evaporated, and the residue was distilled *in vacuo* to give compound Ia (24.1 g., 71.9%), b.p. 78–79° (1.5 mm.). The infrared spectrum in CCl_4 exhibited a carbonyl peak at 5.6 μ.

Anal. Calcd. for $C_3H_6Cl_3N_2OP$: C, 16.15; H, 2.70; Cl, 47.61; N, 12.53; P, 13.86. Found: C, 13.66; H, 2.65; Cl, 47.75; N, 12.00; P, 14.29.

2,4-Di-*n*-Butyl-1,1,1-trichloro-1,2,4-phosphadiazetidin-3-one (Ib).—Phosphorus pentachloride (23 g., 0.11 mole) was added to a solution of 1,3-di-*n*-butylurea (17.2 g., 0.1 mole) in carbon tetrachloride (180 ml.), the mixture was refluxed for 90 min. at 79–80° and then purged 10 min. with nitrogen, the solvent was evaporated, and the residue was distilled *in vacuo* to give compound Ib (21.8 g., 71%), b.p. 105–108° (0.3 mm.). The infrared spectrum (in CCl_4) exhibited a carbonyl peak at 5.6 μ.

Anal. Calcd. for $C_9H_{18}Cl_3N_2OP$: C, 35.14; H, 5.89; Cl, 34.58; N, 9.10; P, 10.07. Found: C, 35.36; H, 6.15; Cl, 34.53; N, 9.42; P, 9.84.

2-*n*-Butyl-4-phenyl-1,1,1-trichloro-1,2,4-phosphadiazetidin-3-one (Ic).—Phosphorus pentachloride (20.8 g., 0.1 mole) was added to a solution of 1-*n*-butyl-3-phenylurea (19.2 g., 0.1 mole) in carbon tetrachloride (200 ml.). Slight warming caused a vigorous reaction with hydrogen chloride evolution. The reaction mixture was refluxed for 90 min. with constant nitrogen purgation and the solvent was evaporated to give Ic as a viscous oil (31.7 g., 96%). The infrared spectrum (in CCl_4) exhibited a carbonyl peak at 5.6 μ.

Anal. Calcd. for $C_{11}H_{14}Cl_3N_2OP$: N, 8.55. Found: N, 8.87.

Refluxing in chlorobenzene resulted in rapid isocyanate and carbodiimide formation as evidenced by infrared absorption at 4.42 (—NCO) and 4.7 μ (—N=C=N—).

Reaction of 1-*p*-Toluenesulfonyl-3-*n*-butylurea and PCl_5.—Phosphorus pentachloride (2.1 g., 0.01 mole) was added to a solution of 1-*p*-toluenesufonyl-3-*n*-butylurea (2.7 g., 0.01 mole) in carbon tetrachloride (40 ml.) and the mixture was refluxed for 1 hr., after which time the hydrogen chloride evolution virtually stopped. The *n*-butyl isocyanate generated (0.8 g., 80.8% by titration with excess di-*n*-butylamine) was removed with the solvent, and the residue (3.1 g.) was recrystallized from carbon tetrachloride to give *p*-toluenesulfonyltrichlorophosphazene (2.35 g., 77%), m.p. 88–90°.[10] The infrared spectrum (in CCl_4) exhibited two characteristic SO_2 peaks at 7.43 and 8.63 μ.

Reaction of 1-Benzoyl-3-*n*-butylurea and PCl_5.—1-Benzoyl-3-*n*-butylurea (11 g., 0.05 mole) was added with stirring at room temperature to a solution of phosphorus pentachloride (10.4 g., 0.05 mole) in carbon tetrachloride (150 ml.). A rapid reaction ensued. The mixture was stirred for 60 min., nitrogen purged for 75 min., and fractionally distilled to give phosphorus oxychloride, *n*-butyl isocyanate (3.3 g., 66.7%, b.p. 115°), and benzonitrile (4.1 g., 82%, b.p. 41–44° at 1 mm.). The infrared spectrum of the carbon tetrachloride solution before distillation showed strong absorption at 4.45 (-NCO) and 4.5 μ (-CN).

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The Reaction of Oxalyl Chloride with Substituted Ureas and Thioureas

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Oxalyl chloride reaction with mono- and 1,3-dialkylureas gave the corresponding substituted parabanic acids while reaction with mono- and 1,3-dialkylthioureas afforded the novel thiazolidine-4,5-dione derivatives. Oxalyl chloride reaction with *p*-chlorobenzenesulfonyl-3-*n*-propylthiourea yielded *p*-chlorobenzenesulfonyl chloride and 1-*n*-propylthioparabanic acid.

Earlier studies have shown that the reaction of carbonyl chloride,[2a] thionyl chloride,[2b] and phosphorus pentachloride[3] with 1,3-di(primary alkyl)ureas gives rise to products formed *via* nitrogen attack, while reaction with 1,3-di(secondary alkyl)ureas[2] results in products formed from initial oxygen attack. Oxalyl chloride is reported to react with disubstituted alkylureas to afford either chloroformamidine hydrochlorides[4] or the corresponding parabanic acid derivatives.[5] Mono- and 1,3-dialkylthioureas were reported to react with oxalyl chloride to form thioparabanic acid derivatives,[5] a surprising result in view of the thiourea—acid chloride reactions which occur exclusively at the sulfur atom. These anomalous results led to our present studies on the oxalyl chloride reaction with ureas and thioureas.

Oxalyl chloride reactions with 1,3-disubstituted ureas having primary, secondary, and tertiary alkyl substituents unfailingly gave the corresponding 1,3-dialkylparabanic acid (IV) in high yield (see Table I). Product identification was made on the basis of elemental analysis and infrared spectral evidence. In some cases the parabanic acid was independently synthesized from the corresponding carbodiimide and oxalyl chloride.

Although the reaction of carbodiimides with both acetyl[6] and carbonyl[7,8] chlorides is known to be general, the only carbodiimide reported to have reacted with oxalyl chloride is diisopropylcarbodiimide.[9] Our results indicate the existence of a general oxalyl chloride and alkyl- or arylcarbodiimide reaction which affords the corresponding 1,1-parabanyl dichloride III (see Scheme I). Evidence for structural assignment included C=O absorption at 1760 cm.$^{-1}$ and the absence of both -C=N and a second C=O group in the infrared spectra. The geminate dichlorides III were readily hydrolyzed to the corresponding parabanic acids (IV).

The mechanism for the oxalyl chloride–1,3-dialkylurea reaction may involve initial oxygen attack similar to that which occurs in both the carbonyl chloride–

(1) To whom inquiries should be directed.

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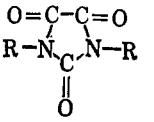
TABLE I

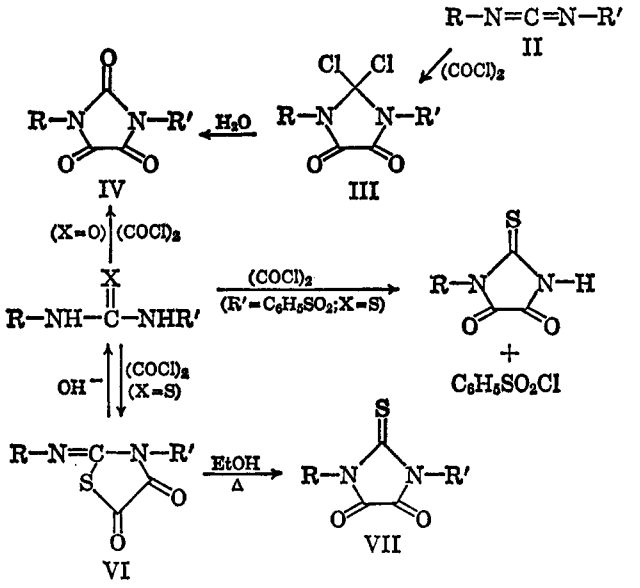
1,3-DIALKYLPARABANIC ACIDS (IV)



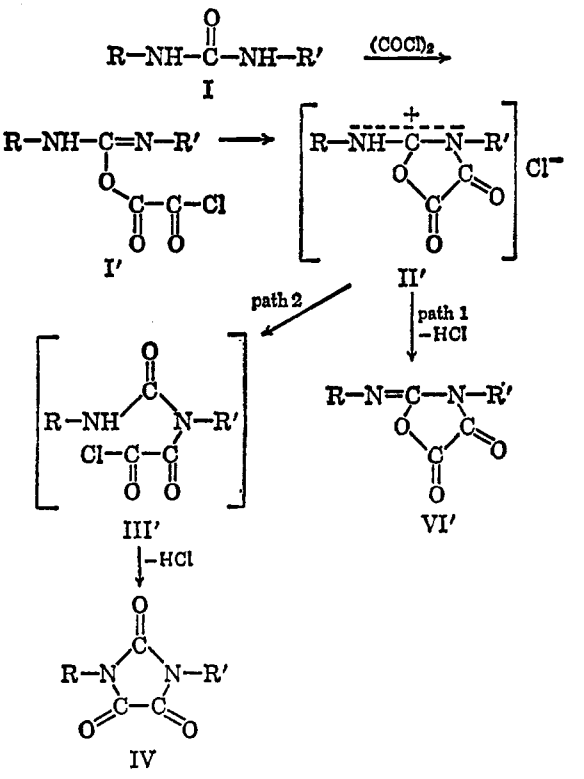
Compd.	R	M.p., °C.	Yield, %	$\nu_{C=O}$,[a] cm.$^{-1}$	Formula	Calcd., % C	H	N	Found, % C	H	N
IVa	Isopropyl	88–90[b,c]	99	1780,[d] 1745	$C_9H_{14}N_2O_3$	...	...	...	...	...	...
IVb	*n*-Butyl	28–29	81.4	1790,[d] 1743	$C_{11}H_{18}N_2O_3$	...	...	12.38	...	...	12.10
		183–185[e]									
IVc	*t*-Butyl	95[b]	95.6	1790,[d] 1745	$C_{11}H_{18}N_2O_3$	...	...	12.38	...	...	12.56
IVd	Cyclohexyl	174–175[b]	96	1730 ($CHCl_3$)	$C_{15}H_{22}N_2O_3$	64.72	7.97	10.07	64.64	8.17	10.37

[a] Infrared spectra in KBr. [b] Recrystallized from isopropyl alcohol. [c] Lit.[9] m.p. 93–94°. [d] Shoulder. [e] Boiling point at 1.5 mm.

SCHEME I



SCHEME II



dialkylurea[2a] and the oxalyl chloride–N-monosubstituted acid amide[10] reactions. The intermediate (I′) could cyclize to the oxazolidinium salt (II′) which in turn could either (1) lose HCl directly to form VI′; or (2) be attacked by chloride ion to give III′ which in turn loses HCl to afford the observed product IV. Chloride ion attack on II′ is apparently faster than HCl elimination from II′, as no evidence for 2-alkylimino-3-alkyloxazolidine-4,5-dione (VI′) formation was found. (See Scheme II.)

Oxalyl chloride reaction with 1,3-di-*n*-butylthiourea in ethylene dichloride gave a liquid product which exhibited C=O infrared absorption at 1755 cm.$^{-1}$ and -C=N absorption at 1660 cm.$^{-1}$ and which regenerated the 1,3-di-*n*-butylthiourea on hydrolysis with dilute NaOH. Both these observations and elemental analysis are in accord with the proposed 2-*n*-butylimino-3-*n*-butylthiazolidine-4,5-dione structure VId (see Table II). Similarly, 1,3-diphenylthiourea afforded 2-phenylimino-3-phenylthiazolidine-4,5-dione (VIe). The formation of iminothiazolidine-4,5-diones as intermediates in the oxalyl chloride–dialkylthiourea reaction was suggested earlier.[11]

Monoalkylthiourea–oxalyl chloride reaction also gave rise to the bright yellow thiazolidine-4,5-diones, and not to the parabanic acid derivatives. Two isomeric products are possible: 2-imino-3-alkyl- and 2-alkyliminothiazolidine-4,5-dione. The former was selected on the basis of theoretical and reported findings. Monoalkylthioureas, on reaction with ethyl chloroacetate, yield the 2-imino-3-alkylthiazolidine derivative, rather than the 2-alkylimino isomer.[12] The 2-iminothiazolidine-4,5-diones prepared appear in Table II.

The thiazolidine-4,5-diones (VI), remarkably stable in aqueous acid, react in dilute base to regenerate the starting thiourea. Pseudothiohydantoins (2-imino-3-alkylthiazolidin-4-ones), compounds similar to VI, are reported to be cleaved readily by base.[13]

Compounds VIa, b, c, and e, on heating in ethanol, isomerized quantitatively to the corresponding thioparabanic acid (VII). The existence of this facile isomerization may be responsible for the difference between our results and those reported by Stoffel[11] and by Biltz and Topp,[5] who on reaction of mono- and 1,3-disubstituted thioureas with oxalyl chloride obtained the corresponding thioparabanic acids. When *n*-propylthiourea was treated with oxalyl chloride in diethyl

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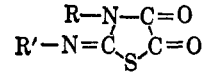
TABLE II

2-IMINOTHIAZOLIDINE-4,5-DIONES (VI)



Compd.	R	R′	M.p., °C.	Yield, %	$\nu_{C=O}$,[a] cm.$^{-1}$	$\nu_{C=N}$,[a] cm.$^{-1}$	Formula	Calcd., % C	Calcd., % H	Calcd., % N	Found, % C	Found, % H	Found, % N
VIa	*n*-Propyl	H	208–209[b]	63	1758, 1745	1660	$C_6H_8N_2O_2S$	41.86	4.68	16.26	41.46	4.75	16.89
VIb	Isopropyl	H	204–205[c]	49	1755, 1740	1660	$C_6H_8N_2O_2S$	41.86	4.68	16.26	42.05	4.78	16.53
VIc	Cyclohexyl	H	204–205[c]	46.1	1765, 1755[d]	1670	$C_9H_{12}N_2O_2S$	...	...	13.20	...	..	13.41
VId	*n*-Butyl	*n*-Butyl	130[e]	80.6	1755[f]	1660[f]	$C_{11}H_{18}N_2O_2S$	54.52	7.49	11.55	54.38	7.27	11.29
VIe	Phenyl	Phenyl	129–130[g]	76.5	1750[f]	1660[f]	$C_{15}H_{10}N_2O_2S$	63.81	3.56	9.92	63.92	3.85	10.20

[a] Infrared spectra in KBr. [b] Recrystallized from chloroform. [c] Recrystallized from ethylene dichloride. [d] Shoulder. [e] Boiling point at 0.2 mm. [f] Infrared spectra in chloroform. [g] Recrystallized from carbon tetrachloride.

ether following Biltz and Topps procedure, we obtained 1-*n*-propylthioparabanic acid in 6.6% yield.

Lastly, the reaction of 1-*p*-chlorobenzenesulfonyl-3-*n*-propylthiourea with oxalyl chloride in ethylene dichloride proceeded with loss of the sulfonyl group to afford 1-*n*-propylthioparabanic acid and *p*-chlorobenzenesulfonyl chloride.

Experimental[14]

1,3-Dialkylparabanic Acid (1,3-Dialkyl-2,4,5-imidazoletrione) Preparation. A. From 1,3-Dialkylureas. General Procedure.—Oxalyl chloride (0.05 mole) was added dropwise with ice cooling and stirring to a solution of the 1,3-dialkylurea (0.05 mole) in ethylene dichloride (86 ml.), the mixture was stirred 30 min. at room temperature and then refluxed an additional 30 min., and the solvent was removed to afford the 1,3-dialkyl-2,4,5-imidazoletriones (IV) in the yields recorded in Table I.

B. From 1,3-Dialkyl-2,2-dichloroimidazolidine-4,5-diones (III). General Procedure.—Aqueous methanol (90%, 35 ml.) and compound III (0.01 mole) were refluxed for 10 min. On cooling, the 1,3-dialkylparabanic acid (IV) crystallized from solution.

The infrared spectrum of the 1,3-dicyclohexylparabanic acid, prepared by method B (in 86.5% yield), was superimposable on the spectrum of the acid prepared by method A (in 96% yield).

1,3-Dicyclohexyl-2,2-dichloroimidazolidine-4,5-dione (III, R = R′ = Cyclohexyl).—Oxalyl chloride (1.27 g., 0.01 mole) was added to a solution of dicyclohexylcarbodiimide (2.06 g., 0.01 mole) in chloroform (25 ml.), a slightly exothermic reaction occurring. (The absence of –N=C=N– infrared absorption at 2125 cm.$^{-1}$ indicated complete reaction.) Solvent evaporation gave a 3.3-g. quantitative yield of 1,3-dicyclohexyl-2,2-dichloroimidazolidine-4,5-dione, $\lambda_{max}^{CHCl_3}$ 1760 (C=O) cm.$^{-1}$, which, without further purification, was converted to the corresponding parabanic acid (IVd).

1,3-Di-*o*-tolyl-2,2-dichloroimidazolidine-4,5-dione (III, R = R′ = *o*-Tolyl).—Oxalyl chloride (1.27 g., 0.01 mole) was added to a solution of di-*o*-tolylcarbodiimide (2.22 g., 0.01 mole) in carbon tetrachloride (20 ml.) which, on standing, yielded 3.0 g. (86%) of crystalline compound (III, R = R′ = *o*-tolyl), m.p. 167–168° dec.

Anal. Calcd. for $C_{17}H_{14}Cl_2N_2O_2$: C, 58.50; H, 4.04; N, 8.01. Found: C, 58.15; H, 4.08; N, 8.16.

The di-*o*-tolylparabanic acids, m.p. 205–207° (lit.[15] m.p. 202–203°), prepared (1) by heating a sample of III (R = R′ = *o*-tolyl) in water and recrystallizing from ethanol and (2) by refluxing di-*o*-tolylguanidine (2.4 g., 0.01 mole) with diethyl oxalate (1.46 g., 0.01 mole) in ethanol and hydrolyzing with concentrated hydrochloric acid to yield 0.5 g. (17%) of product, were found by mixture melting points and infrared spectral results to be identical.

2-Iminothiazolidine-4,5-diones (VI). General Procedure.—Oxalyl chloride (8.89 g., 0.07 mole) was added dropwise with stirring and cooling to a solution of mono- or dialkylthiourea (0.07 mole) in ethylene dichloride (130 ml.), the mixture was refluxed 30 min. at 84–86°, the solvent was evaporated, and the residue was distilled *in vacuo* or crystallized to afford the 2-iminothiazolidine-4,5-diones (VI) recorded in Table II.

Compound VId, b.p. 130° (0.2 mm.), an orange-colored oil, on addition to sodium hydroxide (5% solution) and standing, gave white crystalline di-*n*-butylthiourea (Vd), m.p. 62–63° (lit.[16] m.p. 65°).

Hydrolysis of 2-Imino-3-isopropylthiazolidine-4,5-dione (VIb).—Sodium hydroxide (10 ml. of 5% solution) was added to compound VIb (0.86 g., 0.005 mole) and the reaction mixture was let stand. Isopropylthiourea (0.4 g., 68%), m.p. 172–73° (lit.[17] m.p. 157°), separated.

Anal. Calcd. for $C_4H_{10}N_2S$: N, 23.69. Found: N, 23.86.

Isomerization of 2-Imino-3-*n*-propylthiazolidine-4,5-dione (VIa).—A suspension of compound VIa (0.8 g., 0.005 mole) in ethanol (20 ml.) was refluxed for 30 min., the clear yellow solution was evaporated to the crude yellow 1-*n*-propylthioparabanic acid (0.8 g.), and the crude acid was recrystallized from carbon tetrachloride, m.p. 101–102°, λ_{max}^{KBr} 1780 (C=O) cm.$^{-1}$.

Anal. Calcd. for $C_6H_8N_2O_2S$: C, 41.86; H, 4.68; N, 16.26; S, 18.59. Found: C, 41.60; H, 4.60; N, 15.94; S, 18.54.

Oxalyl Chloride and *n*-Propylthiourea Reaction in Diethyl Ether.—Oxalyl chloride (2.4 g., 0.019 mole) was added with cooling and stirring to a solution of *n*-propylthiourea (2.24 g., 0.019 mole) in diethyl ether (50 ml.), the mixture was refluxed for 7 hr. and filtered, and the ether was evaporated to afford 1-*n*-propylthioparabanic acid (0.2 g., 6.6%), m.p. 101–102° (from carbon tetrachloride).

Oxalyl Chloride and 1-*p*-Chlorobenzenesulfonyl-3-*n*-propylthiourea Reaction.—Oxalyl chloride (2.55 g., 0.02 mole) was added dropwise with cooling and stirring to a solution of 1-*p*-chlorobenzenesulfonyl-3-*n*-propylthiourea[18] (5.85 g., 0.02 mole) in ethylene dichloride (60 ml.), the mixture was refluxed for 90 min., the solvent was evaporated, and the residue was fractionally distilled to give *p*-chlorobenzene sulfonyl chloride (2.8 g., 66.3%), m.p. 47–48° (lit.[19] m.p. 53°), b.p. 91–100° (1.2 mm.), and 1-*n*-propylthioparabanic acid (2.7 g., 85.5%), m.p. 93–95°. Recrystallization of the latter from carbon tetrachloride gave a material, m.p. 101–102°, which was found by mixture melting point and infrared spectral results to be identical with the 1-*n*-propylthioparabanic acid prepared by the above procedures.

Acknowledgment.—We are indebted to Benjamin Tucker for his assistance in the experimental aspects of this work.

(14) Analyses by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.; infrared spectra determined on a Perkin-Elmer 21 spectrometer.

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