at 1730 (-C=C-C̲O̲OCH$_3$), 1665 (CO-C=C), 1645 (C=C), 1270, 1210, 1190 (C-O), and 995 (*trans* olefin). Its NMR spectrum gave a doublet centered at δ 7.05 (1H, J=16 Hz, ascribable to a proton β to ester carbonyl) a doublet of the same magnitude at δ 6.54 (1H, J=16 Hz, *trans* olefinic proton) ascribable to a proton α to ester carbonyl, 3.88 s (3H, -COOC̲H̲$_3$), 2.5 m (2H, -C̲H̲$_2$-CO-CH=CH-), 1.3 br,s (chain-C̲H̲$_2$), and 0.9 t (terminal -C̲H̲$_3$). The mass spectrum of compound 3 absolutely resembled that of methyl 4-oxo-*trans*-2-hexadecenoate reported earlier (7). The mass spectrum of 3 gave the molecular ion at m/e 282 (C$_{17}$H$_{30}$O$_3$) followed by other salient ion peaks at m/e 251 (M-31), 250 (M-32), 223 (M-COOCH$_3$), 169 (δ-cleavage between C-8, C-9), 155 (γ-cleavage between C-7, C-8), 141 (β-cleavage between C-6, C-7), 137 (155-18), 128 (McLafferty, cleavage base peak), 113 (cleavage between C-4, C-5) and other low mass ion peaks.

ACKNOWLEDGMENTS

REFERENCES

1. Swern, D., Organic Reactions, John Wiley and Sons, Inc., New York, NY, 7:378 (1953).
2. Gunstone, F.D., and F.R. Jacobsberg, Chem. Phys. Lipids 9:26 (1972).
3. Abbot, G.G., and F.D. Gunstone, Ibid. 7:290 (1971).
4. Ansari, A.A., and S.M. Osman, JAOCS 53:118 (1976).
5. Ansari, A.A., F. Ahmad and S.M. Osman, Ibid. 55:541 (1976).
6. Ansari, A.A., F. Ahmad and S.M. Osman, Fette Seifen Anstrichm. 79:328 (1977).
7. Ahmad, M.U., M.S. Ahmad and S.M. Osman, JAOCS 55:491 (1978).
8. Ahmad, M.U., M.S. Ahmad, Jr., and S.M. Osman, Ibid. 55:669 (1978).
9. Ahmad, M.S., Jr., M.U. Ahmad and S.M. Osman, Ibid. 56:867 (1979).
10. Ahmad, M.S., Jr., and S.M. Osman, Ibid. 57:363 (1980).
11. Ansari, A.A., B. Schmitz and H. Egge, Chem. Phys. Lipids 29:45 (1981).

☆Reaction of Lithium Naphthalene with Carboxylic Acids Containing the Dichlorocyclopropane Ring System

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ABSTRACT

Carboxylic acids containing the dichlorocyclopropane ring system react with lithium naphthalene to give dechlorinated products. For example, from the reaction of 9,10-dichloromethylene octadecanoic acid and lithium naphthalene, a mixture of 9,10-nonadecadienoic acid as a main product and unidentified minor products were obtained.

INTRODUCTION

The selective dichlorocarbene reaction with phase-transfer catalyst is well known (1). The conversion of the easily accessible carboxylic acids containing the dichlorocyclopropane ring system into other useful products has been a subject of some interest. Their dechlorination is not well known, however, except for reactions of the following compounds. Reactions which serve this purpose include reduction with sodium in liquid ammonia (2), formation of allenes from 1,1-dibromocyclopropanes (3), reaction of magnesium turnings with 9,9-dibromobicyclo [6,1,0] nonane (4), reaction of butyllithium with 13,13-dichlorobicyclo [10,1,0] tridecane (5), the reaction of 1,1-dichlorocyclopropanes with base to obtain the allenic compounds (6) and a dichlorocyclopropane ring opening with base (7).

Recently, it was reported that lithium naphthalene in tetrahydrofuran solution is an excellent reagent for various synthetic organic reactions (8). In connection with our earlier works, an interesting reaction between lithium naphthalene and various carboxylic acids containing the dichlorocyclopropane ring is described in this short Communication.

EXPERIMENTAL PROCEDURES

Methyl esters of oleic acid, erucic acid, undecylenic acid and 3-methyl-3-butenoic acid were used in commercial samples.

Reaction of Methyl Oleate [1] with Chloroform

Forty g of 50% sodium hydroxide solution was added by drops with stirring at a room temperature to a mixture of methyl oleate [1] (23 g), chloroform (60 g) and cetyltrimethylammonium chloride (0.4 g). The mixture was stirred for 5 hr at 60 C. After the mixture was acidified with 50% sulfuric acid, it was extracted with diisopropyl ether. The ether extracts were washed with water, dried over anhyd. sodium sulfate and distilled to give crude methyl 9,10-dichloromethylene octadecanoate [2a]. This [2a] was hydrolyzed with methanol and sodium hydroxide in the usual way to give crude 9,10-dichloromethylene octadecanoic acid [2b] (18 g). The crude product was molecularly distilled with a pot still to give 8 g of 9,10-dichloromethylene octadecanoic acid [2b], bath temperature 150-155 C at 0.1 mm Hg, mp 85-87 C (recrystallized from *n*-hexane). Infrared (IR) (cm^{-1}): 3200-3500, 1710 (-COOH); nuclear magnetic resonance (NMR) 9.9 (1H, s, -COOH), 2.30 (2H, bt, -C̲H̲$_2$COOH), 1.80 (2H, bm, -C̲H̲-C̲H̲-), 1.30 (26H, bs,

$$\underset{Cl \quad Cl}{\overset{\diagdown \; /}{\underset{/ \; \diagup}{C}}}$$
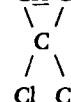
-CH$_2$-), 0.92 (3H, t, CH$_3$-).

TABLE I

Main Products of Reaction of Lithium Naphthalene with Carboxylic Acids
Containing the Dichlorocyclopropane Ring System

Original carboxylic acid	Product	Yield (%)[a]
Erucic acid	13,14-Tricosadienoic acid	52
Oleic acid	9,10-Nonadecadienoic acid	40
Undecylenic acid	10,11-Methylene undecanoic acid	35
3-Octenoic acid	3,3-Nonadienoic acid	30
3-Methyl-3-butenoic acid	3-Methyl-3,4-methylene butanoic acid	40

[a]These yields were calculated from the corresponding carboxylic acids containing the di-
chlorocyclopropane ring system.
The microanalyses of the products were in satisfactory agreement with the calculated values
(C, ±0.32; H, ±0.04).

Reaction of 9,10-Dichloromethylene Octadecanoic Acid [2b] with Lithium Naphthalene

To a tetrahydrofuran solution (100 mL) of lithium naph-thalene prepared from lithium (0.16 mol, 1.12 g) and naphthalene (6 g), 10 g of acid [2b] as a THF solution was added by drops and reacted for 6 hr. The reaction mixture was decomposed with a mixture of methanol and water, and it was extracted with diisopropyl ether to remove the nonacidic material. The remaining solution was acidified with 50% sulfuric acid, and extracted with diisopropyl ether. These ether extracts were washed with water and dried over anhyd. sodium sulfate. The solvent was distilled off to give a crude product [3a] (6 g). It was esterified with methanol in the usual way. The crude methyl ester was mo-lecularly distilled with a pot still to give 4.0 g of crude prod-uct [3b], bath temperature at 130-135 C/0.1 mm Hg. The fraction (2.0 g) was chromatographed over a column of sil-ica gel (50.0 g) and the elution was done with n-hexane con-taining increasing amounts of diethyl ether; each fraction of 10 mL was collected. Elution with n-hexane/diethyl ether (95:5 v/v) gave the starting materials [1] (0.20 g). Elution with n-hexane/diethyl ether (90:10 v/v) gave methyl 9,10-nonadecadienoate [3b] (1.20 g) as an oil.

IR (cm^{-1}): 1955 (allenic bond), 1740 (ester); NMR (δ, ppm): 5.03 (2H, m, -CH=C=CH-), 3.63 (3H, s, -COOCH$_3$), 2.03 (6H, bm, -CH$_2$COO, -CH$_2$-C=C=C-CH$_2$-), 1.31 (22H, bs, -CH$_2$-), 1.00 (3H, t, CH$_3$-CH$_2$).
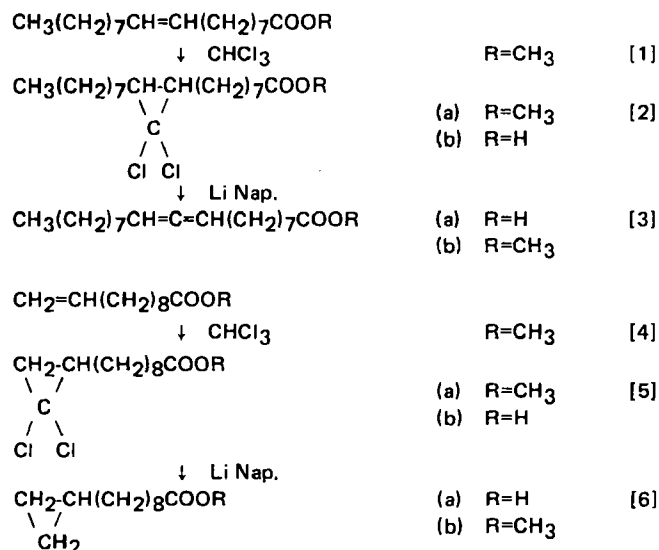
Elution with n-hexane/diethyl ether (93:7 v/v) gave an oil (A) (0.01 g). Elution with n-hexane/diethyl ether (87:13 v/v) gave an oil (B) (0.01 g). IR and NMR spectra of (A) and (B) did not show the absorption of internal acetylenic group. The structures of these oils (A,B) could not be deter-mined.

Other carboxylic acids containing the dichlorocyclopro-pane ring system were treated with lithium naphthalene in the same manner, and the results are listed in Table I.

RESULTS AND DISCUSSION

This paper describes the reaction of lithium naphthalene with various carboxylic acids containing the dichlorocyclo-propane ring system which had been prepared from various carboxylic acids. The chemical structures of the products were studied. Simmons-Smith reaction of various long-chain α,β-unsaturated esters (9) and the chloromethylation of methyl esters (10) are well known. However, dechlorinated reactions of these carboxylic acids have not been known.

9,10-Dichloromethylene octadecanoic acid [2b], which had been prepared from methyl oleate [1] having a disub-stituted double bond, was added to a tetrahydrofuran solution of lithium naphthalene, and treated in the usual manner to give an allenic carboxylic acid [3a] as a main product. The IR spectrum of [3a] gave a band at 1955

$$CH_3(CH_2)_7CH=CH(CH_2)_7COOR$$
$$\downarrow CHCl_3 \qquad R=CH_3 \qquad [1]$$

$$CH_3(CH_2)_7CH\text{-}CH(CH_2)_7COOR$$
$$\underset{Cl\ \ Cl}{\overset{\diagdown\ /}{\underset{/\ \diagdown}{C}}} \qquad \begin{array}{l}(a)\ \ R=CH_3 \qquad [2]\\(b)\ \ R=H\end{array}$$
$$\downarrow \text{Li Nap.}$$
$$CH_3(CH_2)_7CH=C=CH(CH_2)_7COOR \qquad \begin{array}{l}(a)\ \ R=H \qquad [3]\\(b)\ \ R=CH_3\end{array}$$

$$CH_2=CH(CH_2)_8COOR$$
$$\downarrow CHCl_3 \qquad R=CH_3 \qquad [4]$$

$$CH_2\text{-}CH(CH_2)_8COOR$$
$$\underset{Cl\ \ \ Cl}{\overset{\diagdown\ /}{\underset{/\ \diagdown}{C}}} \qquad \begin{array}{l}(a)\ \ R=CH_3 \qquad [5]\\(b)\ \ R=H\end{array}$$
$$\downarrow \text{Li Nap.}$$
$$CH_2\text{-}CH(CH_2)_8COOR$$
$$\underset{CH_2}{\overset{\diagdown\ /}{C}} \qquad \begin{array}{l}(a)\ \ R=H \qquad [6]\\(b)\ \ R=CH_3\end{array}$$

cm^{-1} due to the allenic bond. The assigned structure of methyl 9,10-nonadecadienoate [3b] was further confirmed by the NMR spectrum as shown in Experimental Proce-dures. The IR spectrum did not give the band at 3040 cm^{-1} attributed to the cyclopropane methylene group. An in-ternal acetylenic compound was not confirmed in our experimental conditions. The dichlorocyclopropane com-pounds from methyl erucate gave the corresponding allenic carboxylic acids as a main product.

Reaction of 10,11-dichloromethylene undecanoic acid [5b], prepared from methyl undecylenate [4] containing a vinyl end group, with lithium naphthalene gave 10,11-methylene undecanoic acid [6a]. The IR spectrum of [6a] and the methyl ester [6b] gave band at 3040 cm^{-1}, show-ing the presence of the cyclopropane moiety. The NMR spectrum of [6a] and [6b] gave signals at δ 0.4 ppm due to their cyclopropane ring. A terminal acetylenic com-pound was not detected in our conditions.

From the reaction of 3,4-dichloromethylene-3-methyl-butanoic acid [7], prepared from 3-methyl-3-butenoic acid containing a methylene end group, with lithium naphtha-lene, 3,4-methylene-3-methyl-butanoic acid [8] was pro-duced.

The foregoing observations indicate that the reactions of lithium naphthalene with carboxylic acids containing the dichlorocyclopropane ring system prepared from disubsti-tuted olefinic carboxylic acids gave allenic carboxylic acids as a main product. Those carboxylic acids, prepared from end methylene-type olefinic and end vinyl type of olefinic carboxylic acids, gave saturated cyclopropane carboxylic acids as a main product.

REFERENCES

1. Joshii, G.C., N.S. Ingh and L.M. Pande, Tetrahedron Lett. 15:1461 (1972).
2. Hiyama, T., H. Sawada, M. Tsukanaka and H. Nozaki, Ibid. 34:3013 (1975).
3. Crozet, M.P., J.M. Surzur, R. Janffred and C. Ghiglione, Ibid. 33:3077 (1979).
4. Gardner, P.D., and M. Narayama, J. Org. Chem. 26:3518 (1961).
5. Mühlstädt, J., and J. Graefe, Chem. Ber. 100:223 (1967).

6. von Doering, W., and P.M.L. Flumme, Tetrahedron Lett. 2:25 (1958).
7. Hiyama, T., T. Mishima, K. Kitatani and H. Nozaki, Ibid. 37:3297 (1974).
8. Fieser, M., and L. Fieser, Reagents for Organic Synthesis, Vol. 2, Wiley-Interscience, New York, NY, 1969, p. 228.
9. Ahmad, M.S., Jr., and S.M. Osman, JAOCS 57:363 (1980).
10. Starks, C.M., and C. Liotta, Phase Transfer Catalysis, Academic Press, New York, NY, 1978, p. 232.

� Determination of Trace Elements in Oils by Plasma Emission Spectroscopy

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ABSTRACT

An analytical method for the determination of phosphorus and other elements at low concentrations in edible oils has been developed using a plasma emission spectrometer. The method is fast because it eliminates the ashing process in sample preparation and because the actual measurement takes less than 1 min. Reproducibility and accuracy of the measurement are good and very low detection limits have been observed, e.g., 0.5 ppm for phosphorus and 5 ppb for copper. However, the long-term stability of the instrument cannot as yet be guaranteed and a procedure that prescribes regular measurement of samples of known concentration is essential as a means of detecting any drift in the output signal.

INTRODUCTION

A rapid and accurate analysis of the phosphorus content of edible oils constitutes a desirable tool in oil refining. Metals, particularly copper and iron, seriously affect oil quality, or in the case of lead, arsenic and mercury, may be the subject of food legislation, which again calls for analytical methods.

Consequently, a number of analytical methods have been developed and adopted as official methods. These methods have in common that the elements to be determined are first of all concentrated by ashing, or by volatilization, in the case of mercury. Ashing, however, can lead to losses and/or contamination. Improved procedures have been proposed (1), but duplicate analyses still are a necessary precaution. Besides, the ashing process takes up to 9 hr (1) which is often too long for effective process and quality control.

Naturally, other methods have been investigated since novel instruments became available. Flame atomic absorption (2,3) still requires ashing of the sample but carbon rod flameless atomic absorption spectroscopy (4) obviates ashing. Finally, the use of a graphite furnace in flameless atomic absorption spectroscopy was developed for the determination of trace elements in oil (5), which was found to be a further improvement.

When it was reported (6) that the addition of a lanthanum salt to an aqueous solution of a phosphorus compound not only increased the phosphorus signal but probably also minimized the sensitivity difference between various phosphorus compounds, this finding was extended to edible oils (7,8). Apparently necessary improvements have been reported (9) recently, in that the use of an organic lanthanum salt (lanthanum-2,4-pentadionate) dramatically improved the reproducibility as well as the sensitivity. Using sample volumes of 20 μL and photodiode temperature control, a reproducibility of 2% at levels above 20 ppm P is reported with a detection limit of 0.5 ppm P.

Some authors (5,7) mention smoke formation in the graphite furnace as a drawback particular to edible oils. The use of a higher pyrolysis temperature as provided by a plasma solves this problem. Accordingly, plasma emission spectroscopy has been evaluated as a fast analytical method for trace amounts of phosphorus and other elements in edible oils.

The method analyzes the oil as such and thus obviates ashing and its inherent risks of spurious results. The fact that the method to be described requires a much larger sample volume than methods employing atomic absorption spectrometry is not regarded as a serious disadvantage in an industrial environment where speed, reproducibility and low detection limits as provided by plasma emission spectroscopy are essential.

EXPERIMENTAL PROCEDURES

Equipment

A recent survey of plasma emission spectrophotometry equipment (10) and their emission sources, in particular, codetermined the choice of instrument used in this investigation: Spectraspan IV (Spectrametrics Inc.) coupled with an electronic data terminal (Texas Instruments, Model 743 KSR).

In this instrument, a DC argon plasma arc is generated between 2 carbon anodes and a tungsten cathode at a current of 7.5 A at 40 V. The arc has the shape of an inverted Y into which the sample is fed as an aerosol from below. The sample itself is fed by means of a peristaltic pump at a fixed rate of 1.6 mL/min to a nebulizer where about 20% of the sample is introduced into an argon stream as an aerosol; the fraction of the sample that is not nebulized is removed from the nebulizer by the same peristaltic pump. Collection of this fraction permits the nebulizer efficiency to be determined.

At the junction of the plasma the sample is introduced into the 6,000-7,000 K excitation region where the sample molecules are thermally dissociated and the resulting atoms