g. (60%), and 0.025 g., respectively. The spectrum of the solution did not change on standing for 4 hr. at −80° but after warming to room temperature only the peaks due to the pentacyanopropenide ion remained.

Reaction of Bromomalononitrile and Tetracyanoethylene with Triethylamine.—A solution of 1.45 g. (0.01 mole) of bromomalononitrile in 25 ml. of methylene chloride was added over a 15-min. period to a solution of 2.02 g. (0.02 mole) of triethylamine in 25 ml. of methylene chloride at −80°. The absorption spectrum in methylene chloride indicated the presence of 0.21 g. (50%) of the pentacyanopropenide anion [λ_{max} 418 mμ (ε 23,450) and 399 mμ (ε 23,800) for a methylene chloride solution of pure tetramethylammonium pentacyanopropenide]. When the mixture was allowed to warm to room temperature it turned very dark. The solution absorbed throughout the visible, but the maxima at 399 and 418 mμ were still present. Analysis for tetracyanoethylene indicated the presence of 0.015 g. (2%).

The above reaction was performed using tetracyanoethylene in place of bromomalononitrile.[7] To a suspension of 0.64 g. (0.05 mole) of tetracyanoethylene in 50 ml. of methylene chloride at −80° was added 0.5 g. (0.05 mole) of triethylamine in 50 ml. of methylene chloride. Addition was completed in 1 hr. The reaction was stirred for 2 hr. and then analyzed spectrophotometrically. The yield of pentacyanopropenide anion was 0.195 g. (47%) and the yield of tricyanoethenolate anion was 0.26 g. (44%). Analysis for tetracyanoethylene indicated the presence of 0.052 g. (8%).

Reaction of Bromomalononitrile with Morpholine.[2]—To a solution of 2.9 g. (0.02 mole) of bromomalononitrile at −80° was added 3.48 g. (0.04 mole) of morpholine in 20 ml. of ether. A yellow precipitate formed immediately. After stirring for 7 hr. the solution was filtered and the precipitate was washed with ethanol. The residue left on the filter crystallized from acetonitrile in the form of needles, m.p. 203–208°. This material had an infrared spectrum (KBr) that was identical with that of a sample of morpholine hydrobromide prepared from hydrogen bromide and morpholine (m.p. 208–211°).

The filtrate from the morpholine hydrobromide was added to 0.02 mole of tetraethylammonium bromide to yield 0.48 g. (32%) of tetraethylammonium pentacyanopropenide, m.p. 218–220°.

1,1-Dimorpholino-2,2-dicyanoethylene.[6]—Morpholine (7.0 g., 0.08 mole) was added to 5.0 g. (0.039 mole) of tetracyanoethylene dissolved in 50 ml. of pyridine. The mixture became warm and turned dark orange-brown. It was heated slowly to boiling and then allowed to stand at room temperature for 66 hr. Some product crystallized from the solution. The mixture was poured onto 550 g. of ice, filtered, and washed with water to yield 6.3 g. (65%) of tan crystals, m.p. 277–279°. Recrystallization from acetonitrile yielded white rhombs, m.p. 276–278°. The infrared spectrum of this material was identical with that published for dimorpholinofumaric acid dinitrile, lit.[2] m.p. 277.5–278.9°.

Anal. Calcd. for $C_{12}H_{16}N_4O_2$: C, 58.05; H, 6.50; N, 22.56. Found: C, 58.32; H, 6.84; N, 22.44.

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The Acylation of β-Keto Esters. Control of the Position of Acylation by Variation of the Acylating Agent and Solvent[1a]

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The amount of C- and O-acylation has been determined when the magnesium chelates of 2-carbethoxycyclopentanone and 2-carbethoxycyclohexanone are allowed to react in tetrahydrofuran with ethyl chloroformate, chloracetyl chloride, acetyl chloride, acetyl bromide, acetyl perchlorate, and propionyl chloride. The first two acid halides give C-acylation. The other acylating agents yield about 80–95% C-acylated product with the exception of acetyl perchlorate which yields only 60–65% C-acylation. Increasing solvent polarity results in decreased C-acylation. A mechanism is proposed which is consistent with these data.

When the metal salts of β-keto esters are allowed to react with acid halides, it is possible to get products resulting from attack at the carbon atom (*cf.* III) or oxygen atom (*cf.* V) of the β-keto ester system.[2] Numerous examples of β-keto ester acylations have been recorded in the literature with varying yields of C- and O-acylated product reported, but very few systematic studies of this reaction have been recorded.[3] We have undertaken an investigation of the chemistry of the ambident β-keto esters with the hope of delineating the factors which direct the reaction to carbon or oxygen. The cyclic β-keto esters were chosen for this study since the conformational aspects of these rigid systems are well understood, and these compounds are models of more complicated structures where such information will be of synthetic value (*e.g.*, alkaloids and steroids).

When ethyl chloroformate was allowed to react with the sodium chelates of cyclic β-keto esters, we observed that steric factors governed the proportion of carbon and oxygen acylation.[2] A similar steric argument was proposed simultaneously by Rhoads and Decora[4] to explain that the relative rates of alkylation of the cyclic keto esters are 2-carbethoxycycloheptanone > 2-carbethoxycyclopentanone > 2-carbethoxycyclohexanone. Steric effects have also been suggested by Murdoch and Nonhebel[5] to explain the relative amounts of C- and O-acylation of β-diketones.[6]

Since the importance of steric effects is well documented, the present study was undertaken with the hope of discovering other factors which determine the proportion of C- or O-acylation. It was also the aim of this study to look for methods which would yield the synthetically more useful C-acylated product; thus the sodium chelates used in the initial study which

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(1) (a) Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. (b) Inquiries should be directed to J. P. F. at The Salk Institute.

(2) J. P. Ferris, C. E. Sullivan, and B. G. Wright, *J. Org. Chem.*, **29**, 87 (1964).

(3) The early literature is discussed by A. Brandstrom, *Arkiv Kemi*, **6**, 155 (1953). For a recent review of ambident anions, see R. Gomper, *Angew. Chem., Intern. Ed. Engl.*, **3**, 560 (1964).

(4) S. J. Rhoads and A. W. Decora, *Tetrahedron*, **19**, 1946 (1963).

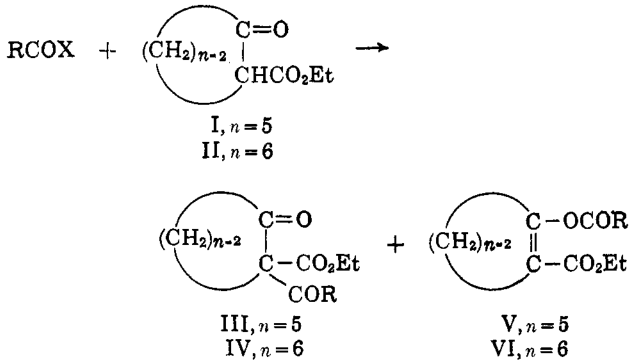
(5) H. D. Murdoch and D. C. Nonhebel, *J. Chem. Soc.*, 2153 (1962).

(6) This effect is referred to as masking[7] and it is similar in nature to the "selective solvation" of Kornblum.[8] See ref. 3 for a discussion of this effect.

(7) M. M. Jones and W. A. Connor, *Ind. Eng. Chem.*, **55**, 14 (1963).

(8) N. Kornblum, P. J. Berrigan, and W. J. LeNoble, *J. Am. Chem. Soc.*, **82**, 1257 (1960).

yielded mainly O-acylated products[2] were abandoned for the more stable magnesium chelates. It was hoped that the magnesium chelates would give a greater proportion of C-acylation because the enol oxygen atom is more tightly bound in a stable chelate ring than it is in the sodium chelate and is therefore a much poorer nucleophile.[3,6] Viscontini and Merckling[9] originally reported a procedure by which the C-acylated product could be obtained by acylation of the ethoxy adduct of the magnesium chelate, and this procedure has been widely adopted for the C-acylation of β-keto esters.[10] However, we have found that this method does not work well with the less reactive acid chlorides owing to the unfavorable competition with the ethoxy group to give the ethyl ester of the acyl halide (*e.g.*, ethyl chloroformate yields only diethyl carbonate).[2] Plesek[11] has obtained good yields by acylating the bromo adduct of the magnesium chelate of 2-carbethoxycyclopentanone. As discussed previously[2] he assumed the formation of the C-acylated product but did not isolate it. Instead, he hydrolyzed directly to the corresponding keto acid with sodium carbonate. The possibility of oxygen to carbon migration of the acyl group (V → III) during hydrolysis was not eliminated in his studies.[12] We undertook an investigation of the bromo adduct of the magnesium chelate because it would provide a system that would not be complicated by side reactions with ethoxide ion and might yield principally C-acylated products.



Preparation of an ether suspension of the magnesium chelate of I with ethylmagnesium bromide and then addition of ethyl chloroformate and heating for 8 hr. according to the procedure of Plesek[11] gave a low yield (Table I, **1**, **8**, and **10**) of mainly C-acylated product (III, R = OEt). The low yields as well as the heterogeneous nature of the reaction and the long reflux time made it desirable to improve the reaction conditions. Substitution of tetrahydrofuran[13] for ether gave a homogeneous reaction mixture, shorter reaction time (15–30 min.), enhanced over-all yield, and a greater proportion of C-acylation (compare **1**, **8**, and **10** with **2**, **9**, and **11**, respectively, Table I). Especially noteworthy is that 50–65% yields of C-acylated β-keto ester were obtained with ethyl chloroformate as the acylation agent where none was obtained when the ethoxy adduct of the magnesium chelate was used.[2]

Application of the modified Plesek procedure to II gave exclusive formation of IV (R = OEt) with ethyl chloroformate. This dramatically demonstrates the important influence of the metal used as the chelating agent since only O-acylation (VI, R = OEt) was observed when the sodium chelate was acylated.[2]

It was also possible to prepare the magnesium chelates indirectly from the sodio derivatives. Reaction of I or II with sodium hydride in tetrahydrofuran gave soluble sodium derivatives which reacted rapidly and exothermically with anhydrous magnesium perchlorate to yield soluble magnesium chelates. The dissolution of the magnesium perchlorate (normally insoluble in tetrahydrofuran) and the exothermic nature of the reaction attest to the greater stability of the magnesium chelate over the sodium chelate. Reaction of the perchlorate adducts of the magnesium chelates with ethyl chloroformate gives products comparable with those from the bromo adducts of the magnesium chelates.

The purity of the above C-acylated products was ascertained by vapor phase chromatography (v.p.c.). The structures were determined by the absence of absorption characteristics of the acrylate systems of V and VI in the infrared and ultraviolet spectra as discussed previously.[2]

The difunctional acyl halide, chloroacetyl chloride, also yielded exclusively C-acylated products (III and IV, R = CH$_2$Cl). The fact that I was recovered when alkylation of the bromo adduct of the magnesium chelate was attempted with ethyl bromoacetate led to the prediction that the isomeric C-alkylated product would not be formed. This was confirmed by lack of infrared absorption at 1800 cm.$^{-1}$ for the acid chloride function in the product. The bromo adduct of the magnesium chelate did yield two different C-acylated products with this acid chloride. The additional product was shown to be due to replacement of the α-chloro group with bromide since none of this product was obtained when the chloro or perchlorate adduct of the magnesium chelate was used.

We then studied the reaction of the β-keto esters with acetyl chloride and propionyl chloride. These acid halides provided us with a sensitive probe by which we could study the factors which direct the acylating agent to carbon or oxygen because, in contrast with the previously studied acid halides, significant amounts of O-acylation were observed. As preliminary results indicated that acetyl halides gave the same reaction products as did the propionyl halides, only the acetyl derivatives were studied in detail.

Increasing the polarity of the reaction solvent tended to increase the proportion of O-acylation (Table II). In some cases the results were ambiguous owing to the formation of precipitates, but the trend is clear. An attempt was made to study the effect of added salts on the proportion of C- and O-acylation (Table I).[14] It is difficult to interpret the results because the yield of acylated product decreased in most instances. When lithium bromide and tetrabutylammonium bromide were added (**19** and **21**, Table I), an additional com-

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(9) M. Viscontini and N. Merckling, *Helv. Chim. Acta*, **35**, 1342, 2280 (1952).

(10) H. Paul, *J. prakt. Chem.*, **21**, 186 (1963); J. Korman, *J. Org. Chem.*, **22**, 848 (1957); A. Triebs and K. Hintermeier, *Ber.*, **87**, 1163 (1954).

(11) J. Plesek, *Collection Czech. Chem. Commum.*, **21**, 1312 (1956); **22**, 49 (1957); **22**, 1661 (1957).

(12) H. Henecka, *Ber.*, **81**, 196 (1948).

(13) S. O. Lawesson and T. Busch, *Acta Chem. Scand.*, **13**, 1717 (1959).

(14) D. P. N. Satchell, *J. Chem. Soc.*, 558, 564 (1963); *J. M. Briody* and D. P. N. Satchell, *ibid.*, 3724 (1964).

TABLE I

THE REACTION OF ACYL HALIDES WITH CYCLIC β-KETO ESTERS

No.	Ring size	Chelate prepd. from	Added salt (mole)	Solvent[a]	Total yield, %	Acylation, %	
						C	O
A. Reaction with $EtOCOCl$							
1	5	EtMgBr	...	Ether[b]	11	95	5
2	5	EtMgBr	...	THF[c]	49	100	..
3	6	EtMgBr	...	THF[d]	51	100	..
4	6	$NaH-Mg(ClO_4)_2$	...	THF[e]	67	100	..
B. Reaction with $ClCH_2COCl$							
5	6	EtMgBr	...	THF[c]	59	100[f]	..
6	6	$NaH-Mg(ClO_4)_2$	...	THF[c]	62	100	..
7	6	EtMgBr	...	THF[d]	79	100	..
C. Reaction with CH_3CH_2COCl							
8	5	EtMgBr	...	Ether[b]	42	90	10
9	5	EtMgBr	...	THF[c]	70	93	7
D. Reaction with CH_3COCl							
10	5	EtMgBr	...	Ether[b]	18	84	16
11	5	EtMgBr	...	THF[d]	63	94	6
12	6	EtMgBr	...	THF	79	87	13
13	6	EtMgCl	...	THF	77	85	15
14	6	EtMgBr	LiCl (0.55)	THF	65	81	19
15	6	EtMgBr	$Mg(ClO_4)_2$ (0.05)	THF	80	72	28
E. Reaction with CH_3COClO_4							
16	5	$NaH-Mg(ClO_4)_2$	...	THF[d]	68	66	34
17	6	EtMgBr	$NaClO_4$ (0.19)	THF	74	60	40
F. Reaction with CH_3COBr							
18	6	EtMgBr	...	THF	75	88	12
19	6	EtMgBr	LiBr (0.55)	THF	54	75	25
20	6	EtMgBr	$LiClO_4$ (0.55)	THF	24	63	37
21	6	EtMgBr	$(n\text{-}C_4H_9)_4NBr$ (0.55)	THF	..	..	..

[a] 600 ml. of solvent was used unless stated otherwise. [b] Exact procedure of Plesek[11] was used. [c] 50 ml. [d] 100 ml. [e] 200 ml. [f] V.p.c. analysis indicates 68% of the desired chloroacetyl derivative and 32% of another C-acylated product, probably the bromoacetyl derivative.

pound was observed in the v.p.c. of the crude reaction product, and this compound was also found when lithium bromide and acetyl bromide were allowed to react with tetrahydrofuran in the absence of the chelate of the β-keto ester. Structure VII was assigned this

$$CH_3CO_2CH_2CH_2CH_2CH_2Br$$

VII

product on the basis of an infrared absorption maximum at 1760 cm.$^{-1}$, a positive silver nitrate test, and similar preparations reported previously.[15]

TABLE II

SOLVENT EFFECTS ON THE REACTION OF ACETYL CHLORIDE WITH THE MAGNESIUM CHELATE OF 2-CARBETHOXYCYCLOHEXANONE

Added solvent[a]	Solubility of chelate	Total yield, %	Acylation, %	
			C	O
Cyclohexane	Insoluble	37	94	6
Dioxane	Part. soluble	61	92	8
Ether	Part. soluble	38	88	12
Tetrahydrofuran	Soluble	68	87	13
Dimethylformamide	Insoluble	36	71	29
Acetonitrile	Soluble	62	57	43

[a] The bromo adduct of the magnesium chelate (0.1 mole) was prepared in 100 ml. of THF and then 500 ml. of the solvent listed was added before addition of acetyl chloride (0.11 mole).

Changing the leaving group on the acylating agent altered the proportion of C- and O-acylation. No significant differences were observed between acetyl chloride and acetyl bromide but, when acetyl perchlorate was used, a substantially greater proportion of O-acylation was observed (**17**, Table I). Acetyl perchlorate is conveniently generated in tetrahydrofuran by adding a solution of sodium perchlorate to acetyl chloride. Sodium chloride precipitates from the reaction. The high proportion of O-acylation found when the magnesium chelate is prepared by adding magnesium perchlorate to the sodium chelate (**16**, Table I) is understood as being caused by the sodium perchlorate generated.[16]

Discussion

The C- and O-alkyl products obtained when the anion of acetoacetic ester reacted with alkyl halides have been explained by Kornblum and co-workers[17] on the basis of the S_N1 or S_N2 nature of the transition state for the reaction. A highly ionic transition state results in an S_N1 process with the alkyl group having preference for the atom of highest electron density (oxygen). Here bond breaking (of

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(15) A. Watanbe, *Himeji Kogyo Daigaku Kenkyu Hokoku*, **6**, 68 (1956); *Chem. Abstr.*, **51**, 3550 (1957); J. A. Barkhash, G. P. Smirnova, and I. V. Machinskaya, *J. Gen. Chem. USSR*, **33**, 2504 (1963).

(16) When tetrahydrofuran solutions of acetyl chloride and sodium perchlorate are mixed, an immediate precipitate is formed. No precipitate is observed when a tetrahydrofuran solution of ethyl chloroformate and sodium perchlorate was allowed to stand for 24 hr.

(17) N. Kornblum, R. A. Smiley, R. K. Blackwood, and D. C. Iffland, *J. Am. Chem. Soc.*, **77**, 6269 (1955).

TABLE III

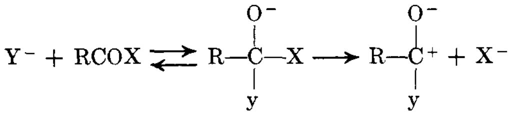
2-ACYL-β-KETO ESTERS

Compd.	R	Formula	B.p., °C. (mm.)	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Infrared max., cm.$^{-1}$
III	OEt	$C_{11}H_{16}O_5$	91 (0.2)	57.89	58.01	7.07	7.09	1765, 1740
III	CH_3	$C_{10}H_{14}O_4$	62 (0.05)	60.59	60.50	7.12	7.44	1760, 1730, 1720
III	CH_2CH_3	$C_{11}H_{16}O_4$	83 (0.5)	62.25	62.06	7.60	7.78	1760, 1730, 1720
IV	OEt	$C_{12}H_{18}O_5$	93 (0.1)	59.49	59.83	7.49	7.64	1765, 1740, 1725
IV	CH_3	$C_{11}H_{16}O_4$	75 (0.05)	62.25	62.65	7.60	7.68	1750, 1720
IV	CH_2CH_3	$C_{12}H_{18}O_4$	90 (0.1)	63.70	63.67	8.02	8.13	1750, 1725
IV	CH_2Cl	$C_{11}H_{15}ClO_4$	115 (0.05)	53.56	53.83	6.15	6.07	1750, 1720

the carbon–halide bond) is the more important process in the transition state. In an SN2 process there is little ionic character in the transition state and bond making predominates. Since the carbon center is a more potent nucleophile than the oxygen center, this process results in C-alkylation. In general, the SN1 reactions with ambident anions are more rapid than SN2 reactions.

The reaction of acyl halides with nucleophiles has been shown to be bimolecular in almost every instance.[18,19] It has been suggested that acetyl perchlorate dissociates into acylium ions[20] so that one might predict that its reaction with nucleophiles would be first order in acetyl perchlorate. However, the evidence for acylium ions is not compelling. Also, it has been shown that acetyl trifluoroacetate, a very reactive acylating agent, reacts in bimolecular fashion with phenol.[21] Therefore, it seems likely that the reaction of acetyl perchlorate with anions is bimolecular in nonpolar solvents. On this basis one might predict *a priori* that all the acylating agents used in our work would yield only the C-acylated product, but acetyl chloride has been found to react with nucleophiles 10^3 times faster than ethyl chloroformate or chloroacetyl chloride.[22-24] This suggests that when acetyl chloride reacts with ambident anions the transition state has considerably more ionic character and O-acylation could result.

The mechanism suggested for the base-catalyzed solvolyses of acid halides[22] is readily adapted to the reaction of acylating agents with ambident nucleophiles.



$$Y^- + RCOX \rightleftarrows R-\overset{O^-}{\underset{y}{C}}-X \longrightarrow R-\overset{O^-}{\underset{y}{C^+}} + X^-$$

With the less reactive acylating agents[24] (CH_3CH_2OCOCl and $ClCH_2COCl$) the transition state is SN2 and bond formation predominates. The carbon atom of the ambident β-keto ester anion is the more nucleophilic so that C-acylation results.

With the more reactive acylating agents (CH_3COX and RCH_2COX) the addition reaction is rapid and nondescriminating and bond breaking predominates. In the limiting case with the reactive acylating agents the relative nucleophilicities of the reaction centers in the ambident ion becomes unimportant, and the product ratio is determined principally by steric effects. This is also true for "reactive anions"[6] since we found previously that steric effects governed the proportion of C- and O-acylation when the more reactive sodium chelates of the β-keto esters were allowed to react with ethyl chloroformate.[2] Obviously, in the present study the relative nucleophilicities of the carbon and oxygen atoms are still an influential factor or else one would have expected complete O-acylation of the magnesium chelate of II as was observed for the sodium chelate.[2]

Changing the leaving group (X) from halide to perchlorate or increasing the solvent polarity both lead to increased O-acylation, a result consistent with the above explanation. Both of these changes would increase the reactivity of the acylating agent by enhancing the ionic character of the C–X bond.[25]

Experimental[26]

Physical constants for the new compounds prepared in this study are given in Table III. The following experiments are typical of those used in this study.

2-Carbethoxy-2-acetylcyclohexanone.—Ethyl bromide (12 g., 0.11 mole) was added to 2.67 g. (0.11 g.-atom) of magnesium turnings in the presence of 30 ml. of tetrahydrofuran. After reaction was complete the solution was diluted to 100 ml. with tetrahydrofuran cooled in an ice bath and 17 g. (0.1 mole) of 2-carbethoxycyclohexanone was added rapidly with stirring. Tetrahydrofuran (500 ml.) was added to this mixture and it was allowed to warm to room temperature. Acetyl chloride (8.63 g., 0.11 mole) was added dropwise to the stirred solution, and it was allowed to stand 30 min. at room temperature. The mixture was acidified with 50 ml. of 1% sulfuric acid and the aqueous layer was extracted several times with ether. The combined ether extracts were washed with dilute sodium bicarbonate solution and dried, and the ether was distilled. V.p.c. analysis of

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[18] P. F. G. Praill, "Acylation Reactions," Pergamon Press Ltd., London, 1963, pp. 13, 35.

[19] Kinetic evidence for the presence of acetylium ions has been found by Satchell and co-workers[14] in the acid-catalyzed reaction of acid halides with phenols. However, the acid is necessary for the formation of these ions; they are not a result of simple dissociation.

[20] H. Burton and P. F. G. Praill, *J. Chem. Soc.*, 1456 (1954), and previous papers in this series; G. Jander and H. F. Surowski, *Z. Elektrochem.*, **65**, 469 (1961); M. Schmerssen, *Angew. Chem.*, **67**, 495 (1955).

[21] T. G. Bonner and E. G. Gabb, *J. Chem. Soc.*, 3291 (1963).

[22] (a) H. Minato, *Bull. Chem. Soc. Japan*, **37**, 317 (1964); (b) M. Bender, *Chem. Rev.*, **60**, 53 (1960); (c) D. P. N. Satchell, *Quart. Rev.* (London), **17**, 161 (1963).

[23] Steric effects due to the acylating agents used should not be important. The steric requirements of each are small and approximately equivalent.

[24] See ref. 22a, ref. 18, pp. 12–20, and J. M. Briody and D. P. N. Satchell, *Proc. Chem. Soc.*, 268 (1964), for listings of the relative reaction rates of the acid halides used in this study.

[25] The solvent effects cited by Burton and co-workers[20] in support of the ionic nature of acetyl perchlorate are also consistent with a modification of the bimolecular mechanism suggested in this discussion.

[26] Infrared spectra were determined on a Perkin-Elmer Model 137 in carbon tetrachloride. Ultraviolet spectra were determined on a Cary Model 14 in 95% ethanol by Mrs. P. Ward. A few of the v.p.c. analyses were determined as described previously but the bulk were performed on an F and M Model 500 chromatograph equipped with disk integrator. A 3-ft. column packed with 20% diethylene glycol succinate on Diatoport S was used with helium flow of 100 cc./min. The column temperature was programmed at 11°/min. starting at 90°. Dry tetrahydrofuran was prepared by distillation from lithium aluminum hydride and was stored over sodium hydroxide pellets. Reagent grade ether was dried over sodium wire before use. The other solvents were purified by distillation and dried by storing over Dri-Na. The acid halides were purified by distillation before use. Analyses were performed by F. Pascher, Bonn, West Germany, and Midwest Microlab, Indianapolis, Ind.

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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[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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