Application of the Ritter Reaction to *a*-Olefins

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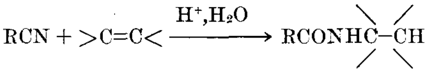
Abstract

By modification of the original Ritter conditions for making substituted amides by addition of nitriles to olefinic compounds, it is possible to apply the reaction to α-olefins. Results are given for addition of hydrogen cyanide, acetonitrile, acrylonitrile, cyanoacetic acid, and some chloronitriles to α-olefins in the range C_{10}–C_{18}. Preliminary attempts to use diolefins containing the vinyl group were unsuccessful. Evidence is adduced to support the carbonium ion mechanism for the reaction.

Introduction

THE FORMATION of N-substituted amides by interaction of nitriles and olefins in the presence of strong acids is now designated the Ritter reaction:



$$RCN + {>}C{=}C{<} \xrightarrow{H^+, H_2O} RCONH\overset{\diagdown\ \diagup}{\underset{\diagup\ \diagdown}{C{-}CH}}$$

Ritter and co-workers showed that this was a general reaction applicable on the one hand to saturated and unsaturated aliphatic and aromatic nitriles and dinitriles and to hydrogen cyanide, and on the other hand to a variety of olefinic compounds (2,6,8,10,11, 15). The scope of the work has been further extended by different workers (1,3–5,7,9,12,14,16–19) and it has been shown that the olefinic component can be replaced by secondary and tertiary alcohols (2,5–8,10, 13) which may be supposed to give rise to secondary and tertiary carbonium ions respectively in acid media.

With the exception of a few isolated cases such as undecylenic acid (17), methyl undecylenate (6), allyl benzene (14), styrene (11,13) and acrylonitrile (11) which can react both as nitrile and olefin, reactions of compounds containing the vinyl group with nitriles do not appear to have been covered. Our interest in this reaction lay in its application to α-olefins which are now appearing as commercial raw materials.

$$RCN + R'CH{=}CH_2 \xrightarrow{H^+, H_2O} RCONHCH(CH_3)R'$$

We summarize here the use of α-olefins in the C_{10}–C_{18} range with hydrogen cyanide, acetonitrile, acrylonitrile, and cyanoacetic acid and also with some chloronitriles. Preliminary attempts to utilize diolefins containing the vinyl group were unsuccessful.

Procedure and Results

α-Olefins. In the straightforward application of the Ritter reaction to α-olefins in sulfuric acid, the reaction was generally started below room temp according to the freezing point of the reaction mixture, which was then allowed to warm up. The reaction was completed at 30–50C for ca. 1 hr followed by addition of iced water. The mixture was extracted with ethyl or petroleum ether and the product recovered in the usual way. Under these conditions, dilution of the acid medium with solvents such as acetic acid or dibutyl ether, which Ritter found useful for highly reactive olefins, gave poor or negative results; acetonitrile, e.g., in acetic acid solution did not react with 1-dodecene even at 50C and substantially the whole of the olefin was recovered. Successful results were obtained by omitting the solvent and using H_2SO_4 (98%) alone, except in the preparation of substituted malonamides from cyanocetic acid when, in order to minimize formation of by-products, a more critical choice of acid at 90–95% strength was found necessary. Subsequent work with α-olefins was generally carried out with excess of 95–98% acid to which water was added to a total of 1 mole as theoretically required by the reaction.

TABLE I

Preparation of N-(2-alkyl) formamides, $RCH(CH_3)NHCHO$

α-Olefin	Yield %	mp °C	Nitrogen content %	
			Found	Calcd
C_{12}	....	Oil[a]	5.3	6.6
C_{14}	37	35–43	5.5	5.8
C_{16}	44	43–47	4.8	5.2
C_{18}	45	48–51	4.4	4.7

[a] bp 122–131C/0.2mm; n_D^{20} 1.4528–1.4546.

The starting materials for these experiments were reagent or technical grade used without further purification. The α-olefins (British Drug Houses, Ltd.) which may have varied throughout the course of the experiments were originally analyzed as follows:

1-decene	96%	1-hexadecene	85%
1-dodecene	90%	1-octadecene	95%
1-tetradecene	86%		

The main impurity in each case was the saturated analogue. The detailed procedure is illustrated by reference to the preparation of substituted acrylamides.

Preparation of N-(2-alkyl) acrylamides. The α-olefin (1 mole) and acrylonitrile (1.1 moles) were well stirred and cooled in a solid carbon dioxide-carbon tetrachloride bath while H_2SO_4 (98%, 4 moles) was added dropwise during 40 min. The mixture was then allowed to warm up for 30 min, and finally heated to 40–45C for 1 hr with continual stirring. Excess water was carefully added with further cooling, and the mixture was then extracted with ether. The extract was washed with 10% sodium carbonate solution, dried, and evaporated. The residue was dissolved in acetone and treated with activated charcoal to remove insoluble polymeric material. After a second treatment the product was successively recrystallized from acetone at low temp.

The overall results of this series of experiments are summarized in Tables I–IV which give the optimum yields of once-recrystallized material obtained from a series of reactions in which variations in the ratio of reactants and the mode of addition were studied. Other features were determined after three recrystallizations from acetone.

Addition of hydrogen cyanide to α-olefins. Crude N-(2-alkyl) formamides were obtained in 70–90% yield by addition of hydrogen cyanide formed *in situ* from H_2SO_4 and sodium cyanide, following the general pattern of Ritter, but with 98% H_2SO_4 alone as the catalyst-medium. A molar ratio of olefin:sodium cyanide:H_2SO_4 of 1:1.2:4 was used, the acid being added to the cooled mixture of olefin and cyanide. The products, after wasteful recrystallization from acetone, were low-melting solids with the exception of that from 1-dodecene which was an oil. This could

TABLE II

Preparation of N-(2-alkyl) acetamides, $RCH(CH_3)NHCOCH_3$

α-Olefin	Yield %	mp °C	Nitrogen content %	
			Found	Calcd
C_{12}	70	52–58	6.0	6.2
C_{14}	80	47–59	5.4	5.5
C_{16}	67	70–74	5.0	4.9
C_{18}	66	75–81	5.0	4.5

TABLE III

Preparation of N-(2-alkyl) acrylamides, $RCH(CH_3)NHCOCH = CH_2$

α-Olefin	Yield %	mp °C	Nitrogen content %	
			Found	Calcd
C_{12}	70	29–34	5.9	5.9
C_{14}	68	36–44	4.9	5.2
C_{16}	58	48–58	4.7	4.7
C_{18}	53	73–77	4.6	4.3

be distilled rapidly in small quantities (<10 g), otherwise decomposition ensued at a bath temp of 180C. IR bands were exhibited by these derivatives at 3250, 3050, 1650 and 1540 cm^{-1}.

In this reaction liquid hydrogen cyanide with correspondingly less acid has given no better yields than sodium cyanide despite possible favorable solvent properties.

Addition of acetonitrile to α-olefins. As already stated, Ritter's conditions for conversion of isobutylene to substituted acetamides, with 98% H_2SO_4 in the presence of acetic acid as solvent, proved inappropriate for 1-dodecene. Small amounts of the required amide were detected in the crude product when the solvent was omitted, and ultimately yields of 65–80% of recrystallized off-white products were obtained, melting in the range 50–80C, by using a molar reactant ratio of 1:1.5:4. (This is given throughout in the order olefin:nitrile:H_2SO_4.) In this case the nitrile and olefin were added successively to the excess of acid.

The IR spectra of these derivatives showed strong absorption at 3300,3100,1650 and 1560 cm^{-1}.

Addition of acrylonitrile to α-olefins. This was carried through as for preparation of the formamides, with a molar reactant ratio of 1:1.1:4, the acid being added to the stirred mixture of olefin and nitrile. Yields of 53–70% were obtained as white or slightly discolored crystalline solids with mp 30–80C.

In addition to strong IR absorption at 3250,3050, 1650 and 1550 cm^{-1} corresponding to the amide group, these compounds also exhibited bands at 1620,985 and 955 due to the vinyl group conjugated with a carbonyl. The non-crystalline materials isolated from the mother liquors showed peaks at 1340,1160 and 895 but were not identified.

Addition of cyano-acetic acid to α-olefins. The addition of cyano-acetic esters to olefins was reported by Ritter and Minieri (13), and of cyano-acetic acid to oleic acid by Roe and Swern (16).

Initial attempts to promote the addition of cyano-acetic acid to α-olefins by means of 98% H_2SO_4 resulted in products of high equivalent weight (despite variations in the mode of addition and ratio of reactants) which could not readily be purified. In a study of acid strength in the range 85–98%, high yields of crude material with satisfactory IR characteristics could be obtained by using 90–95% acid. This was added to the olefin-nitrile mixture in the molar ratio 1:1.1:4. The crude products, which were very soluble in acetone, were crystallized from petroleum ether. With the exception of the C_{10} derivative, the resulting white solids had a mp of 50–80C. The product from 1-decene was an oil which, on attempted distillation at 0.2 mm pressure, decarboxylated smoothly at a bath temp of 135–140C; the residue distilled at 109C/0.1 mm, the distillate being identified by microanalysis and by its IR spectrum as N-(2-decyl) acetamide.

$$C_8H_{17}CH(CH_3)NHCOCH_2COOH \longrightarrow C_8H_{17}CH(CH_3)NHCOCH_3 + CO_2$$

Diolefins. There are few literature references to the reactions of nitriles with diolefins. Bortnick has described the reaction of hydrogen cyanide with 2,5-dimethyl-1, 5-hexadiene (4) and with limonene (3), although in the latter case the presence of terpin hydrate and α- and β-terpineol in admixture with the limonene may have favored the reaction by reducing polymerization side reactions. Roe and Swern reported that no identifiable product could be obtained from the reaction of hydrogen cyanide with linoleic acid (17).

We attempted to apply the Ritter reaction to dipentene, 2,5-dimethyl-1, 5-hexadiene and butadiene, as these compounds were commercially available. With acetonitrile in H_2SO_4 as catalyst-medium, only low yields of nitrogen-containing materials have so far been obtained. Large amounts of polymeric material were obtained, explosively so with butadiene. The hexadiene gave a low yield of amide (plus a high proportion of by-products) with methanesulfonic acid as catalyst.

Chlorinated derivatives. Chlorinated amides were prepared by Ritter via halohydrins and halogenated alkenes (8). An alternative route to such compounds is by way of halogenated nitriles or unsaturated nitriles which can be subsequently halogenated at the amide stage. Since highly-chlorinated nitriles of the type required were not readily available and attempts to prepare them met with little success, the work was confined to using trichloracetonitrile and 2,3-dichloropropionitrile, the latter being prepared by direct chlorination of acrylonitrile at 30–40C without solvent but under 250 W bulb irradiation. In two cases acrylonitrile was used, the chlorine being subsequently introduced into the resulting acrylamide by direct treatment below 0C in CCl_4. Results are summarized in Table V for ether-extractable material recrystallized once.

Mechanism of the reaction. In the results quoted above the difficulty of preparing amides of definite mp was ascribed to the probable operation of a carbonium ion mechanism. This is suggested also by the conditions for the reaction. This subject was considered by Ritter (12) and Smolin (19). Ritter's scheme is illustrated in Figure 1 for an α-olefin and acetonitrile.

Smolin formulated a similar scheme but omitted the participation of the alkyl sulphate at the intermediate stage. Additional evidence for the carbonium ion mechanism was sought by routes given below.

Composition of derived amines. Formation of the primary carbonium ion I should be followed by partial isomerization to an equilibrium mixture, the composition of which would be reflected in that of the amine which can be obtained by hydrolysis of the

TABLE IV

Preparation of N-(2-alkyl) malonamides, $RCH(CH_3)NHCOCH_2COOH$

α-Olefin	Yield %	mp °C	Equiv wt	Nitrogen content %	
				Found	Calcd
C_{10}	....	Gel	......	5.6	5.8
C_{12}	90	48–50	270	5.1	5.2
C_{14}	84	55–61	300	4.6	4.7
C_{16}	53	76–77	327	4.5	4.3
C_{18}	59	81–82	358	3.7	3.9

TABLE V
Preparation of Chlorinated N-alkylamides

Olefin or Alcohol	Nitrile	Amide			
		Yield %	mp C°	Nitrogen %	
				Found	Calcd
1-Octadecene	2,3-Dichloropropionitrile	75[a]	48–54	3.4	3.6
1-Octadecene	Trichloroacetonitrile	56[b]	41–43	3.5	3.4
1-Octene	Trichloroacetonitrile	95[c]	....	4.7	5.1
1-Pentene	Acrylonitrile (+ Chlorine)	25[d]	Gum	....	....
t-Butanol	Acrylonitrile (+ Chlorine)	75[e]	128–132	6.9	7.1

[a] From ethanol at low temp.

[b] From methanol at —70C. Gave also C: found 58.7, calcd: 59.3%; H: found 9.1, calcd: 9.2%.

[c] Crude material; decomposed on distillation.

[d] From chlorination of N-(2 pentyl) acrylamide which was isolated in 25% yield by distillation at 84C/0.3 mm: decomposed on distillation.

[e] From chlorination of N-(t-butyl) acrylamide.

Ritter formamide.

Two series of tests were made, in each of which paired samples of formamides were made from 1-octene and 1-dodecene under identical (standard) conditions from both sodium cyanide and liquid hydrogen cyanide. The resulting reaction mixtures were hydrolyzed, without isolation of the products, by diluting the H_2SO_4 to 50%, and heating the solution at 100–115C for 1½–3 hr. Slight excess of alkali was added and the amine isolated in up to 95% yield by steam distillation and subsequent extraction by ether. The product was examined by GLC analysis on a Pye Argon Chromatograph by means of a stationary phase of glycerol/100 mole ethylene oxide adduct supported on glass microbeads, at 65C for the octylamines and 85C for the dodecylamines. Similar results were obtained with a polyester column (Reoplex) supported on Celite. The fractions were identified by dosing the samples with authentic specimens of the 1-,2-,3- and 4- isomeric amines prepared by independent synthesis. The results for the formamide from 1-octene are given in Table VI. It is recognized that some admixture is possible in the fractions since the GLC results indicate increasing difficulty in separating the isomers as the amino group becomes more remote from the terminal position.

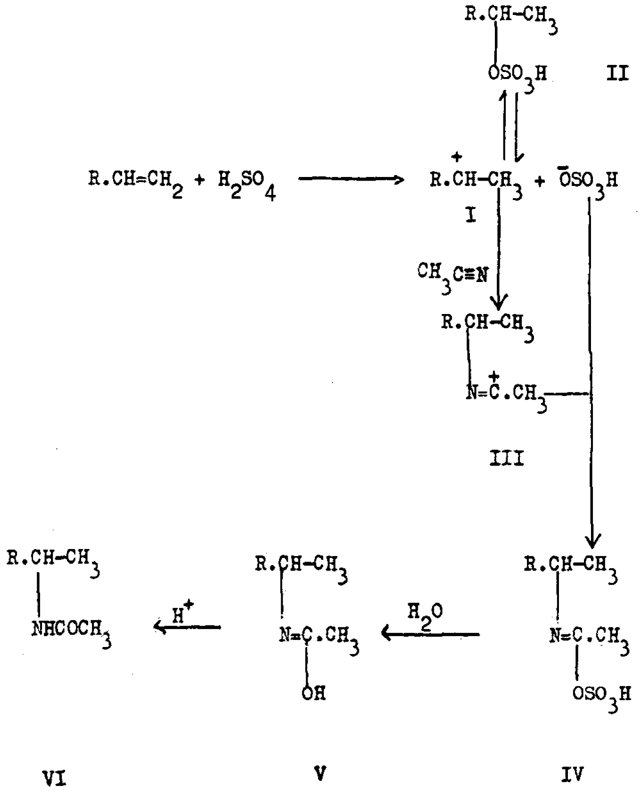


FIG. 1. Mechanism for Ritter reaction.

TABLE VI
Composition of Octylamines from 1-Octene

		2-Octylamine	3-Octylamine
		%	%
From NaCN	Exp 1	44	56
	2	45	55
HCN	3	67	33
	4	64	36

Similar results were obtained for an earlier sample which had been stored for about a year. The results for 1-dodecene are given in Table VII; the GLC results in Figure 2.

Results are consistent with the reaction's proceeding by means of a carbonium ion mechanism. In each case a lower proportion of the 2-isomer is noted in reactions with sodium cyanide than in those with liquid hydrogen cyanide, and this may possibly be due to the slow liberation of hydrogen cyanide from the sodium salt, allowing increased isomerization of the carbonium ion.

Reaction of primary alcohols in the amide synthesis. Reaction of nitrile with the alkylsulfuric ester molecule II rather than with the analogous carbonium ion would imply that primary alcohols can participate in the Ritter reaction as can secondary and tertiary alcohols. Ritter was unable to demonstrate this by reacting primary alcohols with nitrile in the presence of fuming H_2SO_4 for prolonged periods and at elevated temp (2). We have been able to demonstrate that this does occur but only to a slight extent.

1-Dodecanol was sulfated just above its mp by direct treatment with 10% excess of sulfur trioxide (Sulfan) in the form of a 15% mixture with air, and 4 moles of 100% H_2SO_4 were then added. A normal Ritter reaction was carried through with acetonitrile commencing at 0–5C and the mixture being finally heated at 45C for 1 hr before adding water. The ether-soluble product was shown by IR examination to consist mainly of unchanged dodecanol, with traces of didodecyl sulphate and substituted amide. The proportion of the latter could not be increased by varying the preparative procedure. With 1-octanol, however, under more severe conditions (final heating at 50C for 5½ hr) the indications for amide were stronger. Isolation of this fraction by chromatography on alumina gave a 3% yield of N-substituted amide identified by its IR absorption. Some octyl acetate and dioctyl sulphate were isolated, but no unchanged octanol.

While the reaction is therefore demonstrable with primary alcohols the yield is so low as to confirm the probability of the carbonium ion mechanism operating in the second stage.

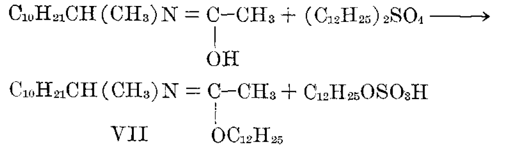
Participation of intermediates. It is difficult to suppose that alkyl sulfuric ester formation does not play a part in the reaction since, firstly, yields up to 90% substituted amide can be obtained by interaction of olefin and H_2SO_4 under appropriate conditions (known to yield the secondary alkyl sulfuric ester) and then adding the nitrile and subsequently water.

Secondly, interaction of olefin and H_2SO_4 can be demonstrated in high yield in as short a time as it is possible to dispel the heat from the exothermic addition of the acid. In a test in which 95% acid was rapidly added to a stirred mixture of 1-dodecene and acetonitrile, and the reaction completed in 5 min at 0C, the mixture was rapidly poured into 10% NaOH solution and the slurry extracted with ether, then butanol. The butanol extract accounted for 62% of the olefin as sodium 2-dodecyl sulphate.

TABLE VII
Composition of Dodecylamines from 1-Dodecene

		2-dodecylamine	3-dodecylamine	4-dodecylamine
		%	%	%
From NaCN	Exp 1	24	36	40
	2	27	37	36
HCN	3	37	35	28
	4	49	25	27

The ether-soluble fraction, after separation on an alumina chromatogram and identification of the fractions by IR analysis, was shown to contain the following: *trans*-dodecenes, 2-dodecanol, 2-dodecyl acetate, N-(2-dodecyl) acetamide, didodecyl sulfate, and N-(2-dodecyl) acetimino-dodecyl ether VII. The presence of this ether was ascribed to the reaction of didodecyl sulfate with N-(2-dodecyl) acetamide in the enol form:



$$C_{10}H_{21}CH(CH_3)N=\underset{\substack{|\\ OH}}{C}-CH_3+(C_{12}H_{25})_2SO_4\longrightarrow$$

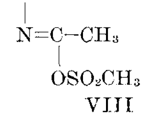
$$\underset{VII}{C_{10}H_{21}CH(CH_3)N}=\underset{\substack{|\\ OC_{12}H_{25}}}{C}-CH_3+C_{12}H_{25}OSO_3H$$

Confirmation of this was obtained by an analogous preparation of the ethyl ether. A stirred mixture of N-(2-dodecyl) acetamide and a 77% molar excess of diethyl sulphate was heated at 100C for 1 hr, and the ethereal solution of the product was washed with 10% aqueous NaOH, and dried to yield a colorless oil. Purification of this by chromatography on alumina afforded a 36% yield of N-(2-dodecyl) acetimino ethyl ether; found: C 75.5, H 13.0, N 5.2, $-OC_2H_5$ 17.9%, mol wt 255; calcd. for $C_{16}H_{33}NO$ C 75.4, H 13.0, N 5.5, $-OC_2H_5$ 17.6%, mol wt 255.

In an attempt to isolate the enol-amide sulfuric ester IV postulated by Ritter, a reaction of acetonitrile with 1-dodecene was carried out in 100% H_2SO_4 and the reaction mixture, instead of being treated with water, was poured into a 10% excess of cold aqueous NaOH to stabilize the compound in the salt form. Extraction of the slurry with ether and subsequent chromatographic separation gave a 54% yield of N-(2-dodecyl) acetamide and 14% of *trans*-olefin, identified by IR analysis and elemental analysis.

Further extraction of the slurry with butanol furnished a pale yellow gum from which a little N-(2-dodecyl) acetamide was removed by ether extraction. The residue which could not be crystallized contained 2.6% nitrogen, and surface-active material calculated as the equivalent of 60% sodium-2-dodecyl sulfate by conventional titration with cetyldimethylbenzylammonium chloride. The IR spectrum showed bands due to hydroxyl, and sulfate or sulfonate groups. This material could not be induced to undergo a Ritter reaction by treatment with 95% H_2SO_4 at 40C for 1 hr, and it was stable to hydrolysis when heated in 10% H_2SO_4 at 100C for 3 hr. It was clearly therefore a sulfonate and was not an intermediate in the Ritter reaction. On the other hand, 65% of the reacted olefin had pursured the normal Ritter route which would have been promoted by the addition of water.

In order to exclude water from the reaction completely another reaction was carried out with azeotropically-dried methanesulfonic acid as the catalyst-medium, designed to give VIII as intermediate.



$$\begin{array}{l}R.CH-CH_3\\ \quad|\\ \quad N=C-CH_3\\ \qquad\quad|\\ \qquad\quad OSO_2CH_3\end{array}$$

VIII

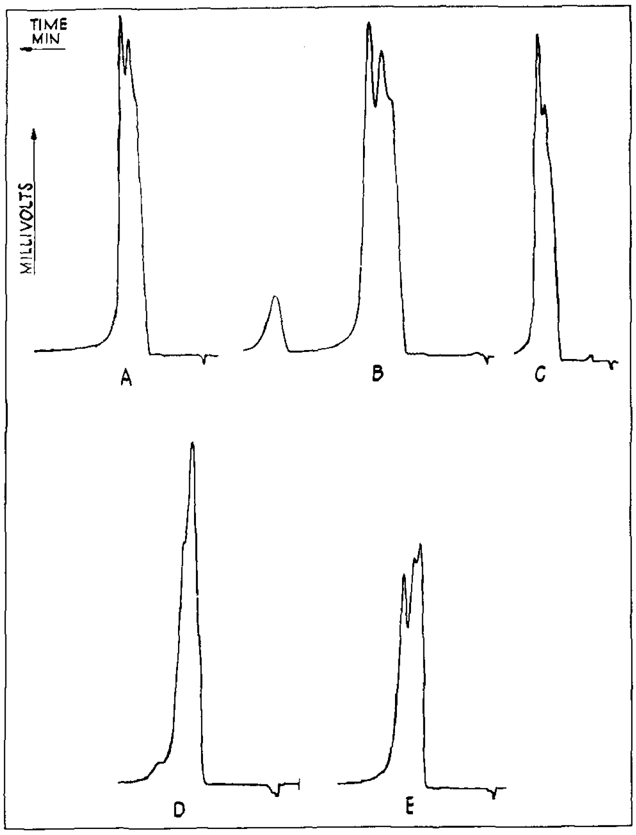


FIG. 2. GLC analysis of dodecylamine mixture from N-dodecylformamide. A, Experimental product; to which is added B, 1-dodecylamine; C, 2-dodecylamine; D, 3-dodecylamine; E, 4-dodecylamine.

Freshly distilled 1-dodecene and acetonitrile were used under anhydrous conditions in an apparatus dried at 200C, the reaction being commenced at −5C and finished at 70C for 2 hr. The system remained heterogeneous, and examination of the top layer during the reaction indicated only *trans*-olefin. As there was a possibility of the supposed intermediate's being held in the lower layer by salt formation, the mixture was cooled in ice and then carefully neutralized with triethylamine which had been dried over NaOH. Extraction of the mixture with sodium-dried petroleum ether furnished a mixture of *trans*-olefin (35%) and N-(2-dodecyl) acetamide which, on the basis of its nitrogen content, amounted to a yield of 35% of the normal Ritter amide, despide efforts to block its formation by complete exclusion of water.

Conclusion

In this paper we have indicated that the Ritter reaction can be applied to the less reactive higher α-olefins by simple modification of the original conditions. This is likely to offer a further synthetic outlet for the appearance of α-olefins in commercial quantities.

Most of our evidence for the course of the reaction is in accordance with a carbonium ion mechanism but we have been unable to isolate the main intermediate postulated by Ritter.

ACKNOWLEDGMENTS

Assistance in preparative work by K. Jones and J. Wagner. Permission for publication granted by Unilever Ltd.

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[Received June 10, 1963—Accepted September 9, 1963]

Preparation and Etherification Reaction of Fatty Dichlorocyclopropanes[1]

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Abstract

Dichlorocarbene was added to *cis*-9-octadecene, methyl oleate, methyl elaidate, and methyl linoleate to form the corresponding mono- or bis-dichlorocyclopropanes in yields of 75–88%. The dichlorocyclopropanes underwent ring-opening substitution on heating with alcohols (or water) to form β-chlorallylic ethers (or alcohols). The ethers were obtained in yields of 46 to 84%. Tetraethylene glycol and methyl lactate, as hydroxyl compounds, gave a polyethenoxy ester and an ether-linked diester, respectively.

Introduction

During the 1950's, the fundamental chemistry of dihalocarbenes was elucidated. Proof was given of their existence (1a,2), their electrophilic character (1b,3b,5), and their *cis*-addition to isomeric 2-butenes (3a,4).

It was desired in the present study to extend the carbene addition reaction, originated with small molecules, to the field of fat chemistry. Dichlorocarbene was chosen as the first carbene to study in this way, and it was added to *cis*-9-octadecene, as a model, and to methyl oleate, methyl elaidate, and methyl linoleate, selected as olefinic fatty esters. These unsaturated compounds were prepared in better than 99% purity by published methods (6,7,8,9).

Procedures

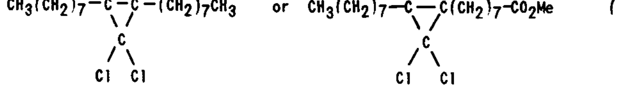
The generation of dichlorocarbene is usually accomplished by the action of an alkoxide on either chloroform (2) or on ethyl trichloroacetate (10), according to the equations:

$$HCCl_3 + R'O^- \rightarrow R'OH + CCl_3^- \quad (1a)$$

$$Cl_3C{-}CO_2R + R'O^- \rightarrow R'OCO_2R + CCl_3^- \quad (1b)$$

$$CCl_3^- \rightarrow Cl^- + :CCl_2 \quad (2)$$

As applied to *cis*-9-octadecene and to methyl oleate, the formation of dichlorocyclopropanes is described by the following equation:



(3)

To methyl linoleate two moles of the carbene were attached. Since in these substrates, the double bonds are all *cis*, and since the mode of addition is *cis* (3a,4), each resultant cyclopropane ring must also have the *cis* structure. The dichlorocyclopropane from methyl elaidate must similarly be *trans*. In assigning product structures any isomerization of the parent olefin by the alkaline conditions has been neglected.

In initial experiments with *cis*-9-octadecene, the ethyl trichloroacetate method (Equations 1b,2,3) gave better results than the chloroform procedure. Yields, however, were still much lower with octadecene than in repetitions of Parham's addition of dichlorocarbene to cyclohexene (10). The yield of *1,1-dichloro-2,3-dioctylcyclopropane* (I) was improved by several techniques. A high speed stirrer with cruciform impeller improved reaction rate, and the ethyl trichloroacetate was added at rates causing substantial but controllable evolution of heat. The exothermicity was accommodated by the use of n-heptane instead of n-pentane as solvent, by large reaction flasks, and by a cooling bath applied as needed. The procedure developed was also applied in the additions to methyl oleate, methyl elaidate, and methyl linoleate. Two typical preparations are described below, while yield and analytical data for products are listed in Table I.

1,1-Dichloro-2-octyl-3-(7-Carbomethoxyheptyl)-Cyclopropane. (II). Methyl oleate, 15g (0.05 mole), was placed with 30 ml of n-heptane and 15g (0.28 mole) of sodium methoxide in a four-necked, round-bottomed 1-liter flask fitted with a thermometer, a by-pass addition funnel, and a condenser protected with a drying tube. Nitrogen was introduced through the addition funnel. The reaction mixture was cooled to 2C with an ice-salt bath and stirred at high speed while 30 ml (0.22 mole) of ethyl trichloroacetate were added dropwise. Heat of reaction caused refluxing of solvent. Upon completion of the addition (1 hr) the mixture was removed from the cooling bath, stirred for 4 hr, and allowed to stand overnight at room temp. After addition of water, the mixture was extracted by shaking with three 100-ml portions of diethyl ether. The ether layer was washed with five 75-ml portions of water and dried over sodium sulfate. Excess ether was removed under vacuum in a rotating evaporator. The product was purified by column chromatography using a Florisil:sample ratio of 20:1. Fractions eluted with hexane afforded the desired dichlorocyclopropane, 15.1g.

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[1] Presented at AOCS meeting, Toronto, October, 1962.
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