potassium carbonate was added to neutralize the solution. The basic solution was extracted with ether, and the ether extract was dried over potassium carbonate and fractionally distilled. The fraction boiling at 157–177° (10 mm) crystallized on standing to give 16.0 g (67%) of crude *trans*-1-methyl-4-phenyl-3-piperidinol (4), mp 50–72°. Recrystallization of the solid from *n*-heptane gave an analytical sample, mp 82.0–84.5°.

Anal. Calcd for $C_{12}H_{17}NO$: C, 75.35; H, 8.96. Found: C, 75.63; H, 8.92.

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Chlorination of Unsaturated Materials in Nonpolar Media. VII. Butadiene: a Reevaluation[1]

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Interaction of butadiene and chlorine in nonpolar solvents not only produces products by polar addition as generally accepted, but also produces free radicals. In fact, previous investigators of this proposed electrophilic reaction were most likely studying a radical chain reaction. In the present study, the spontaneously initiated radical pathway and the polar pathway have been separated. The former is characterized by addition of chlorine atom to butadiene at a rate *not* particulary accelerated over that of a terminal olefin to produce an allylic radical which reacts with molecular chlorine to produce 3,4-dichloro-1-butene (I) and *trans*-1,4-dichloro-2-butene (II) in a ratio of 22:78. The polar pathway, observable in the presence of radical inhibitors such as oxygen, produces I and II in a ratio of *ca.* 55:45; this polar reaction is *slower* than that of 1-butene. In a normal dark chlorination in the absence of inhibitors, the radical pathway dominates in neat olefin, but is gradually replaced by the polar pathway as nonpolar diluents are added. This gross behavior is analogous to that previously observed for linear olefins.

Chlorination of butadiene in nonpolar solvents such as carbon disulfide, ligroin, or chloroform at *ca.* 0° was first reported by Muskat and Northrup[2] to give a mixture of 3,4-dichloro-1-butene (I) and 1,4-dichloro-2-butene (II) richer in the former. Later workers obtained varying amounts of I and II;[3–6] however, formation of tetrachlorides and polymers[4,5] accompanied the dichloride products.

$$CH_2{=}CH{-}CH{=}CH_2 + Cl_2 \longrightarrow \underset{\text{I}}{CH_2{=}CH{-}CHClCH_2Cl} + \underset{\text{II}}{trans\text{-}ClCH_2CH{=}CHCH_2Cl}$$

Products I and II are thermally stable below 130°, and hence the products appear to be kinetically controlled; they can be isomerized by zinc chloride to an equilibrium mixture containing 67–70% of II.[5] Carbonium ion intermediates were invoked by Muskat and Northrup[2] although the concept of allylic resonance was not yet clearly understood. This chlorination has become a standard textbook example[7–10] of electrophilic attack on an unsaturated system followed by kinetic rather than thermodynamic control of product formation. Failure to detect the *cis* isomer of II among the products led Mislow and Hellman[11] to conclude that attack occurred at only one of the double bonds to the exclusion of simultaneous attack at both termini of a cisoid conformation of butadiene.

Our recent finding[12] that interaction of many simple olefins with chlorine in nonpolar solvents leads to production of free radicals and hence to radical rather than polar chlorination prompted us to reinvestigate butadiene, the simplest of conjugated dienes. We wish to report that chlorination of butadiene under conditions comparable to those previously described[2–6] is largely a radical process rather than a polar process as generally assumed.

Results

Treatment of a 2.5 *M* solution of butadiene in carbon tetrachloride with $^1/_3$ equiv of gaseous chlorine diluted with nitrogen in the absence of light at −9° on a preparative scale led to rapid reaction; distillation afforded the expected dichlorides I and II in *ca.* 50% yield along with a liquid residue whose chlorine analysis suggested considerable polychlorination. To obtain quantitative information and avoid secondary reactions, chlorination was run to much lower conversion (always <10%) with slower input rates. Glpc examination of such reaction mixtures revealed I and II as the only significant volatile products (two minor products will be discussed below). However, in several runs under these conditions, small quantities of insoluble material were formed. A study of the effect of butadiene concentration in 1,1,2-trichlorotrifluoroethane as solvent was carried out first. The 1,4-dichloride II makes up 75–80% of the monomeric product at diene concentrations above mole fraction $n = 0.2$; however, below this level, the value of (II)/(I + II) decreases smoothly to *ca.* 0.50 at $n = 0.02$, the lowest concentration studied,

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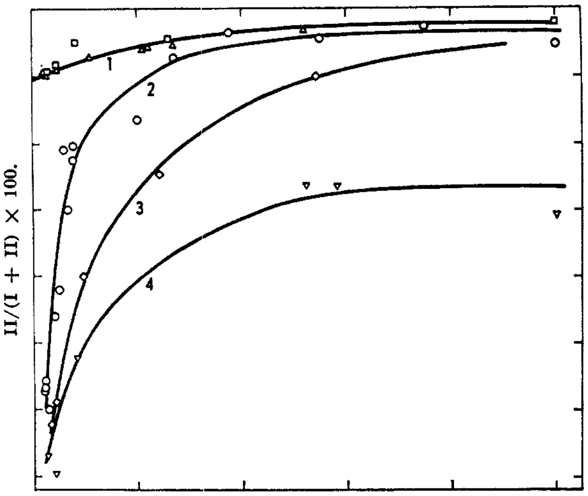


Figure 1.—Dependence of product ratio from chlorination of butadiene at −9°: 1 (□), $C_2F_3Cl_3$, N_2, illuminated; 1 (△), $C_2F_3Cl_3$ + cyclohexane, N_2, illuminated; 2 (○), $C_2F_3Cl_3$, N_2, dark; 3 (◇), cyclohexane, N_2, dark; 4 (▽), $C_2F_3Cl_3$ + cyclohexane, O_2, dark.

as shown in curve 2 of Figure 1. Material balances were checked approximately by use of an internal standard and glpc analysis, and the yields of (I + II) fell in the range 60–95% in random fashion; low yields tended to correlate with formation of insoluble material. The observed effect of concentration on product ratios is reminiscent of the behavior of linear olefins,[12] in which case a solely radical pathway at high concentration is gradually replaced by a polar pathway as the olefin concentration is decreased. In this case, as for olefins,[12] chlorination with external illumination in an attempt to achieve mainly radical reaction gave product ratios essentially independent of concentration and (II)/(I + II) = 0.77 ± 0.02 as shown in curve 1 of Figure 1. These results suggested (1) that purely radical chlorination of butadiene gives I and II in a ratio of *ca.* 22:78; (2) that dark chlorination of concentrated solutions of butadiene is largely an internally initiated radical process; and (3) that ionic chlorination becomes important only at low diene concentration and is characterized by (II)/(I + II) <0.50. This behavior parallels that of linear olefins.

Two lines of additional evidence support the above hypothesis. Firstly, use of cyclohexane as the diluent gave chlorocyclohexane as an additional product. Results of runs under nitrogen with external illumination are shown in entries 1–6 of Table I. Again (II)/(I + II) is essentially constant at 0.77 ± 0.02. The relative reactivity of butadiene compared with that of cyclohexane can be calculated (Experimental Section) and this value shows no trend either with diene concentration or diene: cyclohexane ratio. However, comparable runs in the dark (entries 7–11 of Table I and curve 3 of Figure 1) showed that the apparent relative reactivity of butadiene was the same as in illuminated runs *only* at high diene concentration but increased sharply as the diene concentration was decreased below $n \sim 0.2$. Concurrent with this increase in apparent reactivity was a decrease in the ratio (II)/(I + II). Such behavior is predicted if lowered concentration in the dark leads to more and more participation of a polar pathway which consumes only butadiene superimposed on the radical pathway which consumes both substrates.

TABLE I

PRODUCT DISTRIBUTIONS FROM CHLORINATION OF BUTADIENE AT −9°

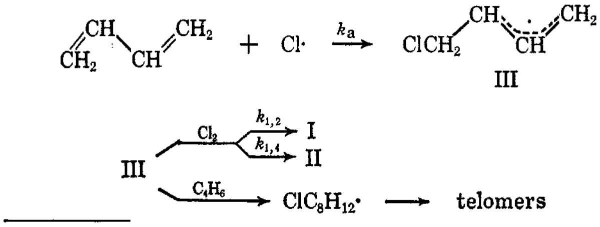
Entry	Mole fraction: Butadiene	Mole fraction: Cyclohexane	Mole fraction: $C_2F_3Cl_3$	[II/(I + II)] × 100	Yield,[a] %	Relative reactivity, C_4H_6/C_6H_{12}[b]
	Nitrogen Illumination					
1	0.52	0.48	...	78.4	100	15.4
2	0.27	0.73	...	74.7	68	16.6
3	0.22	0.084	0.70	77.2	102	19.5
4	0.21	0.25	0.54	77.0	78	20.7
5	0.047	0.050	0.90	75.5	94	18.2
6	0.024	0.016	0.96	75.3	88	18.2
	Nitrogen Darkness					
7	0.54	0.46	...	75.0	112	20.6
8	0.24	0.22	0.54	67.7	99	30.6
9	0.095	0.080	0.82	60.0	104	52.9
10	0.042	0.043	0.92	50.6	95	100
11	0.033	0.014	0.95	48.9	91	133
	Oxygen Darkness					
12	0.58	0.42	...	66.8	65	110
13	0.025	0.019	0.96	46.6	90	>2000

[a] Yield of (I + II) as determined by glpc analysis with internal standard. [b] Defined as $[12(I + II)/(C_6H_{11}Cl)] \cdot [(C_6H_{12})_0/(C_4H_6)_0]$.

Secondly, we considered the effect of oxygen which served as an effective radical inhibitor in our olefin studies.[12] However, with butadiene, chlorination under oxygen was more complex. Insoluble products (which have not been investigated further) were formed along with I and II especially at high diene concentration. In 1,1,2-trichlorotrifluoroethane and/or cyclohexane as solvent, the ratio (II)/(I + II) was consistently lower than in comparable runs at the same concentration without oxygen; however, the ratio was still concentration dependent (curve 4 of Figure 1). At high diene concentration inhibition is not complete as evidenced by residual attack on cyclohexane (entry 12 of Table I). However, at the lowest diene concentration studied ($n = 0.02$), attack on cyclohexane was eliminated (entry 13), and hence here the polar reaction has apparently been isolated and is characterized by (II)/(I + II) ~0.45. The effectiveness of oxygen as an inhibitor in our previous systems undoubtedly results from conversion of reactive alkyl radicals into peroxy radicals which are relatively unreactive towards chain propagation with olefin or chlorine and hence lead to termination. With butadiene, such peroxy radicals add rather readily to diene, as evidenced by autoxidation studies,[13] and hence do not terminate chains effectively.

Discussion

The radical and polar pathway can be discussed separately. The chain steps for the radical reaction can be reasonably written as shown below.



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The value of k_a for 1-butene[12] is 11.7 (compared to $k_t \equiv 1.00$ for abstraction of a single cyclohexyl hydrogen) and that for 1-butyne[1] is 9.7. Considering that these substrates should add chlorine atom predominantly at the terminal position while butadiene is symmetrical (k_a is best expressed as 2×7.5–10), one notes that chlorine atom shows essentially no discrimination between a terminal acetylene, olefin, or diene. Once again the extreme lack of selectivity of chlorine atom is demonstrated.[12] For comparison, the relative rates of addition of methyl radical to propyne,[14] propylene,[15] and butadiene[16] at 65° are 1:2:185; butadiene is 18 times as reactive as 1-octene towards trichloromethyl radical.[17]

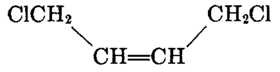
Secondly, the data give information concerning the fate of radical III. The occasional insoluble products, yields of <100%, and previous literature reports[4,5] of polymer formation suggest a certain fraction of telomerization which is, of course, dependent on chlorine concentration. However, this in no way effects the partitioning of III between products I and II; the observed results show $k_{1,4}/k_{1,2} \sim 78/22$. Various radical reagents have been added to butadiene, but only in selected cases has the kinetically controlled 1,4:1,2 product ratio been determined with care. Reaction with hydrogen bromide under conditions designed to promote radical reaction gave 1-bromo-2-butene with <5% 4-bromo-1-butene, the 1,2 product.[18] Both aliphatic and aromatic thiols also gave >95% 1,4 addition[19] as did protonated N-chlorodialkylamines.[20] However, *ca.* 3:1 ratios of 1,4 to 1,2 product have been reported for bromotrichloromethane[17] and *t*-butyl hypochlorite,[21] and cooxidation of butadiene with thiols, in which the allylic radical reacts with oxygen, gave a predominance of 1,2 product.[22] It has been suggested[19a,22] that the lower the activation energy for the chain-transfer step, the greater will be the percentage of attack at the more highly alkylated carbon atom; hence oxygen gives the highest observed amount of 1,2 product. The chlorine results are at least qualitatively consistent since chlorine molecule is a very effective chain-transfer agent.

Obviously butadiene and chlorine do interact to produce free radicals in similar fashion to linear olefins.[12] However, as we have pointed out previously,[12] the amount of radical reaction observed is a function of chain length as well as of initiating efficiency. Therefore, the present data give no quantitative measure of the relative efficiencies of the diene–chlorine and olefin–chlorine radical producing reactions.

The polar reaction is more difficult to evaluate quantitatively, although the present results suggest a 1,2:1,4 product ratio of *ca.* 55:45 under conditions of complete radical inhibition. Bromination of butadiene in a variety of nonpolar solvents under kinetically controlled conditions gave equal amounts of 1,2 and 1,4 products in a reaction assumed to be ionic;[23] whether this reaction has a radical component is not clear. Hydrogen bromide[18] and hydrogen chloride[24] each gave mainly 3-halo-1-butenes under polar conditions. Hence chlorination falls within the range of existing data, although the factors determining 1,2:1,4 product ratios in such polar additions are not well understood.[25] A recent theoretical model[26] has predicted more 1,2 product from addition of a proton acid than from the halogens.

Recently we have measured the relative rates of polar chlorination of a series of alkylated ethylenes in nonpolar solvents by use of oxygen inhibition of radical reactions[27] and have shown that such rates correlate rather well with the cumulative inductive properties of the alkyl groups on the double bond rather than with the stability of the expected carbonium ion. By comparable measurements, butadiene was shown to be considerably *less* reactive than 1-butene but more reactive than allyl chloride;[27] the difficulties associated with complete radical inhibition for butadiene did not allow a more quantitative assessment to be made. Although this result may seem surprising since polar addition to butadiene should generate a stabilized allylic carbonium ion, it is in agreement with our previous conclusions[27] that at the transition state for polar chlorination in nonpolar solvents, very little positive charge has developed on carbon. In that case the main role of the vinyl substituent (if one considers butadiene as vinylethylene) is an electron-withdrawing inductive effect.

Two minor products deserve comment. In all runs, both under radical and ionic conditions, a product with retention time equal to that of *cis*-1,4-dichloro-2-butene (IV) was detected but not isolated; it never exceeded 1.5% of the amount of II. Since butadiene exists predominantly in the transoid form, the failure to observe significant amounts of *cis* product is not surprising in view of the known configurational stability of resonance-stabilized allylic intermediates.[23,28] No special reactivity of the cisoid ground state need be invoked and the original conclusion of Mislow and Hellman[11] that the polar reaction does not proceed to any significant extent through 1,4 attack is correct. However, in light of the present results, it is difficult to determine what mixture of reaction paths these authors studied. In oxygen-inhibited runs, <5% of a volatile product having a retention time equal to that of 1-chlorobutadiene (V) and different from that of 2-chlorobutadiene was detected; if this tentative assignment is correct, a minor sequence of addition of positive chlorine followed by elimination of a proton is suggested for the polar pathway.



IV

$CH_2{=}CH{-}CH{=}CHCl$

V

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Experimental Section

Infrared spectra were determined as 10% carbon disulfide solutions on a Beckman IR-5A instrument; boiling points are uncorrected.

Materials.—Butadiene was Phillips research grade, 99.88% pure. Treatment of all other solvents and gases has been described previously.[12]

Reference Compounds.—3,4-Dichloro-1-butene (I) and *trans*-1,4-dichloro-2-butene (II) were obtained from Columbia Organic Chemicals; the latter was seriously contaminated with I and IV. *cis*-1,4-Dichloro-2-butene (IV) was prepared from the corresponding diol obtained by catalytic reduction of 2-butyn-1,4-diol according to the method of Mislow and Hellman[11] except that Lindlar's catalyst[29] was substituted for Raney nickel. 2-Chlorobutadiene in xylene solution was obtained from K & K Laboratories and served to established its retention time. Dichloride II was gradually heated with solid potassium hydroxide until a volatile product distilled off; the distillate was collected in toluene; and this solution served to establish the retention time of 1-chlorobutadiene (V).[2] Chlorocyclohexane and toluene are commercially available.

Product Isolation.—Butadiene (40 ml, 0.5 mole) was collected at −9° under a Dry Ice condenser and diluted with 200 ml of carbon tetrachloride. The mixture was flushed with nitrogen and 8.1 ml (0.17 mole) of liquid chlorine, condensed in a calibrated trap, was swept into the stirred mixture in 30 min in the absence of light at −9°. Glpc analysis showed I and II as the only significant volatile products with (II)/(I + II) = 0.71. Solvent was removed on a rotary evaporator and the residue distilled through an 18-in. spinning-band column. After a forerun, in which a minor amount of I was lost, the following fractions were collected: (1) 1.62 g, bp 44–47° (50 mm); (2) 9.03 g, bp 75–79° (50 mm); and (3) 5.91 g of liquid residue. Fraction 1 had an infrared spectrum consistent with that of commercial 3,4-dichloro-1-butene (I) and glpc analysis showed it to be >95% I. Fraction 2 had an infrared spectrum generally consistent with that reported[11] for *trans*-1,4-dichloro-2-butene (II); however, glpc analysis revealed 10% of I. The (II)/(I + II) ratio in recovered material is thus 0.77; this increase probably represents some loss of I during distillation since the individual isomers are thermally stable under the distillation and the glpc analysis conditions. Analysis of residue 3 showed C, 29.94; H, 3.77; Cl, 66.29. $(\mathrm{C_4H_6Cl_3})_x$ requires C, 30.08; H, 3.92; Cl, 66.05. This residue may well be a mixture of tetrachlorides and telomeric material.

Quantitative Chlorination Runs.—The general procedure and equipment have been described.[12] Butadiene was introduced as a gas and condensed by use of a Dry Ice condenser; 1,1,2-trichlorotrifluoroethane and cyclohexane were added as liquids. Initial concentrations, as well as final product ratios, wer edetermined by glpc analysis of a 1-μl aliquot (Micro-Tek snap sampler) on a Micro-Tek 2500-R instrument equipped with 2-m Perkin-Elmer "R" columns (polypropylene glycol) by use of a flame ionization detector.

Retention times in minutes at 92° and a helium flow of *ca.* 200 ml/min follow: V, 1.85; 2-chlorobutadiene, 2.1; toluene, 5.2; I, 8.0; chlorocyclohexane, 11.0; IV, 20.6; and II, 24.8. Areas and area calibration factors were determined as before.[12] Yields of (I + II) were calculated by addition of a known amount of toluene after reaction as an internal standard; comparison of the areas of I, II, and toluene with the amount of chlorine introduced (calibrated liquid trap) gave the yield. The relative reactivity of butadiene compared with cyclohexane was determined from the expression

$$\left[\frac{12(\mathrm{I}+\mathrm{II})}{(\mathrm{C_6H_{11}Cl})}\right]\left[\frac{(\mathrm{C_6H_{12}})_0}{(\mathrm{C_4H_6})_0}\right]$$

where $\mathrm{C_6H_{11}Cl}$ is chlorocyclohexane and $(\mathrm{C_6H_{12}})_0$ and $(\mathrm{C_4H_6})_0$ are the initial concentrations of cyclohexane and butadiene. Under purely radical conditions at low conversion, this value becomes equal to k_a/k_t, where k_a is the relative rate of addition of chlorine atom to butadiene as a whole and $k_t \equiv 1.00$ for abstraction of a single cyclohexane hydrogen by chlorine atom.[12]

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Coordination Effects in Organic Reactions. I. A Novel Preparation of *t*-Alkyl Isocyanide Complexes by N-Alkylation of Hydrogen Cyanide

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Reaction of isobutene with hydrogen cyanide in the presence of a cuprous halide was found unexpectedly to give *t*-butyl isocyanide cuprous complexes, $[(\mathrm{CH_3})_3\mathrm{CNC}]_3\mathrm{CuX}$ and $(\mathrm{CH_3})_3\mathrm{CNC{\cdot}CuCN}$. Isocyanide ligands can be liberated from the cuprous complexes by aqueous potassium cyanide. A reaction scheme is proposed to explain the formation of these cuprous complexes. Scope of the novel alkylation reactions was studied and physical properties of a number of new *t*-alkyl isocyanides thus obtained were recorded.

In most metal cyanide complexes neutron-diffraction measurements indicate that $\mathrm{CN^-}$ is bonded to metal by carbon.[2-3] The fact that alkylation of cyanide gives corresponding alkyl isocyanide complexes supports this observation.[4-8] In the parent acid, hydrogen cyanide, it is likely that both of the two σ lone pairs on the carbon and nitrogen of the anion projecting outward along the CN axis are utilized for bonding with hydrogen, since the acid is hydrogen bonded and a weak acid in water ($\mathrm{p}K = 9.21$).[9] Further, hydrogen cyanide is known to be a Lewis base toward acidic metal halides, *e.g.*, $\mathrm{B_2Cl_4}$[10a] or $\mathrm{SbCl_5}$.[10b] Thus it would be of interest to see whether coordination of hydrogen cyanide to certain metals occurs through carbon or nitrogen.

During a course of study on the catalytic syntheses of nitriles from olefins an addition reaction was observed between isobutene and hydrogen cyanide when cuprous bromide was used. The reaction products were apparently cuprous complexes containing organic ligands, but not of alkyl nitriles. This unexpected finding stimulated us to elucidate the structure of the complex products in order to provide an answer to the above question. The purpose of this paper then is to present

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