Acidification with dilute HCl of the trapped volatile solution, evaporation of solvent and water by azeotropic distillation, and drying for 5 hr at 120° yielded diisopropylamine hydrochloride (1.12 g) equivalent to 65% metalation.

A control experiment was carried out on diisopropylamine (1 g, 0.01 m) as a check on the method for the quantitative isolation of the amine salt and to ensure the absence of water of hydration after drying. Acidification, isolation of the salt, and drying gave a dry salt weighing 1.31 g (theory 1.35 g).

C. Isolation of Olefin.—A dianion solution prepared from 2-butylheptanoic acid (3.0 g, 0.016 mol) was alkylated at 25° with 1-bromooctane (3.08 g, 0.016 mol) in THF–HMPA in the manner formerly described. After reaction (1.5 hr), the solution was acidified and extracted with petroleum ether and the extracts were reextracted sequentially with dilute HCl, water, and 5% sodium hydroxide solution. The solvent was removed by distillation and the residue was carefully distilled (bp 120–121°) to give a colorless liquid fraction (1.45 g, 80% yield) which was confirmed to be 1-octene by glpc retention time, ir, and nmr. The same procedure carried out at 25° in the absence of HMPA gave 0.54 g of 1-octene (30% yield).

α Metalation of Oleic Acid. Analysis for Double Bond Migration (von Rudloff Method).[29]—Oleic acid was α metalated in the prescribed manner and regenerated from the salt by acidification.

Samples (0.035 g each) of the treated oleic acid and of untreated oleic acid as a control were separately weighed into Erlenmeyer flasks (50 ml capacity). To each flask were added the oxidant solution [7 ml of an aqueous solution comprised of sodium periodate (21 g) and potassium permanganate (25 ml of 0.1 *N*) diluted to 1 l.], potassium carbonate (0.009 g in 1.4 ml of water), and *tert*-butyl alcohol (8.5 ml). The solutions were stirred (72 hr) until clear. A pellet of potassium hydroxide was added to each solution, the alcohol was removed on a steam bath under a stream of nitrogen, and the solutions were acidified with several drops of concentrated HCl. The materials were extracted three times with chloroform (25 ml portions) and dried, and the combined solutions were evaporated to the organic acid residues under a nitrogen stream. These were each esterified to the methyl esters and analyzed *via* glpc. The samples gave identical chromatograms consisting of only two products, dimethyl azelate and methyl pelargonate, in agreement with the retention times for the authentic compounds.

Registry No.—2-Butyloctadecanoic acid, 33021-13-5; 2-butyl-10-undecenoic acid, 32970-65-3; 2-butyl-*cis*-9-octadecenoic acid, 33016-09-0; ethylheptylmalonic acid, 32970-66-4; actylheptylmalonic acid, 32970-67-5.

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Metal Ion Promoted Dehydrohalogenation of Secondary Alkyl Halides

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Orientation in dehydrohalogenation of 2-alkyl iodides and bromides by silver nitrate, perchlorate, acetate, and nitrite and mercuric nitrate in aprotic and protic solvents under conditions of kinetic control has been determined. Strong preference for formation of internal olefins and *trans*- to *cis*-2-alkene ratios of 1.1–2.8 were observed. In aprotic solvents, metal halide catalysis was negligible, and orientation was somewhat affected by variation of the metal ion, the metal counterion, the leaving group, the solvent, and the 2-alkyl group. Reactions in protic solvents were complicated by metal halide catalysis. The mechanism of metal ion promoted dehydrohalogenation of 2-alkyl halides is discussed.

Electrophilic assistance by mercuric and silver ions in replacement reactions of alkyl halides has been the subject of numerous investigations in recent years.[3–16] Kinetic and stereochemical studies have revealed that silver salt catalyzed substitutions of 2-alkyl halides do not proceed by a simple carbonium ion mechanism.[5,6,12–14] Such conclusions raise questions concerning the mechanism of the competing elimination reactions, about which little is known. An investigation of metal ion promoted dehydrohalogenation from 2-alkyl halides therefore seemed warranted.

Of the available methods for studying β eliminations from 2-substituted alkanes, determination of the effect of experimental variables upon positional and geometrical orientation[17,18] of the olefinic products appeared most suitable for an initial examination.

In only two instances has orientation in metal ion assisted elimination from 2-alkyl halides been considered. Unfortunately, in the reported olefin-forming reaction of 2-bromobutane with silver nitrate in water and *tert*-butyl alcohol,[20] possible complication due to catalysis by silver bromide[16,21] was apparently ignored. In the second study, reaction of 2-octyl bromide with silver nitrate in acetonitrile produced approximately 2% 1-octene and 14% 2-octenes.[12] The isomeric 2-octenes were not separated.

[1] NSF Summer Undergraduate Research Participant, 1970.

[2] Presented by G. M. P. at the 26th Annual Northwest Regional Meeting of the American Chemical Society, Bozeman, Mont., June 1971.

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[16] P. S. Walton and M. Spiro, *J. Chem. Soc. B*, 42 (1969).

[17] For 2-substituted alkanes, positional orientation refers to the relative proportions of 1- and 2-alkenes formed, whereas geometrical orientation compares the relative amounts of *trans*-2-alkene and *cis*-2-alkene produced.

[18] Such studies have given considerable insight into the detailed nature of base-catalyzed β eliminations from 2-substituted alkanes. See ref 19 and references cited therein.

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TABLE I

OLEFINIC PRODUCTS FROM REACTIONS OF 2-BUTYL HALIDES WITH SILVER NITRATE[a] IN DMSO AT 50°

Run	X of 2-BuX	Reaction time, min	Butene yield, %	Total butenes, %			trans-2-Butene: cis-2-butene
				1-Butene	trans-2-Butene	cis-2-Butene	
1	I	2	18	8.5 ± 0.3[b]	59.4 ± 0.2	32.1 ± 0.2	1.85
2	I	10	36	8.3 ± 0.3	58.8 ± 0.2	32.9 ± 0.1	1.79
3	I	10	30	8.5 ± 0.1	58.5 ± 0.1	33.0 ± 0.2	1.77
4	Br	2	1	7.5 ± 0.1	62.5 ± 0.2	30.0 ± 0.1	2.08
5	Br	3	2	7.4 ± 0.2	62.3 ± 0.2	30.2 ± 0.2	2.06
6	Br	10	10	7.4 ± 0.2	61.7 ± 0.1	30.9 ± 0.1	2.00

[a] [2-BuX] = 0.22 M, [$AgNO_3$] = 0.30 M. [b] Standard deviation from repetitive analysis of trapped butene mixture.

TABLE II

OLEFINIC PRODUCTS FROM REACTIONS OF 2-BUTYL HALIDES WITH METAL SALTS IN APROTIC SOLVENTS AT 50°

Run	Silver salt[a]	X of 2-BuX[b]	Solvent	Butene yield, %[c]	Total butenes, %			trans-2-Butene: cis-2-butene
					1-Butene	trans-2-Butene	cis-2-Butene	
3	$AgNO_3$	I	DMSO	36	8.3 ± 0.3[d]	58.8 ± 0.2	32.9 ± 0.1	1.79
6	$AgNO_3$	Br	DMSO	10	7.4 ± 0.2	61.7 ± 0.1	30.9 ± 0.1	2.00
7	$AgNO_3$	I	DMF	50	9.5 ± 0.2	55.4 ± 0.1	35.1 ± 0.2	1.58
8	$AgNO_3$	Br	DMF	20	8.2 ± 0.2	57.5 ± 0.1	34.3 ± 0.1	1.68
9	$AgNO_3$	I	MeCN	24	8.4 ± 0.1	57.8 ± 0.1	33.8 ± 0.1	1.71
10	$AgNO_3$	Br	MeCN	2	7.6 ± 0.4	60.4 ± 0.5	32.0 ± 0.1	1.89
11	$AgClO_4$	I	DMSO	63	8.3 ± 0.3	58.9 ± 0.3	32.8 ± 0.3	1.80
12	$AgClO_4$	Br	DMSO	11	7.0 ± 0.2	61.7 ± 0.1	31.2 ± 0.2	1.98
13	$AgNO_3$	I	DMAC[e]	48	9.0 ± 0.2	57.8 ± 0.3	33.1 ± 0.3	1.74
14	$AgNO_3$	I	NMP[f]	52	9.4 ± 0.5	57.2 ± 0.8	33.3 ± 0.4	1.72
15	$AgNO_3$	I	Pyridine	6	6.8 ± 0.3	67.9 ± 0.4	25.4 ± 0.4	2.68
16	AgOAc[g]	I	DMSO	9	8.4 ± 0.1	57.7 ± 0.1	34.0 ± 0.1	1.70
17	$AgNO_2$[g]	I	DMSO	12	7.2 ± 0.1	60.6 ± 0.1	32.2 ± 0.3	1.88
18	$Hg(NO_3)_2$[g]	I	DMSO	46	9.2 ± 0.1	54.1 ± 0.1	36.6 ± 0.2	1.48

[a] [$AgNO_3$], [$AgClO_4$] = 0.30 M. [b] [2-BuX] = 0.22 M. [c] Ten-minute reaction period. [d] Standard deviation from repetitive analysis of trapped butene mixture. [e] *N,N*-Dimethylacetamide. [f] *N*-Methyl-2-pyrrolidone. [g] Saturated solution.

Results

Reactions were carried out, at 50.0°, in an apparatus continuously bubbled with nitrogen gas and volatile products were collected in a trap cooled in liquid nitrogen. Because of the low stability of silver–olefin complexes,[22] interference by complexation of the liberated alkenes was deemed unlikely. A uniform 10-min reaction period was employed, unless otherwise noted. The relative proportions of the three isomeric olefins were determined by gas–liquid partition chromatography (glpc). Alkene yields were estimated by comparison of the olefin peak areas with those from reaction of 2-bromobutane with potassium *tert*-butoxide in DMSO. Reactions of 2-bromoalkanes with potassium *tert*-butoxide in DMSO produce nearly quantitative yields of alkenes.[23]

Isomerization of product olefins under the reaction conditions was shown to be negligible. As described in the Experimental Section, the isomeric composition of synthetic mixtures of butenes was unaffected by silver nitrate or a mixture of silver iodide and silver nitrate in DMSO or in *tert*-butyl alcohol.

Reactions with Metal Salts in Aprotic Solvents.—Olefinic products from reactions of silver nitrate with 2-butyl iodide and bromide in DMSO are presented in Table I. Under the reaction conditions, 2-butyl chloride produced no olefins when treated with silver nitrate in DMSO.[24] Runs 2 and 3, which were conducted by different researchers with a 1-year time interval, demonstrate the reproducibility of the measured relative olefinic proportions and butene yields. The virtual constancy of the relative butene proportions with varying reaction time indicates little catalytic activity of precipitated silver halides.[25] Kinetic evidence for the relative unimportance of catalysis by silver bromide in reactions of 2-octyl bromide with silver nitrate in acetonitrile has been previously reported.[12]

The effect of leaving groups upon orientation in reactions of 2-butyl iodide and bromide with silver nitrate and perchlorate in aprotic solvents is depicted in Table II. The variations in relative olefinic proportions with change of leaving groups are small, but are outside of experimental error. A consistently lower percentage of 1-butene and higher *trans*- to *cis*-2-butene ratio is observed when the iodide leaving group is replaced by bromide (compare runs 3 and 6, 7 and 8, 9 and 10, 11 and 12).

The consequence of varying the metal cation, the metal anion, and the aprotic solvent may also be inferred from the data in Table II.[26] In DMSO, the relative olefinic proportions in eliminations from 2-butyl iodide are somewhat affected by a change of metal ion from silver(I) to mercury(II) (runs 3 and 18) and exhibit slight sensitivity to variation of the silver counterion (runs 3, 11, 16, 17). A small effect of solvent upon orientation in silver nitrate induced eli-

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(23) R. A. Bartsch, *J. Org. Chem.*, **35**, 1334 (1970).

(24) (a) Small amounts of olefin resulted from treatment of 2-chlorobutane with silver nitrate in pyridine at 68.8° for 27.1 days.[15] (b) Reaction of 2-octyl bromide with silver nitrate in acetonitrile is 450 times more rapid than that of 2-octyl chloride.[12]

(25) In contrast, reactions of 2-butyl halides with silver nitrate and perchlorate in tetramethylene sulfone (sulfolane) were found to be strongly catalyzed by silver halides, producing olefinic proportions markedly different from those in reactions performed in other aprotic solvents.

(26) Lead and thallium nitrates in DMSO were ineffectual in promoting elimination from 2-iodobutane at 50°.

TABLE III

OLEFINIC PRODUCTS FROM REACTIONS OF 2-ALKYL BROMIDES WITH SILVER NITRATE IN DMSO AT 50°[a,b]

Run	Registry no.	R of RBr	Total alkenes, % 1-Alkene	*trans*-2-Alkene	*cis*-2-Alkene	*trans*-2-alkene: *cis*-2-alkene
6		2-Butyl	7.4 ± 0.2[c]	61.7 ± 0.1	30.9 ± 0.1	2.00
19	107-81-3	2-Pentyl	7.5 ± 0.2	68.3 ± 0.9	24.2 ± 1.1	2.82
20	3377-86-4	2-Hexyl	8.8	64.7	26.5	2.44

[a] Ten-minute reaction period. [b] [2-RBr] = 0.22 *M*, [$AgNO_3$] = 0.3 M. [c] Standard deviation from repetitive analysis of trapped alkene mixture.

TABLE IV

OLEFINIC PRODUCTS FROM REACTIONS OF 2-BUTYL HALIDES WITH SILVER AND MERCURIC NITRATE IN PROTIC SOLVENTS AT 50°

Run	X of 2-BuX	Salt	Solvent	Reaction time, min.	Butene yield, %	Total butenes, % 1-Butene	*trans*-2-Butene	*cis*-2-Butene	*trans*-: *cis*-2-Butene
21	I[a]	$AgNO_3$	H_2O	0.5	4	4.9 ± 0.1[b]	54.1 ± 0.2	41.0 ± 0.2	1.32
22				1.5	28	5.0 ± 0.1	53.7 ± 0.1	41.3 ± 0.1	1.30
23				10	38	5.2 ± 0.1	53.3 ± 0.2	41.6 ± 0.3	1.28
24	I[c]	$AgNO_3$	*tert*-BuOH	0[d]		8.7	47.8	43.5	1.12
25				0.5	10	8.5 ± 0.2	47.7 ± 0.5	43.8 ± 0.4	1.09
26				1.5	19	8.0 ± 0.3	47.3 ± 0.3	44.8 ± 0.1	1.06
27				10	89	7.5 ± 0.1	46.3 ± 0.1	46.2 ± 0.1	1.00
28	Br[a]	$AgNO_3$	H_2O	0[d]		3.6	57.2	39.2	1.46
29				1.5	1	3.6 ± 0.2	56.4 ± 0.2	40.0 ± 0.3	1.42
30				3	2	3.6 ± 0.2	55.5 ± 0.2	40.9 ± 0.3	1.36
31				10[f]	9	4.1 ± 0.1	53.0 ± 0.1	42.9 ± 0.1	1.23
32	Br[e]	$AgNO_3$	*tert*-BuOH	0[d]		7.6	56.8	35.6	1.60
33				1.5	1	7.5 ± 0.5	55.1 ± 0.5	37.5 ± 0.2	1.47
34				3	6	6.9 ± 0.2	54.3 ± 0.2	38.9 ± 0.2	1.40
35				10	25	7.0 ± 0.2	46.4 ± 0.1	46.7 ± 0.1	1.00
36	Br[g]	$Hg(NO_3)_2$	*tert*-BuOH	1.5	6	0.8 ± 0.1	70.0 ± 0.4	29.2 ± 0.4	2.40
37				3	32	1.1 ± 0.1	65.2 ± 0.2	33.7 ± 0.2	1.94
38				10	36	3.0 ± 0.1	60.5 ± 0.1	36.5 ± 0.1	1.66
39	Br[e]	$AgNO_3$	*tert*-BuOH	10	24	6.6 ± 0.2	47.4 ± 0.2	46.0 ± 0.1	1.03
40	Br[h]	$AgNO_3$	*tert*-BuOH	10	50	11.6 ± 0.1	29.2 ± 0.3	59.2 ± 0.3	0.49

[a] [2-BuX] = 0.22 *M*, [$AgNO_3$] = 0.30 *M*. [b] Standard deviation from repetitive analysis of trapped alkene mixture. [c] [2-BuI] = 0.10 *M*, [$AgNO_3$] = 0.11 *M*. [d] Extrapolated. [e] [2-BuBr] = [$AgNO_3$] = 0.11 *M*. [f] Reference 20 reports a 29% yield of butenes after 4 hr at 70°. [g] [2-BuBr] = 0.22 *M*, [$Hg(NO_3)_2$] = saturated solution. [h] [2-BuBr] = 0.11 *M*, [$AgNO_3$] = 0.10 *M*, AgBr present.

minations from 2-butyl iodide is also noted (runs 3, 7, 9, 13, 14, 15).

The relative olefinic proportions from reactions of a homologous series of 2-bromoalkanes with silver nitrate in DMSO are displayed in Table III. Variation of the 2-alkyl group affects geometrical orientation with the *trans*- to *cis*-2-alkene ratio increasing in the order 2-butyl < 2-hexyl < 2-pentyl.

Reactions with Metal Salts in Protic Solvents.— In order to assess possible catalytic activity of precipitated metal halides in reactions of 2-butyl iodide and bromide with silver and mercuric nitrates in water and *tert*-butyl alcohol, the effect of reaction time variation upon relative olefinic proportions was examined. The results, which are recorded in Table IV, demonstrate significant metal halide catalysis in four of the five reactions investigated. Such effects are particularly evident in *tert*-butyl alcohol. The apparent order of catalytic activity is AgI < AgBr ~ $HgBr_2$.[27]

For the silver nitrate promoted eliminations, the olefinic products derived solely from the silver nitrate induced reaction may be estimated by extrapolation of the product proportions to zero time. Comparison of the present extrapolated results for reaction of 2-butyl bromide with silver nitrate in *tert*-butyl alcohol (run 32) with those previously reported[20] reveals large discrepancies in both the per cent of 1-butene and *trans*- to *cis*-2-butene ratio. Such variance may be ascribed to complicating silver bromide catalysis in the earlier study.

Examination of the reaction of 2-butyl bromide with silver nitrate in *tert*-butyl alcohol in the presence of silver bromide (run 40) provides confirmation of metal halide catalysis in reactions between 2-alkyl halides and silver or mercuric nitrates in protic solvents. The presence of a small amount of *in situ* generated silver bromide (a milky suspension) strongly affects both the relative proportions of isomeric olefins and the butene yield (compare runs 39 and 40). It is noteworthy that a *trans*- to *cis*-2-butene ratio of much less than unity was observed. Treatment of 2-butyl bromide with externally synthesized silver bromide in *tert*-butyl alcohol in the absence of silver nitrate produced no olefins.

Discussion

Since the observed olefinic proportions for metal ion promoted elimination from 2-butyl halides are similar to the thermodynamic butene distribution from acid-catalyzed butene isomerization,[28] it was necessary to establish the stability of product olefins to the reaction conditions. The relative olefinic proportions of synthetic butene mixtures with composition far from the

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[27] Walton and Spiro have noted greater catalysis by AgI than AgBr in reactions of ethyl iodide with silver nitrate in water.[16]

[28] Sulfuric acid catalyzed equilibration of butenes yields the following butene proportions: 1-butene, 6 ± 1%; *trans*-2-butene, 68 ± 1%; *cis*-2-butene, 26 ± 1%; and *trans,cis*-2-butene, 2.6.[20]

TABLE V

Synthetic mixture	Injected into	% 1-Butene	% *trans*-2-Butene	% *cis*-2-Butene
A		31.0 ± 0.7	52.5 ± 0.2	16.4 ± 0.1
A	$AgNO_3$ in DMSO at 50°	31.0 ± 0.5	53.2 ± 0.3	15.8 ± 0.5
A	AgI–$AgNO_3$ in DMSO at 50°	30.8 ± 0.4	52.9 ± 0.2	16.2 ± 0.4
B		30.3 ± 0.2	52.8 ± 0.2	16.8 ± 0.1
B	$AgNO_3$ in *t*-BuOH at 50°	29.4 ± 0.5	53.8 ± 0.2	16.8 ± 0.4
B	AgI–$AgNO_3$ in *t*-BuOH at 50°	29.2 ± 0.2	53.3 ± 0.3	17.5 ± 0.1

thermodynamic distribution were unaffected by silver nitrate or a mixture of silver iodide and silver nitrate in DMSO or *tert*-butyl alcohol. Therefore, the observed olefinic products are those of kinetic control.

Orientation in Aprotic Solvents.—Before discussion of metal ion promoted eliminations from 2-alkyl halides in aprotic solvents, it is pertinent to establish the orientation anticipated for β eliminations proceeding by concerted and free carbonium ion mechanisms. A characteristic feature of base-catalyzed β elimination from 2-alkyl halides in dipolar aprotic solvents is high *trans*- to *cis*-2-alkene ratios.[19] Thus, ratios of 3.0–4.0 are observed for eliminations from 2-butyl halides induced by a wide variety of bases in DMSO and DMF.[19] For a free 2-alkyl cation, *trans*- to *cis*-2-alkene ratios of unity are anticipated.[20,29,30]

It is immediately apparent from the data presented in Tables II and III that in the metal ion promoted dehydrohalogenation of 2-alkyl halides in aprotic solvents geometrical orientation obtains which is intermediate between that observed in concerted, base-catalyzed elimination and that expected for a free carbonium ion intermediate.

From product and kinetic studies of the reaction of 2-octyl halides with silver nitrate in acetonitrile, Pocker has proposed rate-determining formation of a carbonium nitrate silver halide ion quadruplet which subsequently decomposes to form substitution and elimination products.[12] The observed strong preference for formation of Saytzeff alkenes in the present study is indicative of olefin-forming transition states with a high degree of carbonium ion character.[31] The small but significant variation of orientation with change in the metal ion, the leaving group, the silver counterion, and the 2-alkyl group (Tables II and III) rule out a free carbonium ion intermediate or even a carbonium–metal counterion ion pair. However, these results are consistent with slight encumbrance of a carbonium ion intermediate by the other members of an ion quadruplet in the olefin-forming transition states. The limited sensitivity of the olefinic proportions to variation of the metal counterion and dipolar aprotic solvent (Table II) indicates that proton loss from the high-energy carbonium ion intermediate is quite unselective. Nevertheless, the change in orientation observed for the basic solvent pyridine suggests that proton removal by the solvent obtains.

Orientation in Protic Solvents.—For reactions of 2-butyl iodide and bromide with silver and mercuric nitrates in water and, particularly, in *tert*-butyl alcohol, the relative proportions of the three isomeric olefins change with time (Table IV). Complication due to metal halide produced in the reactions is evident. Graphical extrapolation to zero time produces estimates of the relative olefinic proportions for reactions of silver nitrate with 2-butyl iodide and bromide in water and *tert*-butyl alcohol. Such extrapolated values should be considered more reliable than those previously reported for dehydrohalogenation of 2-butyl bromide with silver nitrate.[20]

In general, the results for silver nitrate promoted elimination from 2-iodo- and 2-bromobutane in water and *tert*-butyl alcohol roughly parallel those in aprotic solvents. Thus, orientation varies with change in leaving group; the ratio of geometric isomers is greater than unity; and strong preference for formation of internal olefins is found (Table IV). Such observations again suggest an ion quadruplet intermediate. The greater sensitivity of orientation to change of leaving group in *tert*-butyl alcohol than in water or the aprotic solvents may be due to a "tighter" ion quadruplet in solvents of low polarity.

It is interesting to speculate briefly concerning the effect of insoluble metal halide upon metal-promoted elimination from 2-alkyl halides. A small amount ($AgNO_3$:AgBr = 10:1) of *in situ* generated silver bromide profoundly influences orientation and olefin yield in reactions of 2-butyl bromide with silver nitrate in *tert*-butyl alcohol (compare runs 39 and 40, Table IV). However, externally synthesized silver bromide in the absence of silver nitrate was ineffectual in inducing elimination. These observations indicate a heterogeneous reaction of alkyl halide with silver ions adsorbed onto the silver bromide surface. The strikingly different geometrical orientation (preferential formation of *cis*-2-butene) observed in the presence of silver bromide is characteristic of contact eliminations.[33]

Experimental Section

Materials.—Reagent grade aprotic solvents were used directly from freshly opened bottles. *tert*-Butyl alcohol was purified as before.[23] 2-Alkyl halides were available from earlier studies.[19,23]

Procedure.—The apparatus, procedure, and glpc analysis previously utilized for study of base-catalyzed dehydrohalogenation of 2-alkyl halides in aprotic solvents were used.[19,23] Solvolytic elimination from 2-butyl iodide in DMF and DMSO was shown to be negligible under the employed conditions. A nitrogen sweep rate of 60 ml/min was used. Olefin yields were estimated by glpc comparison of amounts of butenes derived from a given reaction with that from reaction of 2-bromobutane with potassium *tert*-butoxide in dimethyl sulfoxide. Nearly quantitative olefin yields are anticipated for the latter reaction.[23] Estimated uncertainty in butene yield is ±0.1 times the reported value.

Stability of Olefinic Products to Reaction Conditions.—To test for isomerization of olefinic products under the conditions of silver ion promoted eliminations from 2-alkyl halides, a synthetic

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(29) A. Streitwieser, Jr., and W. D. Schaeffer, *J. Amer. Chem. Soc.*, **79**, 2888 (1957).

(30) In the sulfuric acid catalyzed isomerization of butenes, *trans*- and *cis*-2-butene are formed from the 2-butyl cation at the same rate.[20]

(31) In the solvolysis of 2-butyl iodide in DMSO in the presence of 2,6-lutidine at 50°, 97% of the product olefins are 2-butenes.[32]

(32) R. A. Bartsch, unpublished results.

(33) H. Noller, P. Andreu, and M. Hunger, *Angew. Chem., Int. Ed. Engl.*, **10**, 172 (1971).

mixture of butenes was injected into (1) a 0.30 *M* solution of silver nitrate in DMSO; (2) a mixture of silver iodide and silver nitrate in DMSO which resulted from the reaction of 0.22 *M* 2-butyl iodide with 0.30 *M* silver nitrate in DMSO; (3) a 0.11 *M* solution of silver nitrate in *tert*-butyl alcohol; and (4) a mixture of silver iodide and silver nitrate in *tert*-butyl alcohol which resulted from the reaction of 0.10 *M* 2-butyl iodide with 0.11 *M* silver nitrate in *tert*-butyl alcohol. The results which follow (Table V) demonstrate the stability of olefinic products to the reaction conditions.

Reaction of 2-Butyl Bromide with Silver Nitrate in *tert*-Butyl Alcohol in the Presence of Silver Bromide.—To 5 ml of a 0.11 *N* solution of silver nitrate in *tert*-butyl alcohol in the reaction apparatus was injected 0.2 ml of 0.5 *N* solution of HBr in slightly aqueous *tert*-butyl alcohol. Into the resulting milky white suspension was immediately injected 0.08 g of 2-butyl bromide. The reaction was then carried out in the customary fashion.

It was subsequently demonstrated that reaction of 2-butyl bromide with HBr in *tert*-butyl alcohol produced negligible yields of butenes under the reaction conditions.

Registry No.—$AgNO_3$, 7761-88-8; 2-BuI, 513-48-4; 2-BuBr, 78-76-2; $AgClO_4$, 7783-93-9; AgOAc, 563-63-3; $Hg(NO_3)_2$, 10045-94-0; AgI, 77883-96-2; AgBr, 7785-23-1; $HgBr_2$, 7789-47-1.

Reactions of π-Allylic Nickel(II) Bromide with Organic Halides. A Novel Synthesis of Monoterpenoid Compounds[1]

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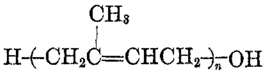
A novel synthesis of monoterpenoid compounds from isoprene as a major starting material is described. Reaction of isoprene with *N*-bromosuccinimide in ethanol or glacial acetic acid gives 1-bromo-4-ethoxy-2-methyl-2-butene and 4-acetoxy-1-bromo-2-methyl-2-butene, respectively. The two allylic bromides react in benzene with 1,1-dimethyl-π-allylnickel bromide prepared by reacting prenyl bromide with excess nickel carbonyl to give geranyl ethyl ether and geranyl acetate, respectively. Under similar condition, ethyl γ-bromosenecioate and 1,1-dimethyl-π-allylnickel bromide give ethyl geranate in a moderate yield.

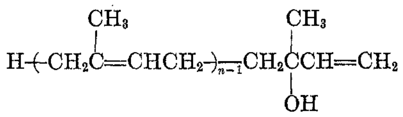
The synthesis of polyprenyl alcohols **1** and **2**, which are not only naturally occurring terpenes but also serve as important materials for synthesis, is achieved by a five-carbon (isoprene skeleton) homologation involving successive two- and three-carbon elongation reactions.[2] This method suffers from low over-all yields in the synthesis of higher analogs of **1** and **2**.

Previously we have reported[3] that such a C-5 homologation can be achieved in one step by using an organophosphorus compound, 4-pentyn-1-ylidenetriphenylphosphorane. This reacted with a isoprenoid ketone to afford its higher analogs *via* the intermediate γ,δ-unsaturated acetylene. In the present paper we describe another method for the desired chain extension, using π-allylnickel complexes.



$$H\text{-}(CH_2\overset{\overset{\large CH_3}{|}}{C}{=}CHCH_2)_n\text{-}OH$$

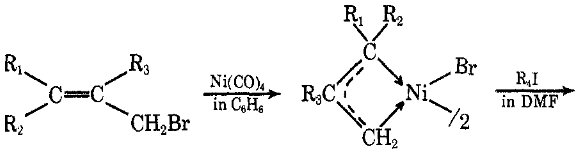
1



$$H\text{-}(CH_2\overset{\overset{\large CH_3}{|}}{C}{=}CHCH_2)_{n-1}CH_2\underset{\underset{\large OH}{|}}{\overset{\overset{\large CH_3}{|}}{C}}CH{=}CH_2$$

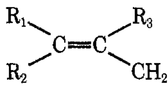
2

During the last decade, organo-transition metal compounds have been shown to be interesting and useful substances in synthetic chemistry. For instance, an efficient and useful method for the attachment of an allylic group **3** to an alkyl, vinyl, or aryl unit by means of π-allylnickel reagents has recently been described by Corey and Semmelhack.[4] However, because these π-allylnickel halides **4**, which can be obtained expeditiously by the reaction of allylic halides **3** with nickel carbonyl in benzene are somewhat unstable and air-sensitive, the purification of these π-allylic complexes must be conducted below room temperature with rigorous exclusion of oxygen. In a preliminary experiment we found that this troublesome purification can be omitted without any noticeable diminution of yields to give **5a–d** (See Experimental Section).



3a–d **4a–d**

a, $R_1 = H; R_2 = H; R_3 = H$
b, $R_1 = H; R_2 = H; R_3 = CH_3$
c, $R_1 = CH_3; R_2 = H; R_3 = H$
d, $R_1 = CH_3; R_2 = CH_3; R_3 = H$



5a–d, $R_4 = C_6H_5$
e, $R_1 = R_2 = R_3 = H; R_4 = (CH_3)_2CHCH_2CH_2$

We intended at first to generate the π-allylnickel complex from an allylic halide possessing a functionalized carbon substituent which can be elaborated to an allylic halide function. Thus, ethyl *trans*-γ-bromocrotonate (**6a**) was heated with nickel carbonyl in benzene, the progress of the reaction being evidenced by evolution of carbon monoxide and the appearance

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[1] A portion of this paper was presented at the 23rd Annual Meeting of the Chemical Society of Japan, Tokyo, April 1970.

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