[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, WEIZMANN INSTITUTE OF SCIENCE]

# The Reactions of β-Hydroxyethylamides and β-Hydroxyethylcarbamates with Phosgene

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β-Hydroxyethylamides (I) on treatment with phosgene are converted to β-chloroethylamides (IV). Under similar experimental conditions β-hydroxyethylcarbamates (V) yield only N-carbalkoxy-2-oxazolidones (VII). The reaction mechanism is discussed.

Schroeter and Lewinski[1] were the first to observe the different response of urethans, as compared with that of amides, to the action of thionyl chloride

$$RCONH_2 + SOCl_2 \longrightarrow RCN$$

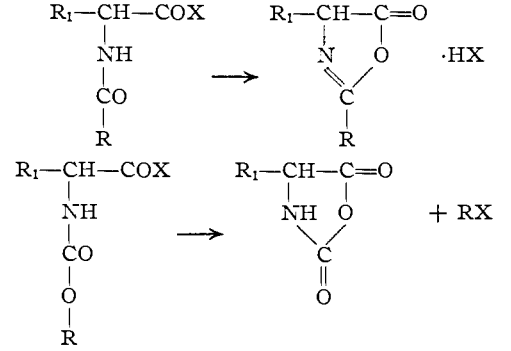
$$2C_2H_5OCONH_2 + SOCl_2 \longrightarrow H_2N{-}CONHCOOC_2H_5$$

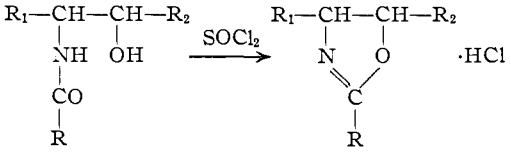
This observation was later confirmed by Raiford and Freyermuth[2] who suggested a mechanism to explain the behavior of urethans in this reaction. According to these authors, urethan is first cleaved by thionyl chloride to cyanic acid, ethyl chloride, sulfur dioxide and hydrogen chloride

$$C_2H_5OCONH_2 + SOCl_2 \longrightarrow HNCO + C_2H_5Cl + SO_2 + HCl$$

The cyanic acid formed reacts with a second urethan molecule to give the ethyl allophanate.

A similar difference in behavior toward electrophilic reagents is known in the intramolecular cyclizations of amino acid derivatives. Acylamino acid halides rearrange rapidly into the corresponding oxazolone hydrohalides,[3] whereas carbalkoxyamino acid halides afford, under similar conditions, 2,5-oxazolidinediones.[4] β-Hydroxyalkylamides resemble acylamino acids and are converted to oxazoline hydrochlorides on treatment with thionyl chloride.[5]



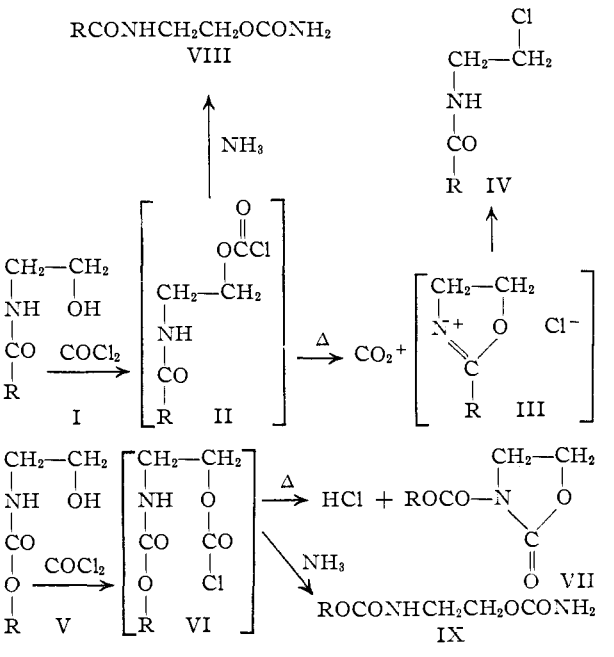


The reaction of one β-hydroxyalkylcarbamate with thionyl chloride was reported by Wenker[6] who found that *N*-(β-hydroxyethyl)-ethylcarbamate is converted to *N*-(β-chloroethyl)-ethylcarbamate on treatment with thionyl chloride

$$C_2H_5OCONH{-}CH_2CH_2OH + SOCl_2 \longrightarrow C_2H_5OCONHCH_2CH_2Cl$$

In the present paper the reactions of β-hydroxyethylamides and β-hydroxyethylcarbamates with phosgene as an electrophilic reagent are described (Chart I). β-Hydroxyethylamides (I) when treated in dioxane solution with phosgene and then heated on a water-bath afforded the corresponding β-chloroethylamides (IV) in over 80% yield (Table I). Under the same experimental conditions β-hydroxyethylcarbamates (V) were converted to *N*-carbalkoxy-2-oxazolidones (VII) in excellent yield (Table II). The β-chloroethylamides thus obtained were identical (mixed m.p.) with authentic samples prepared from β-chloroethylamine hydrochloride and the corresponding acyl chloride in aqueous alkaline solution. The *N*-carbalkoxy-2-oxazolidones showed two characteristic carbonyl absorption bands at 1800 and 1720 cm.$^{-1}$ in the infrared. *N*-Carbobenzyloxy-2-oxazolidone (VII, R = $C_7H_7$) was further degraded to 2-oxazolidone on catalytic hydrogenation and found to be identical (mixed m.p.) with 2-oxazolidone prepared according to Homeyer.[7]

CHART I



(1) G. Schroeter and M. Lewinski, *Ber.*, **26**, 2171 (1893).
(2) L. C. Raiford and H. B. Freyermuth, *J. Org. Chem.*, **8**, 174 (1943).
(3) H. E. Carter and J. W. Hinman, *J. Biol. Chem.*, **178**, 403 (1949).
(4) J. S. Fruton, *Advances in Protein Chem.*, **5**, 21 (1949).
(5) R. H. Wiley and L. L. Bennett, *Chem. Revs.*, **44**, 447 (1949).
(6) H. Wenker, THIS JOURNAL, **58**, 2608 (1936).
(7) A. H. Homeyer, U. S. Patent 2,399,118; *C.A.*, **40**, 4084 (1946).

If the reaction mixtures of *N*-(β-hydroxyethyl)-phenylacetamide (I, R = $C_7H_7$) or *N*-(β-hydroxyethyl)-benzylcarbamate (V, R = $C_7H_7$) with phosgene were poured into aqueous ammonia solution (instead of being heated on water-bath) they yielded β-phenylacetylaminoethylcarbamate (VII, R = $C_7H_7$) or β-carbobenzyloxyaminoethylcarbamate (IX, R = $C_7H_7$), respectively.

This observation, together with the isolation from *N*-(β-hydroxyethyl)-*p*-nitrobenzamide of a crystalline chlorocarbonate which decomposed on heating to yield *N*-(β-chloroethyl)-*p*-nitrobenzamide (IV, R = *p*-$O_2NC_6H_4$), shows the chlorocarbonates II and VI to be intermediates in the reaction of both amides and carbamates with phosgene.

β-Carbobenzyloxyaminoethylcarbamate (IX, R = $C_7H_7$) was further degraded, by the action of hydrogen bromide in glacial acetic acid,[8] to β-aminoethylcarbamate hydrobromide. The latter compound was converted on phenylacetylation to the β-phenylacetylaminoethylcarbamate, identical with VIII (R = $C_7H_7$).

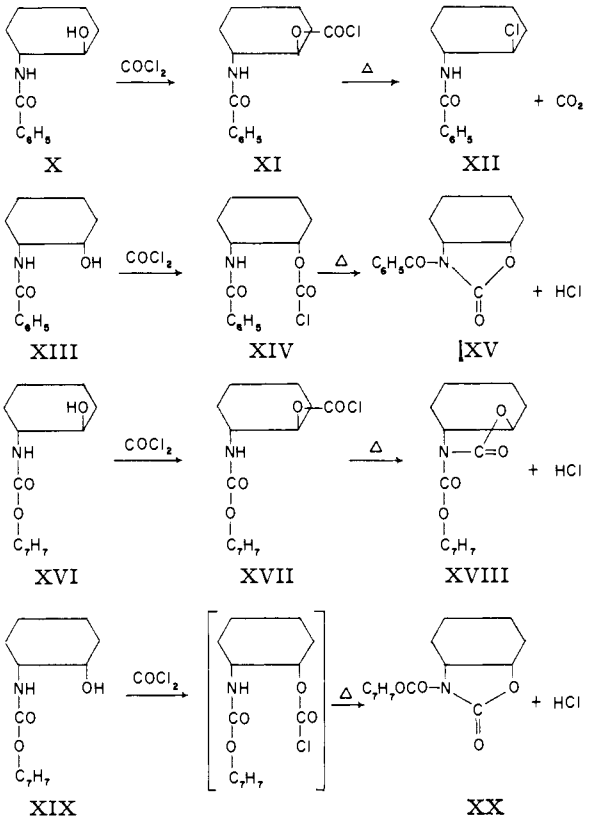
The postulation of oxazolinium chlorides III as intermediates in this reaction would best explain the thermal instability of β-acylaminoethyl chlorocarbonate (II) compared with either that of ethyl chlorocarbonate itself or that of β-chloroethyl chlorocarbonate. A neighboring group effect of this type is known in similar cases.[9] Oxazolinium chlorides were not isolated in the reaction discussed, probably since they are not stable under the conditions under which β-acylaminoethyl chlorocarbonates (II) decompose to yield β-chloroethylamides (IV). They are obtained from β-hydroxyalkylamides only when treated with thionyl chloride in the cold, whereas β-chloroalkylamides are the only products if refluxing thionyl chloride is used.[10]

In order to obtain further information as to the mechanisms of the reactions being discussed, the behavior of *cis*- and *trans-d,l*-β-benzoylaminocyclohexanol and -β-carbobenzyloxyaminocyclohexanol were examined. The results are summarized in Chart II.

*cis*- and *trans*-β-benzoylaminocyclohexanol (X, XIII) on treatment with phosgene afforded crystalline chlorocarbonates XI and XIV, which behaved differently on thermal decomposition. The *trans* isomer XI was converted to *trans*-β-benzoylaminocyclohexyl chloride on heating to 140° for five minutes or by refluxing a xylene solution for a short time. The only product isolated after refluxing a xylene solution of the *cis*-chlorocarbonate XIV was a chlorine-free compound (XV) which showed two carbonyl absorption bands at 1790 and 1680 cm.$^{-1}$ in the infrared. *N*-Benzoyl-2-oxazolidone, prepared by benzoylation of 2-oxazolidone, showed exactly the same absorption bands.

The *cis*- and *trans*-β-carbobenzyloxyaminocyclohexanol isomers (XVI, XIX) were converted, after treatment with phosgene and subsequent heating, into the corresponding 2-oxazolidone derivatives XVIII and XX. Both showed the characteristic carbonyl absorption bands of carbalkoxy-2-oxazolidones (VII) at 1800 and 1720 cm.$^{-1}$. The infrared spectra of the two isomers were not identical and a mixed melting point was depressed. Only the *trans*-chlorocarbonate XVII is stable above 100° and has been obtained as a crystalline compound.

CHART II




These observations support the suggested mechnisms (Chart I). In the case of *cis*-β-benzoylaminocyclohexyl chlorocarbonate (XIV) oxazolinium chloride formation is sterically not favored and therefore formation of an oxazolidone derivative XV is made possible. The *trans* isomer XI behaves normally and is converted on heating to *trans*-β-benzoylaminocyclohexyl chloride (XII). In the case of *trans*-β-carbobenzyloxyaminocyclohexyl chlorocarbonate (XVII) the steric effect is not strong enough to change the course of the reaction and a *trans*-oxazolidone (XVIII) has been obtained.

## Experimental[11]

**Preparation of β-Hydroxyethylamides.**—*N*-(β-Hydroxyethyl)-benzamide and *N*-(β-hydroxyethyl)-phenylacetamide were prepared by the general procedure of Phillips and Baltzly.[12] *N*-(β-Hydroxyethyl)-*p*-nitrobenzamide[13] was prepared from ethanolamine and *p*-nitrobenzoyl chloride in 82% yield by the general procedure of Leffler and Adams.[14]

**N-(β-Hydroxyethyl)-anisamide.**—The general procedure of Leffler and Adams[14] was used. The product melted at 105–106° after recrystallization from ethyl acetate; yield 78%.

*Anal.* Calcd. for $C_{10}H_{13}NO_3$: C, 61.5; H, 6.6; N, 7.1. Found: C, 61.6; H, 6.6; N, 7.4.

(8) D. Ben-Ishai and A. Berger, *J. Org. Chem.*, **17**, 1564 (1952).
(9) S. Winstein and R. Boschan, THIS JOURNAL, **72**, 4669 (1950).
(10) E. M. Fry, *J. Org. Chem.*, **14**, 887 (1949).
(11) All melting points are uncorrected.
(12) A. P. Phillips and R. Baltzly, THIS JOURNAL, **69**, 200 (1947).
(13) R. Hill and G. Powell, *ibid.*, **67**, 1462 (1945).
(14) M. T. Leffler and R. Adams, *ibid.*, **59**, 2259 (1937).

TABLE I

β-CHLOROETHYLAMIDES, R–CONH–$CH_2$–$CH_2$–Cl

| R | Formula | M.p., °C. | Yield, % | Chlorine, % Calcd. | Chlorine, % Found | Nitrogen, % Calcd. | Nitrogen, % Found |
|---|---|---|---|---|---|---|---|
| $C_6H_5$ | $C_9H_{10}ClNO$ | 105–106[10] | 90 | 19.4 | 19.8 | 7.6 | 7.3 |
| $C_6H_5CH_2$ | $C_{10}H_{12}ClNO$ | 78–79 | 90 | 17.9 | 17.4 | 7.1 | 7.2 |
| $C_7H_7OCONHCH_2$ | $C_{12}H_{15}ClN_2O_3$ | 115–116 | 84 | 13.3 | 13.3 | 10.4 | 10.2 |
| $p$-$O_2NC_6H_4$ | $C_9H_9ClN_2O_3$ | 124–125 | 81 | 15.5 | 15.6 | 12.3 | 12.4 |
| $p$-$CH_3OC_6H_4$ | $C_{10}H_{12}ClNO_2$ | 128–129 | 91 | 16.6 | 16.5 | 6.5 | 6.4 |

TABLE II

*N*-CARBALKOXY-2-OXAZOLIDONE (VII)

| R | Formula | M.p., °C. | Yield, % | Carbon, % Calcd. | Carbon, % Found | Hydrogen, % Calcd. | Hydrogen, % Found | Nitrogen, % Calcd. | Nitrogen, % Found |
|---|---|---|---|---|---|---|---|---|---|
| $C_2H_5$ | $C_6H_9NO_4$ | 51–52 | 95 | 45.3 | 45.3 | 5.7 | 5.8 | 8.8 | 8.5 |
| $C_3H_7$ | $C_8H_{11}NO_4$ | 53–54 | 92 | 48.6 | 48.5 | 6.4 | 6.6 | 8.1 | 7.9 |
| $C_3H_5$ | $C_7H_9NO_4$ | 41–42 | 90 | 49.1 | 49.0 | 5.3 | 5.4 | 8.2 | 8.1 |
| $C_6H_5CH_2$ | $C_{11}H_{11}NO_4$ | 101–102 | 89 | 59.7 | 59.5 | 5.0 | 4.8 | 6.3 | 5.9 |
| $p$-$O_2NC_6H_4CH_2$ | $C_{11}H_{10}N_2O_6$ | 171–173 | 82 | 49.6 | 49.8 | 3.8 | 3.7 | 10.5 | 9.9 |

**N-(β-Hydroxyethyl)-carbobenzyloxyglycineamide.**—A solution of 10 g. of ethyl carbobenzyloxyglycinate and 6 g. of ethanolamine in 50 ml. of ethanol was refluxed for one hour and then distilled *in vacuo* to dryness. The solid residue was crystallized from ethyl acetate, giving 7 g. (66%) of colorless leaflets, m.p. 113–114°.

*Anal.* Calcd. for $C_{12}H_{16}N_2O_4$: C, 57.1; H, 6.4; N, 11.1. Found: C, 57.3; H, 6.2; N, 10.9.

**N-(β-Hydroxyethyl)-allylcarbamate.**—A mixture of 30.5 g. (0.5 mole) of ethanolamine and 75 g. (0.75 mole) of powdered potassium bicarbonate in 250 ml. of methylene chloride was cooled in an ice-bath and, while stirring, 60.3 g. (0.5 mole) of allyl chlorocarbonate was added over a period of one hour. The potassium salts were filtered off, washed with more methylene chloride and the washings added to the filtrate. The solvent was removed *in vacuo* and the oily residue distilled. The yield was 62 g. (84%), b.p. 122–123° (0.8 mm.), $n^{25}D$ 1.4704.

*Anal.* Calcd. for $C_6H_{11}NO_3$: C, 49.6; H, 7.6; N, 9.7. Found: C, 49.2; H, 7.4; N, 10.0.

*N*-(β-Hydroxyethyl)-ethylcarbamate[15] and *N*-(β-hydroxyethyl)-propylcarbamate[16] were prepared in 73 and 78% yield as described above for the allyl derivative. *N*-(β-Hydroxyethyl)-benzylcarbamate was prepared from ethanolamine and benzyl chlorocarbonate by the method of Rose.[17]

**N-(β-Hydroxyethyl)-*p*-nitrobenzylcarbamate.**—This compound was prepared from ethanolamine and *p*-nitrobenzyl chlorocarbonate by the general procedure of Leffler and Adams.[14] The product melted at 102–103° after recrystallization from ethyl acetate; yield 68%.

*Anal.* Calcd. for $C_{10}H_{12}N_2O_5$: C, 50.0; H, 5.0; N, 11.7. Found: C, 50.4; H, 5.3; N, 11.5.

**Reaction of β-Hydroxyethylamides with Phosgene. General Procedure.**—A suspension of 5 g. of the amide in 25 ml. of dry dioxane was saturated with phosgene for half an hour. During the reaction the temperature rose to 40° and the starting material dissolved. The excess phosgene was removed by bubbling dry carbon dioxide through the solution, the dioxane was evaporated under reduced pressure and the residue was heated on the water-bath for another hour. The β-chloroethylamides thus obtained were crystallized from ethyl acetate–heptane (Table I).

**β-*p*-Nitrobenzoylaminoethyl Chlorocarbonate.**—*N*-(β-Hydroxyethyl)-*p*-nitrobenzamide (10 g.) was suspended in 50 ml. of dry dioxane and treated with phosgene as described above (general procedure). The chlorocarbonate melted at 106–107° dec. after recrystallization from benzene; yield 8 g. (62%).

*Anal.* Calcd. for $C_{10}H_9ClN_2O_5$: Cl, 13.0; N, 10.3. Found: Cl, 12.6; N, 10.6.

**Reaction of β-Hydroxyethylcarbamates with Phosgene.**—A solution of 5 g. of the carbamate in 25 ml. of dry dioxane was treated with phosgene as described above (general procedure). The *N*-carbalkoxy-2-oxazolidones thus obtained were recrystallized from ethyl acetate–heptane (Table II)).

**β-Phenylacetylaminoethylcarbamate** (VIII, R = $C_7H_7$).—*N*-(β-Hydroxyethyl)-phenylacetamide (5 g.) dissolved in 20 ml. of dry dioxane was treated with phosgene as described above (general procedure). After removal of the excess phosgene, the solution was poured into aqueous ammonia containing crushed ice. The white precipitate thus obtained was filtered and crystallized from ethanol–water. The product melted at 161–162°; yield 3.7 g. (58%).

*Anal.* Calcd. for $C_{11}H_{14}N_2O_3$: C, 59.5; H, 6.4; N, 12.6. Found: C, 59.4; H, 6.4; N, 12.4.

**β-Carbobenzyloxyaminoethylcarbamate** (IX, R = $C_7H_7$).—The procedure just described was repeated using 10 g. of N-(β-hydroxyethyl)-benzylcarbamate dissolved in 30 ml. of dioxane. The product melted at 115–116° after recrystallization from ethanol–water; yield 11 g. (92%).

*Anal.* Calcd. for $C_{11}H_{14}N_2O_4$: C, 55.5; H, 5.9; N, 11.7; Found: C, 55.8; H, 5.7; N, 11.4.

**β-Aminoethylcarbamate Hydrobromide.**—β-Carbobenzyloxyaminoethylcarbamate was treated with hydrogen bromide in glacial acetic acid.[8] The hydrobromide melted at 147–148° after recrystallization from alcohol–ether; yield 84%.

*Anal.* Calcd. for $C_3H_9BrN_2O_2$: Br, 43.1; N, 15.1. Found: Br, 42.7; N, 14.8.

**2-Oxazolidone.**—*N*-Carbobenzyloxy-2-oxazolidone (2 g.) was suspended in 60 ml. of alcohol and catalytically hydrogenated under 4 atm. pressure and in the presence of 10% palladized charcoal (0.2 g.). After three hours, the solution was filtered from the catalyst and evaporated *in vacuo* to dryness. The product melted at 89° after recrystallization from benzene and this m.p. was not depressed on admixture with an authentic sample of 2-oxazolidone.[7] The yield was 0.68 g. (86%).

**Preparation of 2-Aminocyclohexanol Derivatives.** ***d,l-trans*-2-Benzoylaminocyclohexanol X.**—The procedure of McCasland, Clark and Carter was used.[14,18] The product melted at 174–175° after recrystallization from ethyl acetate.

***d,l-cis*-2-Aminocyclohexanol Hydrochloride.**—*d,l-trans*-2-Benzoylaminocyclohexanol (X) was converted to *d,l-cis*-2-aminocyclohexanol by the method of Johnson and Schubert.[19]

***d,l-cis*-2-Benzoylaminocyclohexanol (XIII).**—The procedure of McCasland, Clark and Carter was used.[18] The product melted at 188–189° after recrystallization from ethyl acetate.

***d,l-trans*-2-Carbobenzyloxyaminocyclohexanol (XVI).**—This compound was prepared from *d,l-trans*-2-aminocyclohexanol and benzyl chlorocarbonate by the Schotten–Baumann procedure. The product melted at 101–102° after recrystallization from heptane; yield 84%.

*Anal.* Calcd. for $C_{14}H_{19}NO_3$: C, 67.4; H, 7.6; N, 5.6. Found: C, 67.2; H, 7.4; N, 5.7.

(15) A. P. M. Francimont and A. Lublin, *Rec. trav. chim.*, **21**, 45 (1902).

(16) K. Hess and Cl. Uibrig, *Ber.*, **48**, 1974 (1915).

(17) W. G. Rose, THIS JOURNAL, **69**, 1384 (1947).

(18) G. E. McCasland, R. K. Clark and H. E. Carter, *ibid.*, **71**, 637 (1949).

(19) W. S. Johnson and E. N. Schubert, *ibid.*, **72**, 2187 (1950).

*d,l-cis*-2-Carbobenzyloxyaminocyclohexanol (XIX).—*d,l-cis*-2-Aminocyclohexanol was carbobenzoxylated as described above for the *trans* isomer. The product melted at 72–73° after recrystallization from heptane; yield 88%.

*Anal.* Calcd. for $C_{14}H_{19}NO_3$: C, 67.4; H, 7.6; N, 5.6. Found: C, 67.4; H, 7.3; N, 5.5.

*d,l-trans*-2-Benzoylaminocyclohexyl Chlorocarbonate (XI).—One gram of the benzamido alcohol X was suspended in 15 ml. of dry dioxane and treated with phosgene as described above (general procedure). After removal of the solvent the residue was recrystallized from benzene–petroleum ether and melted at 134° dec. The yield was 1.1 g. (90%).

*Anal.* Calcd. for $C_{14}H_{16}ClNO_3$: Cl, 12.6; N, 5.0. Found: Cl, 12.7; N, 5.3.

*d,l-trans*-2-Benzoylaminocyclohexyl Chloride (XII).—This compound was obtained in 64% yield by heating the chlorocarbonate XI to 140° for 5 minutes in an oil-bath. The product melted at 165–166° after recrystallization from benzene and this m.p. was not depressed on admixture with a sample prepared according to Johnson and Schubert.[19]

*d,l-cis*-Benzoylaminocyclohexyl Chlorocarbonate (XIV).—The procedure described above for the preparation of the *trans* isomer was used. The product melted at 112–113° dec. after recrystallization from benzene–petroleum ether; yield 88%.

*Anal.* Calcd. for $C_{14}H_{16}ClNO_3$: Cl, 12.6; N, 5.0. Found: Cl, 12.9; N, 5.3.

N-Benzoyl-*d,l-cis*-4,5-cyclohexano-2-oxazolidone (XV).—This compound was obtained by refluxing a xylene solution of the chlorocarbonate XIV for 3 hours and distillation *in vacuo* to dryness. The product melted at 114–115° after recrystallization from hexane; yield 74%.

*Anal.* Calcd. for $C_{14}H_{15}NO_3$: C, 68.6; H, 6.1; N, 5.7. Found: C, 68.8; H, 5.8; N, 5.8.

N-Benzoyl-2-oxazolidone.—2-Oxazolidone was benzoylated by the procedure of Close.[20] The product melted at 171–172° after recrystallization from ethyl acetate–hexane; yield 54%.

*Anal.* Calcd. for $C_{10}H_{10}NO_3$: N, 7.3. Found: N, 7.1.

*d,l-trans*-2-Carbobenzyloxyaminocyclohexyl Chlorocarbonate (XVII).—One gram of the carbobenzyloxaminoalcohol XVI was dissolved in 10 ml. of dry dioxane and treated with phosgene as described above. The chlorocarbonate melted at 112–113° dec. after recrystallization from heptane; yield 1.05 g. (85%).

*Anal.* Calcd. for $C_{15}H_{15}ClNO_4$: Cl, 11.4; N, 4.5. Found: Cl, 11.6; N, 4.6.

N-Carbobenzyloxy-*d,l-trans*-4,5-cyclohexano-2-oxazolidone (XVIII).—This compound was obtained by refluxing a xylene solution of the chlorocarbonate XVII for one hour and distillation *in vacuo* to dryness. The product melted at 88–89° after recrystallization from ethyl acetate–hexane: yield 80%.

*Anal.* Calcd. for $C_{15}H_{17}NO_4$: C, 65.5; H, 6.2; N, 5.1. Found: C, 65.9; H, 6.2; N, 5.2.

N-Carbobenzyloxy-*d,l-cis*-4,5-cyclohexano-2-oxazolidone (XX).—One gram of the carbobenzyloxyaminoalcohol XIX was dissolved in 10 ml. of dioxane and treated with phosgene as described above. The oily residue left after evaporation of the solvent was heated for 2 hours on a water-bath. The product melted at 92–93° after recrystallization from heptane; yield 0.9 g. (82%).

*Anal.* Calcd. for $C_{15}H_{17}NO_4$: C, 65.5; H, 6.2; N, 5.1. Found: C, 65.9; H, 6.4; N, 5.4.

(20) W. J. Close, THIS JOURNAL, **73**, 95 (1951).

REHOVOTH, ISRAEL

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[CONTRIBUTION FROM THE ROHM & HAAS COMPANY]

# *t*-Carbinamines, $RR'R''CNH_2$. IV. The Addition of Isothiocyanic Acid to Olefinic Compounds[1]

BY LEO S. LUSKIN, G. E. GANTERT AND W E CRAIG

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Isothiocyanates were obtained by addition of isothiocyanic acid to diisobutylene, styrene and α-methylstyrene. Similar addition to acrylic esters gave 3-thiocyanatopropionates.

The addition of isothiocyanic acid to unsaturated hydrocarbons[2] and α,β-unsaturated ketones[3] has been reported to give thiocyanates or isothiocyanates. However, the identification of the products often has been confusing. The possibility of the formation of mixtures also has been recognized, but these have been carefully examined only in the products obtained from isobutylene.[2c]

The addition of isothiocyanic acid to several olefins has now been studied. The structure of the resulting products was determined by physical examination and by comparison with the compounds obtained by alternative methods.

In the addition reactions, nascent isothiocyanic acid was generated by the addition of aqueous sulfuric acid to sodium thiocyanate slurried with the olefin. Successful additions were achieved with typical branched aliphatic and aromatic olefins and with acrylic esters (Table I). Attempts to extend the reaction to acrylonitrile and to methacrylates failed.

Infrared spectrophotometry was used to distinguish possible thiocyanates which have a strong, very sharp *peak* at 2130–2160 cm.$^{-1}$ [4] while isothiocyanates show a broad, very strong *band* at 2040 to 2180 cm.$^{-1}$.[5] When measured in dilute

(1) Presented at the Delaware Valley Regional Meeting of the American Chemical Society, Philadelphia, Penna., February 16, 1956.

(2) (a) F. Challenger, A. L. Smith and F. J. Patton, *J. Chem. Soc.*, **123**, 1046 (1923); (b) W. Lee, U. S. Patent 1,992,533; (c) M. S. Kharasch, E. M. May and F. R. Mayo, THIS JOURNAL, **59**, 1580 (1937); E. M. May, Ph.D. Thesis, University of Chicago, 1938; (d) H. Bruson and T. W. Riener, U. S. Patent 2,393,746; (e) H. Bruson, U. S. Patents 2,395,454, 2,395,456 and 2,411,869; (f) R. F. Naylor, *J. Chem. Soc.*, 247 (1945).

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(4) W. Gordy and D. Williams, *J. Chem. Phys.*, **3**, 664 (1935); **4**, 85 (1936); F. Pristera, *Appl. Spectroscopy*, **6**, No. 3, 29 (1952); E. C. Taylor, Jr., J. Wolinsky and H. Lee, THIS JOURNAL, **76**, 1866 (1954); National Research Council–National Bureau of Standards Compound Cards No. 481 to 483; Sadtler Infrared Spectra No. 3104 to 3115, 5753, etc. In our work, ethyl thiocyanate was used as a standard, peak at 2160 cm.$^{-1}$.

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