ethanol is stable on standing overnight at 50°, but a parallel solution containing 0.100 *M* $CuCl_2$ undergoes 56% conversion into an equimolar mixture of acetal and ethyl acetate (basis gc areas). Vinyl chloride (approximately 5% by volume) is similarly stable in pure ethanol at 50° but in the presence of 0.10 *M* $CuCl_2$ undergoes substantial conversion into acetal. With 0.020 *M* $PdCl_2$ and 0.100 *M* $CuCl_2$ vinyl chloride yields a mixture of acetal and chloroacetaldehyde diethyl acetal in ratio 10:1

Registry No.—Ethylene, 74-85-1; 1-butene, 106-98-9; 1-hexene, 592-41-6; 1-octene, 111-66-0; cyclohexene, 110-83-8; *trans*-3-hexene, 13269-52-8; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; 2,5-dihydrofuran, 1708-29-8; acrylonitrile, 107-13-1; $PdCl_2$, 7647-10-1.

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Metalation Reactions. III. Metalation of Octadecynols and Octadecynyl Methyl Ethers

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Octadecynyl alcohols and methyl ethers were metalated with butyllithium in ether and yielded on carbonation mono- and diacids. The two carboxyls in the diacids were situated on the same carbon atom. The alcohols were metalated faster than the ethers. The composition of the products was determined. The proton abstraction from both propargylic positions proceeded to a similar extent. Carbonation was more pronounced at the initially sp-hybridized atoms. The distance from the functional group was of little influence on the protonation and carbonation reactions, except for the case when the triple bond was very near the functional group.

The transformation of unsaturated fatty acids into new products by addition to double bonds[1] has been studied for many years. Allylic oxidations and halogenations of these compounds have also been investigated.[1] Some years ago our laboratory embarked on a study of allylic metalation of derivatives of unsaturated acids with a view to the transformation of the metalated adducts into difunctional compounds. We now report our results on the metalation of octadecynols and octadecynyl methyl ethers.

The metalations were at first performed with amylsodium in hexane. Stearolyl alcohol (I) gave precipitates containing the alkoxide, and no metalation was observed. Stearolyl methyl ether (II) did not precipitate under these conditions, and yielded carboxylic acids after carbonation of the reaction mixture with Dry Ice. Since butyllithium did not form precipitates with I, all subsequent metalations were carried out with this reagent in ether solution or in ether–hexane (1:1). The metalated compounds were carbonated with Dry Ice and the products were shown to be a mixture of mono- and diacids. The ratio of these acids was analyzed by glpc, after esterification, etherification, and hydrogenation of the reaction products. The results are recorded in Table I. The metalation of the alcohol is faster than that of the ether, in agreement with the known catalytic influence of alkoxides on the metalation reaction,[2] which is probably due to depolymerization of the organometallic reagent by the catalyst.[3]

The metalation is faster in ether than in a mixture of ether–hexane (1:1), and proceeds to a very limited extent (5%) in hexane alone, even after long reaction periods. However, the addition of tetramethylethylenediamine (TMEDA) speeds up the reaction in hexane, making it approximately as fast as in ether. The catalytic effect of this substance has been previously observed.[4]

TABLE I

METALATION[a] OF STEAROLYL ALCOHOL I AND METHYL ETHER II

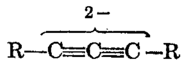
Compd	Duration, hr	Yield[b] of monoesters, %	Yield[b] of diester, %	Uv,[c] λ_{max}, mμ (ε)
I	48	45	15	220 (5200)
I	72	32	39	220 (4400)
I[d]	72	44	16	. . .
II	72	45	2	218 (3600)[e]
II	93	44	6	218 (3400)[e]
II	120	24	30	. . .[f]
II[d]	98	43	23	. . .
I[g]	96	34	9	. . .
II[g]	96	29	4	. . .

[a] In ether solution at room temperature, with subsequent carbonation and esterification. [b] Determined on the saturated esters. [c] Determined on the mixture of unsaturated esters before their separation. [d] In hexane at room temperature, using TMEDA as a catalyst. [e] ν_{max} 1710, 1740, and 1950 cm^{-1}. [f] ν_{max} 1710, 1740, 1950 (w), and 2750 cm^{-1} (w). [g] In ether–hexane (1:1).

The reaction proceeds largely to the dimetalated derivative after long reaction times. The second proton is abstracted from the same carbon as the first (see below). The formation of such dianions (III), called by us extended acetylenes or sesquiacetylenes,[5] was proved directly for similar propargylic systems.[5] Other metalations on the propargylic posi-

$$CH_3(CH_2)_7C\equiv C(CH_2)_8OR$$

I, R = H
II, R = CH_3



$$R—\overbrace{C\equiv C\equiv C}^{2-}—R$$

III

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(1) H. J. Harwood, *Chem. Rev.*, **62**, 99 (1962).

(2) A. A. Morton and A. E. Brachman, *J. Amer. Chem. Soc.*, **73**, 4363 (1951); A. A. Morton, C. E. Claff, Jr., and F. W. Collins, *J. Org. Chem.*, **20**, 428 (1955); M. Schlosser, *J. Organometal. Chem.*, **8**, 9 (1967).

(3) R. A. Benkeser, T. F. Crimmins, and W. Tong, *J. Amer. Chem. Soc.*, **90**, 4366 (1968).

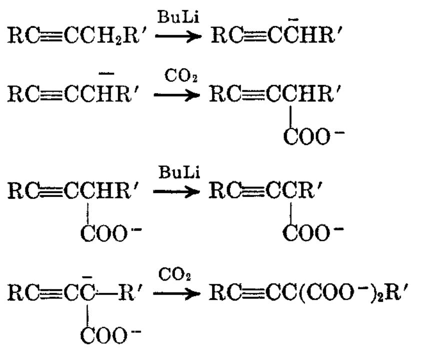
(4) G. G. Eberhardt and W. A. Butte, *J. Org. Chem.*, **29**, 2928 (1964).

(5) J. Klein and S. Brenner, submitted for publication.

tion were reported recently for 1-butyne,[6] propyne,[7] and 1-phenylpropyne.[8]

A series of transmetalations and carbonations (Scheme I) involving only monometalated compounds which takes place during the carbonation reaction has been shown to occur in other instances.[9] However, the introduction of the second carboxyl group in this case is not due to such a reaction, in view of the gradual rise in the percentage of diacids with the time of reaction. A higher ratio of di- to monocarboxylic acids would be expected at the beginning of the reaction, when a larger excess of butyllithium was present, should the formation of dicarboxylic acids have proceeded by Scheme I.

SCHEME I



$$RC{\equiv}CCH_2R' \xrightarrow{BuLi} RC{\equiv}C\bar{C}HR'$$

$$RC{\equiv}C\bar{C}HR' \xrightarrow{CO_2} RC{\equiv}C\underset{COO^-}{\underset{|}{C}}HR'$$

$$RC{\equiv}C\underset{COO^-}{\underset{|}{C}}HR' \xrightarrow{BuLi} RC{\equiv}C\underset{COO^-}{\underset{|}{\bar{C}}}R'$$

$$RC{\equiv}C\underset{COO^-}{\underset{|}{\bar{C}}}{-}R' \xrightarrow{CO_2} RC{\equiv}CC(COO^-)_2R'$$

The second carboxyl was found to be on the same carbon as the first, since, on heating to 180°, the saturated dicarboxylic acids are converted totally to monocarboxylic acids. Formation of malonic acids by a mechanism other than that of Scheme I could occur only if both abstracted protons came from the same carbon atom.

All monocarboxylic acids were isomers, as were the dicarboxylic acids. No products were obtained by addition of butyllithium to the triple bond and subsequent carbonation of the vinylic anion, as evidenced by analysis and comparison with synthetic samples.

The next problem to be solved was therefore the position of the carboxyl in the chain of the product and the disposition of the multiple bonds.

In Table I are recorded the uv and ir absorptions of the mixture of unsaturated esters obtained from the reaction studied with I and II. Two carbonyl frequencies are observed at 1710 and 1740 cm^{-1}, which can be attributed to a conjugated and nonconjugated ester function, respectively. A band at 1950 cm^{-1} shows the presence of an allene group and, at 2240 cm^{-1}, of an acetylenic function. A maximum absorption at 220 mμ also shows the presence of a conjugated chromophore. The extinction of this band decreases with the reaction time, this decrease being associated with the decrease in the intensity of the initially strong bands at 1710 and 1950 cm^{-1} and the increase in the intensity of the weak 1740- and 2240-cm^{-1} bands. All these changes can be associated with the increase in the ratio of dicarboxylic to monocarboxylic acids. The latter are therefore mostly of allenic structure, and the dicarboxylic acids are acetylenic as expected, both carboxyls being situated on the same carbon. This assignment is confirmed by the spectral properties of the two fractions, containing separately the mono- and diesters. In particular, an allenic band at 1950 cm^{-1} was present in the monoesters and absent in the diesters.

The position of the multiple bonds in each acid is determined by the position of the carboxyl group, as shown in Scheme II, provided that no isomerization occurs in the metalation step. Such isomerization would also be detected by a carboxyl group at a position different from that indicated in Scheme II.

Separation experiments were carried out on saturated esters in order to diminish the number of isomers and to avoid possible decarboxylation during the work-up. Fruitless efforts were made to separate the isomers by glpc. Thin layer chromatography, however, proved itself to be a good separation technique in this case, but for qualitative analysis only. Four spots were separated corresponding in number to the monocarboxylic acids expected according to Scheme II. In order to attribute these spots to the expected isomers and to exclude the possibility of positional isomerization of the charged carbon during the transmetalation reaction, we synthesized several of the desired acids.

12-Methoxycarbonyloctadecanol-1 (IV) was synthesized (Scheme III) by alkylation of diethyl malonate first with undec-10-enyl bromide and then with hexyl bromide. The dialkylated malonate was hydrolyzed, decarboxylated to the monoacid, esterified with diazomethane, hydroborated, and oxidized to IV.

11-Methoxycarbonyloctadecanol-1 (V) was synthesized by a procedure similar to that in the initial steps above, but involving ozonolysis instead of hydroboration at the end (Scheme IV).

10-Methoxycarbonyloctadecanol-1 (VI) was prepared by alkylation of diethyl octaylmalonate with 9-bromononyl acetate, with subsequent saponification of the product, decarboxylation, and esterification (Scheme V).

The preparation of 9-methoxycarbonyloctadecyl methyl ether (VII) proceeded along similar lines (Scheme VI).

A similar synthesis afforded 8-methoxycarbonyloctadecylmethyl ether (Scheme VII).

The synthesized hydroxy esters were transformed into methyl ethers by treatment with diazomethane in the presence of fluoroboric acid.[10]

Comparison by tlc with the ether esters obtained by the metalation–carbonation reaction of I and II and subsequent hydrogenation and esterification (and etherification in case of I) has resulted in the identification of four isomers present in the monocarboxylic ester fraction as the expected 8-, 9-, 10-, and 11-methoxycarbonyloctadecyl alcohols or methyl ethers, respectively, for I and II.

The position of the carboxyls in the dicarboxylic acid fraction was found by decarboxylation of these acids after their hydrogenation. Analysis by tlc as above showed the presence of the same four isomers as in the

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[6] K. C. Eberly and H. E. Adams, *J. Organometal. Chem.*, **3**, 165 (1965).

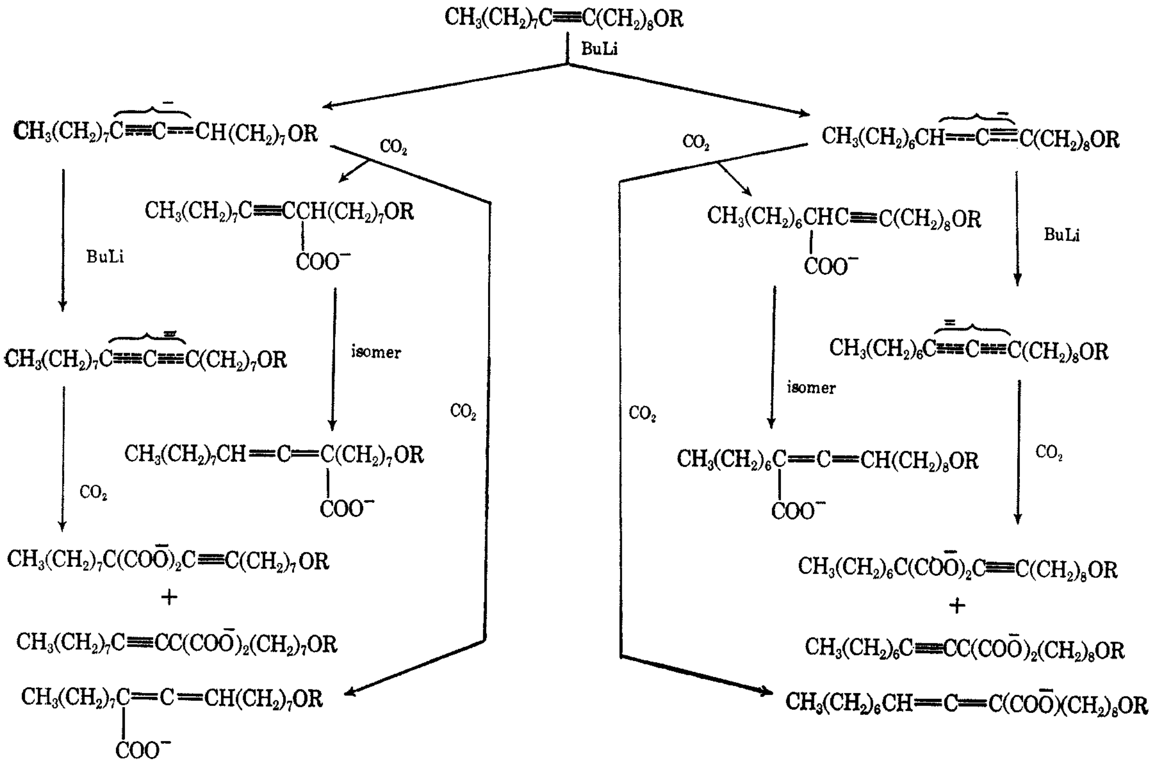
[7] R. West, P. A. Carney, and I. C. Mineo, *J. Amer. Chem. Soc.*, **87**, 3788 (1965).

[8] J. E. Mulvaney, T. L. Folk, and D. J. Newton, *J. Org. Chem.*, **32**, 1675 (1967).

[9] A. A. Morton, F. Fallwell, Jr., and L. Palmer, *J. Amer. Chem. Soc.*, **60**, 1426 (1938).

[10] M. Neeman, M. C. Caserio, J. D. Roberts, and W. S. Johnson, *Tetrahedron*, **6**, 36 (1959).

Scheme II



Scheme III

$$\mathrm{CH_2(COOEt)_2 + CH_2{=}CH(CH_2)_9Br \xrightarrow{B}}$$
$$\mathrm{CH_2{=}CH(CH_2)_9CH(COOEt)_2 \xrightarrow{CH_3(CH_2)_5Br}}$$
$$\mathrm{CH_3(CH_2)_5C(COOC_2H_5)_2(CH_2)_9CH{=}CH_2 \longrightarrow}$$
$$\mathrm{CH_3(CH_2)_5CH(COOCH_3)(CH_2)_9CH{=}CH_2 \xrightarrow[oxidation]{B_2H_6}}$$
$$\mathrm{CH_3(CH_2)_5\ CH(COOCH_3)(CH_2)_{11}OH}$$

IV

Scheme IV

$$\mathrm{CH_2{=}CH(CH_2)_9CH(COOC_2H_5)_2 + CH_3(CH_2)_6Br \xrightarrow{B}}$$
$$\mathrm{CH_3(CH_2)_6C(COOC_2H_5)_2(CH_2)_9CH{=}CH_2 \longrightarrow}$$
$$\mathrm{CH_3(CH_2)_6CH(COOCH_3)(CH_2)_9CH{=}CH_2 \xrightarrow[reduction]{O_3}}$$
$$\mathrm{CH_3(CH_2)_6CH(COOCH_3)(CH_2)_{10}OH}$$

V

Scheme V

$$\mathrm{CH_3(CH_2)_7CH(COOC_2H_5)_2 + Br(CH_2)_9OCOCH_3 \longrightarrow}$$
$$\mathrm{CH_3(CH_2)_7C(COOC_2H_5)_2(CH_2)_9OCOCH_3 \longrightarrow}$$
$$\mathrm{CH_3(CH_2)_7CH(COOH)(CH_2)_9OH \longrightarrow}$$
$$\mathrm{CH_3(CH_2)_7CH(COOCH_3)(CH_2)_9OH}$$

VI

Scheme VI

$$\mathrm{CH_3(CH_2)_8CH(COOC_2H_5)_2 + Cl(CH_2)_8OCOCH_3 \longrightarrow}$$
$$\mathrm{CH_3(CH_2)_8C(COOC_2H_5)_2(CH_2)_8OCOCH_3 \longrightarrow}$$
$$\mathrm{CH_3(CH_2)_8CH(COOH)(CH_2)_8OH \longrightarrow}$$
$$\mathrm{CH_3(CH_2)_8CH(COOCH_3)(CH_2)_8OCH_3}$$

VII

Scheme VII

$$\mathrm{CH_3(CH_2)_9CH(COOC_2H_5)_2 + Br(CH_2)_7OCOCH_3 \longrightarrow}$$
$$\mathrm{CH_3(CH_2)_9C(COOC_2H_5)_2(CH_2)_7OCOCH_3 \longrightarrow}$$
$$\mathrm{CH_3(CH_2)_9CH(COOH)(CH_2)_7OH \longrightarrow}$$
$$\mathrm{CH_3(CH_2)_9CH(COOCH_3)(CH_2)_7OCH_3}$$

VIII

case of the monocarboxylic acids. This easy decarboxylation of the diacids proves that they contain both carboxyls on the same carbon.

These results prove the course of metalation and the lack of isomerization. We were, however, also interested in the relative amounts of the isomers formed and, specifically, in the effect of the terminal group on the position of metalation. The extent of carbonation at the two ends of each ion having a delocalized charge was also of interest. Such effects were found by us in other systems.[11] In addition, the influence of the distance of the terminal functional group on the course of the metalation and carbonation reactions was also investigated.

A series of acetylenic alcohols and methyl ethers of the general formulas IX and X was prepared by reduction of the corresponding esters.

$$\mathrm{CH_3(CH_2)_{15-\mathit{x}}C{\equiv}C(CH_2)_{\mathit{x}}OH} \qquad \mathrm{CH_3(CH_2)_{15-\mathit{x}}C{\equiv}C(CH_2)_{\mathit{x}}OCH_3}$$

X

IXa, $x = 4$ e, $x = 8$
b, $x = 5$ f, $x = 9$
c, $x = 6$ g, $x = 11$
d, $x = 7$

The alcohols IX and methyl ethers X were metalated by butyllithium in ether–hexane and carbonated, and the acids obtained were esterified with diazomethane. In the infrared, the unsaturated esters showed an allenic band at 1950 $\mathrm{cm^{-1}}$ and two carbonyl bands at 1710 and

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[11] J. Klein and S. Glily, unpublished data.

1740 cm^{-1}. These esters were hydrogenated, etherified when necessary, and separated into a mono- and diester fraction by glpc (Table II).

TABLE II

COMPOSITION OF THE PRODUCTS OF METALATIONS[a]

Starting material	Yield of monoesters, %	Yield of diesters, %
IXa	20	30
IXb	45	5
Xb	41	7
IXc	48	5
IXd	38	7
IXe	34	9
Xe	29	4
IXf	44	2
IXg	40	10

[a] The metalations were carried out for 96 hr by butyllithium (5 mol) in ether–hexane (1:1) at room temperature.

Table II shows the relative amounts of these two fractions, as obtained from the starting materials in question. The yields of all reactions are approximately the same and so are the relative amounts of mono- and diesters, except in one case, that of IXa, where a large amount of diester was formed. Note that the metalation in hexane–ether is somewhat slower than in ether alone (compare the results for IXe and I of Tables II and I).

The fractions were analyzed by tlc, which showed the presence of four spots in almost all products. This proved the absence of isomerization. Moreover, the overlap in position between the right number of ester products obtained during the metalation–carbonation of the series of triple-bond positional isomers of IX and X permitted the assignment of each spot to a particular isomeric ester.

Evaluation of the amount of the esters in the chromatoplates having proved very difficult, we used mass spectrometer techniques for the analysis of the ratio of isomeric esters in the reaction products. The fragmentation pattern of the synthetic esters was as expected.[12,13] The molecular ions (M^+) of IV, V, VI, VII, and VIII did not appear. The intensity of the peaks corresponding to $[M - H_2O]^+$ and $[M - CH_3OH]^+$, and to fragments containing both functional groups, such as $[CH_3OC(OH){=}CH(CH_2)_yOCH_3]^+$ and $[OC{=}CH(CH_2)_yOCH_3]^+$, was low. The most intense large fragments were those containing the ester with the alkyl group $[CH_3(CH_2)_zCH{=}C(OH)OCH_3]^+$[14] The intensity of this fragment was used to measure the ratios of the isomeric esters in the mixtures. All determinations were made in similar conditions. The reliability of this method was checked by analyzing three different mixtures of synthetic V and VII. The results, recorded in Table III, show that the relative peak intensities are approximately linearly correlated with the relative amount of the compound in the mixture. The percentages of the isomeric esters having the methoxycarbonyl groups at the positions x, $x + 1$, $x + 2$, and $x + 3$ obtained from the various starting alkynols IX and alkynyl methyl ethers X are recorded in Table IV. The sum of the percentages of the products with the methoxycarbonyl groups at the positions x and $x + 2$ gives the percentage of metalation at the position x, and the sum of ester groups at $x + 1$ and $x + 3$ shows the percentage of metalation at $x + 3$. The sum of products with the ester group at the $x + 1$ and $x + 2$ positions reflects the amount of allenic products formed. This analysis is correct if the diesters have a distribution of the carboxylic groups similar to that of the monoesters, and this is what in fact occurred (Table V). It can be observed that the allenic products are formed in larger amounts than the other isomers.

TABLE III

RELATIVE ABUNDANCE OF $[CH_3(CH_2)_7CH{=}C(OH)OCH_3]^+$ AND $[CH_3(CH_2)_5CH{=}C(OH)OCH_3]^+$

	Ratio of m/e 172/200	Molar ratio of V/VII
Mixture 1	74/26	70/30
Mixture 2	48/52	55/45
Mixture 3	22/78	24/76

TABLE IV

COMPOSITION OF MONOESTERS OBTAINED FROM METALATION

	% carboxyl at position					% carboxyl at position			
Starting material	x	$x + 1$	$x + 2$	$x + 3$	Starting material	x	$x + 1$	$x + 2$	$x + 3$
IXa[a]	3	11	72	14	IXf[a]	9	37	39	15
IXb[a]	11	33	25	31	IXg[a]	12	36	36	17
Xb[a]	20	19	38	23	IXe[b]	17	24	36	23
IXc[a]	19	38	28	15	Xe[b]	14	29	41	16
IXd[a]	15	30	33	22	IXb[b]	16	35	24	25
IXe[a]	10	26	38	26	Xb[b]	17	29	34	20
Xe[a]	9	25	46	20					

[a] In hexane–ether. [b] In hexane using TMEDA as catalyst.

TABLE V

RATIO OF THE MALONIC ESTERS OBTAINED AFTER METALATION

	Method A:[a] % isomers with carboxyl at position				Method B:[b] % isomers with carboxyl at position			
Starting material	x	$x + 1$	$x + 2$	$x + 3$	x	$x + 1$	$x + 2$	$x + 3$
IXa	..	13	66	21	..	17	63	20
IXe	20	23	30	27	17	21	31	31
Xe	17	23	32	28	16	23	32	29
IXb	13	30	26	31	18	27	28	27

[a] Method A: using peak intensities of the fragment $[CH_3(CH_2)_zCH{=}C(OH)OCH_3]^+$. [b] Method B: using peak intensities of the fragment $[CH_3(CH_2)_yC(COOCH_3){=}C(OH)OCH_3]^+$.

The abstraction of protons proceeded to a similar extent at both propargylic positions, except in the first case. It seems that neither inductive nor field effects carry to the fifth carbon in the chain. The absence of direct field effects in the case of the alkoxides could be attributed to the presence of ion pairs or clusters in which the effect of one charge was balanced by the effect of the other. A large diminution in the extent of proton abstraction at the position x was observed only in the case of IXa, where the triple bond was on the fifth carbon. This was due perhaps to the inductive effect of the alkoxide ion or to some coiling of the molecule. On the other hand, there is a possibility that

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(12) R. Ryhage and E. Stenhagen in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963, p 399.

(13) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., New York, N. Y., 1967, p 174.

(14) The relation between x, y, and z is as follows. The triple bond is at the $x + 1$ position of the starting material and the metalation can take place at the propargylic position x or $x + 3$. For metalation at the x position, y can be equal to $x - 1$ or to $x + 1$. For metalation at the $x + 3$ position, y can be $x + 2$ or x (see Scheme II). In this manner, y can be $x - 1$, x, $x + 1$, or $x + 2$. Similarly, z can be $14 - x$, $15 - x$, $16 - x$, or $17 - x$.

the method of analysis based on the relative intensities of $[CH_3(CH_2)_2CH{=}C(OH)OCH_3]^+$ is no longer reliable because of the proximity of the functional group. The presence of coiling can also be inferred from the consistently lower yields of acids with carboxyls at position x than of the isomers with carboxyls at the other propargylic position. This was observed for the ethers as well as for the alkoxides. It is possible that the oxygen of the functional group helps to solvate the lithium cation in the metalated product, thus hindering carbon dioxide attack at the position nearer to the functional group.

The position of the carboxyls in the dicarboxylic acids was determined by mass spectrometric analysis of the diesters (method B), and also of the monoesters obtained by decarboxylation of the diacids (method A). The ratio of the diesters in method B was obtained from the relative intensities of the fragments $[CH_3(CH_2)_2C(COOCH_3){=}C(OH)OCH_3]^+$. The results, recorded in Table V, were similar for both methods. They also show that the ratio of the positional isomers in the dicarboxylic esters correspond to that of the monoesters given in Table IV.

The influence of the conditions of the reaction on the extent of dimetalation was investigated for two additional compounds: tariryl alcohols (IXb) and tariryl methyl ether (Xb). The recorded results (Table VI) (based on the amounts of esters obtained after carbonation, esterification, and hydrogenation) confirm that longer reaction periods increase the extent of dimetalation, as in the case of I and II. The ether was metalated more slowly than the alcohol. TMEDA proved itself an excellent catalyst in these reactions.

TABLE VI

METALATION[a] OF TRIAYL ALCOHOL AND METHYL ETHER

Starting compd	Time of reaction, hr	Yield of monoester, %	Yield of diester, %
IXb	48	34	12
IXb	96	27	38
IXb	168	27	63
IXb[b]	95	59	11
Xb	69	26	10
Xb	90	41.5	4.5
Xb	170	15	40
Xb[b]	144	50	10

[a] With butyllithium in ether. [b] With butyllithium in hexane in the presence of TMEDA.

Experimental Section

9-Octadecynol (I).—A solution of 45 g of methyl stearolate[15] in 100 ml of anhydrous ether was added dropwise for 1 hr to 3.8 g of $LiAlH_4$ in 300 ml of ether with stirring and under nitrogen. The reaction mixture was then refluxed for 1 hr and cooled, and excess reagent was decomposed with ethyl acetate. Dilute acid was added, the layers were separated, and the solvent of the organic layer was distilled, yielding 36 g of I:[16] mp 25°; $\bar{\nu}_{max}$ 3300 cm^{-1}.

9-Octadecynyl Methyl Ether (II).—A solution of diazomethane in dichloromethane[17] (prepared from 13.8 g of nitrosomethylurea) was added dropwise to a solution of 10 g of stearolyl alcohol in 20 ml of dichloromethane containing 8 drops of 50% fluoroboric acid. The temperature of the reaction mixture was not allowed to exceed 0° during the addition. The acid was then neutralized by a solution of KOH. The organic layer was washed with water and distilled, yielding 9.3 g of II, bp 125–130° (0.1 mm).

Anal. Calcd for $C_{19}H_{36}O$: C, 81.4; H, 12.8. Found: C, 81.3; H, 12.8.

6-Octadecynol (IXb) was prepared by lithium aluminum hydride reduction of methyl 6-octadecyanoate, which was prepared by esterification of tariric acid[18] by diazomethane: bp 153–155° (0.4 mm); mp 29–30°; $\bar{\nu}_{max}$ 3370 cm^{-1}.

Anal. Calcd for $C_{18}H_{34}O$: C, 81.2; H, 12.8. Found: C, 81.4; H, 12.7.

6-Octadecynyl methyl ether (Xb) was prepared from the alcohol and diazomethane as described for II in 85% yield, bp 152–155° (0.7 mm).

Anal. Calcd for $C_{19}H_{36}O$: CH_3O, 11.1. Found: CH_8O, 11.0.

5-Octadecynol, 7-octadecynol, 8-octadecynol, 10-octadecynol, and 12-octadecynol were prepared by lithium aluminum hydride reduction of the corresponding acetylenic esters, which were prepared by esterification with diazomethane of the acetylenic acids, kindly donated to us by Dr. van Dorp of Unilever Laboratories. The methyl ethers of these alcohols were prepared as described above for stearolyl methyl ether.

5-Octadecynol had mp 28–29° (hexane).

Anal. Calcd for $C_{18}H_{34}O$: C, 81.2; H, 12.7. Found: C, 81.2; H, 12.8.

7-Octadecynol had mp 27–29° (hexane).

Anal. Calcd for $C_{18}H_{34}O$: C, 81.2; H, 12.7. Found: C, 81.3; H, 12.5.

8-Octadecynol had mp 26–27° (hexane).

Anal. Calcd for $C_{18}H_{34}O$: C, 81.2; H, 12.7. Found: C, 80.7; H, 12.3.

10-Octadecynol had mp 28–29°.

Anal. Calcd for $C_{18}H_{34}O$: C, 81.2; H, 12.7. Found: C, 81.1; H, 12.6.

12-Octadecynol had mp 28–29°.

Anal. Calcd for $C_{18}H_{34}O$: C, 81.2; H, 12.7. Found: C, 81.1; H, 12.8.

Diethyl Octylmalonate.—A 14.4-g sample of a 50% suspension of NaH was washed with hexane. Then 500 ml of toluene was added, followed by 48 g of diethyl malonate and 38 g of octyl bromide. The reaction mixture was refluxed for 6 hr, cooled, and acidified with acetic acid. Water was then added, the layers were separated, and the organic layer was distilled, giving 35 g, bp 120° (0.1 mm).[19]

Diethyl nonylmalonate[19] and diethyl decylamlonate[19] were prepared by the same procedure.

12,12-Diethoxycarbonyloctadecene-1 was prepared as above from diethyl undec-10-enyl malonate[20] and hexyl bromide: bp 160–170° (0.3 mm); $\bar{\nu}_{max}$ 1730 and 1640 cm^{-1}.

Anal. Calcd for $C_{24}H_{44}O_4$: C, 72.7; H, 11.1. Found: C, 73.05; H, 11.07.

12-Methoxycarbonyloctadecene-1.—A solution of 12 g of 12,12-diethoxycarbonyloctadecene-1 in 60 ml of ethanol was refluxed with a solution of 15 g of KOH in 15 ml of water for 18 hr, then acidified, diluted with water, and extracted with ether. The residue, after distillation of ether from the organic layer, was heated at 180° until CO_2 evolution ceased. The product obtained was treated with an excess of an ethereal diazomethanol solution and distilled, giving 6 g: bp 155–160° (1.5 mm); $\bar{\nu}_{max}$ 1740 and 1640 cm^{-1}.

Anal. Calcd for $C_{20}H_{38}O_2$: C, 77.4; H, 12.3. Found: C, 77.48; H, 12.2.

12-Methoxycarbonyloctadecanol-1 (IV).—Diborane, generated by addition of 7 g of $BF_3 \cdot OEt_2$ in 10 ml of diglyme to 1.5 g of $NaBH_4$ in 20 ml of diglyme, was bubbled at 0° through a solution of 6 g of 12-methoxycarbonyloctadecene in 50 ml of THF. The solution was left for 30 min at 0°, and 10 ml of water was added dropwise, followed by 15 ml of 10% NaOH and 15 ml of 30% H_2O_2. The reaction mixture was stirred for 1 hr and extracted with dichloromethane. Distillation gave 5 g: bp 155–160° (0.5 mm); $\bar{\nu}_{max}$ 3350 and 1740 cm^{-1}.

Anal. Calcd for $C_{20}H_{40}O_3$: C, 73.2; H, 12.2. Found: C, 72.9; H, 12.2.

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12,12-Diethoxycarbonylnonadecene-1 was prepared as described above from diethyl undec-10-enylmalonate and heptyl bromide: bp 175–178° (0.4 mm); $\tilde{\nu}_{max}$ 1740 and 1640 cm^{-1}.

Anal. Calcd for $C_{25}H_{46}O_4$: C, 73.1; H, 11.2. Found: C, 73.1; H, 11.05.

11-Methoxycarbonyloctadecene-1 was prepared as described for 12-methoxycarbonyloctadecene: bp 155–160° (0.4 mm); $\tilde{\nu}_{max}$ 1740 and 1640 cm^{-1}.

Anal. Calcd for $C_{20}H_{38}O_2$: C, 77.8; H, 12.3. Found: C, 77.8; H, 12.2.

11-Methoxycarbonyloctadecanol-1 (V).—A solution of 3.5 g of 11-methoxycarbonylnonadecene in 50 ml of CH_2Cl_2 was ozonized at −60° until a blue coloration appeared. Excess ozone was removed in a stream of N_2, the solvent was distilled off, and the residue was dissolved in 50 ml of ethanol and treated dropwise with a solution of 1 g of $NaBH_4$ in 10 ml of ethanol. The reaction mixture was stirred for 16 hr, diluted with water, and extracted with ether. Distillation gave 2.2 g: bp 176° (0.7 mm); $\tilde{\nu}_{max}$ 3400 and 1740 cm^{-1}.

Anal. Calcd for $C_{20}H_{40}O_3$: C, 73.2; H, 12.2. Found: C, 73.15; H, 12.1.

Methyl 9-bromononanoate was prepared by the procedure of Cristol[21] from 21 g of methyl hydrogen sebacate.[22] Distillation gave 13 g: bp[23] 95–96° (0.6 mm); $\tilde{\nu}_{max}$ 1740 cm^{-1}. Reduction of 9 g of methyl 9-bromononanoate with $LiAlH_4$ as above yielded 6 g of 9-bromononanol:[24] bp 90–100° (0.2 mm); $\tilde{\nu}_{max}$ 3350 cm^{-1}. Acetylation of this alcohol with acetic anhydride in pyridine gave 6 g of the acetate: bp 90–92° (0.2 mm); $\tilde{\nu}_{max}$ 1740 cm^{-1}. The reaction of octyl malonate and 9-bromononyl acetate in toluene using sodium hydride as base gave 10,10-diethoxycarbonyloctadecyl acetate: bp 175–180° (0.5 mm); $\tilde{\nu}_{max}$ 1740 cm^{-1}. Saponification of the triester, decarboxylation, and esterification with diazomethane gave 10-methoxycarbonyloctadecanol-1 (VI): bp 160–170° (0.1 mm); $\tilde{\nu}_{max}$ 3400 and 1740 cm^{-1}.

Anal. Calcd for $C_{20}H_{40}O_3$: C, 73.2; H, 12.2. Found: C, 73.2; H, 12.0.

8-Chlorooctyl acetate was prepared by treating 8-chlorooctanol with acetic anhydride in pyridine: bp 94–98° (0.3 mm); $\tilde{\nu}_{max}$ 1740 cm^{-1}.

Anal. Calcd for $C_{10}H_{19}ClO_2$: C, 58.1; H, 9.2; Cl, 17.1. Found: C, 58.2; H, 9.30; Cl, 16.9.

9-Methoxycarbonyloctadecyl Methyl Ether (VII).—The reaction of diethylnonylmalonate, sodium hydride, 8-chlorooctyl acetate, and sodium iodide in toluene gave 9,9-diethoxycarbonyloctadecyl acetate: bp 175° (0.4 mm); $\tilde{\nu}_{max}$ 1740 cm^{-1}. This triester gave 9-methoxycarbonyloctadecyl methyl ether (VII) on saponification, decarboxylation, esterification, and etherification with diazomethane: bp 145–155° (0.5 mm); $\tilde{\nu}_{max}$ 1740 cm^{-1}.

Anal. Calcd for $C_{21}H_{42}O_3$: C, 73.7; H, 12.3. Found: C, 74.0; H, 12.0.

Methyl 7-bromoheptanoate[23] was prepared by Cristol's procedure[21] from hydrogen methyl suberate.[24]

7-Bromoheptyl acetate was obtained by reduction of methyl 7-bromoheptanoate with $LiAlH_4$ in ether, with subsequent acetylation of the alcohol with acetic anhydride in pyridine: bp 76–78° (0.3 mm); $\tilde{\nu}_{max}$ 1740 cm^{-1}.

Anal. Calcd for $C_9H_{17}BrO_2$: C, 45.6; H, 7.2; Br, 33.7. Found: C, 45.7; H, 7.4; Br, 33.54.

8-Methoxycarbonyloctadecyl methyl ether (VIII) was obtained by condensing diethyl decylmalonate with 7-bromoheptyl acetate in the presence of NaH in toluene. The 8,8-diethoxycarbonyloctadecyl acetate thus formed, bp 175–180° (0.3 mm), was saponified, decarboxylated, esterified, and etherified with diazomethane, yielding VIII: bp 145–148° (0.3 mm); $\tilde{\nu}_{max}$ 1740 cm^{-1}.

Anal. Calcd for $C_{21}H_{42}O_3$: C, 73.7; H, 12.3. Found: C, 73.9; H, 12.1.

Metalation. Procedure A (Table IV).—A 40-ml portion of 1.5 *M* butyllithium in hexane (Foote) was added under N_2 to a solution of 1.5 g of the octadecynol in 40 ml of ether. The reaction mixture was stirred for 96 hr at room temperature, and poured slowly onto an excess of pulverized Dry Ice in ether. The reaction mixture was left overnight, and washed with water, dilute NaOH, and again water. The aqueous solutions were acidified, extracted with ether, esterified, and etherified with diazomethane in the presence of $BF_3 \cdot OEt_2$.[10] The mixture of unsaturated esters was analyzed and then separated by glpc on a 1.5 m × 0.25 ft column of 10% stabilized polydiethyleneglycol succinate on acid-washed Chromosorb P at 230°.

The mixture of unsaturated esters dissolved in acetic acid was hydrogenated at 50 psi. The saturated esters showed a band at 1740 cm^{-1}, and no bands at 1710, 1950, and 2150 cm^{-1}. They were analyzed by glpc as above and by tlc.

Procedure B (Table I).—A solution of 2.8 g of the octadecynol in 20 ml of ether was added to a solution formed by evaporation *in vacuo* of the solvent from 50 ml of 1.5 *M* butyllithium in hexane and subsequent addition of 30 ml of ether. The solution was left for the indicated period of time, and carbonate, worked up, and analyzed as above.

Procedure C (Table I).—A solution of 3 g of the octadecynol was added to 47 ml of 1.5 *M* butyllithium in hexane, and 7 g of tetramethylethylenediamine (TMEDA) were added. The reaction mixture was stirred for the indicated period of time worked up, and analyzed.

Thin layer chromatography was performed on silica gel, using for the elution a mixture of hexane, benzene, and ether (175:50:14). A separation was obtained after four elutions. Preparative separation between the mono- and diesters was easily achieved on a layer 1 mm thick.

Preparative Metalations. II with Amylsodium.—A 9-g sample of II was added to a solution of amylsodium prepared from 33 g of sodium dispersion and 75 g of pentyl chloride.[25] The solution was left under nitrogen at room temperature for 84 hr, and cooled in a Dry Ice–acetone bath. Ether and Dry Ice were added in excess. The acids formed were separated, esterified, and distilled at 175–185° (0.7 mm): $\tilde{\nu}_{max}$ 1740, 1710, and 1650 cm^{-1}; λ_{max} 220 mμ (ϵ 7000).

Anal. Found: CH_3O, 18.2.

II with Butyllithium.—A 100-ml solution of 1.6 *M* butyllithium in hexane was added to a solution of 8 g of II in 100 ml of ether. The reaction mixture was left for 150 hr under nitrogen at room temperature. Carbonation with Dry Ice and esterification with diazomethane yielded 4.5 g of esters: bp 160–165° (0.2 mm): $\tilde{\nu}_{max}$ 1710, 1740, and 1950 cm^{-1}; λ_{max} 220 mμ (ϵ 5000).

Anal. Found: C, 73.16; H, 10.31; CH_3O, 19.6.

This product was separated by preparative tlc into two fractions, 1 and 2.

Fraction 1: $\tilde{\nu}_{max}$ 1710, 1740, and 1950 cm^{-1}; λ_{max} 225 mμ (ϵ 6000).

Anal. Calcd for $C_{21}H_{38}O_3$: C, 74.5; H, 11.2; CH_3O, 18.2. Found: C, 74.5; H, 11.2; CH_3O, 17.8.

This fraction contained the monoesters.

Fraction 2 contained the diesters: $\tilde{\nu}_{max}$ 1710 (w) and 1740 cm^{-1}; λ_{max} 225 mμ (ϵ 1700).

Anal. Calcd for $C_{23}H_{40}O_5$: C, 69.2; H, 10.1; CH_3O, 23.4. Found: C, 69.2; H, 10.3; CH_3O, 22.9.

Tariryl Methyl Ether (Xb) with Butyllithium.—A 100-ml solution of 1.6 *M* butyllithium in hexane was added to a solution of 11.2 g of Xb in 100 ml of ether. The reaction mixture was left for 118 hr and worked up as above, giving 7 g of esters: $\tilde{\nu}_{max}$ 1710, 1740, and 1950 cm^{-1}. This product was separated by glpc on a 1.5 m × 0.25 ft column of 10% Apiezon L on Celite into two fractions. The first had bands at 1710, 1740, and 1950 cm^{-1}.

Anal. Calcd for $C_{21}H_{38}O_3$: CH_3O, 18.2. Found: CH_3O, 17.9.

Stearolyl Alcohol I with Butyllithium.—A 140-ml solution of 1.6 *M* butyllithium in hexane was added to a solution of 13.5 g of I in ether (cooled in an ice bath). The reaction mixture was left for 96 hr at room temperature and poured onto pulverized Dry Ice covered with ether. Work-up as before and etherification left 10.5 g of esters: $\tilde{\nu}_{max}$ 1710, 1740, and 1950 cm^{-1}; λ_{max} 220 mμ (ϵ 5000). This product was hydrogenated and separated by glpc into mono- and diesters. The diesters were saponified, decarboxylated at 180°, reesterified, and analyzed by glpc and tlc. No diesters remained after this treatment.

Mass spectra were determined on a CH4 mass spectrometer using a 70-eV ionizing potential and a high temperature inlet system (H. T. E.) operated at 125°.

Registry No.—IV, 21720-90-1; V, 21720-91-2; VI, 3647-63-0; VII, 21720-93-4; VIII, 21720-94-5; IXa, 676-43-7; IXb, 2861-50-9; IXc, 17643-37-7; IXd,

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Alkyldihydroaryllithiums. IV. Stereochemistry of Reactions of 9-Alkyl-9,10-dihydroanthracenyllithiums[1]

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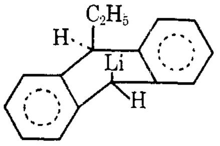
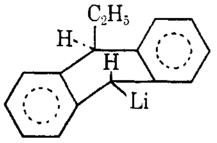
A stereospecific synthesis of *cis*-9-methyl-10-ethyl-9,10-dihydroanthracene from the known *cis*-9,10-dihydro-10-methylanthracene-9-carboxylic acid utilized coupling with lithium dimethylcopper and *cis* tosylate **5c**. The existence of 9-lithio-10-alkyl-9,10-dihydroanthracenes as an equilibrium mixture of *cis* and *trans* stereoisomers is inferred from *cis*/*trans* product ratio variations obtained with alkyl halides, deuterium oxide, and carbon dioxide.

Recently, we reported that an ethyllithium-N,N,N′,N′-tetramethyl-*o*-phenylenediamine (TMOPD) complex in cyclohexane adds ethyllithium to anthracene to form a mixture of *cis*- and *trans*-9-lithio-10-ethyl-9,10-dihydroanthracene (dihydroanthracene = DHA) (**1a** and **2a**).[2]



1a



2a

Reaction of these intermediates with methyl iodide gave 88–95% yields of *cis*-9-methyl-10-ethyl-9,10-DHA (**1c**).[3] Treatment of the intermediates with deuterium oxide gave both *cis*- and *trans*-9-deuterio-10-ethyl-9,10-DHA (**1b** and **2b**) as judged by comparison of nmr spectra for the mixed product (Figure 1) with the published spectrum for **1b**.[6] In fact, our early deuterolysis results (*cis*/*trans* = 39:61 ± 3) corresponded better with data reported by Winkler for the existence of the homologous 10-butyl-9-deuterio-9,10-DHA as nearly a 1:1 mixture of *cis* and *trans* isomers.[7a] The observation of two products under photolytic conditions[7a] or in the presence of bisamine[2] and only one isomer[6,7b] in the absence of uv radiation or bisamine might be interpreted as implying the need for some agent to catalyze the interconversion of **1a** and **2a**. However, neither of these organolithium compounds would be expected to maintain its steriochemical integrity in ether (or THF) at temperatures above 0°.[8] The detection[6,7b] of a single deuterioethyl-DHA isomer was surprising and not in harmony with other results.[2,7a] Accordingly, it was decided to reinvestigate the addition of ethyllithium to anthracene in THF.

Results

Deuterolysis of the adducts formed by addition of ethyllithium to anthracene in THF in the absence of tertiary bisamine gave a 1:1 mixture of *cis*- and *trans*-deuterioethyl-DHA, **1b** and **2b**, regardless of the order of mixing of the intermediates and D_2O. When a dilute solution of D_2O in dry THF was added slowly during 1 hr at −20° to the organolithium intermediates, the *cis*/*trans* ratio changed to 64:36. The slow mixing result may be attributed to a higher rate of reaction of D_2O with **1a** than with **2a**. An alternate explanation of product variation involving a transmetalation process (*i.e.*, reaction of **2b** with **1a** or **2a**) is not supported by nmr data. Since protolyses with oxygenated acids are known to be faster processes than protonations by weak carbon acids,[9] transmetalation would be expected to be a much slower process than either deuterolysis or equilibration of stereoisomeric organolithium intermediates.[10] If transmetalation was involved, detectable amounts of 9-ethyl-9,10-DHA (**3**) should be observed by nmr; **3** was not detected.

Attempts to secure a single deuterioethyl-DHA isomer by deuterolysis with deuteriotriphenylmethane also gave 57:43 mixtures of **1b** and **2b**.

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(3) We appreciated receiving timely advance notice from Professor R. G. Harvey that alkyl halide quenching of alkyllithium-anthracene adducts affords *cis*-9,10-dialkyl-9,10-DHAs.[4] A *cis* stereochemistry was also assigned by Redford[5] to the 9-methyl-10-ethyl-9,10-DHA of mp 108° using the unproven criterion that *cis*-9,10-dialkyl-9,10-DHAs feature a singlet for the aromatic protons while *trans* isomers exhibit an A_2B_2 (or AA′BB′) pattern.

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