.5 mmol in 1.5 h). The mixtures were washed and concentrated. From each mixture, solid **4** was isolated, and the supernatant liquid was shown by NMR analysis to be mainly reactant dihalide plus some **5**. Separate experiments, during which several samples were removed at different times and analyzed gave the following data (time in s, concentration of **2** in mM, concentration of **3** in mM): 0, 49.8, 49.8; 600, 42.6, 47.1; 1500, 30.4, 42.6; 2400, 28.4, 42.2; 3900, 15.5, 32.2; 5225, 10.7, 31.1. From these data, the pseudo-first order rate constants for these brominations were found to be $k_2' = 3.0 \times 10^{-4} \text{ s}^{-1}$ and $k_3' = 9.6 \times 10^{-5} \text{ s}^{-1}$.

An experiment in the dark in an NMR tube containing a solution of **2**, bromine, and carbon tetrachloride produced no NMR spectral evidence of **4** after 1 h at about 29 °C.

Intermolecular Competitive Brominations. According to the general bromination procedure above, a mixture of approximately equal, accurately measured amounts of chloroalkane and alkane (~2.5 mmol for **2** and **3**; 7–10 mmol for others) in carbon tetrachloride (25 mL total volume) was brominated. The time for introduction of the bromine was 100–250 min. A sample of the solution was removed at several different times, quenched by 5% sodium thiosulfate solution, washed with saturated sodium bicarbonate solution and with water, dried over 4A molecular sieve, and analyzed by GC. At least three GC analyses for remaining reactants were made on each sample; the carbon tetrachloride served as an internal standard. The GC data were used for the calculation of the rate ratio, $k_{\text{chloroalkane}}/k_{\text{alkane}}$.¹⁴ The data for the several competitions are summarized as follows in the form reactants, temperature, calculated rate ratio: **2** and **3**, 32 °C, 3.4 \pm 0.5; 1-chloro-2,3-dimethylbutane and 2,3-dimethylbutane, 32 °C, 2.23 \pm 0.27; 2-chloro-2,3-dimethylbutane and 2,3-dimethylbutane, 32 °C, 2.20 \pm 0.19; 1-chloropentane and pentane, 26 °C, 0.39 \pm 0.05; 3-chloropentane and pentane, 26 °C, 1.11 \pm 0.10; 1-chloro-2-meth-

ylpropane and 2-methylbutane, 19 °C, 3.61 \pm 0.50 (When this pair was brominated with a mixture of bromine and NBS^{8d} at 20 °C, the rate ratio was 3.66 \pm 0.23.); 1-chloro-2-methylpropane and 2-methylhexane, 32 °C, 5.04 \pm 0.45 (When this pair was brominated at 19 °C by adding bromine in portions instead of in a nitrogen stream, the rate ratio was 4.94 \pm 0.55.); 2-methylbutane and 2-methylhexane, 19 °C, 1.33 \pm 0.11 (calcd from RCl-RH competitions, 1.37).

Bromination of 3-Chloropentane (13). A 10% solution of **13** in carbon tetrachloride was brominated in the usual way. NMR analysis of the reaction mixture showed the principal product to be 3-bromo-3-chloropentane: ^1H NMR (CCl_4) δ 1.16 (t, $J = 7$ Hz, 6, CH_3) and 2.23 (q, $J = 7$ Hz, 4, CH_2). GC analysis showed two products to be present; the earlier, larger peak (74%) was assigned to 3-bromo-3-chloropentane and the later, smaller one (26%) to 2-bromo-3-chloropentane.

Bromination of 2-Chloro-2,3-dimethylbutane (10). A 10% solution of **10** in carbon tetrachloride was brominated in the usual way. NMR analysis of the reaction mixture (at 100% reaction) showed that only one product, 2-bromo-3-chloro-2,3-dimethylbutane, was produced: ^1H NMR (CCl_4) δ 1.81 [s, 6, $\text{CCl}(\text{CH}_3)_2$] and 1.93 [s, 6, $\text{CBr}(\text{CH}_3)_2$]. There was no evidence for the formation of 2,3-dibromo-2,3-dimethylbutane (δ 2.01), the product to be expected from an elimination-addition sequence, or of 1,4-dibromo-2,3-bis(bromomethyl)-2-butene.

Bromination of 2,3-Dimethylbutane (12). A 10% solution of **12** in carbon tetrachloride was brominated in the usual way. NMR analysis of the reaction mixture showed that only one product, 2,3-dibromo-2,3-dimethylbutane, was produced: ^1H NMR (CCl_4) δ 2.01 (s). This spectrum was identical with that of the 2,3-dibromo-2,3-dimethylbutane produced by the addition of bromine to 2,3-dimethyl-2-butene.

Chlorination of 1. A procedure substantially the same as that for the brominations was used for the chlorination (0.25 molar equiv of chlorine) of **1** at 30–40 °C. The reaction mixture was partially separated by distillation at reduced pressure (2 mm) through a short-path distillation apparatus, or better, by preparative GC on a 0.5 in. \times 9.8 ft Carbowax 20M column at 150 °C. The major products, identified by their ^1H NMR (CCl_4) spectra, were, in order of increasing GC retention time, 1,2-dichloro-2,3-dimethylbutane²² (**17**) [δ 1.05 (2 d, 6, $J = 6.6$ Hz, $(\text{CH}_3)_2\text{CH}$), 1.64 (s, 3, CH_3CCl), 2.25 (septet, 1, $J = 6.6$ Hz, $(\text{CH}_3)_2\text{CH}$), and 3.74 (2 d, 2, $J = 11.1$ Hz, CH_2Cl)]; 1,3-dichloro-2,3-dimethylbutane (**18**) [δ 1.20 (2 d, 3, $J = 6.7$ Hz, CH_3CH), 2.03 and 2.12 (s, 3 each, $(\text{CH}_3)_2\text{CCl}$), 1.7–2.3 (m, 1, MeCH), 3.30 (dd, 1, $J = 8.7$ and 10.6 Hz, one of CH_2Cl), and 3.90 (dd, 1, $J = 3.4$ and 10.6, other of CH_2Cl)];¹⁷ and 1,4-dichloro-2,3-dimethylbutane (**19**) [δ 0.92–1.15 (2 d, 6, $J = 6$ Hz, CH_3), 1.75–2.3 (m, 2, MeCH), and 3.43–3.63 (m, 4, CH_2Cl)]; this spectrum is consistent with a mixture of meso and racemic **19**. Irradiation of the δ 1.75–2.3 m at different positions decoupled only one of the d at δ 0.92–1.15 at a time. The proportions of **17**:**18**:**19** were determined by NMR and GC data to be 3:4:5. Two minor components (GC peaks) were not identified but, on the basis of GC retention times, were presumed to be other isomeric dichlorides.

When the chlorination of **1** was carried out at –70 °C in chloroform (lower freezing point than carbon tetrachloride), the ratio of products **17**:**18** was found to be 4:3.

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- (11) The chloro substituent in radicals **6** and **7** must promote loss of bromine atom, because bromination of 2,3-dimethylbutane under the same conditions gave only 2,3-dibromo-2,3-dimethylbutane.
- (12) A mixture of **8** and its isomer, 3-chloro-2,3-dimethyl-1-butene (3:2 by GC and NMR data), prepared by addition of hydrogen chloride to 2,3-dimethyl-1,3-butadiene at -30°C [L. F. Hatch and G. E. Journey, *J. Am. Chem. Soc.*, **75**, 3712 (1953)] and dissolved in carbon tetrachloride, was rapidly converted by excess bromine to products identified by ^1H NMR (CCl_4) data as a 3:2 mixture of **5** and its isomer, 1,2-dibromo-3-chloro-2,3-dimethylbutane.
- (13) If $[\text{Br}\cdot]$ is constant and selective reversal of hydrogen abstraction from isomeric positions is unimportant, the rate of disappearance of **1** can be represented by the pseudo-first order equation
- $$-\frac{d[\mathbf{1}]}{dt} = (k_2 + k_3) \quad [1]$$
- from which the integrated expression
- $$\ln(1 - F) = -(k_2 + k_3)t$$
- is obtained (F = fraction of reaction). By a nonlinear least-squares treatment, the slope of the linear plot was $-2.90 \times 10^{-4} \text{ s}^{-1}$.
- (14) Analysis by GC was performed to determine the ratio of reactants relative to carbon tetrachloride in the unreacted starting mixture and in each sample. The relative rate was then calculated from the relationship
- $$\frac{k_{\text{halide}}}{k_{\text{alkane}}} = \frac{\log \frac{(\text{halide}/\text{CCl}_4)_{\text{final}}}{(\text{halide}/\text{CCl}_4)_{\text{initial}}}}{\log \frac{(\text{alkane}/\text{CCl}_4)_{\text{final}}}{(\text{alkane}/\text{CCl}_4)_{\text{initial}}}}$$
- For further discussion of this method, see ref 5.
- (15) For the 11:12 competition, the rate ratio was not changed significantly by the addition of *N*-bromosuccinimide to the reaction mixture to remove hydrogen bromide and maintain bromine concentration.^{8d} Earlier workers reported 0.4 for this rate ratio.^{8d} Since our value of 3.6 is consistent with all the other competitions we measured between a vicinal tertiary position in RCl and a tertiary position in the alkane, we are not able to account for the lower value reported.
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Cyclohexadienyl Cations. 7. Kinetics and Mechanism of the Acid-Catalyzed Dienol-Benzene Rearrangement

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Abstract: The rates of the acid-catalyzed dienol-benzene rearrangement for 4-trichloromethyl-4-methylcyclohexadienol (**3**) and 4,4-dimethylcyclohexadienol (**4**) are reported. While **3** undergoes the dienol-benzene rearrangement in concentrated mineral acids, **4** undergoes the same reaction in dilute buffers. Interestingly **4** also undergoes a concomitant allylic rearrangement not observed for **3**. Certain mechanistic conclusions for **3** and **4** are derived and compared. α -D effects are reported for both **3** and **4**. Stereochemical assignments for both isomers of **3** and of solvolysis products are made using NMR shift reagents.

For some time now we have been interested in the molecular details of the dienone-phenol and related rearrangements.³⁻⁸ All of the results thus far obtained in our laboratory, as well as the work of Waring,⁹ provide substantial support for the mechanism outlined in Scheme I for the dienone-phenol rearrangement.

In this paper we report results for the dienol-benzene rearrangement, a reaction which is formally similar to the dienone-phenol rearrangement but which provides several interesting differences. A representative scheme for this reaction is provided in Scheme II.

A notable difference between this reaction and the dienone-phenol rearrangement is the absence of a protonated

carbonyl group as an intermediate. This is thought to seriously affect the kinetic acidity dependence of the dienone-phenol rearrangement because of strong intermolecular hydrogen bonding to neighboring water molecules. In the dienol-benzene rearrangement no such interaction is possible and it is of some significance to determine the kinetic acidity dependence for this reaction.

Although 4,4-dimethylcyclohexadienone (**1**) undergoes the dienone-phenol rearrangement readily,³⁻⁹ 4-trichloromethyl-4-methylcyclohexadienone (**2**) protonates in acid, but does not rearrange unless very forcing conditions are used, where more complex reactions can occur.¹⁰ In contrast, both of the corresponding dienols **3** and **4** do rearrange in acid,