was then removed and the residual liquid was distilled under reduced pressure to give 9.0 g (70%) of a yellow liquid (**11**): bp 78–79° (3.6 mm); n^{27}D 1.5552; λ_{max}^{EtOH} 271 mμ (ε 11,600) and 230 mμ (ε 6250). The infrared spectrum of **11** had an N–H peak at 3300, a C=N peak at 1625, and a C–N stretch at 1125 cm^{-1}. Its nmr spectrum showed a multiplet of olefin peaks centered at 5.9, an N-methyl singlet at 2.9, and a cyclohexyl multiplet between 2.4 and 1.6 ppm.

Anal. Calcd for $C_7H_{12}N_2$: C, 67.26; H, 10.32; N, 22.41. Found: C, 66.84; H, 9.88; N, 22.60.

Oxidation of 2-Cyclohexen-1-one Monomethylhydrazone with Lead Tetraacetate.—To 10.0 g (0.08 mole) of **11** dissolved in 200 ml of methylene chloride was added slowly with stirring and cooling 42.4 g (0.08 mole) of lead tetraacetate. The solution was allowed to stir at ambient temperature for 2 hr. Work-up in the manner previously described followed by distillation of the residual liquid afforded 9.7 g (70%) of a yellow liquid (**12**): bp 81–81.5° (3.5 mm); n^{28}D 1.4739; λ_{max}^{EtOH} 356 mμ (ε 27). The infrared spectrum of **12** had no N–H peak but had strong acetate peaks at 1750 and 1240 cm^{-1}. The nmr spectrum of **12** had an olefinic signal at 5.95, an N-methyl singlet at 3.75, an acetyl methyl singlet at 2.0, and a methylene multiplet at 2.2–1.6 ppm. The relative intensities were 2:3:3:6, respectively.

Anal. Calcd for $C_9H_{14}N_2O_2$: C, 59.32; H, 7.74; N, 15.37. Found: C, 59.17; H, 7.63; N, 15.45.

Oxidation of 2-Cyclohexen-1-one Monomethylhydrazone with Peracetic Acid.—To 10.0 g (0.08 mole) of **11** dissolved in 200 ml of anhydrous ether was added with stirring and cooling in an ice water bath 15.5 g (0.08 mole) of 40% peracetic acid. The solution was stirred at ambient temperature for 2 hr. The usual work-up followed by distillation of the residual liquid afforded 4.75 g (35%) of 1-(methylazo)-2-cyclohexen-1-ol acetate (**12**), bp 82.5° (3.7 mm). The ultraviolet, infrared, and nmr spectra of this product were identical with those of **12** prepared by the oxidation of **11** with lead tetraacetate. Back extraction of the first two aqueous bicarbonate washes with methylene chloride afforded 2.1 g of a liquid whose infrared spectrum showed it to be mainly 2-cyclohexen-1-one.

Registry No.—**1** (*syn*), 15023-24-2; **1** (*anti*), 15023-25-3; **2**, 15023-26-4; **3**, 15023-27-5; **4**, 15023-28-6; **5** (*syn*), 15023-29-7; **5** (*anti*), 15026-11-6; **6**, 15023-30-0; **7**, 15023-31-1; **8** (*syn*), 15023-32-2; **8** (*anti*), 15023-33-3; **9**, 15023-34-4; **10**, 15023-35-5; **11**, 15023-36-6; **12**, 15023-37-7; *trans*-cinnamaldehyde dimethylhydrazone, 15023-38-8.

Pseudo-Halogens. X. Effect of Some Electronic or Steric Factors on the Addition of N,N-Dichlorourethan to Unsaturated Compounds[1,2]

THOMAS A. FOGLIA AND DANIEL SWERN

Fels Research Institute and Department of Chemistry, Temple University, Philadelphia, Pennsylvania 19122

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The addition of N,N-dichlorourethan (DCU) to unsaturated compounds with special electronic or steric factors has been investigated. Yields of β-chlorocarbamates range from 35 to 80%. Electron-withdrawing groups slow down the addition reaction; extensive electron withdrawal completely arrests it. Perfluorocyclohexene, ethyl vinyl sulfone, and diethyl maleate do not react. Addition of DCU to substituted alkenes is subject to steric retardation and is also complicated by allylic chlorination. With 2,3-dimethyl-2-butene allylic chlorination is the exclusive process. DCU adds to all terminally unsaturated compounds studied in anti-Markownikow fashion. Nmr and chemical evidence have been used to prove the structures of the adducts. By controlled pyrolysis of methyl β-(N-carboethoxyamino)-α-chloropropionate and N-(2-chloro-2-cyanoethyl)carbamate, 5-carbomethoxy- and 5-cyano-2-oxazolidones, respectively, have been obtained in 65 and 35% yields. These oxazolidones are difficult to obtain by the usual alkali-catalyzed ring-closure methods.

Study of the scope, limitations, and mechanisms of the addition of pseudo-halogens (iodine isocyanate, nitrosyl acylates, N,N-dichlorourethan) to unsaturated compounds is of considerable interest in our laboratory.[1,3] In an earlier paper,[3a] we described the addition of N,N-dichlorourethan (DCU) to a series of monoolefinic compounds and showed that the reaction has many of the characteristics of a free-radical addition reaction. The initial group of unsaturated compounds studied comprised straight-chain terminal olefins (RCH=CH_2), internal olefins (RCH=CHR), a branched-chain terminal olefin (RC(R)=CH_2), an unsaturated compound with an electron-withdrawing group attached to the double bond (methyl acrylate) and two cyclic olefins (cyclohexene and norbornene). In most cases addition was rapid; the reaction provides a facile, one-step synthesis of compounds containing the carbon–nitrogen bond from monounsaturated compounds.

DCU is an unusual pseudo-halogen. Although it is extremely reactive, it can be distilled under vacuum and stored for long periods in the dark without excessive decomposition. Redistillation just before use provides the pure pseudo-halogen. This combination of properties makes DCU an attractive halogenoid reagent for chemical investigations.

In the present paper we are reporting (a) the reaction of DCU with selected unsaturated compounds having special electronic or steric features and (b) proof of structure of the addition products. When pure β-chlorocarbamates could be isolated, their pyrolysis and reaction with base were also studied in attempts to prepare unusual 2-oxazolidones and aziridines, respectively. Table I lists the β-chlorocarbamates prepared.

Addition of DCU to Unsaturated Compounds with Polar Substituents.—In all cases shown, yields of analytically pure, isolated β-chlorocarbamates are fair to good (35–80%) whether electron-donating or certain electron-withdrawing groups (–CN, $-CO_2C_2H_5$, $-CO_2CH_3$, Cl_2, $-COCH_3$) are attached to the double bond. This result is consistent with the generally

(1) Pseudo-Halogens. IX: *J. Org. Chem.* **32**, 3665 (1967). Work submitted by T. A. Foglia in partial fulfillment of the requirements for the Ph.D. degree, Temple University.

(2) The authors acknowledge with thanks support of this investigation by Public Health Service Grants No. CA-07803 and CA-07174 from the National Cancer Institute.

(3) (a) T. A. Foglia and D. Swern, *J. Org. Chem.*, **31**, 3625 (1966), and references therein; (b) H. C. Hamann and D. Swern, *Tetrahedron Letters*, 3303 (1966).

TABLE I

β-CHLOROCARBAMATES BY ADDITION OF DCU TO UNSATURATED COMPOUNDS WITH SPECIAL FEATURES

Unsaturated compd	β-Chlorocarbamate	Bp (mm) or mp, °C	Reacn time, hr	Temp, °C	C, %		H, %		N, %		Cl, %		% yield
					Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	
$(CH_3)_3CCH{=}CH_2$	$(CH_3)_3CCH(Cl)CH_2NHCO_2C_2H_5$ (1)	70–71.5	4.5	85	52.0	52.1	8.74	8.61	6.74	6.93	17.1	16.9	80
$(CH_3)_2CHC(CH_3){=}CH_2$	$(CH_3)_2CHC(CH_3)(Cl)CH_2NHCO_2C_2H_5$ (3)	71–72 (0.2)	2.0	45	52.0	51.9	8.74	8.54	6.74	6.65	17.8	17.4	40
$CH_2{=}CHCN$	$H_5C_2O_2CNHCH_2CH(Cl)CN$ (7)	101–102 (0.3)	5.0	85	40.8	40.8	5.14	5.27	15.9	15.8	20.1	19.9	60
$C_6H_5CH{=}CHCO_2C_2H_5$ (*trans*)	$C_6H_5CH(Cl)CH(CO_2C_2H_5)NHCO_2C_2H_5$ (9)[a]	30–35	4.0	85	56.1	56.8	6.05	6.20	4.67	4.65	11.9	12.0	60
$CH_2{=}CHCO_2CH_3$	$H_5C_2O_2CNHCH_2CH(Cl)CO_2CH_3$ (4)	104–106 (0.2)	4.5	85	40.1	40.2	5.77	5.67	6.68	6.49	16.9	17.2	55
$CH_2{=}CCl_2$	$H_5C_2O_2CNHCH_2CCl_3$ (8)	51–52	2.0	85	27.2	27.4	3.66	3.70	6.35	6.51	48.2	48.4	75
$CH_2{=}CHO_2CCH_3$	$H_5C_2O_2CNCH_2CH(Cl)O_2CCH_3$ (5)	114–116 (0.2)	4.0	85	39.9	38.7	6.13	5.98	6.66	6.93	16.9	16.4	*b*
$CH_2{=}CHCOCH_3$	$H_5C_2O_2CNHCH_2CH(Cl)COCH_3$ (6)	107–108 (0.3); 33–33.5	4.0	85	43.4	43.2	6.25	6.08	7.23	7.28	18.3	18.1	35

[a] Major isomer present. [b] Unstable product; yield of crude product with expected spectral characteristics was quantitative.

accepted conclusion that radical reactions are less sensitive to polar effects than are ionic reactions.

Polar effects play an important role on the rates of addition, however. Not shown in Table I are perfluorocyclohexene and ethyl vinyl sulfone; they give no detectable reaction with DCU after 72 hr in refluxing benzene. Thus, extensive electron withdrawal completely arrests the addition reaction. In all the cases listed in Table I when an electron-withdrawing group is present in the unsaturated compound the rate of addition is slower than when electron-donating groups are present that impose no special steric limitations on the unsaturated compound.[3a] With this information at hand, it was predicted that diethyl maleate would be unreactive; experiment (>30 hr of reaction time) confirmed this conclusion.

Vinylidene chloride reacts essentially quantitatively in less than 2 hr; the delocalization effect of the two chlorine atoms effectively neutralizes their electron-withdrawing inductive effect. Vinyl acetate, ethyl cinnamate, and methyl vinyl ketone react completely within 4 hr. The yield of crude β-chlorocarbamate from vinyl acetate is essentially quantitative, as shown spectrally, but the reaction product is somewhat unstable and could not be obtained in the hoped for analytical purity. The yield of β-chlorocarbamate from ethyl cinnamate is about twice that from methyl vinyl ketone. It is noteworthy that Chabrier[4] reported that cinnamaldehyde and cinnamic acid do not react with DCU. Methyl acrylate reacts slightly more slowly than does methyl vinyl ketone, and acrylonitrile is the slowest. In an earlier paper,[3a] we had employed inhibited methyl acrylate; as expected the reaction time was longer and the yield lower than with uninhibited monomer.

Vinyl polymerization is not observed in any of the addition reactions. We had shown earlier[3a] that styrene gives an almost quantitative yield of the 1:1 adduct (β-chlorocarbamate) and no polymer. We conclude from these results that either "free" radicals are never present or the termination step to form the 1:1 addition product from the first-formed radical adduct is a much faster process than the polymerization propagation step. It is tempting to suggest that the reaction proceeds by an essentially concerted but nonsynchronous molecule-induced homolysis (four-center attack) in which the transition state has some free-radical character on that carbon atom of the original double bond better able to accommodate it.[5] The failure to obtain stereoselective addition with *trans*-3-hexene and stilbene, however, argues against a concerted completely synchronous four-center attack mechanism.

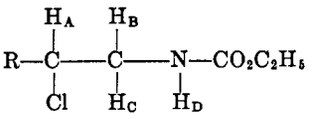
Information on the effect of steric factors was obtained from a study of the reaction of DCU with isomeric hexenes. This phase of the investigation was complicated by the fact that variations in structure not only change steric parameters but also introduce different numbers and kinds of hydrogen atoms subject to allylic attack. Thus, disappearance of olefin, shown by glpc, cannot always be correlated with double bond addition.

(4) P. Chabrier, *Ann. Chim.*, **17**, 353 (1942).

(5) A molecule-induced homolysis has also been suggested by C. Walling, L. Heaton, and D. Tanner, *J. Am. Chem. Soc.*, **87**, 1715 (1965), for another system.

TABLE II

NMR SPECTRAL ASSIGNMENTS OF β-CHLOROCARBAMATES



Compd	Chemical shifts, ppm (J, cps) (TMS = 0)[a] H_A, δ	H_B, H_C, δ	H_D, δ
$CH_3(CH_2)_3CH(Cl)CH_2NHCO_2C_2H_5$[b]	3.92 (m)	3.44 (m)	5.6 (s)
$CH_3(CH_2)_7CH(Cl)CH_2NHCO_2C_2H_5$[b]	3.90 (m)	3.40 (m)	5.6 (s)
$C_6H_5CH(Cl)CH_2NHCO_2C_2H_5$[b]	5.05 (q)	3.70 (m)	5.4 (s)
1	3.72 (m)	2.94 (sep)	5.2 (s)
2		3.40 (d, J = 7)	5.5 (s)
3		3.52 (d, J = 7)	5.5 (s)
4	4.46 (t, J = 6)	3.68 (m)	5.85 (t)
5	6.66 (t, J = 6)	3.78 (t, J = 6)	6.0 (t)
6	4.40 (t, J = 6)	3.62 (m)	5.3 (s)
7	4.74 (t, J = 6)	3.68 (t, J = 6)	6.2 (t)
8		4.16 (d, J = 7)	6.25 (s)

[a] Abbreviations used are s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, sep = septuplet. [b] See ref 3a.

1-Hexene reacts completely with an equimolar quantity of DCU in refluxing benzene in less than 1 hr.[3a] Addition to the double bond appears to be the exclusive reaction. 2-Methyl-1-pentene is even more reactive and requires a lower reaction temperature (5-25°) to control the addition reaction which is also complete in less than 1 hr.[3a] These results show that electron donation to the double bond can overcome the steric effect of a single methyl group, and is consistent with the earlier conclusion that DCU has considerable electrophilic character. β-Chlorocarbamates are isolated in good yields from both 1-hexene and 2-methyl-1-pentene.

With 2,3-dimethyl-1-butene, however, a compound of comparable nucleophilicity to 2-methyl-1-pentene, disappearance of olefin is considerably slower. This is attributed to a steric factor. The double bond of 2,3-dimethyl-1-butene carries a methyl and an isopropyl group, whereas 2-methyl-1-pentene has a methyl and an *n*-propyl group on the double bond. 2,3-Dimethyl-1-butene also has one tertiary hydrogen atom and, in this case, a 25% yield of monochlorinated alkenes and only a 40% yield of β-chlorocarbamate are isolated. 2,3-Dimethyl-2-butene, on the other hand, disappears very rapidly but no addition to the double bond is observed. The products isolated (45% yield) are those arising from allylic monochlorination.

3,3-Dimethyl-1-butene reacts extremely slowly, as anticipated on steric grounds, and requires a reaction time of 4.5 hr in refluxing benzene for complete disappearance of olefin. The reaction product isolated is exclusively the β-chlorocarbamate, isolated in analytical purity in 75–80% yield.

Structure of Addition Products.—With the exception of the product from vinyl acetate, all β-chlorocarbamates listed in Table I had acceptable elemental analyses and infrared spectra. The final structural assignment, namely, the location of the chlorine atom and the urethan group ($-NHCO_2C_2H_5$), was made from nmr spectra by analysis of the chemical shifts and multiplicity of the relevant protons and comparison of the spectra with those of β-chlorocarbamates of known structures. Table II lists the nmr spectral assignments of protons H_A, H_B, H_C, and H_D for various β-chlorocarbamates.

The first three compounds listed were described previously[3a] and unequivocal proof of their structure was given in that and a subsequent paper.[6] The methine proton, H_A, is split by the nonequivalent protons H_B and H_C and by the adjacent methylene protons in R. Thus, H_A appears as a complex multiplet centered at about 3.9 ppm. In these cases (and in all the others to be discussed shortly) the resonance of this proton—attached to a carbon bearing a chlorine atom—is downfield from the protons H_B and H_C, attached to a carbon bearing the urethan group. On this basis, the addition product of DCU to 3,3-dimethyl-1-butene (neohexene) is given the structure, **1**, shown in Table II, because the methine proton, H_A, appears as a complex multiplet at 3.72 ppm (1 H), downfield from the septet of H_B and H_C at 2.94 ppm (2 H). The H_D (1 H) signal appears as a broad singlet at 5.2 ppm, in the usual region for a proton attached to nitrogen in a urethan group.

Confirmation of the structural assignment of the neohexene adduct was obtained by chemical evidence. Ethyl N-(2-chloro-2-*t*-butylethyl)carbamate (**1**) was pyrolyzed at a maximum temperature of 210°, a reaction that readily converts unhindered β-chlorocarbamates to 2-oxazolidones with the elimination of alkyl chloride.[6] No ethyl chloride was obtained and the starting material was recovered completely unchanged except for a slight yellow color. Examination of models show that the methyl groups effectively prevent the carbonyl oxygen of the urethan group from performing a backside nucleophilic attack on the carbon bearing chlorine. If **1** is treated with base, however, *t*-butylaridine is obtained in 60% yield although the ring-closure reaction required 48 hr refluxing with alcoholic potassium hydroxide for completion; whereas in the other cases studied, where steric effects are not involved and chlorine is also secondary, 4 hr at 50° is usually sufficient.[6] The successful preparation of the aziridine can be readily understood from models as it involves attack on carbon by the nitrogen anion to displace the chlorine atom. Attack by the nitrogen anion does not involve the same steric limitations by the methyl groups as

(6) T. A. Foglia and D. Swern, *J. Org. Chem.*, **32**, 75 (1967).

does attack by the carbonyl oxygen, two atoms removed, in attempting to form a 2-oxazolidone.

Finally, structure **1** is the expected product on steric grounds as attack of neohexene by DCU either by the free radical, $\cdot N(Cl)CO_2C_2H_5$, or by a molecule-induced homolysis involving a four-center transition state should place the larger urethan moiety on the more accessible terminal carbon atom. Even ionic addition of iodine isocyanate and iodine azide to neohexene, recently discussed by Fowler, Hassner, and Levy,[7] proceeds in anti-Markownikow fashion whereas with numerous other less-hindered alkenes addition is predominantly Markownikow.

The structure of the addition product of DCU to 2-methyl-1-pentene (**2**, Table II) is clearly demonstrated by nmr. The absence of H_A simplifies the character of the signal from H_B and H_C which appears as a doublet centered at 3.40 ppm (2 H) and $J = 7$ cps. Compound **3**, the addition product of DCU to 2,3-dimethyl-1-butene, is assigned an analogous structure to that of **2**. The signal of H_B and H_C appears as a doublet at 3.52 ppm (2 H) and $J = 7$ cps. With the exception of neohexene, in all cases studied in which the urethane group appears on the terminal carbon atom of a 1-alkene, the chemical shift of protons H_B and H_C is in the range of 3.4–3.5 ppm. In both **2** and **3**, H_D appears as a broad singlet at 5.5 ppm (1 H).

Addition of DCU to methyl acrylate yields **4**. The signal of H_A appears as a downfield triplet centered at 4.46 ppm (1 H) and that of H_B and H_C as a complex multiplet centered at 3.68 ppm (2 H). If the chlorine atom and urethan group were reversed, such a pattern would not be obtained. The signal of H_A is slightly farther downfield from the usual position of H_A in alkene adducts. Also, the signal of H_D appears as a broad, ill-defined triplet centered at 5.85 ppm (1 H). This serves as additional confirmation of the structure assigned to **4** as the alternative possible structure could produce a doublet at most.

In the vinyl acetate adduct (**5**, Table II), the signal of the methine proton, H_A, is shifted downfield to 6.66 ppm (1 H) where it appears as a triplet with $J = 6$ cps. Protons H_B and H_C, however, appear in the normal position (3.78 ppm) as a triplet with $J = 6$ cps (2 H). H_D, the proton on nitrogen, appears as a broad, ill-defined triplet centered at 6.0 ppm (1 H).

Interpretation of the nmr spectrum of the adduct of DCU with methyl vinyl ketone (**6**, Table II) is analogous to that of **5**, and the structural assignment is made on the same basis. H_D appears as a broad singlet centered at 5.3 ppm (1 H), not as the hoped-for triplet seen with the methyl acrylate adduct **5**.

The nmr spectrum of the adduct of DCU with acrylonitrile **7** shows a well-defined triplet (H_D) with broadened peaks centered at 6.2 ppm (1 H). Structure **7** is therefore correct. The signal of H_A appears as a downfield triplet at 4.74 ppm (1 H) and $J = 6$ cps. H_B and H_C also appear as a triplet at 3.68 ppm (2 H) and $J = 6$ cps.

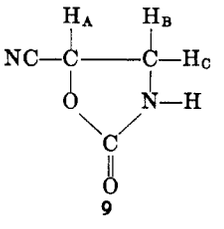
The nmr spectrum of the adduct of DCU with vinylidene chloride (**8**) shows a sharp doublet for H_B and H_C at 4.16 ppm (2 H) and $J = 7$ cps. The alternative structure requires a singlet.

(7) F. W. Fowler, A. Hassner, and L. A. Levy, *J. Am. Chem. Soc.*, **89**, 2077 (1967).

The adduct of DCU with ethyl cinnamate had an extremely complex nmr spectrum suggesting that it was a mixture of *erythro* and *threo* and perhaps even positional isomers. The broad melting range (30–35°) of the product having correct elemental analyses is consistent with this view. Treatment of the product with silver nitrate in aqueous ethanol gave only 79% of the calculated quantity of silver chloride as an immediate precipitate. In our previous paper we showed that the yield of silver chloride precipitated immediately is over 90% if the chlorine atom is entirely on the benzylic carbon atom (styrene adduct). We conclude therefore, that the adduct with ethyl cinnamate is a mixture of isomers with the majority of the chlorine being benzylically located.

In five cases attempts were made to confirm nmr structural assignments by pyrolytic conversion of the β-chlorocarbamates to 2-oxazolidones. Ethyl N-(2-chloro-2-*t*-butylethyl)carbamate and ethyl N-(2,2,2-trichloroethyl)carbamate were recovered unaltered on heating to 210 and 190°, respectively. Ethyl N-(2-cyano-2-chloroethyl)carbamate and ethyl N-(2-acetyl-2-chloroethyl)carbamate were converted to insoluble black, granular, carbonized masses at 190°. At 160°, the former gave a 35% yield of 5-cyano-2-oxazolidone, mp 95°, isolated by column chromatography. Methyl β-(N-carboethoxy)-α-chloropropionate, however, when pyrolyzed at 170° rapidly evolved a gas (ethyl chloride). By column chromatography of the pyrolysis residue a 65% yield of 5-carbomethoxy-2-oxazolidone, mp 66°, was obtained. These 2-oxazolidones are difficult to obtain by conventional ring-closure methods with alkaline catalysts.

If the proposed β-chlorocarbamate structures proposed are correct, the 2-oxazolidones should be substituted at the 5 position. The nmr spectra of these 2-oxazolidones were obtained. The methine proton, H_A, of 5-cyano-2-oxazolidone (**9**) appears as a doublet of doublets centered at 5.7 ppm (1 H). The signal of the protons H_B and H_C appears as a multiplet (octet) centered at 4.1 ppm (2 H). 5-Carbomethoxy-2-oxazolidone (**10**) shows a similar pattern. The methine proton, H_A, appears as a doublet of doublets centered at 5.05 ppm (1 H), farther upfield than the corresponding proton in **9**. H_B and H_C appear as a multiplet, overlapping the methyl protons, centered at 3.8 ppm (2 H). Comparison of these spectra with those of known 4- and 5-substituted 2-oxazolidones[6] confirms the structures shown (**9** and **10**).



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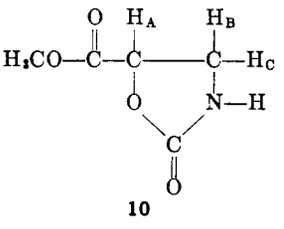

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Three β-chlorocarbamates were treated with alcoholic potassium hydroxide. In only one case, already discussed, was an aziridine isolated. Base treatment of ethyl N-(2-acetyl-2-chloroethyl)carbamate and ethyl N-(2,2,2-trichloroethyl)carbamate yielded dark brown, viscous oils which did not yield any aziridine on vacuum distillation.

Experimental Section

Materials and Equipment.—The unsaturated compounds used were the best quality commercial reagents. Their purity in all cases was checked by glpc; purity exceeded 98%. N,N-Dichlorourethan was prepared by the method of Foglia and Swern.[3a] Infrared spectra were obtained on a Perkin-Elmer Infracord, Model 137. Nmr spectra were obtained on a Varian A-60 spectrometer using TMS as internal standard. Glpc was carried out on a Wilkens Aerograph Autoprep, Model A-700. Refractive indices were taken on a Bausch and Lomb refractometer. Microanalyses were performed by Microanalysis, Inc., Wilmington, Del.

Addition of DCU to Olefins. General Procedure.—A solution of DCU (8.0 g, 0.050 mole) in benzene (25 ml) was placed in a 100-ml flask and the solution was purged with and kept under an atmosphere of nitrogen. The olefin (0.050 mole) was then added dropwise and the reaction mixture was maintained at the indicated temperature (see below) until disappearance of olefin was complete as shown by glpc. A 20% aqueous solution of sodium bisulfite (50 ml) was then added at 5–10° and the organic layer was separated. The aqueous phase was extracted with two 25-ml portions of ether and combined organic layers were then washed with two 25-ml portions of water and dried over anhydrous Na_2SO_4. The crude reaction product was isolated as a residue by vacuum evaporation of the solvent. Purification was by vacuum distillation and/or recrystallization. Table I shows results and analyses.

A. 3,3-Dimethyl-1-butene.—Olefin disappearance was complete after 4.5 hr at 85°. The product, ethyl N-(2-chloro-2-*t*-butylethyl)carbamate (**1**), was recrystallized from hexane at low temperature, mp 70–71.5° (yield 75–80%). Infrared bands are at $\lambda_{max}^{CCl_4}$ 3500 (NH), 1735 (C=O), 1530 (amide II), 1390 and 1360 (*t*-Bu), and 1240 cm^{-1}.

B. 2,3-Dimethyl-1-butene.—Olefin disappearance was complete after 2 hr at 45°. The reaction product was distilled under vacuum: fraction A, mixture of monochlorinated alkenes, bp 58–62° (10 mm) (1.50 g, yield 25%); fraction B, ethyl N-(2-chloro-2,3-dimethylbutyl)carbamate (**3**), bp 71–72° (0.20 mm) (4.20 g, yield 40%) and n^{25}D 1.4620. Infrared bands are at λ_{max}^{neat} 3400 (NH), 1730 (C=O), 1520 (amide II), and 775 cm^{-1} (C–Cl).

An analytical sample of fraction A was obtained by preparative glpc at 150° using a 10 ft × 3/8 in. column packed with 20% SE-30 on Chromsorb P. Infrared bands are at λ_{max}^{neat} 1640 (C=C), 1110, 915, and 760 cm^{-1} (C–Cl). The product is a mixture of monochlorinated alkenes, as shown by nmr.

Anal. Calcd for $C_6H_{11}Cl$: C, 60.76; H, 9.35; Cl, 29.89. Found: C, 60.60; H, 9.21; Cl, 29.76.

C. 2,3-Dimethyl-2-butene.—Olefin disappearance was complete after 2 hr at 40°. The product, a mixture of monochlorinated alkenes, was distilled under vacuum, bp 52–53° (4.0 mm) (yield 45%). An analytical sample was obtained by preparative glpc at 170° using a 10 ft × 3/8 in. column packed with 15% Apiezon-L on Anakrom ABS. Infrared bands are at λ_{max}^{neat} 3000, 1650 (C=C), 1120 and 770 cm^{-1} (C–Cl). The product is a mixture of isomeric monochlorinated alkenes as shown by nmr.

Anal. Calcd for $C_6H_{11}Cl$: C, 60.76; H, 9.35; Cl, 29.89. Found: C, 60.72; H, 9.05; Cl, 29.93.

D. Acrylonitrile.—Disappearance of unsaturated compound (inhibitor free) was complete after 5 hr at 85°. The product, ethyl N-(2-chloro-2-cyanoethyl)carbamate (**7**), was isolated by distillation under vacuum, bp 101–102° (0.30 mm) (yield 59%) and n^{23}D 1.4642. Infrared bands are at λ_{max}^{neat} 3400 (NH), 2280 (CN), 1730 (C=O), 1540 (amide II), 1260, 1070, 1030, and 780 cm^{-1} (C–Cl).

E. Ethyl Cinnamate.—Disappearance of unsaturated compound was complete after 4 hr at 85°. The crude reaction product was dissolved in a minimum volume of chloroform and placed on a Florisil column (2.0 g of crude carbamate to 80 g of Florisil) and eluted successively with pentane (150 ml), 25% ether–pentane (150 ml), 50% ether-pentane (150 ml), 75% ether–pentane (150 ml), and then ether (150 ml). The carbamates, mainly ethyl N-(2-chloro-2-phenyl-1-carboethoxyethyl)carbamate (**9**), were obtained from the 50% ether–pentane eluate. They had mp 30–35° (1.36 g, 60% yield) and probably consisted of a mixture of *erythro*, *threo*, and positional isomers. Infrared bands are at $\lambda_{max}^{CCl_4}$ 3450 (NH), 1750, 1730 (carbonyl), 1520 (amide II), 1240, 1050, 1030, 860, and 700 cm^{-1}.

Treatment of the carbamate with silver nitrate in aqueous ethanol by the procedure previously reported[3a] gave an immediate precipitate of silver chloride (79% yield). The yield of silver chloride was less than that anticipated if the chlorine atom was on the benzylic carbon atom exclusively.

F. Methyl Acrylate.—Disappearance of unsaturated compound (inhibitor free) was complete in 4.5 hr at 85°. The crude reaction product was distilled under vacuum. Methyl β-(N-carboethoxyamino)-α-chloropropionate (**4**), bp 104–106° (0.20 mm), was obtained in 55% yield, n^{25}D 1.4594 (lit.[3a] bp 99–100 (0.15 mm), n^{26}D 1.4588). Infrared bands are at λ_{max}^{neat} 3350 (NH), 1750, 1720 (C=O), 1520 (amide II), and 780 cm^{-1} (C–Cl).

G. Vinylidene Chloride.—Disappearance of unsaturated compound (inhibitor free) was complete in 2 hr at 85°. The crude product, ethyl N-(2,2,2-trichloroethyl)carbamate (**8**), was recrystallized from hexane at low temperature, mp 51–52° (yield 75%). Infrared bands are at $\lambda_{max}^{CCl_4}$ 3450 (NH), 1730 (C=O), 1540 (amide II), 1260, 1080, and 825 cm^{-1}.

H. Vinyl Acetate.—Disappearance of unsaturated compound was complete in 4 hr at 85°. The product, ethyl N-(2-chloro-2-acetoxyethyl)carbamate (**5**), was distilled under vacuum, bp 114–116° (0.20 mm). It was slightly unstable and decomposed upon standing. It could not be obtained in analytical purity; its spectra were consistent with the assigned structure. Infrared bands are at λ_{max}^{neat} 3400 (NH), 1770, 1730 (C=O), 1540 (amide II), 1260, 1210, 1080, 1040, and 780 cm^{-1} (C–Cl).

I. Methyl Vinyl Ketone.—Disappearance of unsaturated compound was complete in 4 hr at 85°. The product, ethyl N-(2-chloro-2-acetylethyl)carbamate (**6**), was distilled under vacuum, bp 107–108° (0.30 mm). It crystallized on cooling to −30° and was recrystallized from ether–pentane, mp 33–33.5° (yield 35%). Infrared bands are at $\lambda_{max}^{CCl_4}$ 3500 (NH), 1740 (C=O), 1520 (amide II), 1220, 1260, 1030, and 870 cm^{-1}.

Attempted Preparation of 5-*t*-Butyl-2-Oxazolidone from Ethyl N-(2-Chloro-2-*t*-Butylethyl)carbamate.—The β-chlorocarbamate (3.12 g, 0.015 mole) was heated as a neat liquid at 210° for 2.5 hr. No evolution of gas was observed. The reaction product was cooled and recrystallized from hexane at low temperature. The recovered product (2.60 g) had a melting point and an infrared spectrum identical with those of starting material.

Attempted Preparation of 5,5-Dichloro-2-oxazolidone from Ethyl N-(2,2,2-Trichloroethyl)carbamate.—The carbamate (2.20 g, 0.010 mole) was treated as above but at 190°. Recrystallization from hexane at 0° gave unchanged starting material (1.70 g, mp 51° and identical infrared spectra).

Attempted Preparation of 5-Acetyl-2-oxazolidone from Ethyl N-(2-Acetyl-2-chloroethyl)carbamate.—Pyrolysis at 190° yielded a black, insoluble mass. It was discarded.

Preparation of 5-Cyano-2-oxazolidone from Ethyl N-(2-Cyano-2-chloroethyl)carbamate.—Pyrolysis of the carbamate as a neat liquid at 190° yielded a black, carbonized, granular mass insoluble in common organic solvents. At 160–165° the carbamate (1.77 g, 0.010 mole) was converted to a brown viscous liquid that was placed on a Florisil column (15 g). Elution was carried out successively with ether (100 ml) and methanol (100 ml). Evaporation of the methanol eluate yielded crude 2-oxazolidone. It was recrystallized from ethanol–hexane, mp 94.5–95.5° (0.40 g, 35% yield). Infrared (Nujol) bands are at 3350 (NH), 1760 (C=O), 1270, 1220, 1090, 1070, 1010, and 940 cm^{-1}.

Anal. Calcd for $C_4H_4N_2O_2$: C, 42.9; H, 3.60; N, 25.0. Found: C, 42.8; H, 3.71; N, 25.1.

Preparation of 5-Carbomethoxy-2-oxazolidone from Methyl β-(N-Carboethoxyamino)-α-chloropropionate.—The chlorocarbamate (2.10 g, 0.010 mole) was heated at 170° until evolution of gas ceased. The residue was dissolved in a minimum quantity of chloroform and placed on a Florisil column (30 g of adsorbent/1.5 g crude 2-oxazolidone). Elution was conducted successively with pentane (150 ml), ether (100 ml), 25% acetone–ether (200 ml), and 50% acetone–ether (50 ml). The oxazolidone (pale yellow) was obtained by evaporation of the 25% acetone–ether solution followed by crystallization from methanol (3 ml of solvent/1 g) at low temperature, mp 66–67° (1.0 g, 65% yield). Infrared bands are at $\lambda_{max}^{CHCl_3}$ 3350 (NH), 1770 and 1750 (oxazolidone and ester C=O), 1230, 1090, and 930 cm^{-1}.

Anal. Calcd for $C_6H_7NO_4$: C, 41.4; H, 4.86; N, 9.65. Found: C, 41.4; H, 4.86; N, 9.80.

Preparation of *t*-Butylaziridine.—Ethyl N-(2-*t*-butyl-2-chloroethyl)carbamate (29.7 g, 0.145 mole) in 95% ethanol (100 ml) was added in one portion to a solution of potassium hydroxide (30.0 g, 0.550 mole) in 95% ethanol (150 ml). The solution was refluxed for 48 hr, at which time the separation of solids was complete. The reaction mixture was poured into water (1 l.) and extracted with five 200-ml portions of ether. The combined extracts were dried over anhydrous sodium sulfate and the ether was removed by distillation. The residual oil was then distilled using a 6 in. × 3/8 in. column packed with glass helices to yield 2-*t*-butylaziridine, bp 116–116.5° (760 mm), and $n^{23}D$ 1.4244, as a colorless liquid (8.95 g, 60% yield). Infrared bands are λ_{max}^{neat} 3300 (NH), 1480, 1360, 1200, 895, and 860 cm^{-1}.

Anal. Calcd for $C_6H_{13}N$: C, 72.66; H, 13.21; N, 14.12. Found: C, 72.52; H, 13.32; H, 13.88.

Attempted Preparation of 2-Acetylaziridine.—Repetition of the above procedure with ethyl N-(2-acetyl-2-chloroethyl)carbamate on a 0.001-mole scale and with 2 hr of reflux time yielded a dark brown viscous oil which did not yield the aziridine on vacuum distillation.

Attempted Preparation of 2,2-Dichloroaziridine.—Repetition of the above procedure with ethyl N-(2,2,2-trichloroethyl)carbamate on a 0.01-mole scale and reaction with base for 18 hr at room temperature yielded a dark brown intractable viscous liquid.

Attempted Addition of DCU to Perfluorocyclohexene, Ethyl Vinyl Sulfone and Diethyl Maleate.—The unsaturated compound (0.05 mole) was added in one portion to a solution of DCU (8.0 g, 0.05 mole) in benzene (25 ml). With the first two unsaturated compounds, the solutions were refluxed for 72 hr; in the third case refluxing was continued for only 31 hr. There was no detectable disappearance of unsaturated compound as shown by glpc.

Registry No.—**1**, 15044-22-1; **3**, 15042-62-3; **4**, 13698-14-1; **5**, 15042-64-5; **6**, 15042-65-6; **7**, 15042-66-7; **8**, 762-07-2; **9**, 15042-67-8; **9a** (*erythro*), 15042-68-9; **9a** (*threo*), 15042-72-5; **10**, 15042-69-0; DCU, 13698-16-3; 2-*t*-butylaziridine, 13639-44-6.

The Isomerization and Cyclization of Octatrienes

E. A. ZUECH, D. L. CRAIN, AND R. F. KLEINSCHMIDT

Phillips Petroleum Company, Research and Development Department, Bartlesville, Oklahoma 74003

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Interactions of the readily available mixture of 1,3,6- and 1,3,7-octatrienes with the alkali metal salts of alkyl amides have resulted in both a selective isomerization and a cyclization. In the first instance, potassium salts have selectively transformed the 1,3,6-octatrienes to 2,4,6-octatrienes and, in the second, the octatriene mixture has been converted into methylcycloheptadienes (IV). By a series of glpc and nmr determinations and by conversion to a Diels–Alder derivative, the dienes IV have been shown to be composed primarily of 1-methyl- and 2-methyl-1,3-cycloheptadiene.

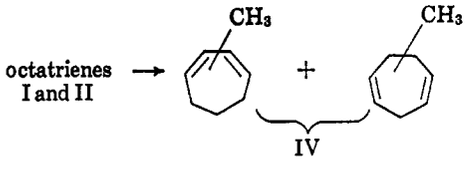
The field of hydrocarbon acidity, proton exchange, and carbanions has been and remains an extremely active one in current research.[1] In this connection, we have observed that the linear trienes, 1,3,6-octatrienes (I) and 1,3,7-octatrienes (II), will undergo some unusual reactions upon treatment with strong bases. On the one hand, I in mixtures of these trienes has been found to be selectively isomerized, while, on the other, both isomers have been found to cyclize.

A mixture of 49% of I and 49% of II (2% of 4-vinylcyclohexene impurity) upon interaction with piperidinopotassium gave a product containing 46% of 2,4,6-octatrienes (III) and 48% of recovered II (eq 1). Only a trace of nondistillables was observed.

$$\underset{\text{I}}{CH_2{=}CH{-}CH{=}CH{-}CH_2{-}CH{=}CH{-}CH_3} + \underset{\text{II}}{CH_2{=}CH{-}CH{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2} \longrightarrow \underset{\text{III}}{CH_3{-}CH{=}CH{-}CH{=}CH{-}CH{=}CH{-}CH_3} + \underset{\text{II}}{CH_2{=}CH{-}CH{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2} \quad (1)$$

This selective isomerization appears to be general with potassium compounds of alkyl monoamines, since diethylaminopotassium and 1,1 3,3-tetramethylbutylaminopotassium were found to be equally as effective. The reaction proceeds slowly at room temperature and rapidly near 100°. Just as the compounds I and II were mixtures of at least two configurational isomers, the resultant triene III was composed of three isomers which were readily resolved by gas–liquid partition chromatography (glpc). The two major components were isolated and identified by their infrared spectra.

This selective isomerization was not observed when sodium alkyl amides were employed; instead, both I and II were consumed to give new products. These products were found to be the result of a unique cyclization which furnished a mixture of isomeric methylcycloheptadienes (IV) (eq 2). The presence of



(2)

the seven-membered ring was readily demonstrated since upon hydrogenation exactly 2 moles of hydrogen were absorbed to give methylcycloheptane. This cyclization has been effected under a variety of conditions. Treatment of a mixture of octatrienes (neat) with piperidinosodium at room temperature for 19 hr gave IV in 43% yield, along with the formation of higher molecular weight materials. When the octa-

(1) (a) A. I. Shatenshtein, "Advances in Physical Organic Chemistry," Vol. 1, V. Gold, Ed., Academic Press Inc., New York, N. Y., 1963, p 155; (b) A. Streitwieser, Jr., and J. H. Hammons, "Progress in Physical Organic Chemistry," Vol. 3, S. G. Cohen, A. Streitwieser, Jr., and R. W. Taft, Ed., Interscience, Publishers, Inc., New York, N. Y., 1965, p 41.