mixture containing NF_2 compounds continued to decompose on standing at room temperature which precluded any attempts toward isolation. Weakly nucleophilic olefins have previously been shown to resist the N_2F_4 addition reaction.[2]

This study has shown that olefinic nitrogen compounds undergo the addition of N_2F_4 in the expected manner. It has been further demonstrated that compounds containing the 1,6-heptadienyl structure are prone to undergo an addition–cyclization reaction with the ultimate formation of bis(difluoramino) derivatives. It is important to stress the explosive character of these reaction mixtures and products. Mixtures of organic materials and N_2F_4 are potentially explosive and the products are impact-sensitive materials; hence, the experimental work should be performed with requisite precautions.

Experimental Section

Most olefins were purchased from commercial sources and used as received. The tetrafluorohydrazine employed was of 95–99% purity containing CF compounds as impurities. Infrared spectra were obtained with a Perkin-Elmer Infracord spectrophotometer using a sodium chloride prism while nmr spectra were obtained with a Varian Associates Model V-4310 high-resolution spectrometer using a 40-Mc probe (^{19}F). An Aerograph Instrument, Model A-100-C, with a dinonyl phthalate on Chromosorb column was used for all gas chromatography work. The general experimental technique used in all reactions is described for the reaction of tetrafluorohydrazine with N,N-dimethylmethacrylamide. Experimental data for the other reactions are presented in Table II.

Tetrafluorohydrazine-N,N-Dimethylmethacrylamide.—As a typical preparative example, a thick-walled glass Aerosol tube with high-pressure fittings containing 25 ml of carbon tetrachloride and 25 mmol of N,N-dimethylmethacrylamide was attached to a high-pressure stainless steel manifold and the system deaerated by alternately evacuating to low pressure and flushing with nitrogen. The system was then charged with N_2F_4 to 65 psi, placed in an oil bath at 85°, and heated for 6 hr. The pressure was maintained between 30 and 65 psi by frequently recharging the system as necessary. On cooling the excess N_2F_4 was vented, the tube was flushed thoroughly with nitrogen, and the contents were transferred to a round-bottomed flask. On evaporation of the solvent, a dark liquid residue remained which was distilled at reduced pressure on an 18-in. Holtzman column to give 4.9 g (90%), bp 53° (0.6 mm), $n^{20}\mathrm{D}$ 1.4262, of N,N-dimethyl-2-methyl-2,3-bis(difluoramino)propionamide. Its infrared spectrum showed absorption at 1665 (–C=O–) and 800–1000 cm^{-1} (NF_2). The ^{19}F nmr spectrum showed signals as a triplet centered at ϕ 54.3 (CH_2NF_2) and a singlet at 26.7 (CNF_2).

Anal. Calcd for $C_6H_{11}F_4N_3O$: C, 33.12; H, 5.07; F, 35.00; N, 19.35. Found: C, 33.61; H, 5.03; F, 34.77; N, 19.66.

Registry No.—Tetrafluorohydrazone, 10036-47-2; N,-N-dimethyl-2-methyl-2,3-bis(difluoramino)propionamide, 19639-91-9.

Acknowledgment.—The technical assistance of Mr. F. Hooper and Mr. J. O. Woods is greatly appreciated.

The Mechanism of Alcoholysis of Carboxylic Acid Halides in the Presence of Triethylamine

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The alcoholysis of carboxylic acid halides in the presence of triethylamine and a hydrocarbon solvent proceeds by two competing pathways, an elimination-addition process involving a ketene intermediate and a substitution process involving an acyl quaternary ammonium intermediate. Evidence for the ketene intermediate was obtained by performing the reaction in the presence of methanol-*d* and measuring the proportion of monodeuterated ester (in the absence of polydeuterated ester). The products obtained from the isomeric butenoyl chlorides provide further evidence for the competitive processes and suggest the interconversion of the two intermediates. The effects of the leaving group and of the structure of the acyl halide are also presented.

The reaction of acyl chlorides, possessing α hydrogens, with tertiary amines is an old and commonly used method for the synthesis of ketenes,[1] and is often used for *in situ* generation as in cycloadditions[2] and other reactions typical of ketenes. Having demonstrated the role of sulfene intermediates in the triethylamine-induced alcoholysis of sulfonyl chlorides,[3] the mechanism of alcoholysis of acid chlorides in the presence of triethylamine was investigated by like methods and is reported herein. To determine the relative participation of ketene intermediates, the alcoholysis was carried out using methanol-*d* (MeOD). The ester arising from the reaction of ketene with methanol-*d* would be monodeuterated. The absence of dideuterated ester would preclude deuterium incorporation by simple exchange.

Results

A number of carboxylic acid halides and acetic anhydride were treated with ordinary methanol and methanol-*d* in the presence of triethylamine. The procedure involved adding a solution of the acid halide to a stirred solution of methanol and triethylamine in an inert solvent (pentane, hexane, or octane) at 0°. The identity of the esters was verified by comparison of physical properties with literature values and by nmr[4] analysis. Nmr analysis was also used to show that deuterium incorporation occurred on the carbon α to the carbonyl carbon. The esters were subjected to low voltage mass spectral analysis[5] (used to eliminate the P − 1 peak) to determine the amount of deuterium incorporation[6] and

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(1) W. E. Hanford and J. C. Sauer, *Org. Reactions*, **3**, 124 (1947).

(2) G. Opitz and M. Kleeman, *Ann. Chem.*, **665**, 114 (1963).

(3) W. E. Truce and R. W. Campbell, *J. Amer. Chem. Soc.*, **88**, 3599 (1966).

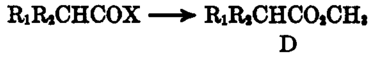
(4) The nmr spectra were obtained using a Varian A-60 or A-60A spectrometer at a sweep width of 500 cps with tetramethylsilane (TMS) as internal standard.

(5) Mass spectra were run at the Purdue Mass Spectral Center on a Hitachi RMU-6a instrument.

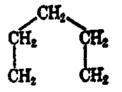
(6) K. Biemann, "Mass Spectrometry," McGraw Hill Book Co., Inc., New York, N. Y., 1962, pp 212–228.

TABLE I

MASS SPECTRAL DATA AND PER CENT MONODEUTERATION FOR ESTERS



$$R_1R_2CHCOX \longrightarrow R_1R_2\underset{D}{C}HCO_2CH_3$$

R_1[a]	R_2	X	P − 1[b]	P + 1	P + 2	% mono deuteration[c]
H	H	F	0	3.8		0
H	H	Cl	0	67.5	3.6	39
H	H	Br	0	45.2	3.5	29
H	H	I	0	23.4	3.3	16
H	H	CH_3CO_2	0	8.4		5
CH_3	H	Cl	9.9	52.3	4.5	33
CH_3	H	Br	8.7	45	2.9	29
CH_3CH_2	H	Cl	44.5	41.9	5.8	30
CH_3	CH_3	Cl	20.3	6.1		0
CH_3	CH_3	Br	4.7	6.2		0
CH_3CH_2	CH_3CH_2	Cl	0[d]	8.7		0
		Cl	0	9.4		0
Cl	H	Cl	0	51	40	32
Cl	Cl	Cl	3[e]	72	67	41
C_6H_5O	H	Cl	0	39.2	4.1	22
C_6H_5	H	Cl	0	74	8.8	39
C_6H_5[f]	H	Cl	0	72	8.5	38
C_6H_5	H	Cl	0	344	35.1	77[g]
C_6H_5	C_6H_5	Cl	0	30	3.9	12

[a] Solvents: When $R_1 = R_2 = H$, octane was used as solvent. When $R_1 = C_6H_5O$ and $R_2 = H$ and when $R_1 = R_2 = C_6H_5$, hexane was used as solvent. In all other cases (except footnote *f*), pentane was used as solvent. [b] P, parent peak (molecular ion) in mass spectra. P = 100 in all cases except as noted. [c] All values were reproducible within ±1%. [d] *m/e* 99 used as P. [e] *m/e* 83 used as P. [f] Benzene used as solvent. [g] Eight equivalents of CH_3OD were used in the reaction.

TABLE II

ALCOHOLYSIS OF BUTENOYL CHLORIDES

Acid chloride	Alcohol	% CH_2=$CHCH_2CO_2R$	% CH_3CH=$CHCO_2R$
CH_2=$CHCH_2COCl$	CH_3OD	100 (40% deuterated)[a]	0
CH_3CH=$CHCOCl$	CH_3OD	60 (67% deuterated)[a]	40
CH_3CH=$CHCOCl$	CH_3CH_2OH	92	8

[a] Nmr shows that deuterium incorporation occurs α to the carbonyl carbon.

to establish that monodeuteration occurred exclusively. Mass spectral data and per cent monodeuteration for the following reaction are summarized in Table I.

$$R_1R_2CHCOX + Et_3N + MeOD \longrightarrow R_1R_2CH(D)CO_2Me + Et_3NH(D)Cl$$

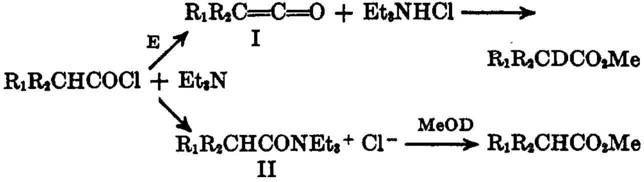
That deuterium incorporation occurs only from the addition of methanol-*d* to the ketenes and not by any simple exchange mechanisms is supported by the following experimental observations. (1) Only monodeuteration occurs. Any exchange process should give significant polydeuteration. (2) When methyl phenylacetate or methyl dichloroacetate, methanol-*d*, triethylamine, and triethylamine deuteriochloride (100% deuterated by nmr) are stirred in hexane for 4 hr at 0°, no deuterium incorporation occurs.[7] (3) When phenylacetyl chloride, triethylamine, and methanol are allowed to react in the presence of triethylamine deuteriochloride (insoluble in medium), again no deuterium incorporation is detected.

2-Butenoyl chloride and 3-butenoyl chloride were subjected to reactions with methanol and methanol-*d* in the presence of triethylamine. 3-Butenoyl chloride yielded only methyl 3-butenoate which was 40% monodeuterated, whereas 2-butenoyl chloride yielded a mixture of the isomeric esters.[8] The isomer distribution and per cent deuterium incorporation are given in Table II and nmr data is presented in Table III.

Discussion

The formation of both monodeuterated and undeuterated esters under the reaction conditions suggests a competition between two reaction pathways, the most likely being competing substitution and elimination processes involving the acyl halide and triethylamine (Scheme I). A ketene (I) would arise from an elimina-

SCHEME I



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[7] When methyl phenylacetate was stirred *8 days* at room temperature with the same materials 9% monodeuteration was measured.

[8] The product ratios were determined by nmr. The deuterium incorporation was measured by mass spectral analysis on the product from 3-butenoyl chloride and was determined by nmr on the products from 2-butenoyl chloride. The isomer distributions were determined on crude material prior to distillation.

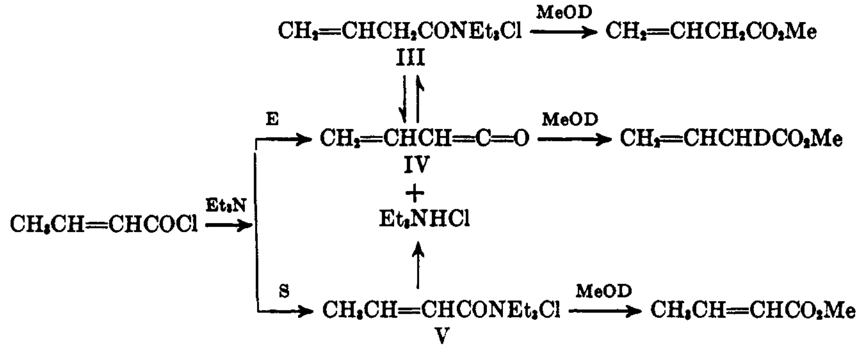
TABLE III

NMR DATA FOR BUTENOATE ESTERS

$\overset{a}{CH_2}=\overset{b}{CH}-\overset{c}{CH_2}CO_2\overset{g}{CH_3}$ $\overset{d}{CH_3}\overset{e}{CH}=\overset{f}{CH}CO_2\overset{g}{CH_3}$

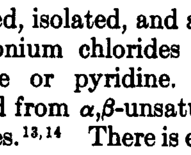
	δ						
Ester	1.9	3.2	3.8	5.2	6.0	7.1	Relative area
$CH_2=CHCH_2CO_2CH_3$		c (two triplets)	g (singlet)	a (two multiplets)	b (multiplet)		2:3:2:1
$CH_3CH=CHCO_2CH_3$	d (two doublets)		g (singlet)		f (two quartets)	e (sextet)	3:3:1:1
Products from 2-butenoyl chloride + methanol	d (two doublets)	c (two triplets)	g (doublet)	a (two multiplets)	b, f (multiplet)	e (sextet)	1.4:1.1:3 1:1:0.4

SCHEME II



tion reaction and would yield a monodeuterated ester upon reaction with methanol-*d*. However, the intermediate of the substitution reaction, possibly the acyl quaternary ammonium salt (II), would undergo displacement by methanol-*d* to yield an undeuterated ester.

The formation of monodeuterated ester is ample evidence for the ketene intermediate. There is also strong precedent for the acyl quaternary ammonium salt. It is well known that tertiary amines catalyze the acylation of amines, alcohols, and phenols by acid chlorides and anhydrides.[9] Even the hydrolysis of some acid derivatives such as acetyl phosphate[10] and acetic anhydride[11] is strongly catalyzed by even small amounts of pyridine. In most of these reactions an acyl quaternary ammonium salt intermediate has been proposed and in some instances these salts have been prepared and shown to be intermediates. Adkins and Thompson[12] have prepared, isolated, and analyzed several acyl quaternary ammonium chlorides from acid chlorides and triethylamine or pyridine. These salts have also been prepared from α,β-unsaturated acid chlorides and tertiary amines.[13,14] There is evidence that a tetrahedral adduct may precede formation of the salt.[11,15,16]


$$Et_3{}^+N-\overset{\displaystyle O^-}{\underset{\displaystyle CHR_1R_2}{C}}-Cl$$

When phenylacetyl chloride reacts in the presence of excess methanol-*d*, the amount of monodeuteration almost doubles (39 to 77%). This indicates that a considerable amount of the initially formed ketene (I) collapses with triethylamine hydrochloride yielding the quaternary ammonium intermediate (II), which then reacts with methanol-*d* producing undeuterated ester. In the presence of excess methanol-*d* the ketene is trapped more efficiently, thus accounting for the tremendous increase in deuterium incorporation.

Further evidence for the competing elimination and substitution pathways and the proposed interconversion of I and II is provided using the isomeric butenoyl chlorides (Table II and Scheme II). The following experimental observations should be considered.

(1) When 3-butenoyl chloride is treated with methanol-*d* under the reaction conditions only methyl 3-butenoate (40% monodeuterated) is formed. This indicates that only 1,2 addition of methanol-*d* to the ketene ($CH_2=CHCH=C=O$) is possible since 1,4 addition would result in the conjugated isomer.

(2) When 2-butenoyl chloride is treated with methanol-*d* and triethylamine, 60% methyl 3-butenoate (67% deuterated[17]) and 40% methyl 2-butenoate (undeuterated) are formed. Methyl 2-butenoate can arise only from the substitution pathway since the intermediate ketene (IV) produced by elimination can only yield methyl 3-butenoate by 1,2 addition. Therefore in this system, the elimination is favored 3:2. Further, since the final product of the elimination route, methyl 3-butenoate, is not completely deuterated (67%), it is probable that some of ketene IV is collapsing to the triethylammonium complex (III) which gives undeuterated ester.

(3) When 2-butenoyl chloride is treated with *ethanol*, 92% ethyl 3-butenoate and 8% ethyl 2-butenoate are formed in contrast to 60 and 40% for the corresponding methyl esters. Since the formation of intermediates from the acyl chloride and triethylamine is the same in both cases, it is probable that the reaction of ethanol with the quaternary ammonium derivative (V) is slower than methanol, thus giving V a greater opportunity to

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[9] M. L. Bender, *Chem. Rev.*, **60**, 77 (1960).

[10] D. E. Koshland, Jr., *J. Amer. Chem. Soc.*, **74**, 2286 (1952).

[11] V. Gold and E. G. Jefferson, *J. Chem. Soc.*, 1406 (1953).

[12] H. Adkins and Q. E. Thompson, *J. Amer. Chem. Soc.*, **71**, 2242 (1949).

[13] H. E. Baumgarten, *ibid.*, **75**, 1239 (1953).

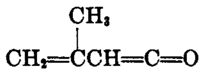
[14] P. W. Hickmott, *J. Chem. Soc.*, 883 (1964).

[15] C. A. Bunton and T. A. Lewis, *Chem. Ind.* (London), 180 (1956).

[16] R. F. Hudson, *Chimia* (Aarau), **15**, 394 (1961).

[17] The methyl 3-butenoate is more highly deuterated than that formed from 3-butenoyl chloride since in its formation it must proceed through a ketene intermediate, whereas that produced from 3-butenoyl chloride can result from either the elimination or substitution mechanism.

convert into ketene IV. Payne[18] has shown that the acyl quaternary ammonium chloride formed from 3-methylcrotonyl chloride and trimethylamine is convertible into the following corresponding ketene which was trapped by 1,2 cycloaddition to ethyl vinyl ether.

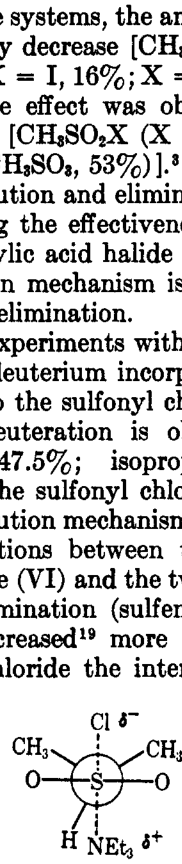


$$CH_2{=}\overset{CH_3}{C}CH{=}C{=}O$$

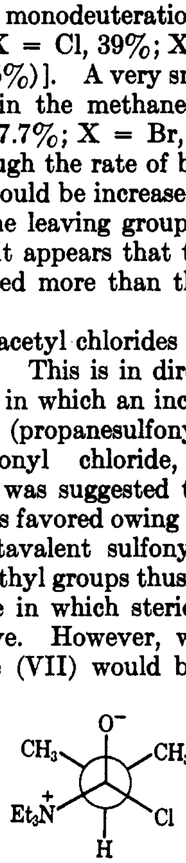
Thus the experiments with the isomeric butenoyl chlorides are consistent with the existence of competing elimination–addition and substitution mechanisms and indicate that the respective intermediates are interconvertible.

As the effectiveness of the leaving group is increased in these systems, the amount of monodeuteration shows a steady decrease [CH_3COX (X = Cl, 39%; X = Br, 29%; X = I, 16%; X = OAc, 5%)]. A very small but opposite effect was observed in the methanesulfonyl system [CH_3SO_2X (X = Cl, 47.7%; X = Br, 48.3%; X = CH_3SO_3, 53%)].[3] Although the rate of both the substitution and elimination should be increased by increasing the effectiveness of the leaving group, in the carboxylic acid halide system it appears that the substitution mechanism is enhanced more than the competing elimination.

All experiments with dialkylacetyl chlorides resulted in no deuterium incorporation. This is in direct contrast to the sulfonyl chlorides[3] in which an increase in monodeuteration is observed (propanesulfonyl chloride, 47.5%; isopropanesulfonyl chloride, 57%). With the sulfonyl chlorides it was suggested that the substitution mechanism was less favored owing to steric interactions between the pentavalent sulfonyl intermediate (VI) and the two α-methyl groups thus making the elimination (sulfene) route in which steric effects are decreased[19] more attractive. However, with the acyl chloride the intermediate (VII) would be tetravalent and inhibition to the substitution mechanism would not be so important. Ugi and Beck[20] have shown that α,α-alkyl disubstitution has little effect on the rate of hydrolysis of acid chlorides in aqueous acetone [$k \times 10^4$/sec; $CH_3CH_2CH_2COCl$, 5.85; $(CH_3)_2CHCOCl$, 4.41]. However, it is known[21] that alkyl substitution can greatly affect the rate of ionization of acidic hydrogens (k_1; $CH_3COCH_2COCH_3$, 1.0; $CH_3COCHCH_3COCH_3$, 5×10^{-3}). Thus with alkyl disubstituted acid chlorides the elimination sequence is less favorable owing to decreased acidity of α hydrogens. However, if the acidity of the α hydrogens is increased sufficiently, even disubstituted acetyl chlorides will undergo elimination and incorporate deuterium (See dichloro- and diphenylacetyl chloride in Table I).



VI



VII

It should be realized that, since the intermediates of the two pathways are interconvertible, no strict rules can be laid down to explain each case. For example, the fact that propionyl chloride, chloroacetyl chloride and phenylacetyl chloride give similar results is rather distressing. However, it is reasonable that the chlorine and phenyl group are able to stabilize the ketene by π overlap, making it less reactive with the alcohol and thus giving it a greater opportunity to recombine with the triethylamine hydrochloride to give the intermediate of the substitution pathway.

In summary the preceeding work has shown that the alcoholysis of acyl halides possessing α hydrogens proceeds by competing elimination–addition and substitution mechanisms, the intermediates of which are interconvertible.

Experimental Section

Materials.—Triethylamine (Matheson Coleman and Bell reagent), methanol-*d* (Volk, 100% O–D; Merck Sharp and Dohme, 99% O–D), methanol (Baker Analyzed Reagent), *n*-pentane (Phillips 66, 99% pure), hexane (Baker Analyzed Reagent), *n*-octane (Matheson Coleman and Bell), benzene (Baker Analyzed Reagent), acetyl chloride (Mallinckrodt), acetyl bromide (Eastman), acetyl iodide (Columbia), acetyl fluoride (Hynes, Columbia) phenylacetyl chloride (Eastman, Matheson Coleman and Bell), propionyl chloride (Eastman), propionyl bromide (Eastman), isobutyryl chloride (Eastman), isobutyryl bromide (Eastman), 2-ethylbutyryl chloride (Eastman), cyclohexane carbonyl chloride (Eastman), phenoxyacetyl chloride (Eastman), diphenylacetyl chloride (Columbia), chloroacetyl chloride (Eastman), dichloroacetyl chloride (Eastman), crotonyl chloride (Eastman), butyryl chloride (Eastman), and 3-butenoic acid (Columbia) were used. 3-Butenoyl chloride was prepared from 3-butenoic acid and thionyl chloride.

General Procedure for the Reaction of Acyl Halides with Alcohol and Triethylamine.—The following procedure was used for all acyl halides except the acetyl halides. The acyl halide (0.10 mol) dissolved in pentane (50 ml) or hexane (50 ml) was added dropwise to a stirred solution of triethylamine (0.10 mol) and alcohol (0.10 mol) in pentane (60 ml) or hexane (60 ml) at 0–5° in a 200-ml three-neck round-bottom flask equipped with an addition funnel, mechanical stirrer, and reflux condensor. The system was flame dried prior to use and the reactions were run under nitrogen. After stirring for a total of 4 hr at 0° the triethylamine hydrohalide (almost quantitative yield) was removed by filtration. The solvent was then removed on a Rinco rotary evaporater and the ester was purified by distillation.[22]

General Procedure for the Reaction of Acetyl Halides and Acetic Anhydride with Alcohol and Triethylamine.—The acetyl halide (0.10 mol) dissolved in octane (25 ml) was added dropwise to a stirred solution of triethylamine (0.10 mol) and alcohol (0.10 mol) in octane (25 ml) at 0–5° in a 100-ml three-neck flask equipped with an addition funnel, mechanical stirrer, and reflux condensor. The mixture was allowed to stir a total of 4 hr. Any solid ammonium salt was removed by filtration,[23] and the methyl acetate was then distilled directly from the reaction solution.

Check on Hydrogen–Deuterium Exchange between Methyl Phenylacetate and Methanol-*d* in the Presence of Triethylamine and Triethylamine Deuteriochloride under the Reaction Conditions.—Methyl phenylacetate (0.05 mol), triethylamine (0.05 mol), methanol-*d* (0.055 mol), and triethylamine deuteriochloride[24] (0.05 mol) were stirred in pentane (60 ml) at 0° for 4 hr. The pentane, methanol-*d*, and triethylamine were removed on a rotary evaporater and the remaining methyl phenylacetate was

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[18] G. B. Payne, *J. Org. Chem.*, **31**, 718 (1966).

[19] E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., Inc., New York, N. Y., 1962, p 488.

[20] I. Ugi and F. Beck, *Chem. Ber.*, **94**, 1839 (1961).

[21] R. G. Pearson and R. L. Dillon, *J. Amer. Chem. Soc.*, **75**, 2439 (1953).

[22] Methyl diphenylacetate was sublimed [45° (1 mm), mp 60–61°). The product ratio of methyl butenoates was determined by nmr after evaporation of pentane but prior to distillation.

[23] No ammonium salt was isolated from acetyl fluoride or acetic anhydride.

[24] The triethylamine deuteriochloride was isolated from the reaction of isobutyryl chloride with methanol-*d* and triethylamine and was shown to be 100% deuterated by nmr.

purified by distillation. Low voltage mass spectral analysis showed the ester to be completely undeuterated.

A similar check on hydrogen–deuterium exchange between methyl dichloroacetate and methanol-*d* was made. Before workup the reaction mixture was treated with acetyl chloride. The triethylamine hydrochloride was filtered, and the pentane and methyl acetate were removed on a rotary evaporater, leaving the methyl dichloroacetate which was shown to be undeuterated by nmr analysis.

Reaction of Phenylacetyl Chloride with Methanol in the Presence of Triethylamine and Triethylamine Deuteriochloride.—Phenylacetyl chloride (0.10 mol) dissolved in pentane (50 ml) was added dropwise to a stirred mixture of methanol (0.10 mol), triethylamine (0.10 mol), and triethylamine deuteriochloride (0.10 mol) in pentane (60 ml) at 0°. The reaction was worked up according to the general procedure yielding methyl phenylacetate which was shown to be completely undeuterated by mass spectral analysis.

Registry No.—Triethylamine, 121-44-8; methyl 3-butenoate, 3724-55-8; methyl 2-butenoate, 18707-60-3.

Acknowledgment.—The authors wish to express their appreciation for financial support of this work by Public Health Service Research Grant No. CA 04536-10 from the National Cancer Institute and by National Science Foundation Grant No. GP 05175.

Photochemical Oxidations. II. Rate and Product Formation Studies on the Photochemical Oxidation of Ethers

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Received October 28, 1968

The rates of oxygen uptake during the photochemical oxidation of ethers have been determined. The rates correlate with the orders of basicity of acyclic and cyclic ethers to substantiate further the earlier postulated role of charge-transfer complexes in the photochemical oxidation of ethers. The products of the ether oxidations were determined for an acyclic ether, diethyl ether, and for a cyclic ether, tetrahydrofuran. Mechanisms are postulated for the products formed which involve hydroperoxide intermediates.

Work done by Chien has shown that the excitation of charge-transfer complexes is partially responsible for the photooxidation of hydrocarbons.[2] Also, in a previous publication we have presented evidence that the initial step in the photooxidation of diethyl ether is the absorption of light by a charge-transfer complex of molecular oxygen with ether.[3] In this paper we shall discuss additional studies on this reaction in which a series of ethers, both cyclic and acyclic, were used. The discussion will center on the mechanistic implications of the results of an analysis of the products formed and the relative rates of reaction as indicated by both the rates of oxygen uptake and product formation during irradiation.

TABLE I

O_2 UPTAKE AFTER 1 HR AND pK_a VALUES FOR ETHERS

	O_2 uptake, mol	pK_a
Diethyl ether	2.0×10^{-3}	−3.59
Di-*n*-propyl ether	1.3×10^{-3}	−4.40
Diisopropyl ether	1.1×10^{-3}	−4.30
Di-*n*-butyl ether	0.9×10^{-3}	−5.40
Propylene oxide	0.1×10^{-3}	
Trimethylene oxide	2.7×10^{-3}	
Tetrahydrofuran	2.2×10^{-3}	−2.08
Tetrahydropyran	1.2×10^{-3}	−2.79

All of the ethers studied (Table I) reacted when they were saturated with oxygen and irradiated. The ethers had been previously subjected to a rigorous purification to eliminate the possibility of impurities participating in the reactions. On being irradiated for several hours, each of the ethers gave a mixture of products, but a major product was always the ester or lactone. In addition, each irradiated reaction mixture contained peroxides. Since it has been previously shown that trimethylene oxide[4] and propylene oxide[5] may undergo photochemical decomposition, these compounds were first irradiated under a nitrogen atmosphere to see if they would decompose under the conditions used in these experiments. The results indicate that they do not decompose, and therefore we can be sure that the reaction observed with oxygen is not due to photodecomposition of ethers.

Diethyl ether and tetrahydrofuran, as representative cyclic and acyclic compounds, were chosen for a more detailed examination. As the irradiation time was decreased to a few minutes, it was found that tetrahydrofuran gave three products, butyrolactone, α-hydroxytetrahydrofuran, and water (see Figure 1). Thus the other unidentified compounds found for the longer irradiation times are formed as the result of secondary reactions. It is likely that some of these are the products of the photodecomposition of butyrolactone.[6] On the other hand, the products found when diethyl ether is irradiated, *i.e.*, ethyl acetate, ethyl formate, ethyl alcohol, and acetaldehyde,[7] appear even when the reaction is run for a very short time (Figure 2). Thus, it would seem that the cyclic and acyclic ethers may have slightly different reaction mechanisms.

That the mechanism involves the excitation of charge-transfer complexes for both cyclic and acyclic ethers with the difference in the reaction path for the two series occurring after this step can be inferred also from an examination of the relative rates of oxygen

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[1] Taken in part from Ph.D. thesis, C. T. Wang, University of North Dakota, 1969.

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[6] R. Simonaites and J. N. Pitts, Jr., *ibid.*, **90**, 1389 (1968).

[7] The presence of acetaldehyde was verified by vpc. It could not be trapped owing to its low concentration. Its well-known photodecomposition most probably is the cause of its low concentration.