

Metalation Reactions. V. The Metalation of Octadecadienyl Alcohols and Methyl Ethers

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Linoleyl alcohol and methyl ether are metalated by butyllithium, the first compound more easily than the second. Carbonation of the metalated product gives a mixture of carboxylic acids, and the position of carbonation is influenced by the methyl ether function and even more so by the lithium alkoxide group. An intramolecular isomerization of the metalated product occurs. Linoleyl alcohol and methyl ether are isomerized at room temperature with dimethylsodium in DMSO to conjugated dienes. These dienes are not metalated by butyllithium in ether, but in hexane they undergo in presence of TMEDA an addition of butyllithium to one of the double bonds. This addition depends on the stereochemistry of the double bond.

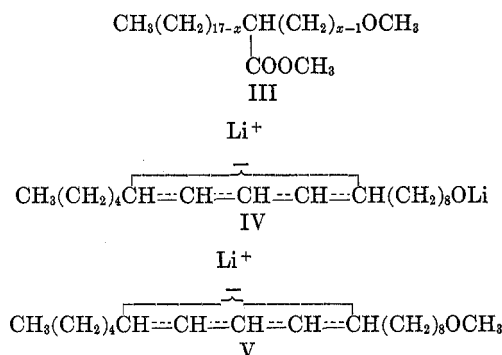
The metalation of olefins is very slow relative to that of aromatic compounds.¹⁻³ Alkylsodium compounds and prolonged reaction periods are usually employed to carry out these reactions. We found some years ago⁴ that linoleyl alcohol (I) and linoleyl methyl ether (II) undergo metalation with amylsodium and butyllithium. We report now the details of these reactions. Metalation of other aliphatic 1,4-dienes with butyllithium were reported recently.⁵

Linoleyl alcohol (I) was metalated in hexane solution with amylsodium and treated with Dry Ice to give a mixture of carboxylic acids. A similar reaction could be obtained in ethyl ether using butyllithium as metalating agent. The latter reaction was studied in detail, because of the commercial availability and safer handling of the lithium reagent. The carboxylic acids obtained on carbonation of the metalation product were separated from the neutral compounds, then esterified, and etherified with diazomethane.⁶

The metalation was relatively fast and a high yield of products was obtained after 6 hr in the studied conditions (Table I). The lower yields after longer reaction periods were probably due to the partial decomposition of the anion. Diesters were obtained in some cases on metalation and carbonation of I. Their formation is probably due to a metalation⁷ of the initial product of carbonation by excess butyllithium present in solution and a repeated carbonation. This explanation is supported by the structure of the diesters which were found to be disubstituted malonates.

The obtained unsaturated esters showed a strong absorption at 235 m μ with an extinction coefficient of ca. 16,000 and no bands at higher wavelengths. The conjugation revealed by these spectra could be attributed either to two double bonds in 1,3 positions or to one double bond α,β to the ester function. However, the second possibility was excluded by the presence of a strong band at 1740 cm⁻¹ in the infrared. It could therefore be concluded that the carbanion IV, formed during the metalation, is attached by carbon dioxide preferentially at the extremities and not at the central

position of the pentadienylic system, giving in this manner two conjugated double bonds. This mode of attack is different from the course of protonation of cyclohexadienyl systems.⁸⁻¹⁰ The absence or low extent of conjugation with the ester group proved also that no isomerization occurred during the carbonation and work-up procedures. The position of the carboxyl group could therefore be assumed to determine the location of the double bonds in the products. The mixture of isomers formed in these reactions gave rise to inordinate analytic difficulties. Direct separation of the isomers was impossible even by glpc. Various methods of degradative oxidation, e.g., by ozonolysis or by permanganate-periodate treatment did give some of the expected products in low yields or not at all. The following analytical procedure was therefore adopted. The ester-ethers obtained were distilled, hydrogenated, and purified by glpc; the composition of the saturated esters III was analyzed by mass spectrometer techniques, using the ratio of the fragments [CH₃(CH₂)_{18-x}-



COOCH₃]⁺ with varying x to evaluate the ratio of the isomeric ethers III having the carboxyl group at the position x . This method was found to give a good picture¹¹ of the ratio of the studied isomeric esters III. The esters III formed in this reaction could also be separated and identified by tlc, but quantitative evaluation of the relative amount of the isomers formed has proved very difficult by this method. Glpc could not afford the separation of the isomers. The relative amounts of the isomers III with the carboxyls at different positions as determined by mass spectrometer

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(3) M. Schlosser, *Angew. Chem. Int. Ed. Engl.*, **287**, 362 (1964).

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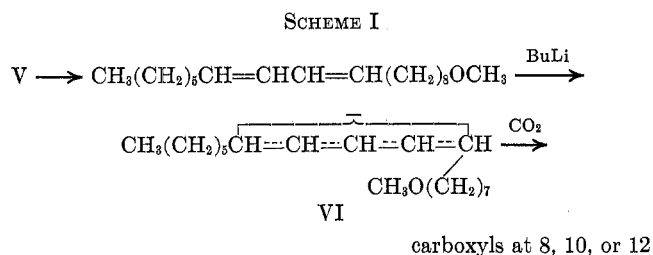
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(9) R. B. Bates, R. H. Carnighan, and C. E. Staples, *J. Amer. Chem. Soc.*, **85**, 3032 (1963).

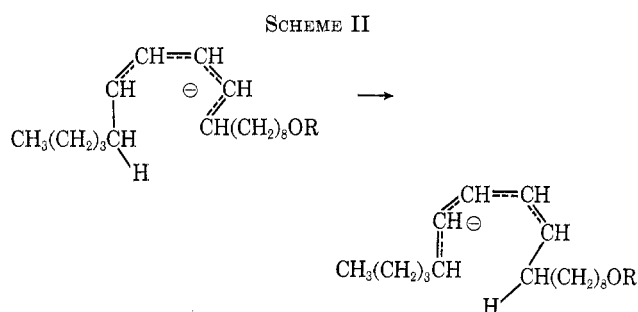
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The isomerization of the pentadienylic anion could proceed by a proton transfer from the solvent to the anions IV or V with the formation of isomeric conjugated dienes and subsequent renewed metalation of these dienes, *e.g.*, Scheme I. The new anion VI formed



could give on carbonation three isomeric acids. The anion VI in its turn could be isomerized in the same way. However, the conjugated dienes derived from linoleyl alcohol (I) and linoleyl methyl ether (II) did not undergo metalation with butyllithium in ether solution and an addition to the diene system occurred in hexane in the presence of TMEDA with formation of butyl-substituted allylic anions (see below). These results exclude the two-step mechanism of Scheme I. We conclude therefore that the isomerizations are intramolecular and a proton is transferred from a position α to the pentadienyl system to a carbon of this system. This is an unencountered sigmatropic rearrangement, to which the rules of Woodward and Hoffmann¹⁷ could be applied. The most probable course taken by the isomerization is a 1,6-sigmatropic migration since in this case a new pentadienylic system is formed from the original one (Scheme II). According to the rules,^{17,18}



an antarafacial migration of hydrogen is predicted for this system. Such a migration will be accompanied by some strain in the transition state but can be performed even on molecular models.

The intramolecular isomerization is favored for carbanions that are not coordinated to the lithium cation, as in the TMEDA catalyzed reaction. It is of interest that the rate of this isomerization drops very strongly when the pentadienylic system reaches the fifth carbon from one of the extremities of the chain. There is a possibility that in this position the anionic sites are exposed to the solution and therefore less apt

(17) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 2511 (1965).

(18) R. B. Woodward, Special Publication No. 21, The Chemical Society, London, 1967, p 217; R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

to isomerize. This explanation infers that the pentadienylic system in locations nearer the center of the molecule is protected from the solvent during the isomerization by coiling the chain around it.

This intramolecular isomerization by proton transfer resulting in a migration of a pentadienylic anion along an aliphatic chain could be observed only in a long-chain molecule. The fact that this isomerization stopped at the positions 6 and 15 at one and the other end of the molecule, respectively, requires a minimum number of 14 carbons in the chain to make this process observable. The long molecules should therefore not be regarded as an inert extension of short-chain compounds, but the aliphatic chain itself has the properties of a functional group.

Isomerization of linoleyl methyl ether (II) was performed at room temperature with solutions of dimethylsodium in DMSO.¹⁹ The reaction was fast and terminated after a few minutes resulting in the formation of conjugated products, as shown by their uv absorption at 233 m μ . Linoleyl alcohol is isomerized more slowly. A mixture of 9,11- and 10,12-dienes was obtained from I and II. The two dienes were obtained in similar amounts as evidenced by the ratio of capraldehyde and heptaldehyde obtained on ozonolysis of the mixture of products of the isomerization (Table II).

TABLE II
OZONOLYSIS OF THE ISOMERIZATION PRODUCTS OF LINOLEYL ALCOHOL AND LINOLEYL METHYL ETHER IN DMSO

Starting compound	Duration of the isomerization, hr	Ratio of products of ozonolysis		Composition of the isomerization product	Ratio of absorbance at 985 and 947 cm ⁻¹ in the product
		Capraldehyde/heptaldehyde	VII/VIII		
II	1	0.9	1.2	XIb + XIIb	1.1
II ^a	40	0.9	1.3	IXb + Xb	4.0
I	40	1		XIa + XIIa ^b	2.0

^a The product of ozonolysis contains also approximately 10% CHO(CH₂)₈OCH₃ and 10% CHO(CH₂)₁₀OCH₃. ^b This product contains a considerable amount of IXa and Xa.

The relative amounts of the two ω -methoxyaldehydes VII and VIII formed in this reaction confirmed these

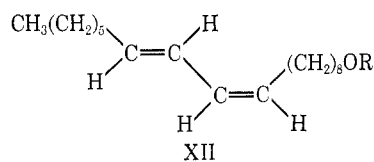
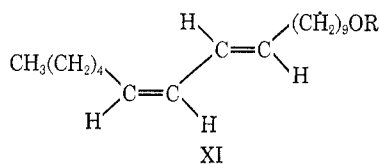
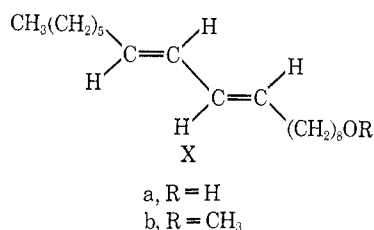
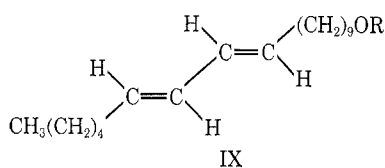


results. The obtained dienes contain *cis* and *trans* double bonds, since two bands of similar intensity were found in the infrared at 985 cm⁻¹ and 947 cm⁻¹. Prolonged treatment of I and II with larger amounts of dimethylsodium produced a product rich in the *trans-trans*-dienes IX and X, as revealed by the ratio of intensities of the bands at 985 cm⁻¹ and 947 cm⁻¹. Ozonolysis of the *trans-trans* isomers gave a product composed predominantly of capraldehyde and heptaldehyde and only 10% 8-methoxyoctaldehyde and 10% 11-methoxyundecaldehyde, showing that migration of the double bonds occurred to a small extent. This result indicates that metalation at an allylic position is not the exclusive mechanism for the *cis-trans* isomerization of the conjugated dienes, since protonation of the

(19) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1345 (1965).

pentadienylic anion should produce in this case 33% double-bond migration. We conclude therefore that the *cis-trans* isomerization of the conjugated dienes proceeded differently from that of the 1,4 isomers by addition of dimethylsodium to one double bond with formation of an allylic anion that subsequently eliminated dimethylsodium. Similar additions of dimethylsodium to conjugated olefins were observed by Cram.²⁰

The disposition of the substituents around the double bonds in the 9,11- and 10,12-octadecadienols and octadecadienyl methyl ethers was of interest. The product could have been a mixture of *cis-cis*-, *trans-trans*-, and *cis-trans*-dienes or composed of *cis-trans*-dienes only. The selective reactivity of one bond in each diene (see below) led us to assume that it was



constituted of *cis-trans*-dienes predominantly. The structures XI and XII were tentatively attributed to the alcohols and ethers formed after short-time isomerization reactions on the assumption of a *trans* configuration around the double bond that migrated, whereas the double bond, that did not change its position, was assumed to retain its original *cis* configuration. This was not a very safe conclusion. Allylic anions are known to retain their configuration²¹ for some time, and the pentadienylic anion formed during the isomerization is in the essentially protic DMSO (certainly a short-lived species) and is expected to retain its configuration around the nonmigrating bond. However, *cis* olefins are known to be formed kinetically in base-catalyzed migrations of double bonds,^{22,23} and it could also be argued that it was the migrating bond that had the *cis* configuration since the kinetic product

was isolated after short reaction time. We preferred, nevertheless, the first assignment of XI and XII to the short-time isomerization products, since the explanation (assuming a more stable *cis* than *trans* conformation in the allylic anion²³) advanced previously for the preferential formation of *cis* products during the protonation of these anions has proved to be inaccurate in the case of pentadienylic,⁵ phenylallylic,²⁰ or pentenylic²² anions, where *trans* conformations were found by nmr, or product study and kinetic methods. In order to support this assignment we subjected the isomerization products to a partial epoxidation and subsequent ozonolysis. Analysis of the formed aldehydes showed that the double bond, to which the *cis* configuration was assigned, was attacked to a greater extent than the *trans* one. A higher reactivity of *cis* relative to *trans* olefins was found before in the reaction with disiamylborane,²⁴ or in the Simmons-Smith reaction.^{25,26} Epoxidation,²⁷ having a mechanism similar to that of the last reaction, should show also a similar discrimination between the *cis* and *trans* bonds.

The compounds obtained either after short (XI + XII) or prolonged (IX + X) isomerization times of I or II did not undergo metalation with butyllithium in ether. Only traces of carboxy derivatives of I and II were obtained, and these were formed probably from small amounts of unisomerized I or II present in the starting material. However, metalation of the same compounds in hexane solution in presence of N-tetramethylethylenediamine (TMEDA) and subsequent carbonation gave a good yield of monocarboxylic acid, that contained a butyl group in the chain (elemental analysis). A small amount (less than 20% of the product) of the carboxylated linoleyl alcohol or methyl ether exempt of an additional butyl group was also obtained. The butyl-substituted acidic product was a mixture of several isomeric compounds. Their methyl esters could be separated analytically by tlc, but isolation of the individual esters for further study was very difficult. Only traces of butyl-substituted acids were obtained on metalation of unisomerized linoleyl alcohol or linoleyl methyl ether in hexane in presence of TMEDA, and these were formed probably from traces of conjugated isomers in the starting material.

The formation of butyl-substituted acids was rationalized by an addition of butyllithium to the conjugated system of the double bonds. If this occurred, eight isomeric acids (XIII, XIV, XV, XVI, XVII, XVIII, XIX, and XX) could be obtained after carbonation and hydrogenation (Scheme III). It was assumed that the butyl group added always to one of the extreme carbons of the conjugated system to give an allylic anion. Since the separation of the isomers was difficult, mass spectrometer techniques were used for the analysis of the composition of this acidic product after hydrogenation (in the form of methyl ethers and esters) and also to evaluate the relative amounts of the isomeric esters. This method was proved itself in the analysis of the isomeric α -methoxycarbonyloctadecyl

(20) D. H. Hunter and D. J. Cram, *J. Amer. Chem. Soc.*, **88**, 5765 (1966).

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(22) J. Klein and S. Brenner, unpublished work.

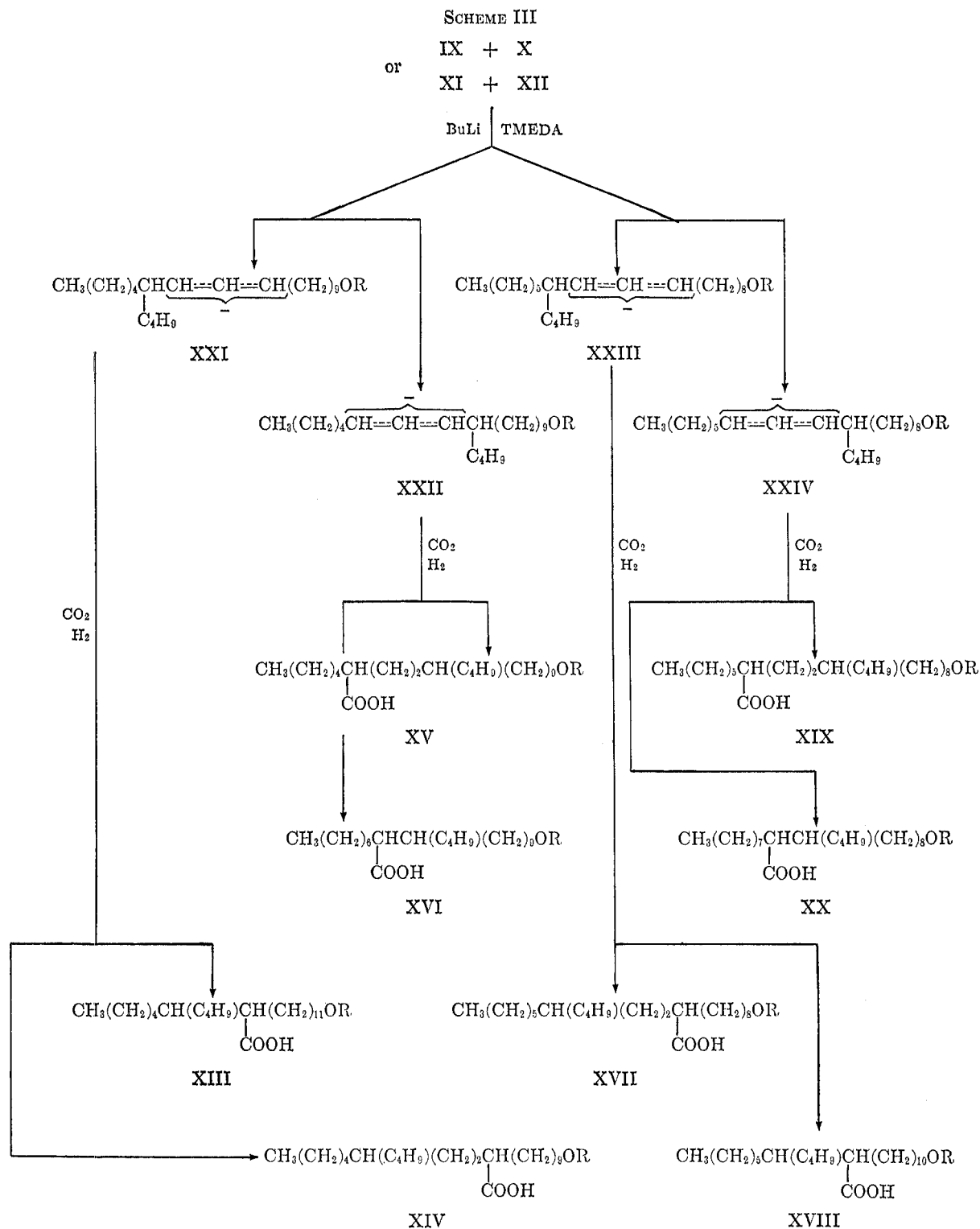
(23) S. Bank, A. Schriesheim, and C. A. Rowe, Jr., *ibid.*, **87**, 3224 (1965).

(24) H. C. Brown and A. W. Moerikofer, *ibid.*, **85**, 2063 (1963).

(25) H. E. Simmons and R. D. Smith, *ibid.*, **80**, 5323 (1958); **81**, 4256 (1959).

(26) E. P. Blanchard and H. E. Simmons, *ibid.*, **86**, 1337 (1964); H. E. Simmons, E. P. Blanchard, and R. D. Smith, *ibid.*, **86**, 1347 (1964).

(27) B. Rieckborn and J. H. H. Chan, *J. Org. Chem.*, **32**, 3576 (1967).



methyl ethers,¹¹ since the relative abundance of the fragments $[\text{CH}_3(\text{CH}_2)_{18-x}\text{COOCH}_3]^+$ was in a 1:1 correspondence with the relative amounts of the corresponding synthetic esters $\text{CH}_3(\text{CH}_2)_{17-x}\text{CH}(\text{COOCH}_3)(\text{CH}_2)_{x-1}\text{OCH}_3$.

β cleavage²⁸ of the butyl-substituted esters can give rise to four kinds of fragments, depending on the position of the butyl relative to that of the ether and ester groups. Two of these fragments, $[\text{C}_{18-x}\text{H}_{36-2x}(\text{C}_4\text{H}_9)\text{COOCH}_3]^+$ and $[\text{C}_x\text{H}_{2x-1}(\text{C}_4\text{H}_9)(\text{COOCH}_3)\text{OCH}_3]^+$, are

(28) R. Ryhage and H. Stenhagen in "Mass Spectrometry," F. W. McLafferty, Ed., McGraw-Hill Book Co., New York, N. Y., 1962.

of low abundance due to additional bond breaking on the branched carbon. The ratio of the intensities of the unbranched fragments $[\text{CH}_3\text{O}(\text{CH}_2)_x\text{COOCH}_3]^+$ and $[\text{CH}_3(\text{CH}_2)_{18-x}\text{COOCH}_3]^+$ was therefore used to determine the relative amounts of the isomeric esters.

The relative abundances of the $[\text{CH}_3\text{O}(\text{CH}_2)_x\text{COOCH}_3]^+$ fragments with m/e of 216, 230, 244, and 258 derived from the esters of XVII, XIV, XVIII, and XIII, respectively, were 24:6:8:2 for the products of metalation of the mixture of the *cis-trans*-dienes XIb and XIIb and 14:9:8:4, respectively, for the product of metalation of the mixture containing predominantly

the *trans-trans*-dienes IXb and Xb. Similarly, the relative abundances of the $[\text{CH}_3(\text{CH}_2)_{18-x}\text{COOCH}_3]^+$ fragments with m/e of 172, 158, 144, and 130 derived from the esters of XX, XVI, XIX, XV, respectively, was 24:20:100:4, respectively, for the products of metalation of the mixture XIb and XIIb, and 36:50:67:21 for the products of the mixture rich in IXb and Xb.

In the case of the butyl-substituted esters no pure compounds were available to verify the 1:1 correspondence between the relative amounts of these esters and the relative intensities of the mentioned fragments. Such a correspondence was nevertheless assumed and it was supported by the following internal evidence. Each allylic anion formed by addition of butyllithium to the diene gave rise to two carboxylic acids, one with the carboxyl on a carbon vicinal and another with the carboxyl in a position three carbons away from the butyl group. The ratio of these two acids should be similar for all allylic ions, since the environment in the chain is similar. In fact, the ratios of the fragments 28 mass units apart and arising from the same anion are between 1:2 and 1:3 for all anions. Thus, the 3:1 ratio of the intensities of the fragments $[\text{CH}_2\text{OCO}(\text{CH}_2)_x\text{OCH}_3]^+$ with m/e 216 and 244 formed from the esters of the acids XVII and XVIII, both derived from the anion XXIII formed during the metalation of the *cis-trans*-diene mixture XIb and XIIb, is the same as the ratio of m/e 230 and 258 derived from the anion XXI via the acids XIV and XIII, although their absolute intensities are different. This supports the use of the concentration-intensity correspondence at least to determine qualitatively the ratio of components in the mixture. The ratio of the two acids from the same anion reflects the greater hindrance to carbonation on the vicinal than on the carbon more remote from the butyl group.

The fivefold difference in the intensities of the fragments derived from the anions XXIV and XXI formed during the metalation of the mixture XIb and XIIb is significant, particularly when it is observed that a similar fivefold difference is observed between the sum of the intensities of the $[\text{CH}_3(\text{CH}_2)_{18-x}\text{COOCH}_3]^+$ fragments (m/e 144 and 172) obtained from the esters of XV and XVI derived from the anion XXII during the metalation of XIb and XIIb and that of similar fragments obtained from the esters of XIX and XX (m/e 158 and 186) derived from the anion XXIV. This difference is not due to a lack of correspondence between the intensities of the fragments and the amounts of the esters, since a ratio of only 2:1 instead of 5:1 of these fragments is observed during the mass spectral analysis of the same esters formed from the product of metalation of the *trans-trans*-dienes IXb and Xb. It is reasonable to expect that the symmetrical dienes IXb and Xb will be attacked equally well from both extremities of the conjugated system and the comparable intensities of the fragments confirm again the assumption of an approximate 1:1 correspondence between the intensities of the fragments and the amounts of the corresponding esters. Therefore, the difference in the intensities of the fragments from the products of metalation of XIb and XIIb has to be ascribed to the preferential attack of butyllithium on one of the double bonds of the *cis-trans*-dienes. It can

be seen that the bond attacked is the one that has migrated during the isomerization and to which the *trans* configuration was ascribed. The selectivity of the attack of butyllithium is not due to the influence of the methoxyl group, since the olefinic carbon nearest to this group in XIb, but the furthest in XIIb was attacked by butyllithium. The 2:1 ratio of the fragments obtained from the products of metalation of IXb and Xb is probably due to the presence of XIb and XIIb in this mixture. Since the mixture of XIb and XIIb contains also probably *cis-cis*- and *trans-trans*-dienes that should not exhibit preferential attack on one of the two double bonds, it can be assumed that the ratio of rates of attack of the *trans* and *cis* double bonds is higher than 4:1.

The reason for selective attack of butyllithium on *cis-trans*-dienes is not clear. One possibility is the faster formation of an allylic anion with a *cis* conformation that is assumed to be more stable.²³

Experimental Section

Linoleyl alcohol (I) was prepared by reduction²⁹ of methyl linoleate.

Linoleyl Methyl Ether (II).—A solution of diazomethane in dichloromethane⁶ (prepared from 13.8 g of nitrosomethylurea) was added dropwise to a solution of 10 g of linoleyl alcohol in 20 ml of dichloromethane containing 8 drops of 40% HBF_4 . The temperature of the reaction 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 10 g, bp 128° (0.2 mm).

Metalation of I with Amylsodium.—Amylsodium in hexane was prepared from 9.2 g of Na by the method described by Schlosser.³ A solution of 13.3 g of I in 25 ml of hexane was then added dropwise at 10°. The reaction mixture was left for 1 hr at room temperature and excess Dry Ice was then added in pieces. Water was added after several hours. The layers separated; the aqueous solution was acidified and extracted with ether. Evaporation of the solvent and of the caproic acid *in vacuo* left 6 g of an acid, showing by titration a molecular weight of 300.

Metalation of I with Butyllithium.—A solution of 26.5 g of I in 50 ml of ether was added dropwise to a solution of butyllithium³⁰ prepared from 7 g of lithium. The solution was left for 24 hr at room temperature, then added dropwise to a stirred suspension of powdered Dry Ice in ether. Water and hydrochloric acid were added; the ether layer was washed with aqueous NaOH. Acidification of the alkaline solution gave the acid that was extracted with ether and esterified with diazomethane. Distillation gave 60% yield of hydroxy esters, boiling at 175–185° (0.4 mm): $\bar{\nu}_{\text{max}}$ 1740, 1710 (sh), 3350 cm^{-1} ; λ_{max} 234 μ (ϵ 16,000).

Anal. Calcd for $\text{C}_{20}\text{H}_{36}\text{O}$: C, 74.07; H, 11.11. Found: C, 74.21; H, 11.15.

Metalation with Butyllithium. See Table I. Method A (Run 7).—A solution of 7 g of linoleyl methyl ether (II) in 100 ml of ether was added under nitrogen to 40 ml of 1.6 *M* butyllithium in hexane. The solution was left at room temperature for 24 hr, then added dropwise to a suspension of Dry Ice in ether and left overnight. Water and hydrochloric acid was added, the organic layer was washed with 10% NaOH, and the aqueous solutions were acidified and extracted with ether. Esterification with diazomethane yielded 1.8 g of the unsaturated ester: $\bar{\nu}_{\text{max}}$ 1740 cm^{-1} ; λ_{max} 231 μ (ϵ 17,000).

Anal. Calcd for $\text{C}_{21}\text{H}_{38}\text{O}_2$: CH_3O , 18.34. Found: CH_3O , 18.02.

Hydrogenation of 1 g of the unsaturated methoxy esters, in acetic acid in presence of PtO_2 , yielded 1 g: bp 160° (0.4 mm); $\bar{\nu}_{\text{max}}$ 1740 cm^{-1} .

(29) S. P. Lighthelm, E. Von Rudloff, and D. A. Sutton, *J. Chem. Soc.* 3187 (1950).

(30) R. G. Jones and H. Gilman, *Org. React.*, **6**, 352 (1951).

Anal. Calcd for $C_{21}H_{42}O_3$: CH_3O , 18.1. Found: CH_3O , 17.5.

Method B (Run 5).—The solvent was distilled off *in vacuo* from 30 ml of 1.6 *M* butyllithium in hexane and the residue was dissolved in 25 ml of dry ether. Linoleyl alcohol (2.7 g, 0.01 mol) was then added and the solution left 6.5 hr at room temperature. Carbonation, separation of the acid, esterification, and finally etherification⁸ gave 2.6 g: bp 160–170° (0.5 mm); $\bar{\nu}_{max}$ 1740 cm^{-1} ; λ_{max} 234 $m\mu$ (ϵ 16,200). Hydrogenation gave pure saturated esters.

The neutral fraction gave on distillation 0.6 g of I: bp 140° (0.2 mm); $\bar{\nu}_{max}$ 3250–3450 cm^{-1} ; λ_{max}^{EtOH} 233 $m\mu$ (ϵ 1950).

Method C (Run 2).—Linoleyl alcohol (5.4 g, 0.02 mol) was added to 60 ml of an ether solution of butyllithium prepared from 1 g of lithium. The usual work-up gave a 60% yield of unsaturated ether-esters: bp 170–180° (0.5 mm); $\bar{\nu}_{max}$ 1740 cm^{-1} ; λ_{max}^{EtOH} 233 $m\mu$ (ϵ 21,000). Hydrogenation in acetic acid gave the saturated esters: bp 165° (0.5 mm); $\bar{\nu}_{max}$ 1740 cm^{-1} .

Anal. Calcd for $C_{21}H_{42}O_3$: C, 73.68; H, 12.25. Found: C, 73.67; H, 12.30.

Distillation of the neutral fraction gave 0.8 g of I: bp 148–155° (0.5 mm); $\bar{\nu}_{max}$ 3300–3400 cm^{-1} ; λ_{max}^{EtOH} 233 $m\mu$ (ϵ 1180).

Method D (Run 8).—Tetramethylethylenediamine (3.4 g) was added to 28 ml of 1.6 *M* butyllithium in hexane. Linoleyl methyl ether (2.8 g) was then added to the solution; the reaction mixture was left for 72 hr at room temperature and carbonated. The acids were separated, hydrogenated, esterified, and re-etherified with diazomethane, giving 46% yield of the saturated product. This product was purified from a small amount of diester by glpc.

Isomerization of Linoleyl Methyl Ether (II).—II (2.8 g) was added to 5 ml of dimethylsodium in DMSO;¹⁹ the solution was left for 1 hr, then poured on dilute HCl. The product was extracted with hexane and the hexane solution washed several times with water, and distilled, yielding 2.5 g of XIb + XIIb, boiling at 148° (0.4 mm): λ_{max}^{EtOH} 230 $m\mu$ (ϵ 25,000), 268 (190), 279 (155). This compound showed ir bands at 985 and 947 cm^{-1} ; the ratio of absorbances at these wavelengths is 1.1.

II (2.8 g) was left for 24 hr with 15 ml of dimethylsodium solution,¹⁹ an additional 15 ml of the catalyst solution was added, and the reaction mixture was left for another 24 hr. Work-up as above yielded 2.5 g of IXb + Xb: bp 140° (0.4 mm); λ_{max} 233 $m\mu$ (ϵ 25,000). The ratio of absorbances at 985 and 947 cm^{-1} was 4.0.

Isomerization of Linoleyl Alcohol (I).—I (5 g) was added to 30 ml of dimethylsodium in DMSO¹⁹ and the solution left for 3 hr. Water was then added. Work-up as for II gave 4.6 g of XIa + XIIa, boiling at 148–150° (0.4 mm): λ_{max}^{EtOH} 234 $m\mu$ (ϵ 16,300), 247 (270), 280 (280). The ratio of absorbances at 985 and 947 cm^{-1} was 1.1.

The product (4.6 g) obtained in the preceding experiment and 20 ml of the catalyst solution was left overnight at room temperature. Work-up as above gave 3.6 g IXa + Xa + XIa + XIIa: bp 142° (0.4 mm); λ_{max} 233 $m\mu$ (ϵ 18,300). The ratio $A_{985\text{ cm}^{-1}}/A_{947\text{ cm}^{-1}} = 2.0$.

I (3 g) and 60 ml of the catalyst solution were left overnight at room temperature. Then 30 ml of the same catalyst solution was added and the reaction mixture left for 24 hr. Work-up as above gave 2.8 g of IXa + Xa + XIa + XIIa: bp 142° (0.4 mm); λ_{max} 233 $m\mu$ (ϵ 23,000). The ratio $A_{985\text{ cm}^{-1}}/A_{947\text{ cm}^{-1}} = 2.0$.

Ozonolysis.—Ozone was bubbled through a solution of 20 mg of the product in 1.5 ml of dichloromethane cooled to -70° until a blue coloration appeared. Excess ozone was then removed by passing a stream of N_2 through the solution and 200–300 mg of triphenylphosphine²¹ was then added. The reaction mixture was left until it reached room temperature, $MgSO_4$ was added, the solution was filtered and concentrated to 0.5 ml by passing a stream of N_2 , and the products were analyzed by glpc. The ratio of hexanal to heptanal was analyzed on a 2 m \times 0.25 ft

column of 10% polydiethylene glycol succinate on Chromosorb and the methoxyaldehydes on a 1 m \times 0.25 ft column of 20% SE-30 on Chromosorb. The ratio of hexanal to heptanal did not change when the solution was analyzed before concentration. Linoleyl alcohol and linoleyl methyl ether were ozonolyzed in the same conditions for comparison.

Epoxidation.—A solution of 77 mg of *m*-chloroperoxybenzoic acid in 1 ml of CH_2Cl_2 was added to a solution of 103 mg of the mixture of XIb and XIIb in 0.5 ml of CH_2Cl_2 ²² and the reaction mixture was left for 20 min at room temperature. This solution was then washed with 10% aqueous sodium metabisulfite, then with $NaHCO_3$ solution, and the solvent was evaporated. The product showed a *trans* double bond at 970 cm^{-1} . Ozonolysis of this product gave a 1:2 ratio of capraldehyde to heptaldehyde and of VII to VIII instead of the 1:1 ratio of these compounds in the ozonolysis of the conjugated dienes.

Metalation of Isomerized Linoleyl Methyl Ether.—The solvent was distilled off *in vacuo* from 25 ml of 1.6 *M* butyllithium in hexane. The residue was dissolved in 25 ml of dry ether. The *cis-trans* isomers XIb and XIIb (1.5 g) were then added and the solution was left for 184 hr at room temperature. Carbonation, separation of the acids, their esterification, and distillation of methyl valerate left only a trace of an ester. Only a part of the neutral fraction could be distilled since some polymerization occurred.

TMEDA (1.7 g, 15 mmol) was added to 10 ml of butyllithium (15 mmol) in cyclohexane, followed by 1.4 g (5 mmol) of the mixture of VIIIb and IXb. The reaction mixture was left for 2 days under N_2 , then added dropwise, with stirring, to a suspension of Dry Ice in anhydrous ether. The mixture was left overnight, then water and dilute acid were added, and the ether layer was separated. The organic layer was washed with dilute NaOH and the alkaline solution was acidified and extracted with ether. The carboxylic acid was esterified with diazomethane yielding 0.9 g of esters: λ_{max}^{EtOH} 233 $m\mu$ (ϵ 4000); $\bar{\nu}_{max}$ 1730 cm^{-1} . Hydrogenation of these esters in acetic acid in presence of PtO_2 gave a product which was separated by glpc—on 1.5 m \times 0.25 ft column of 10% stabilized polydiethylene glycol succinate on Chromosorb—into two fractions. The first fraction (18% of the product) was a mixture of α -methoxy-carbonyloctadecyl methyl ethers, identified by tlc and mass spectrometer analysis. The second fraction (82%) was composed of octadecyl methyl ethers having butyl and carboxy substituents.

Anal. Calcd for $C_{25}H_{50}O_3$: C, 75.65; H, 12.56. Found: C, 75.88; H, 12.45.

The mixture of IXb and Xb (2.8 g) was added to 15 ml of butyllithium in hexane (25 mmol), containing 2.8 g of TMEDA. The solution was left for 72 hr, then worked up as above, yielding 1.1 g of saturated esters that were separated as above into two fractions, the first (13%) containing carboxy-substituted octadecyl methyl ethers and the second (87%) composed of octadecyl methyl ethers having butyl and carboxyl substituents.

Metalation of Isomerized Linoleyl Alcohol.—Metalation of 2.6 g of the mixture of XIa and XIIa with butyllithium in ether for 72 hr as described above yielded 0.3 g of esters.

The mixture of isomerized linoleyl alcohols (1.5 g, 6 mmol), λ_{max} 233 $m\mu$ (ϵ 18,300), was metalated in 16 ml of butyllithium (26 mmol) in hexane for 79 hr. Carbonation, esterification of the acids, then etherification,⁸ and hydrogenation yielded 1.1 g of saturated esters that were separated by glpc into two fractions, the first (21%) being the product of metalation and the second (79%) that of butyllithium addition as in the case of the ethers IXb and Xb.

Registry No.—I, 506-43-4; II, 23405-45-0.

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