esterification of oleic acid with *n*-butanol obtained specific rates very nearly proportional to the external area of the resin particle employed, indicating that only acid groups near the exterior of the particles are active catalytically. The present results on the effect of particle size of resin, obtained with much smaller molecules, also indicate a superiority of the external acid groups, but one which is of almost negligible total effect. One might attribute this effect to the intrusion of diffusion into the interior of the particle as a significant factor in the control of the over-all rate except that the effect of particle size is unchanged by a change in the size of the reacting molecule which produces a large change in the over-all rate.

Summary

A method in which reproducible rate constants can be obtained has been developed for following the hydrolysis of esters in 70% acetone with a cation exchange resin as the catalyst. A comparison of the catalytic effect of the exchange resin with that of hydrochloric acid showed that the free energy of activation relative to the hydrogen chloride-catalyzed reaction increased almost linearly with the chain length of the ester in the series methyl acetate, ethyl acetate, ethyl *n*-butyrate, ethyl *n*-caproate at 25°.

Measurements of the temperature coefficients of the rates of hydrolysis of methyl acetate and of ethyl *n*-butyrate showed that the lower rates with the exchange resin were accompanied by lower entropies of activation and lower heats of activation than with hydrochloric acid, the former effect being strongly dependent on the chain length of the ester, the latter relatively independent.

The major factor determining these effects appears to be the loss in internal entropy of the ester molecule which accompanies its fixation on the skeleton of the resin catalyst in the formation of the transition state.

NEW YORK, N. Y. RECEIVED SEPTEMBER 3, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF ILLINOIS INSTITUTE OF TECHNOLOGY AND RCA LABORATORIES]

Absorption Spectra of Some Double Salts Containing Bivalent Cobalt[1]

BY MELVIN L. SCHULTZ[2]

The absorption spectra of crystals of five double salts of cobaltous chloride all containing the tetrahedral $CoCl_4^{--}$ ion have been shown[3] to consist, at room temperature, of a large number of relatively narrow bands. The details of these spectra were found to be almost completely independent of the identity of the cation and therefore it was concluded that the absorption was characteristic of the complex ion.

Prominent among the wave number differences of adjacent bands in these spectra is one of approximately 370 cm.$^{-1}$. This frequency was identified tentatively as one of the characteristic frequencies of the $CoCl_4^{--}$ ion. The validity of this interpretation has, in the present work, been investigated by studying the spectra of two salts, $(PyH)_2CoBr_4$ and $(QuH)_2CoBr_4$,[4] containing the corresponding bromo- complex ion. Substitution of one halogen for another would be expected to lead to changes in frequency differences if the structure of the spectrum is determined by the coupling of vibrations of the complex with electronic transitions.

Such an effect has, in fact, been observed by Brode and Morton[5] for solutions of cobaltous halides in concentrated aqueous solutions of the corresponding hydrogen halides.[6] They found decreasing separations of bands in passing from the chloride to the bromide and to the iodide. Their analysis is subject to some uncertainty, however, since the absorption bands of the solutions are broad and incompletely resolved. The comparison in the case of the crystals is much more clear cut since the bands are considerably sharper and therefore more completely resolved. The expected frequency shifts have been found for many, but not all, of the bands in the spectra of the crystals.

Confirmation of the hypothesis that the detailed structure of the spectra of these complexes of bivalent cobalt is determined essentially by the configuration of the complex ion was obtained by studying the absorption spectrum of crystals of $2(en\ H_2)Cl_2 \cdot CoCl_2$.[7] Although the structure of the complex ion in this compound has not been determined, the coördination number of cobalt is probably six[8] with probably an octahedral arrangement of chloride ions about the central co-

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[1] The spectra described here were photographed in 1943 while the author was a member of the staff of Illinois Institute of Technology. The plates obtained were measured and the present paper was written after the author became associated with RCA Laboratories.

[2] Present address: RCA Laboratories Division, Radio Corporation of America, Princeton, N. J.

[3] M. L. Schultz and E. F. Lilek, THIS JOURNAL, **64**, 2748 (1942).

[4] The abbreviations Py, Qu and en represent pyridine, quinoine and ethylenediamine, respectively.

[5] W. R. Brode, *Proc. Roy. Soc. (London)*, **118A**, 286 (1928); W. R. Brode and R. A. Morton, *ibid.*, **120A**, 21 (1928).

[6] These solutions also contain the CoX_4^{--} ion; see reference 3.

[7] Due to lack of time, this spectrum was only incompletely investigated. Structure in the region of very strong absorption in the red was not resolved since sufficiently thin absorbing layers were not used.

[8] J. Meyer and K. Hoehne, *Z. anorg. allgem. Chem.*, **222**, 161 (1935).

balt ion. Although the spectrum of this salt shows the same general arrangement of groups of bands as do the tetrahalide complexes, the detailed structure of the groups is completely different.

Experimental

The experimental methods employed were, with some modifications, those previously described.[3] The double salts used were prepared according to published methods.[8,9] In each case, the composition of the preparation was established by the determination of halogen by precipitation and weighing as silver halide.

When large single crystals of the double salts could be obtained these were mounted in Canada balsam between microscope slides and cover glasses. For (en $H_2)_2CoCl_6$ which could not be obtained as large crystals or for very thin absorbing layers of the bromides, the micro crystals were suspended in Canada balsam and mounted between slides. In this manner, the transparency of the preparations was increased and, in addition, the crystals were protected from attack by water vapor in the atmosphere. In the case of $(QuH)_2CoBr_4$, crystals obtained from hydrobromic acid solution and material prepared by recrystallization from ethyl alcohol solution gave identical spectra.

The wave lengths of the band maxima were determined from microphotometer tracings, made with a Leeds and Northrup recording microphotometer, of the comparison spectra produced by either a copper arc or a neon discharge tube and of the absorption spectra. Except for the very weak or very diffuse bands, the uncertainties in the wave numbers calculated from the measured wave lengths are about 10 cm.$^{-1}$. In the extreme red where the dispersion of the spectrograph was small, the uncertainty is somewhat greater.

Results and Discussion

The wave numbers and estimated relative intensities of the observed band maxima for the two bromides are listed in Table I. Except for differences in the region between 18,100 cm.$^{-1}$ and 20,300 cm.$^{-1}$ and for the very weak doublet at 25,300 cm.$^{-1}$, which was observed for $(PyH)_2CoBr_4$ but not for $(QuH)_2CoBr_4$, there is a complete correspondence between the two spectra. The differences in wave lengths of corresponding bands are small and are of the same order of magnitude as the uncertainties in the determination of the band positions. The differences between the two spectra mentioned above represent the only effects of the identity of the cation within the portion of the spectrum studied. A similar situation was observed in the spectra of the chlorides where the specific cation effects appeared between 19,200 cm.$^{-1}$ and 20,600 cm.$^{-1}$.

TABLE I

ABSORPTION BANDS OF COBALT(II) BROMIDE DOUBLE SALTS

$(PyH)_2CoBr_4$		$(QuH)_2CoBr_4$	
ν, cm.$^{-1}$	Intensity	ν, cm.$^{-1}$	Intensity
13604	10	13625	10
14193	7	14217	9
14876	7	14903	7
15170	8	15179	8
15538	9	15506	9
15828	7	15789	7
16597	5	16542	3
16985	4	16974	4
17276	6	17239	5
17669	4	17589	3
17866	5	17793	3
18250	3		
		18490	2
18611	3		
		19066	1
19197	2		
19981	1		
20702	4	20643	4
21181	6	21139	6
21482	6	21450	6
21812	4	21786	4
22287	1	22216	1
22993	5	22972	5
23432	4	23411	4
23594	3	23562	3
25205	1		
25360	1		

In order to facilitate comparison of the bromide and chloride spectra, the slight differences among the spectra of the individual salts with a common anion have been neglected and a composite chloride and a composite bromide spectrum have been obtained by averaging wave number values and intensities of corresponding bands. These composite spectra are summarized in Table II and are illustrated in Fig. 1. For convenience, the bands have been numbered consecutively beginning with the one of longest wave length and, in addition, have been classified into groups designated by Roman numerals. In the figure, the band centers are represented by the positions of the vertices of the triangles representing the bands, the relative intensities by the altitudes of the triangles and the approximate band widths by the lengths of their bases. The solid triangles represent bands whose positions are independent of the identity of the cation while the open triangles represent those which are not. For comparison with the tetrahalide spectra, that portion of the spectrum of (en $H_2)_2CoCl_6$ which was photographed is also illustrated in the figure. The wave numbers and relative intensities of the bands in this spectrum are listed in Table III.

It is apparent from an examination of Fig. 1, that Groups I and II of the two tetrahalide spectra are essentially identical except for a shift of about 700 cm.$^{-1}$ of the entire bromide spectrum to the red relative to that of the chloride; for small differences in the spacing of the bands and for

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(9) E. G. V. Percival and W. Wardlaw, *J. Chem. Soc.*, 1505 (1929).

TABLE II

COMPOSITE SPECTRA OF COBALT(II) TETRAHALIDE COMPLEX IONS

Group	Band	$CoBr_4^{--}$ ν, cm.$^{-1}$	$CoBr_4^{--}$ Int.	$CoCl_4^{--}$ ν, cm.$^{-1}$	$CoCl_4^{--}$ Int.
I	1	13615	10	14265	10.0
	2	14205	8	15009	10.0
	3	14890	7	15462	8.2
	4	15175	8	15829	9.2
	5	15522	9	16277	8.4
	6	15809	7	16651	7.4
II	7	16570	4	17248	3.6
	8	16980	4	17684	2.4
	9	17258	5.5	18066	3.4
	10	17629	3.5	18618	5.4
	11	17830	4	18878	6.0
III	12	18250[a]	3	19279[c]	2.3
	13	18490[b]	2		
	14	18611[a]	3	19643	3.0
	15	19066[b]	1		
	16	19197[a]	2	20250[d]	1.3
	17	19981[a]	1		
IV	18	20673	4		
	19	21160	6	21898	2.8
	20	21466	6	22162	3.6
	21	21799	4	22452	3.4
	22	22252	1	22819	0.4
V	23	22983	5	24025	1.0
	24	23422	4	24480	0.8
	25	23578	3		
VI	26	25205[a]	1		
	27	25360[a]	1		

This band observed only for [a] $(PyH)_2CoBr_4$. [b] $(QuH)_2CoBr_4$. [c] Cs_3CoCl_5, $(PyH)_2CoCl_4$, and $(QuH)_2CoCl_4\cdot H_2O$. [d] All of the tetrachloride double salts except Cs_2CoCl_4.

some differences in relative intensities. The groups lying at higher frequencies show more pronounced differences but nevertheless, the correspondence between the two spectra is sufficiently close to justify the conclusion that both spectra are due to absorbing groups having the same configuration.

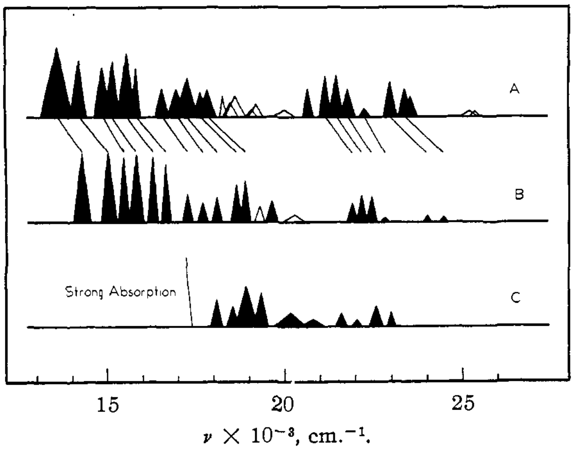

Fig. 1.—Absorption bands of cobalt(II) comple: ions: A, $CoBr_4^{--}$; B, $CoCl_4^{--}$; C, $CoCl_6^{4-}$.

TABLE III

ABSORPTION BANDS OF $(en\ H_2)_2CoCl_6$

Group	ν, cm.$^{-1}$	Intensity
I	17400[a]	
II	18082	4
	18529	3
	18919	6
	19320	5
III	20144	2
	20773	1
IV	21603	2
	22036	1
	22579	3
	23001	2

[a] Short wave length edge of unresolved group.

On the other hand, the spectrum of $(en\ H_2)_2CoCl_6$ is distinctly different. For it, Groups II and IV are similar in structure (which is not the case for the tetrahalides) and consist of doublets with an average separation of 426 ± 14 cm.$^{-1}$ and with similar relative intensities within each doublet. In each group the less intense doublet occurs displaced to the long wave length side of the more intense one. This displacement is 814 cm.$^{-1}$ in Group II and 970 cm.$^{-1}$ in Group IV.

The comparative sharpness of most of the bands in these spectra suggests that for the transitions responsible for the observed absorption both the initial and final states are rather effectively shielded from perturbing effects of surrounding ions. The absorption is probably due to an unpaired electron in one of the 3d orbitals of the cobalt ion and the shielding is provided by the electron clouds of the coördinated halide ions. The complexity of the spectra may be due to the multiplet nature of the energy levels of the cobalt ion or to the coupling of vibrations characteristic of the complex with the electronic transitions or possibly to both. If vibrational structure is present, then, as has been pointed out above, substitution of one halogen by another should give rise to changes in the characteristic frequencies. The direction and magnitude of such changes will be determined both by the masses of the halide ions and by the force constants of the cobalt–halogen bonds. Examination of Table II and Fig. 1 reveals that a number of intervals between adjacent bands in Groups I and II are smaller in the spectrum of the bromide than in the spectrum of the chloride. This is to be expected if vibrational structure is present and if the force constants of the Co–Br and Co–Cl bonds are not very different in magnitude.

All of the bands, with the exception of number 7, in these two groups can be represented by the energy level diagrams shown in Fig. 2 in which the transitions representing observed bands are indicated by arrows numbered to correspond to Table II. The ground state consists of two levels separated by 263 cm.$^{-1}$ for the bromide and by 346 cm.$^{-1}$ for the chloride. The excited states are also doublets separated by about 600 cm.$^{-1}$ for the bromide and by about 800 cm.$^{-1}$ for the chloride. The comparison between wave numbers calculated from the term values shown in the figure and the observed wave numbers of these bands is made in Table IV. For the bromide the average difference between calculated and observed values is 12 cm.$^{-1}$ while for the chloride it is 17 cm.$^{-1}$.

TABLE IV

COMPARISON OF CALCULATED AND OBSERVED WAVE NUMBERS

		$CoBr_4^{--}$			$CoCl_4^{--}$	
Band	ν calcd.	ν obs.	Diff.	ν calcd.	ν obs.	Diff.
1	13615	13615	0	14265	14265	0
2	14205	14205	0	15009	15009	0
3	14901	14890	+11	15472	15462	+10
4	15164	15175	−11	15818	15829	−11
5	15534	15522	+12	16291	16277	+14
6	15797	15809	−12	16637	16651	−14
8	16987	16980	+ 7	17702	17684	+18
9	17250	17258	− 8	18048	18066	−18
10	17598	17629	−31	18575	18618	−43
11	17861	17830	+31	18921	18878	+43

Although no attempt to give a complete interpretation of this energy level diagram will be made, the separation in the ground state will be identified tentatively as the totally symmetric valence vibration of the tetrahedral CoX_4^{--} complex. The magnitude of the observed frequencies is about that to be expected for such an assignment. For example, for several tetrahalides of elements of the fourth group of the Periodic Table, the values of the frequency in question range from 220 cm.$^{-1}$ to 265 cm.$^{-1}$ for the bromides and from 367 cm.$^{-1}$ to 459 cm.$^{-1}$ for the chlorides.[10]

If this assignment is correct and if it be assumed that the vibration may be represented by a simple harmonic force function, the force constants, calculated from the above frequencies, for the Co–X bond in these complexes are 3.25×10^5 dynes/cm. and 2.50×10^5 dynes/cm. for the bromide and chloride, respectively. Since the force constant can be taken as being roughly proportional to the dissociation energy of the bond,[11] it may be concluded that in these complexes, the Co–Br bond is stronger than the Co–Cl bond.

From these relative bond strengths, certain conclusions regarding the nature of the binding may be drawn. If ion–ion attractive forces alone were responsible for the binding, the Co–Cl bond would be expected to be stronger than the Co–Br bond since the interionic distance is smaller for the former than for the latter. Clearly, then, other forces must be operative in order to account for the observed relative magnitudes of the bond energies. These are presumably ion-induced dipole forces between the cobalt ion and the dipoles produced by polarization of the halide ions in the field of the cobalt ion. Since the polarizability of the bromide ion is larger than that of the chloride ion, this type of force will make a larger contribution in the case of the Co–Br bond than in that of the Co–Cl bond. The ratio of the polarizabilities of the bromide and chloride ions is 1.40[12] while the ratio of the force constants for the complex ions is 1.30. The contribution of the ion–ion forces to the binding is reflected in the smaller value of the latter ratio as compared with the former.

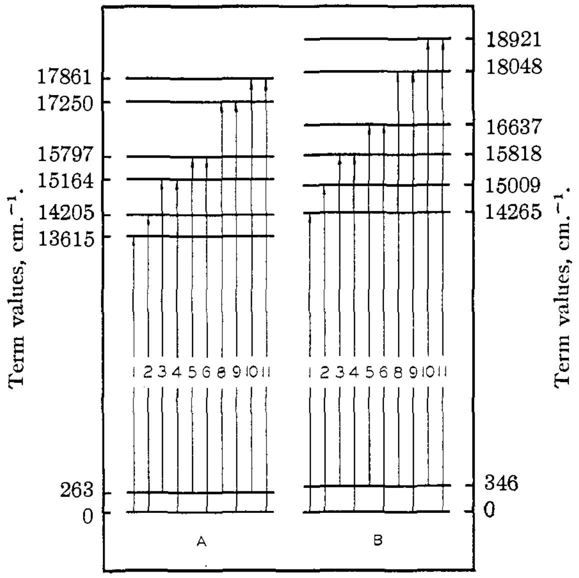

Fig. 2.—Energy level diagram: A, $CoBr_4^{--}$; B, $CoCl_4^{--}$.

Additional evidence that the binding is not purely of ion–ion type is obtained from a consideration of the interionic distance for the $CoCl_4^{--}$ complex ion. From an analysis of X-ray diffraction measurements upon Cs_3CoCl_5,[13] the Co–Cl distance in the complex ion has been found to be 2.34 Å. The sum of the ionic radii[14] for Co^{++} and Cl^- is 2.53 Å. Since the experimental distance is significantly smaller than this sum, a considerable deformation of the electron distribution of the chloride ion is indicated.

The question as to whether the observed relative intensities of the bands agree with those to be expected may now be considered. Since the population of the higher level in the ground state relative to that of the lower is determined by a Boltzmann factor, the intensities of bands originating in the upper level ought to be smaller than that of those from the lower. This condition is satisfied for all of the pairs of bands except numbers 5 and 6 for both the bromide and chloride. Since band 6 occurs at the short wave length edge of Group I where the continuous background absorption is falling very rapidly with decreasing wave length, the estimated relative intensities of bands 5 and 6 may well be in error. It must be emphasized that

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[10] J. H. Hibben, "The Raman Effect and its Chemical Applications," Reinhold Publishing Corporation, New York, N. Y., 1939, pp. 138, 348.

[11] A. Eucken, *Ann.*, **440**, 111 (1924).

[12] O. K. Rice, "Electronic Structure and Chemical Binding," McGraw-Hill Book Company, Inc., New York, N. Y., 1940, p. 178.

[13] H. M. Powell and A. F. Wells, *J. Chem. Soc.*, 359 (1935).

[14] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, pp. 326, 330.

the relative intensities reported here are based on visual estimates of blackening of the photographic plate at the band maxima. No account of deviations from linearity of the characteristic curve of the plate or of the effect of the appreciable width and overlapping of the absorption bands has been taken in making the estimates. Therefore the discrepancy in the relative intensities mentioned above cannot be considered to be a serious objection to the suggested interpretation of the spectra; at least not until accurate intensity measurements are made and until the changes of relative intensities with changes of temperature of the absorbing crystals are investigated.

Summary

1. The room temperature absorption spectra of crystals of pyridinium tetrabromocobaltate(II), quinolinium tetrabromocobaltate(II) and ethylenediaminium hexachlorocobaltate(II) have been photographed.

2. The spectra of pyridinium tetrabromocobaltate(II) and quinolinium tetrabromocobaltate(II) were found to be essentially identical and to bear a very close resemblance to the previously observed spectra of similar double salts containing the tetrahedral tetrachlorocobaltate(II) ion. Therefore the bromides may be assumed to contain the tetrahedral tetrabromocobaltate(II) ion. The spectrum of ethylenediaminium hexachlorocobaltate(II) is distinctly different.

3. A vibration frequency of the tetrahedral complex ions has been identified from an analysis of the tetrahalide spectra. From the magnitude of this frequency, the force constants of the cobalt-bromine and cobalt-chlorine bonds have been determined.

PRINCETON, N. J. RECEIVED SEPTEMBER 28, 1948

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

The Preparation of the Six *n*-Octynoic Acids[1,2]

BY MELVIN S. NEWMAN AND JOHN H. WOTIZ[3]

In this paper are described the syntheses of the six *n*-octynoic acids and of many intermediates. This work was undertaken with a multiple purpose: (1) to add to our knowledge of the reactivity of the acetylenic function in acids having the triple bond at varying distances from the carboxyl group; (2) to study various methods of synthesis for such acids; (3) to obtain information about the odors of the methyl esters. Inasmuch as the synthetic problems consumed most of our efforts, the first objective must remain for future study. It was deemed of interest to investigate the odors of the methyl esters of these acids because of the commercial use of methyl heptynecarboxylate in perfumery. The odors have been evaluated by men skilled in the art and are described as follows.[4]

$HC\equiv C(CH_2)_5COOCH_3$, very green but sharp, chemical, fatty, unpleasant; $CH_3C\equiv C(CH_2)_4COOCH_3$, reseda-like, fatty, weak, green seaweed; $CH_3CH_2C\equiv C(CH_2)_3COOCH_3$, leafy, cucumber-like, something like talia, sweet, violet; $CH_3(CH_2)_2C\equiv C(CH_2)_2COOCH_3$, cucumber-like but sharp, chemical, somewhat fruity; $CH_3(CH_2)_3C\equiv CCH_2COOCH_3$, something like fresh cut grass, but crude and fatty.

The synthetic methods used are described below and are summarized in a series of charts. Since many bifunctional acetylenic intermediates of either rare or previously non-existent types were prepared, we prefer to discuss the preparation of these compounds according to the functional group other than the triple bond. In this way the scope and limitations of the methods of synthesis will be emphasized.

Alkynes and Alkynols

The required 1-alkynes were prepared in high yields by known procedures.[5] 2-Alkyn-1-ols were made in high yield by condensation of 1-alkynylmagnesium bromides with gaseous formadehyde[6] while 3-alkyn-1-ols were prepared in poor yield by the reaction of acetylenic organometallic reagents with ethylene oxide.[7]

Acetylenic Halides

One useful method for preparation of halogenated acetylenes involved the reaction of alkynylsodium in liquid ammonia with polymethylene chlorobromides.[8] This reaction failed with ethylene

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[1] The material herein presented was taken from the Ph.D. thesis of John H. Wotiz, The Ohio State University, June, 1948. Present address of John H. Wotiz, Chemistry Department, University of Pittsburgh.

[2] Presented before the Organic Division of the American Chemical Society at Chicago, Illinois, April, 1948.

[3] The authors wish to express their gratitude to The Ohio State University for a grant from funds donated by The Ohio State University Research Foundation and administered by the Graduate School.

[4] We are indebted to Dr. Ernst T. Theimer of the research department of van Ameringen-Haebler, Inc., Elizabeth, New Jersey, for securing the data on odor.

[5] (a) Vaughn, *et al.*, *J. Org. Chem.*, **2**, 1 (1937); (b) Henne and Greenlee, THIS JOURNAL, **67**, 484 (1945).

[6] Lai, *Bull. soc. chim.*, **53**, 682 1533 (1933); Bartlett and Rosen, THIS JOURNAL, **64**, 545 (1942)

[7] Compare Faucounau, *Compt. rend.*, **199**, 605 (1934); Danehy, Vogt and Nieuwland, THIS JOURNAL, **57**, 2327 (1935); Greenlee, Ph.D. thesis, The Ohio State University, 1942, p. 60.

[8] In a paper which appeared while this manuscript was in preparation, Ahmad and Strong, THIS JOURNAL, **70**, 1699 (1948), mention a 36% yield of 1-chloro-5-decyne from 1-chloro-4-iodobutane and 1-hexynylsodium.