this crude reaction product on a DEGS column gave the following retention times: 5.7 (1%), 6.9 (1%), 10.2 (16%), and 12.5 min. (82%). Distillation through a 12-in. Vigreux column yielded 16.8 g. (79%) of a fraction boiling at 75–77° (0.05 mm.) with two v.p.c. retention times of 10.1 (13%) and 11.8 min. (87%).

Inorganic salts were added to the reaction mixture by dissolving in the 500 ml. of tetrahydrofuran.

The presence of O-acylated products was ascertained not only by v.p.c. but also by ultraviolet absorption at 222 mμ and infrared absorption at 1660 cm.$^{-1}$.[2]

2,2-Dicarbethoxycyclohexanone.—Sodium hydride (5.5 g. of 50% dispersion in mineral oil, 0.11 mole) was rinsed with tetrahydrofuran and then suspended in 100 ml. of the same solvent. To this was added dropwise 17 g. (0.1 mole) of 2-carbethoxycyclohexanone with stirring. The precipitate that formed redissolved on addition of 24.5 g. (0.11 mole) of magnesium perchlorate. An additional 100 ml. of tetrahydrofuran was added to the mixture and then 10.8 g. (0.1 mole) of ethyl chloroformate was added. The mixture was heated for 15 min., cooled to room temperature, acidified with 1% sulfuric acid, and extracted into ether. Distillation of the residue at 92–95° (0.1 mm.) through a 12-in. Vigreux column yielded 16.1 g. (67%) of product. V.p.c. analysis on a silicone rubber column gave one peak of retention time 6.5 min. When a DEGS column was used the peak had a retention time of 12.6 min.

Measurements on Isolated Double-Bond Systems. Ultraviolet Absorption Spectra of Fatty Acid Esters

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The far-ultraviolet spectra of a series of *cis* and *trans* mono-, and poly-, substituted-unsaturated fatty acid esters were examined with a commercially available spectrophotometer to approximately 177 mμ. The results are compared with those of several related studies, and certain inconsistencies in earlier results are considered. Some observations concerning interaction between substituents and unsaturated centers and a technique for assessing the number of olefinic bonds in various nonconjugated systems are discussed.

Measurements of the absorption spectra of isolated double bonds have been relatively few because the maxima, which lie in the far-ultraviolet, have been accessible only by use of vacuum spectrographs or spectrometers. Since spectrophotometers that can routinely record down to about 175 mμ have become available, the spectra of compounds containing di-, tri-, and tetrasubstituted olefinic bonds can be conveniently obtained. With a commercial instrument, Micheli and Applewhite[2] studied a group of steroids and triterpenoids and found their results correlated well with those of Turner[3] who used a vacuum spectrophotometer.

Unsaturated fatty acids are interesting compounds for study because the effects on ultraviolet light absorption of increasing the number of isolated double bonds and of *cis–trans* isomerization may be inspected with minimum complication by the configuration of the rest of the molecule. Several groups have investigated fatty acid spectra. Barnes, *et al.*,[4] reported the spectra of methyl octadecanoate, methyl *cis*-9-octadecenoate, methyl *cis*-9-*cis*-12-octadecadienoate, methyl *cis*-9-*cis*-12-*cis*-15-octadecatrienoate, and methyl *cis*-5-*cis*-8-*cis*-11-*cis*-14-eicosatetraenoate in the region 210–250 mμ. Schauenstein and Benedikt[5] extended the curves for the unsaturated esters to 200 mμ but did not observe maxima. By using a vacuum spectrograph over the range 170–250 mμ, Rusoff, *et al.*,[6] observed maxima in the spectra of a variety of fatty acids or esters having one to four isolated *cis* olefinic bonds and also of some of the possible *trans* isomers.

Absorption by the isolated olefinic bond has been used for quantitative analysis. Two groups[4,6] were able to correlate the ultraviolet absorption of several vegetable oils with the fatty acid composition. In another use, Paschke, *et al.*,[7] determined the double-bond content of methyl oleate dimer by comparison of its absorption with the absorptions of methyl oleate and methyl elaidate.

This paper reports the results of spectral measurements in the far-ultraviolet region on 30 fatty acid esters and *cis*- and *trans*-2-octene. In addition to the compounds studied previously,[4–7] we include a number of substituted unsaturated fatty acid derivatives that allow some assessment of interaction effects on absorption in this spectral region.

Experimental[8]

Instrumentation.—An extended-range Beckman Model DK-2 spectrophotometer was employed as previously described[2] but the scale selected was absorbance −0.3 to +0.7. Sample and reference cells were fused quartz and had path lengths of 0.01099 and 0.01004 cm.

Preparation of Sample Solutions.—All measurements were made in cyclohexane solutions. One lot of Eastman Kodak cyclohexane did not show a peak at 187 mμ and accordingly was used without further purification. Cyclohexane purified through Davison No. 923 silica gel, as described by Potts,[9] was used also. Liquid samples of 2 to 20 mg. (±0.02 mg) were weighed by difference in sections of disposable 50-μl. pipets: the pipet section was weighed, partially filled with sample, reweighed, transferred to a 10-ml. volumetric flask, and crushed under cyclohexane. Solid samples were weighed directly. Sample sizes were adjusted to attain absorbances between 0.3 and 0.6 to minimize error due to stray light.[10]

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[1] A laboratory of the Western Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

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[8] Reference to a company or product name does not imply approval or recommendation of the product by the U. S. Department of Agriculture to the exclusion of others that may be suitable.

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Purity of Standard Samples.—National Institutes of Health standard fatty acid esters were used as received. Methyl *cis*-6-octadecenoate (petroselinate), *cis*-11-octadecenoate, *cis*-11-eicosenoate, *cis*-13-docosenoate (erucate), and *cis*-15-tetracosenoate (nervonate) were labeled >99% pure by gas–liquid chromatography (g.l.c.). The methyl *cis*-12-octadecenoate had a listed impurity of 3.4% octadecanoate. Calculations for this sample were based on the weight of 12-octadecenoate present. The all-*cis*-5,8,11,14,17-eicosapentaenoate was a sample described as 96.2% C_{20} with five double bonds and 3.8% C_{20} with four double bonds: *trans* unsaturation (infrared) ~2% as methyl elaidate; $a_{233} = 0.835$; 0.1% propyl gallate added. The composition of all-*cis*-4,7,10,13,16,19-docosahexaenoate was described as 95.4% C_{22} with six double bonds, 2.6% C_{22} with five double bonds, 1.2% C_{20} with five double bonds, and 0.8% C_{18} with four double bonds: *trans* unsaturation ~1.2% as methyl elaidate; $a_{233} = 0.92$; 0.1% propyl gallate added. Calculations for this sample were based on an average molecular weight of 341.83 and an average of 5.952 double bonds per molecule.

The Hormel Foundation's methyl *cis*-9-hexadecenoate (palmitoleate), *trans*-9-octadecenoate (elaidate), *cis*-9-octadecenoate (oleate), *cis*-9-*cis*-12-octadecadienoate (linoleate), octadecanoate (stearate)—all with estimated purity of >99%—were similarly used as received. A methyl arachidonate (all-*cis*-5,8,11,14-eicosatetraenoate) sample of apparent 90% arachidonate content was purified to better than 98% (g.l.c.) by chromatography on a silver nitrate–silicic acid column[11] followed by preparative thin layer chromatography (t.l.c.) on chromatostrips.[12]

Preparation of Samples.—Methyl 12-hydroxy-*cis*-9-octadecenoate (ricinoleate) was purified to >99% (g.l.c. and t.l.c.) by silicic acid chromatography.[13] Methyl 12-hydroxyoctadecanoate, m.p. 57–58°, was prepared by hydrogenation of methyl ricinoleate and recrystallization. A sample of methyl 12-hydroxy-*trans*-9-octadecenoate (ricinelaidate), prepared as described by McCutchon, *et al.*,[14] was chromatographed on silicic acid to yield product of >99% purity.

Methyl 12-methoxy-*cis*-9-octadecenoate, 12-methoxy-*trans*-9-octadecenoate, and 12-methoxyoctadecanoate were prepared by reaction of diazomethane with methyl ricinoleate, ricinelaidate, and 12-hydroxyoctadecanoate in the presence of fluoroboric acid.[15] The 12-methoxy methyl esters were obtained in >99% purity by silicic acid chromatography.

Methyl 14-hydroxy-*cis*-11-eicosenoate[16] (lesquerolate) of >98% purity (g.l.c. and t.l.c.) was prepared by distillation of *Lesquerella fendleri* methyl esters.

Base-catalyzed transesterification of trivernolin with methanol in an Amberlite 401 ion-exchange resin column[17] gave methyl *cis*-12,13-epoxy-*cis*-9-octadecenoate (vernolate).[18] After chromatography on silicic acid, it had a purity of >99% (g.l.c. and t.l.c.).

A mixture of hydroxy acid esters including methyl 12-hydroxy-*cis*-9-*cis*-15-octadecadienoate (densipolate)[19] was prepared by sodium methoxide catalyzed methanolysis of *Lesquerella densipila* seed oil and separated from nonhydroxy esters by distillation. The sample was dissolved in acetone and held at −50° to crystallize a substance, probably a plant sterol, that otherwise persists through subsequent purification procedures. Hydroxy monoene esters were removed on a silver ion–macroreticular ion-exchange resin[20] by elution with methanol. Methyl densipolate remained on the column but was displaced with acetonitrile. Chromatography on silicic acid afforded methyl densipolate that showed no impurity by g.l.c. or t.l.c.

Methyl *cis*-5-*cis*-13-docosadienoate[21] was isolated from *Limnanthes douglasii* seed oil methyl esters. Mixed esters were fractionated in a 50-ml. buret that contained 24 g. of Amberlyst XN-1005 resin converted to the silver ion form.[20] As expected, saturated and monoene esters separated from dienes but, contrary to earlier results,[20] dienes eluted with methanol, perhaps because of partial reduction of silver ion on the column. Preparative g.l.c. separated two diene impurities of shorter chain length from the C_{22} diene. A silica gel G chromatostrip[12] impregnated with silver nitrate[22] showed only one spot for this sample and indicated that only *cis,cis*-diene was present. However, g.l.c. suggests that the 5,13-diene sample contains 2–3% of an impurity that may be a methylene-interrupted C_{22} diene.[23]

Methyl *cis*-9-*cis*-12-*cis*-15-octadecatrienoate (linolenate) was concentrated from linseed oil methyl esters by urea fractionation and separated from methyl linoleate on the argentation column described above. After chromatography on silicic acid, the sample showed no impurity by g.l.c. and t.l.c.

Anal. Calcd. for $C_{19}H_{32}O_2$: C, 78.03; H, 11.03. Found: C, 78.2; H, 10.9.

Methyl *trans*-9-*trans*-12-octadecadienoate (linolelaidate) was prepared by the nitrous acid isomerization[24] of high-purity methyl linoleate. Isomerized esters were extracted from the reaction mixture with commercial pentane. Most of the remaining polar impurities were removed by chromatography on a silicic acid column. The infrared absorption of *trans* olefinic bonds at 10.3 μ was then used to monitor the urea fractionation of the isomerized esters. One fraction with high *trans* bond content was recrystallized from acetone (1:6) at −40°. The resulting methyl linolelaidate did not show any impurity during g.l.c. (polyester column), but did show a trace of *cis,trans*- or *trans,cis*-diene (estimated at <2%) on a silver nitrate impregnated silica gel G chromatostrip.[12,22]

Workers at the USDA Southern Regional Research Laboratory isolated methyl ω-(2-*n*-octylcyclopropenyl)octanoate (sterculate) from mixed methyl esters of *Sterculia foetida* seed oil by urea fractionation and recrystallization. We further purified the compound by chromatography on silicic acid. The final sample showed only traces of two impurities on a chromatostrip and had the correct cyclopropenoid proton count in the n.m.r. spectrum (2.04 found *vs.* 2.00 calculated).

Methyl 12-oxo-*cis*-9-octadecenoate, prepared by oxidation of methyl ricinoleate,[25] was chromatographed on silicic acid to provide a sample of >98% purity as estimated by chromatostrip analysis.

Methyl 12-oxooctadecanoate, m.p. 46.1–46.4°, was prepared by chromic acid oxidation of methyl 12-hydroxyoctadecanoate[26] and purified by crystallization.

cis-2-Octene was isolated from a sample containing *trans*-2-octene by preparative g.l.c. on a 6 ft. × 0.25 in. column packed with 32% (17% silver nitrate in ethylene glycol) on 70–80-mesh Gas Chrom P operated at 28°.

A sample of *trans*-2-octene contained no *cis* isomer but did have about 3.3% of an impurity which is probably an isomeric *trans*-octene.

Spectral Curve Measurements.—Absorption curves were examined for absorption maxima and absorbance, the molar absorptivity (ϵ) was calculated, and the area under the curve was measured by planimetry. In all cases, correction was made for solvent absorption. (Errors in recording λ_{max} values may approach +0.5 mμ because of pen tracking error.)

The area under the absorption curve gives the integrated intensity $\int \epsilon d\nu$, where ϵ is in units of 1000 cm.²/mole and the wave number ν is in cm.⁻¹. Our absorption spectra were recorded linearly in mμ and then replotted to be linear in cm.⁻¹. Because the total absorption curve could not be recorded with our instrument, the areas between λ_{max} and λ_{min} and between 180 mμ and λ_{min} were determined instead. Oscillator strengths, $f = 4.315 \times 10^{-9} \int \epsilon d\nu$, were calculated from the integrated intensities between λ_{max} and λ_{min} by assuming that the absorption curves are symmetrical for the N → V electronic transition in monoene esters.

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TABLE I

SPECTRAL DATA FOR PURE COMPOUNDS

Methyl ester	Curve	λ_{max}, mμ (ϵ_{max})	$\int_{\lambda_{max}}^{\lambda_{min}} \epsilon d\nu$, cm./mole × 10^8	f^a	$\int_{180}^{\lambda_{min}} \epsilon d\lambda$, cm.^{3}/mole
cis-9-Hexadecenoate		184.0 (12,900)	442	0.38	21.1
cis-6-Octadecenoate		184.0 (13,000)	452	0.39	21.2
cis-9-Octadecenoate	II	184.0 (13,000)	441	0.38	21.8
cis-11-Octadecenoate		184.0 (13,150)	458	0.40	22.2
cis-12-Octadecenoate		184.0 (13,100)	453	0.39	21.8
cis-11-Eicosenoate		184.0 (13,150)	452	0.39	21.5
cis-13-Docosenoate		184.0 (12,850)	449	0.39	21.3
cis-15-Tetracosenoate		184.5 (12,950)	445	0.38	21.8
12-Hydroxy-*cis*-9-octadecenoate	XI	184.0 (13,800)	476	0.41	23.2
14-Hydroxy-*cis*-11-eicosenoate	XII	184.5 (13,700)	460	0.40	23.1
cis-12,13-Epoxy-*cis*-9-octadecenoate	XIV	184.0 (13,900)	453	0.39	21.8
12-Methoxy-*cis*-9-octadecenoate	XVI	185.0 (12,800)	439	0.38	22.4
12-Methoxy-*trans*-9-octadecenoate	XV	189.0 (11,200)	342	0.29	22.4
trans-9-Octadecenoate	I	187.0 (11,900)	372	0.32	21.8
12-Hydroxy-*trans*-9-octadecenoate	X	186.5 (11,450)	383	0.33	21.4
cis-9-*cis*-12-Octadecadienoate	IV	190.0 (18,750)	687		44.2
cis-5-*cis*-13-Docosadienoate	V	184.5 (25,750)	873		43.1
12-Hydroxy-*cis*-9-*cis*-15-octadecadienoate	XIII	184.0 (27,800)	959		44.8
trans-9-*trans*-12-Octadecadienoate	III	192.0 (16,050)	590		41.7
All-*cis*-9,12,15-octadecatrienoate	VI	192.5 (25,150)	888		65.3
All-*cis*-5,8,11,14-eicosatetraenoate	VII	193.5 (31,800)	1193		89.1
All-*cis*-5,8,11,14,17-eicosapentaenoate	VIII	193.5 (37,400^b)	1439		106.8
All-*cis*-4,7,10,13,16,19-docosahexaenoate	IX	194.0 (43,600^b)	1690		130.8
ω-(2-*n*-Octylcyclopropenyl)octanoate	XIX	(ϵ_{195} 5,440)			20.4
12-Oxo-*cis*-9-octadecenoate	XVII	(ϵ_{183} 10,900)			22.4
12-Oxooctadecanoate	XVIII	(ϵ_{183} 940)			1.3
cis-9,10-Epoxyoctadecanoate		(ϵ_{184} 315)	4.5^c		0.6
12-Methoxyoctadecanoate		(ϵ_{185} 1,026)	18^d		1.4
		(ϵ_{189} 493)	10^e		
12-Hydroxyoctadecanoate		(ϵ_{184} 430)	11.5^c		0.8
Octadecanoate		(ϵ_{184} 110)			0.2
cis-2-Octene		181.5 (13,450)	438	0.38	
trans-2-Octene		184.0 (10,450)	350	0.30	

[a] Oscillator strength calculated from integrated intensity between λ_{max} and λ_{min}. [b] Average of three determinations. [c] 184 mμ to λ_{min}. 185 mμ to λ_{min}. [e] 189 mμ to λ_{min}.

Results and Discussion

Straight-chain methyl esters that contain one isolated, disubstituted *cis* olefinic bond but no other functional group (curve II, Figure 1, is representative) have λ_{max} 184.0–184.5 mμ (ϵ_{max} 13,000 ± 150) (Table I). This ϵ_{max} is considerably higher than the value reported by Rusoff, *et al.*,[6] for oleic acid (*ca.* 7400). The difference in apparent intensity is probably attributable to inherent limitations of their photographic recording method. Paschke, *et al.*,[7] report ϵ 11,000 at 183 mμ (maxinum) for methyl oleate but give no details of the determination.

The molar absorptivity at the wave length of maximum absorption, ϵ_{max}, is generally used to measure the intensity of an absorption band, but, as Jaffé and Orchin[27] state, "the value of ϵ_{max} is not directly related to any quantity obtainable from theory." It is rather the integrated intensity and the oscillator strength that are of theoretical interest. We find oscillator strengths for *cis*-monoenes, $f = 0.38$–0.40 (Table I), that are in excellent agreement with the value, $f = 0.40$, calculated by use of the free-electron approximation.[28]

Esters with two to six methylene-interrupted *cis* olefinic bonds show a bathochromic shift of λ_{max}, augmentation of ϵ_{max}, and broadening of the absorption curve. The λ_{max} of methyl *cis*-9-*cis*-12-octadecadienoate (curve IV) is 6 mμ longer than the λ_{max} 184.0 mμ of methyl *cis*-9-octadecenoate (curve II). Successive shifts are smaller and methyl all-*cis*-4,7,10,13,16,19-docosahexaenoate has λ_{max} of 194.0 mμ, but, when the double bonds are farther apart (curves V and XIII, Figure 2), λ_{max} lies closer to λ_{max} for methyl octadecenoate. Increase in molar absorptivity in the methylene-interrupted series is linear but not a simple multiple of ϵ_{max} for methyl octadecenoate (Figure 3). For example, the molar absorptivity of methyl *cis*-9-*cis*-12-octadecadienoate is only 44% greater. However, in *cis*-5-*cis*-13-docosadienoate the olefinic bonds are widely separated and its ϵ_{max} is about double the ϵ_{max} of methyl *cis*-9-octadecenoate. Jones and Taylor[29] similarly found that the two intervening methylene groups insulated the double bonds in 1,5-hexadiene. This compound has an ϵ_{max} value double that of 1-pentene, whereas the ϵ_{max} for 1,4-hexadiene is only about 40% greater. Interaction between nonconjugated chromophores is well known. It has been ascribed to hyperconjugation of an intervening methylene group[30] and to 1,3 interaction or homoallylic resonance.[31] It is also instructive to consider the interaction in methyl

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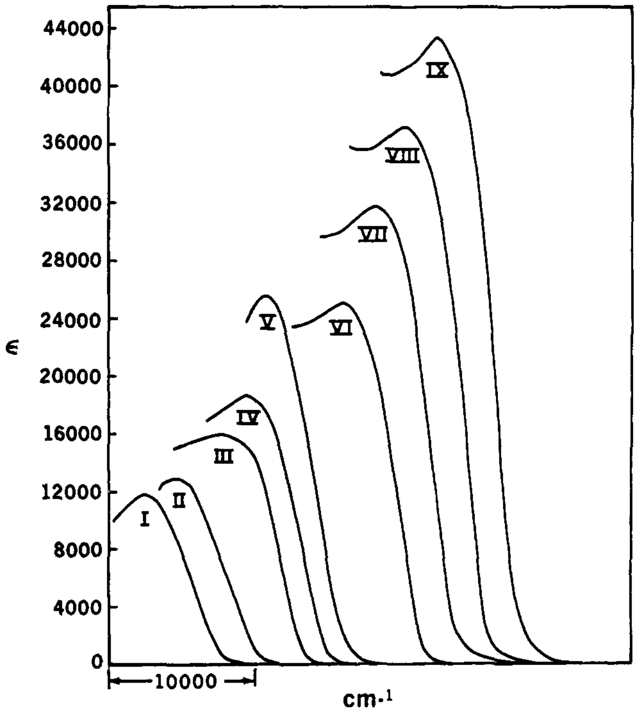

Figure 1.—Absorption spectra of unsubstituted fatty acid esters containing one to six isolated olefinic bonds. Each curve begins at 55,555 cm.$^{-1}$ (180 mμ). Compounds are listed in Table I.

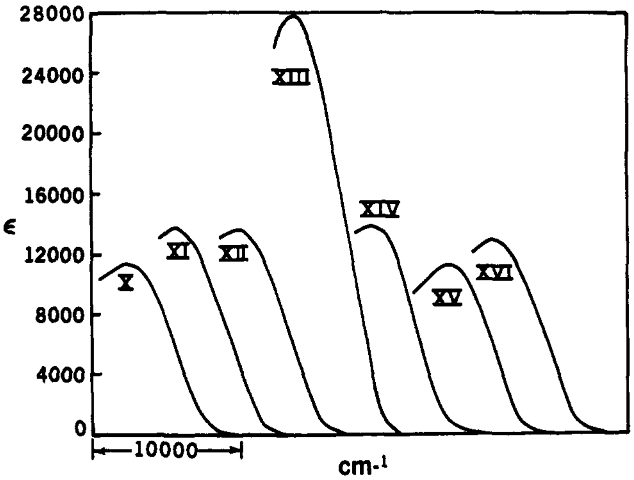

Figure 2.—Absorption spectra of fatty acid esters having a substituent β to an olefinic bond. Each curve begins at 55,555 cm.$^{-1}$ (180 mμ). Compounds are listed in Table I.

cis-9-*cis*-12-octadecadienoate on the basis of a free-electron model that has the π electrons disposed as a free-electron gas in two potential energy boxes along the molecular axis. The width and height of the boxes may be taken as 3 Å.[32] and the length, 4.09 Å., is calculated from[28] $L = (3\lambda/329.7)^{1/2}$ by use of $\lambda_{\max}$ for methyl *cis*-9-octadecenoate. The boxes intersect. This interaction may also be ascribed to the first-order splitting of the excited states, due to energy delocalization, of the neighboring olefinic bonds.[33] An estimate of the interaction in methyl *cis*-9-*cis*-12-octadecadienoate, calculated by use of the dipole–dipole approximation[33] on a simple model, agrees with the experimental results (calculated shift 2220 cm.$^{-1}$, observed 1720 cm.$^{-1}$).

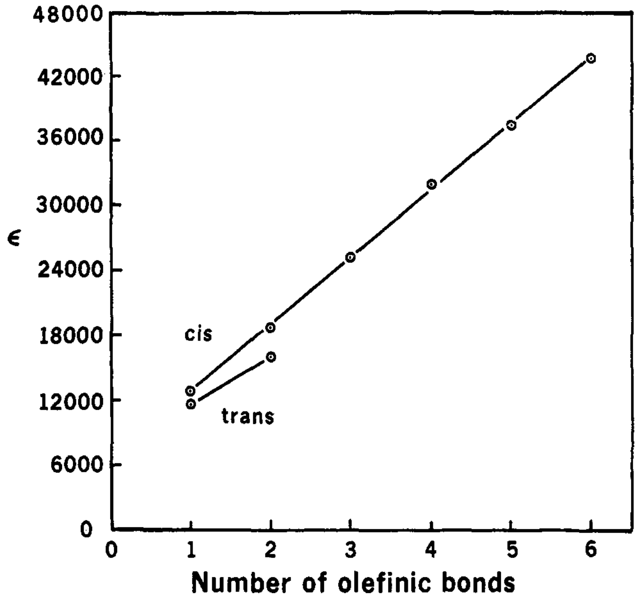

Figure 3.—Change in molar absorptivity with increasing number of methylene-interrupted olefinic bonds.

Although our $\lambda_{\max}$ values generally correspond well to those of Rusoff, *et al.*,[6] our intensity values do not. Our values are considerably higher except for linoleic acid for which they show $\epsilon_{\max}$ *ca.* 19,600 (as estimated from their graphic[6] data). They show that linolenic acid, with one more olefinic bond, has molar absorptivity essentially equivalent to linoleic acid but ethyl linolenate has $\epsilon_{\max}$ *ca.* 15,500. These inconsistencies make comparison of our absorption data with theirs difficult.

The absorptivity of the esters containing methylene-interrupted *cis* olefinic bonds is not proportional to the degree of unsaturation, but the area $\int \epsilon d\lambda$ under the absorption curve between 180 mμ and $\lambda_{\min}$, recorded linearly in mμ, indicates the number of nonconjugated olefinic bonds. For this region, $\int \epsilon d\lambda$ for the monoene esters is within 3% of 21.7 cm.^{3}/mole and as the number of olefinic bonds increases the area increases proportionally (Table I). This rule is also valid for methyl *cis*-5-*cis*-13-docosadienoate (Table I) and mixtures of unsubstituted esters. The integrated intensity $\int \epsilon d\nu$ between 180 mμ and $\lambda_{\min}$ or between $\lambda_{\max}$ and $\lambda_{\min}$ is a less satisfactory measure, since the area, as we determined it, does not increase proportionally with the number of double bonds.

When the isolated double bond is *trans*, $\lambda_{\max}$ increases and absorption decreases. Methyl *trans*-9-octadecenoate and methyl 12-methoxy-*trans*-9-octadecenoate have $\lambda_{\max}$ 3–4 mμ longer than the corresponding *cis* isomers and $\epsilon_{\max}$ are 8.5 and 12.5% lower. Methyl *trans*-9-*trans*-12-octadecadienoate has $\lambda_{\max}$ 2 mμ longer and $\epsilon_{\max}$ 14% less than methyl *cis*-9-*cis*-12-octadecadienoate. Rusoff, *et al.*,[6] report that isomerization of oleic acid (*cis*) to elaidic acid (*trans*) causes a 4-mμ bathochromic shift of the absorption curve and a 15% increase in maximum absorption. However, they also show the maximum absorption for ethyl elaidolinolenate to be 11% less than for ethyl linolenate. Paschke, *et al.*,[7] give values for methyl elaidate, ε

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[32] H. Kuhn, *Experientia*, **9**, 41 (1953).

[33] J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," John Wiley and Sons, Inc., New York, N. Y., 1963, p. 137.

11,400 at 186 mμ (maximum), that are essentially equivalent to ours. Stray light may have caused their ϵ value for methyl oleate at 183 mμ to be low. Similar differences have been noted and discussed before.[10] Other work[29,34-36] on isomeric 2-butenes, 2-pentenes, and dichloroethylenes indicates that an isolated *trans* bond has a maximum at longer wave lengths and of lower intensity than the *cis* bond. Platt, *et al.*,[37] find the reverse order of band positions and intensities for *cis*- and *trans*-2-octene, but our results for the same compounds contradict theirs (*cf.* Table I). In view of our results and the correlations found in all other studies, it seems likely that the earlier measurements[37] were in error.

The ground state for *cis*-2-butene is of higher energy than for *trans*-2-butene, as indicated by heats of hydrogenation,[38] whereas the band maximum of the *cis* isomer[34] corresponds to a more energetic electronic transition. This implies a stabilization of the excited state of the *trans* olefin relative to the *cis* olefin.[35] For molecules of similar configuration but different molecular weight, Semenow, *et al.*,[35] noted a bathochromic shift of the N → V band for the larger molecules. We observe similar shifts for *cis* and *trans* isomers of 2-octene and methyl 9-octadecenoate.

An oxygenated substituent β to an olefinic bond may increase or decrease the molar absorptivity. Subtraction of the absorptions of unsubstituted esters from the absorptions of corresponding substituted esters establishes a basis for noting a change in molar absorptivity attributable to the substituent. For example, the difference between molar absorptivities at 184 mμ for methyl 12-hydroxyoctadecanoate and methyl octadecanoate is 320 but for methyl 12-hydroxy-*cis*-9-octadecenoate and methyl *cis*-9-octadecenoate is 800. Thus, some interaction between the hydroxyl group and the olefinic bond seems to be indicated. On this basis, a β-methoxyl group decreases molar absorptivity and an epoxy group β to a *cis* olefin increases it. The β-hydroxyl group causes an increase when the double bond is *cis* but a decrease when it is *trans*.

However, the most striking example of influence by the β substituent is in methyl 12-oxo-*cis*-9-octadecenoate (Figure 4). At 184 mμ, the molar absorptivity attributable to the olefinic bond is 22% less than in methyl *cis*-9-octadecenoate and there is no absorption maximum in the 180–250-mμ region. Nevertheless, the integrated absorption $\int \epsilon d\lambda$ is approximately the sum of the absorptions of methyl *cis*-9-octadecenoate and methyl 12-oxooctadecanoate (Table I and Figure 4). Although the decrease in intensity and change in curve shape indicate some interaction, our results do not reproduce the more striking interactions observed in other β,γ-unsaturated ketones.[39,40] This is perhaps to be expected since the acyclic compound described here does not have the relatively rigid conformation that provides a stereoelectronic situation favoring interaction as discussed by Winstein, *et al.*[40] The spectra of the acyclic homoallylic olefins we have examined can be interpreted similarly. For example, whereas the spectrum of methyl *cis*-9-*cis*-12-*cis*-15-octadecatrienoate shows some interaction, it does not display the rather striking ultraviolet spectrum which was interpreted as arising from interaction in the case of *cis*-*cis*-*cis*-1,4,7-cyclononatriene.[41]

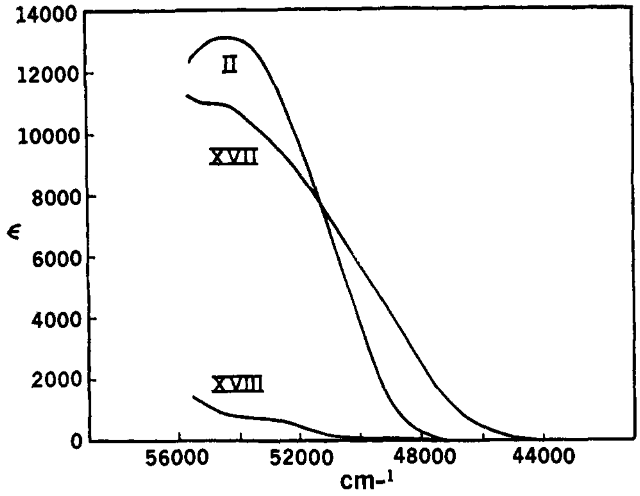

Figure 4.—Absorption spectrum of methyl 12-oxo-*cis*-9-octadecenoate (XVII) compared with spectra of methyl *cis*-9-octadecenoate (II) and methyl 12-oxooctadecanoate (XVIII). Compounds are listed in Table I.

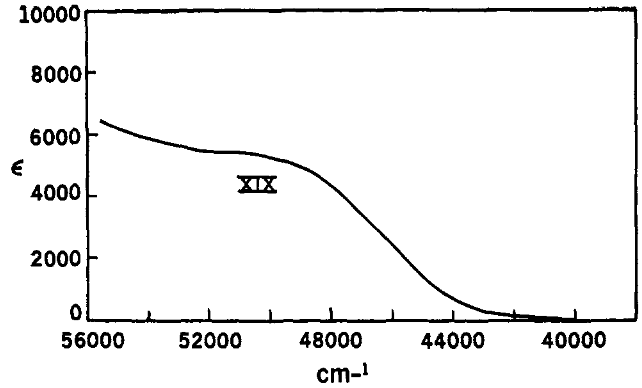

Figure 5.—Absorption spectrum of methyl sterculate (180–250 mμ). Spectral data are given in Table I.

The methyl sterculate spectrum (Figure 5) shows continually increasing absorption from 250 to 180 mμ, with an inflection point at about 193 mμ. The curve resembles the curve for cyclopropene[42] but displays higher molar absorptivity (*e.g.*, ϵ 5900 *vs.* ϵ 2000 at 185 mμ) and extends to longer wave lengths.

Most of the esters investigated have λ_{max} in the region 183–194 mμ. This narrow range limits information on structure obtainable from the position of maxima. Nevertheless, a methylene-interrupted diene can be distinguished from other nonconjugated dienes and *cis* isomers can be distinguished from *trans*. The methylene-interrupted diene also has lower molar absorptivity than other dienes. Evaluation of $\int \epsilon d\lambda$ between 180 mμ and λ_{min} affords a more reliable esti-

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mate of total unsaturation than do the molar absorptivities.

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Amidation of Esters with Amides in the Presence of Methoxide Ion

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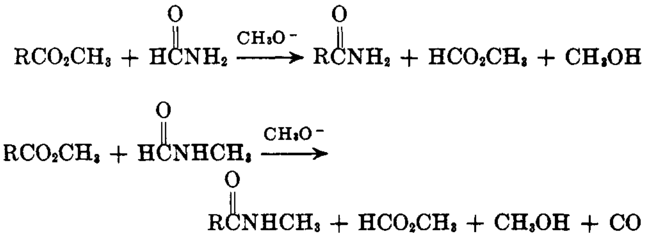
Methyl esters have been found to undergo amidation when treated with formamide or N-methylformamide in the presence of catalytic amounts of sodium methoxide. In addition to the new amide, other reaction products are methyl formate and methyl alcohol. Carbon monoxide is an additional product with N-methylformamide. Amidation also can be effected with esters other than methyl esters and with amides other than formamides. Amide anions are the actual reactive species with the ester. In this regard, the sodium salts of formamide and N-methylformamide are efficient catalysts. The amidation mechanism appears to consist of a complex series of reversible addition–elimination steps which include N-acylformamides and N-acylamides as reaction intermediates.

The conversion of carboxylic acid derivatives to one another by the action of appropriate nucleophiles has been one of the more extensively studied classes of chemical reactions.[2] In view of this, it is surprising to find that the reaction of amide anions with other carboxylic acid derivatives has received only limited attention. With one exception, the published results appear to deal entirely with intramolecular amidation by a neighboring amide function. Most of the reports have been concerned with demonstrating neighboring-group participation,[3-7] with only one study specifically utilizing the ring closure for synthetic purposes.[8] The one reference to intermolecular amidation describes only limited use of the reaction for synthesis.[9]

This paper reports our investigation of the reaction of amides with esters in the presence of catalytic amounts of methoxide ion, and discusses our cursory examination of the amidation mechanism for formamides. A unique decarbonylation reaction of a formyl imide also is reported.

Results and Discussion

Amidation Reactions Promoted by Methoxide Ion.—Preliminary experiments revealed that the reactions of formamide and N-methylformamide with esters in the presence of sodium methoxide proceed quite differently. These results prompted us to scrutinize the details of the reactions, as well as to investigate the synthetic scope.



$$\mathrm{RCO_2CH_3} + \mathrm{H\overset{\overset{O}{\|}}{C}NH_2} \xrightarrow{\mathrm{CH_3O^-}} \mathrm{R\overset{\overset{O}{\|}}{C}NH_2} + \mathrm{HCO_2CH_3} + \mathrm{CH_3OH}$$

$$\mathrm{RCO_2CH_3} + \mathrm{H\overset{\overset{O}{\|}}{C}NHCH_3} \xrightarrow{\mathrm{CH_3O^-}} \mathrm{R\overset{\overset{O}{\|}}{C}NHCH_3} + \mathrm{HCO_2CH_3} + \mathrm{CH_3OH} + \mathrm{CO}$$

Germane to a study of these reactions was the observation that mixtures of the reactants were not completely homogeneous. The very low solubility of sodium methoxide in aprotic solvents made difficult the examination of the reactions in a nonreactive solvent under strictly comparable homogeneous conditions. For this reason, the reactions for this preliminary investigation were carried out in the absence of solvent under one set of conditions. This standard set of conditions consisted of stirring an equal molar mixture of the anhydrous ester and amide with 5 mole % sodium methoxide (based on amide) at a bath temperature of 94–96° for 23 (or 72) hr. As the reaction proceeded, the low-boiling products were allowed to distil through a short column packed with Heli-Pak into a trap cooled with Dry Ice and acetone. The volume of any gas evolved was estimated with a gas buret assembly similar to one described by Wiberg.[10] Following the heating period, the remaining volatile products were removed under vacuum. Product analysis of both the low- and high-boiling products was by gas phase chromatography. Identification was made by comparison of the individual components with samples of the known compounds. Representative results for the reactions of a number of esters with formamide and N-methylformamide are collected in Tables I and II. The yields are estimated to be accurate to within *ca.* ±2%, based on checks with known mixtures of the products. Carbon monoxide gas was identified by the infrared spectrum which consisted of a doublet absorption at 4.65 and 4.76[11] μ. From each reaction,

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