

d,l-cis-2-Carbobenzyloxyaminocyclohexanol (XIX).—*d,l*-cis-2-Aminocyclohexanol was carbobenzyloxylated 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-Benzoylamino-cyclohexyl 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 $C_{14}H_{18}ClNO_3$: Cl, 12.6; N, 5.0. Found: Cl, 12.7; N, 5.3.

d,l-trans-2-Benzoylamino-cyclohexyl 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-Benzoylamino-cyclohexyl 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 $C_{14}H_{18}ClNO_3$: 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 $C_{14}H_{17}NO_3$: 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 $C_{16}H_{18}ClNO_4$: 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 carbobenzyloxaminoalcohol 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).

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[CONTRIBUTION FROM THE ROHM & HAAS COMPANY]

t-Carbinamines, RR'R''CNH₂. IV. The Addition of Isothiocyanic Acid to Olefinic Compounds¹

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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 hydrocarbons² and α,β -unsaturated ketones³ 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 sul-

furic 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

(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} .

(5) W. Gordy and D. Williams, *J. Chem. Phys.*, **4**, 85 (1936); D. Williams, *ibid.*, **8**, 513 (1940); J. Carol and L. L. Ramsey, *J. Assoc. Offic. Agr. Chemists*, **36**, 967 (1953); R. A. Ludwig, G. D. Thorn and C. H. Unwin, *Can. J. Botany*, **33**, 42 (1955); M. G. Ettlinger and J. E. Hodgkins, *THIS JOURNAL*, **77**, 1831 (1955); M. G. Ettlinger and A. J. Lundeen, *ibid.*, **78**, 1952 (1956). In this work, *t*-butyl isothiocyanate^{6b} was used as a standard, peaks at 2090 and 2000 cm^{-1} . A similar shift in location has been observed for nitriles and isonitriles; J. J. McBride and H. C. Beachell, *THIS JOURNAL*, **74**, 5247 (1952); D. Samuel, B. Weintraub and D. Ginsburg, *J. Org. Chem.*, **21**, 376 (1956).

(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).

(3) H. Bruson, U. S. Patent 2,395,453; R. A. Mathes, F. D. Stewart and F. Swedish, Jr., *THIS JOURNAL*, **70**, 1452 (1948).

carbon tetrachloride, the isothiocyanate band peaked at $2095 \pm 15 \text{ cm}^{-1}$ and, in many cases, also showed a second weak peak at 2000 cm^{-1} . The above products obtained from the hydrocarbons (except trimethylethylene) showed almost exclusive isothiocyanate absorption. Those prepared from acrylic esters showed almost exclusively the thiocyanate peak. Very small inflections near the site of the alternative peaks suggested the possible presence of small amounts of the isomers in each case. The isomeric peaks were not observed in the spectra of the compounds prepared by alternative methods. Attempts to demonstrate the presence of thiocyanate in the isothiocyanate products by chemical means failed.

Molar refractions based on Vogel's constants⁶ were helpful in certain cases. The molar refraction of the mixed product obtained from trimethylethylene, compared with those of the individual *t*-amyl isomers, indicated a predominance of the thiocyanate form.⁷ The mixture was not further examined.

Comparison of the boiling points of the products obtained from acrylates to those of the known α -substituted propionates⁸ and measurement of molar refraction indicated a β -thiocyanato structure.

The isothiocyanates were also prepared from the corresponding amines by the customary decomposition of the dithiocarbamates.⁹ *t*-Amyl and *t*-octyl thiocyanates were obtained from the corresponding mercaptans by treatment of the lead mercaptides with cyanogen chloride.^{2c} The reaction of aqueous sodium thiocyanate with β -bromopropionates gave the corresponding β -thiocyanatopropionates (Table II). Comparison of the properties of these compounds with those of the addition products established the structure of the latter.

Thiourea derivatives were produced from the isothiocyanates by treatment with amines. Alkaline hydrolysis gave the symmetrical disubstituted thioureas.^{9b,10}

A brief study of the method of preparation of *t*-octyl isothiocyanate was made. The best result was obtained in half-mole runs with 73% sulfuric acid in some excess added slowly to an equimolar mixture of sodium thiocyanate and diisobutylene at $40\text{--}60^\circ$. Potassium thiocyanate gave somewhat lower yields, while ammonium thiocyanate was a definitely inferior reagent. The importance of stirring and contact in this heterogeneous reaction system was suggested by somewhat reduced yields obtained in larger runs.

Some indications concerning the mechanisms of these reactions were obtained. In general, the re-

sults parallel the substitution reactions of ambident ions.¹¹ May has shown that the formation of the two species is independent and concurrent.^{2c}

The isothiocyanates are similar in skeletal structure to the addition products obtained from olefins and other acidic substances. Their formation must therefore proceed by attack of a carbonium ion on the ambident thiocyanate ion. The proportion of isothiocyanate therefore measures the carbonium ion character of each addition and the stability of carbonium ion generated from each olefinic substrate. By analogy with similar reactions of ambident ions, there must be a preferential distribution of the negative charge of the thiocyanate ion toward the nitrogen atom.

Acrylic esters do not form carbonium ions. The thiocyanate product indicates attack by the more nucleophilic sulfur atom in a process resembling a nucleophilic displacement in which the leaving group may be considered to be the electron pair.

Experimental¹²

***t*-Octyl Isothiocyanate.**—To a vigorously stirred slurry of diisobutylene (56 g., 0.5 mole) and sodium thiocyanate (42 g., 0.5 mole), 73% sulfuric acid (50 g., 0.75 mole) was added during two hours at $40\text{--}45^\circ$. Stirring was continued for 6 hours. Water (200 ml.) was then added and the upper layer was separated, filtered if necessary, washed with dilute sodium carbonate and water, and dried over magnesium sulfate. Distillation gave 57 g. (66%) of almost colorless liquid, b.p. $83\text{--}85^\circ$ (12 mm.).

Other addition reactions were run in a similar manner (Table I).

The isothiocyanates were also prepared from the amines via the dithiocarbamate⁹ (Table II).

***t*-Amyl Thiocyanate.**—A solution of lead acetate (76 g.) in 50% aqueous alcohol (600 ml.) was added to 85% *t*-amyl mercaptan (49 g., 0.39 mole) in 95% ethanol (300 ml.). The bright yellow mercaptide was collected, washed with alcohol, and dried in a vacuum desiccator; yield 44 g. Cyanogen chloride (18.5 g., 0.30 mole) was added to a mixture of the mercaptide (41.3 g., 0.10 mole) and anhydrous ether (160 ml.) at 10° in a pressure bottle. The stoppered bottle was stored for 3 days in the refrigerator. After removal of lead chloride, the filtrate was distilled to give 18 g. (30%) of a colorless oil, b.p. $57\text{--}60^\circ$ (10 mm.).

***t*-Octyl thiocyanate** was prepared similarly (Table II).

Ethyl 3-Thiocyanatopropionate.—A mixture of ethyl β -bromopropionate (45 g., 0.25 mole), sodium thiocyanate (41 g., 0.5 mole) and water (20 g.) was stirred and heated under reflux for 6 hours. The solids were filtered off and washed with benzene. The combined organic layers were washed with water, saturated aqueous sodium bicarbonate solution and water, then dried over calcium chloride. Distillation gave 23.5 g. (59%) of a pale yellow oil, b.p. $101\text{--}105^\circ$ (3 mm.).

Methyl 3-thiocyanatopropionate was obtained similarly (Table II).

1,1-Dimethyl-3- α -phenylethyl-2-thiourea.—A 40% aqueous solution of dimethylamine (15.8 g., 0.14 mole) was added to α -phenylethyl isothiocyanate (16.8 g., 0.10 mole) in ethanol (20 ml.) and heated at 70° overnight. The separated oil crystallized upon cooling to give a waxy solid, 15.7 g. (75%); recrystallized from carbon tetrachloride, m.p. $108\text{--}109^\circ$.

Anal. Calcd. for $\text{C}_{11}\text{H}_{16}\text{N}_2\text{S}$: N, 13.5; S, 15.4. Found: N, 13.6; S, 15.4.

1,1-Dimethyl-3-(α,α -dimethylbenzyl)-2-thiourea was obtained similarly as needles, m.p. $73\text{--}75^\circ$.

Anal. Calcd. for $\text{C}_{12}\text{H}_{18}\text{N}_2\text{S}$: N, 12.6; S, 14.4. Found: N, 12.4; S, 14.4.

(11) N. Kornblum, R. A. Smiley, R. K. Blackwood and D. C. Ifland, *THIS JOURNAL*, **77**, 6269 (1955).

(12) We wish to thank A. J. McFaul and Rita Cerruti for experimental assistance, T. P. Callan, Jr., and staff for analyses and Helen Miklas for infrared measurements.

(6) A. I. Vogel, *J. Chem. Soc.*, 1833 (1948); the molar refractive constant of *t*-octyl (1,1,3,3-tetramethylbutyl) is 37.85.

(7) It is possible that products with rearranged alkyl chains were also present.

(8) H. L. Wheeler and B. Barnes, *Am. Chem. J.*, **24**, 60 (1900); T. B. Johnson and A. A. Ticknor, *THIS JOURNAL*, **40**, 636 (1918).

(9) (a) M. L. Moore and F. S. Crossley in E. C. Horning, "Organic Syntheses," Coll. Vol. III, John S. Wiley & Sons, Inc., New York, N. Y., 1955, p. 599; (b) N. Bortnick, L. S. Luskin, M. D. Hurwitz and A. W. Rytina, *THIS JOURNAL*, 4358 (1956).

(10) O. Rundqvist, *Arch. Pharm.*, **236**, 472 (1898); J. Gadamer, *ibid.*, **237**, 99 (1899).

TABLE I
 PRODUCTS OF ADDITION OF ISOTHIOCYANIC ACID TO OLEFINS

Olefin	Product	Yield, %	$^{\circ}\text{C.}$	B.p., Mm.	n_D^{25}	d_4^{25}	Nitrogen, %		Sulfur, %	
							Calcd.	Found	Calcd.	Found
$(\text{CH}_3)_2\text{C}=\text{CHCH}_3$	Mixture ^a	30	73-78	29	1.470-1.474	0.928	10.9	10.7	24.8	24.6
$(\text{CH}_3)_3\text{CCH}=\text{C}(\text{CH}_3)_2$	$(\text{CH}_3)_3\text{CCH}_2\text{C}(\text{CH}_3)_2\text{NCS}$	66	83-85	12	1.4811	0.9045	8.2	8.0	18.8	18.6
$\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$	$\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{NCS}$	52	135-137	23	1.5784	1.0754	8.6	8.4	19.6	19.7
$\text{C}_6\text{H}_5(\text{CH}_3)=\text{CH}_2$	$\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2\text{NCS}$	66	82-86	23	1.5678	1.0565	7.9	7.8	18.1	17.6
$\text{CH}_2=\text{CHCOOCH}_3$	$\text{NCSCH}_2\text{CH}_2\text{COOCH}_3$	20	78-80	0.5	1.4772	1.1839	9.7	9.5	22.1	22.3
$\text{CH}_2=\text{CHCOOC}_2\text{H}_5$	$\text{NCSCH}_2\text{CH}_2\text{COOC}_2\text{H}_5$	38	124	10	1.4699 ^b	1.1381 ^b	8.8	8.6	20.1	20.0

^a Mixture of amyl thiocyanate and isothiocyante; $[M]_D$ calcd. for $\text{C}_5\text{H}_{11}\text{SCN}$, 37.64; for $\text{C}_5\text{H}_{11}\text{NCS}$, 39.82; found, 38.09.
^b At 20 $^{\circ}$.

 TABLE II
 THIOCYANATES AND ISOTHIOCYANATES

Compound	$^{\circ}\text{C.}$	B.p., Mm.	n_D^{25}	d_4^{25}	Nitrogen, %		Sulfur, %	
					Calcd.	Found	Calcd.	Found
$\text{C}_2\text{H}_5\text{C}(\text{CH}_3)_2\text{SCN}$	57-60	10	1.4620 ^a	0.9369 ^a	10.9	10.7
$\text{C}_2\text{H}_5\text{C}(\text{CH}_3)_2\text{NCS}$	67-72	23	1.4820 ^a	.9198 ^a	10.9	10.4
$(\text{CH}_3)_3\text{CCH}_2\text{C}(\text{CH}_3)_2\text{SCN}$	88-92	10	1.4749 ^a	.926 ^a	8.2	8.3
$(\text{CH}_3)_3\text{CCH}_2\text{C}(\text{CH}_3)_2\text{NCS}^b$	108-112	28	1.4811	0.9043	8.2	8.0	18.8	18.8
$\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{NCS}$	133-134	20	1.5780	1.0719	8.6	8.3	19.6	19.5
$\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2\text{NCS}$	83	0.7	1.5670	1.0537	7.9	7.9	18.1	17.9
$\text{CH}_3\text{OOCCH}_2\text{CH}_2\text{SCN}$	73-76	0.3	1.4770	1.1840	9.7	9.6	22.1	22.4
$\text{C}_2\text{H}_5\text{OOCCH}_2\text{CH}_2\text{SCN}$	101-105	3	1.4678	1.1281	8.8	8.7	20.1	20.0

^a At 20 $^{\circ}$.

1,3-Bis-(α -phenylethyl)-2-thiourea.— α -Phenylethyl isothiocyante (56 g., 0.34 mole) was heated under reflux with 20% aqueous sodium hydroxide solution (100 g., 0.5 mole) for 6 hours. Crystals gradually deposited on standing. They were collected (42 g., 87%) and recrystallized from ether, m.p. 158-159 $^{\circ}$.¹³

Anal. Calcd. for $\text{C}_{17}\text{H}_{20}\text{N}_2\text{S}$: N, 9.9; S, 11.3. Found: N, 9.6; S, 11.4.

(13) A. Michaelis and E. Linow, *Ber.*, **26**, 2168 (1893), reported m.p. 163 $^{\circ}$.

1,3-Bis-(α,α -dimethylbenzyl)-2-thiourea, m.p. 150-152 $^{\circ}$, was obtained similarly but required 48 hours heating. The yield was low.

Anal. Calcd. for $\text{C}_{19}\text{H}_{24}\text{N}_2\text{S}$: N, 9.0. Found: N, 8.7.

Infrared absorption was measured with a Perkin-Elmer spectrophotometer, model 21, using sodium chloride prisms. Ethyl thiocyanate and *t*-butyl isothiocyante^{2b} were reference compounds.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, NORTHWESTERN UNIVERSITY]

The Mechanism of γ -Bromoester Pyrolysis

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It has been shown that the pyrolysis of a γ -bromoester to form lactone and alkyl bromide proceeds with inversion of configuration both in the formation of the new carbon-oxygen bond and in the formation of the new carbon-bromine bond. This has been interpreted as indicating an ionic two-stage mechanism for this reaction.

The pyrolysis of γ -bromoesters to form γ -lactones and alkyl bromides has been known for many years.¹ A more recent example was the observation of Linstead and Mead² that a sample of ethyl 2-bromocyclopentaneacetate was unstable at room temperature and that on heating it gave ethyl bromide, 2-hydroxycyclopentaneacetic acid lactone, hydrogen bromide and ethyl 1-cyclopentene-1-acetate. This reaction was investigated by Kharasch³ during his classical work on the free radical addition of α -bromoesters to olefins to form γ -bromoesters. He found that pyrolysis of aliphatic

γ -bromoesters proceeded smoothly at 160-180 $^{\circ}$ to give good yields of the corresponding γ -lactones and the alkyl bromide derived from the alcohol portion of the ester. In connection with another problem it became necessary for us to learn the mechanism of this reaction.

The stereochemistry of the replacement of bromine by oxygen during the pyrolysis was studied using alicyclic bromoesters. The required ethyl *trans*-2-bromocyclopentaneacetate was prepared by treating *cis*-2-hydroxycyclopentaneacetic acid lactone with hydrogen bromide in ethanol.² Since the replacement of oxygen by bromine in this reaction is a nucleophilic displacement,⁴ the product must be *trans*. The isomeric ethyl *cis*-2-bromocy-

(1) See C. D. Hurd, "The Pyrolysis of Carbon Compounds," The Chemical Catalog Co., (Reinhold Publ. Corp.), New York, N. Y., 1929, p. 550, for a review of the older literature.

(2) R. P. Linstead and E. M. Mead, *J. Chem. Soc.*, 935 (1934).

(3) M. S. Kharasch, P. S. Skell and P. Fisher, *THIS JOURNAL*, **70**, 1055 (1948).

(4) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 393.