Reactions of Group IV Organometallic Compounds. I. The Reaction of Trimethylsilyldialkylamines with β-Propiolactone

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Received December 20, 1965

The reaction of β-propiolactone with six trimethylsilyldialkylamines was studied at 80° in ethylene dichloride. The alkyl oxygen bond in β-propiolactone was cleaved selectively, giving the trimethylsilyl esters of N,N-dialkyl-β-alanine (I). Further moles of β-propiolactone would add to I and the first product was a betain (VI). Stepwise additions of β-propiolactone to VI occurred easily and gave poly-β-propiolactone.

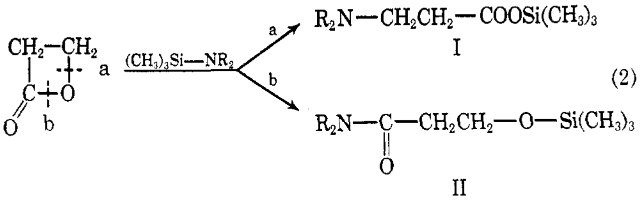
Compounds containing a silicon–nitrogen bond were reported to react with some polar double bonds as in carbon dioxide,[1] carbon disulfide,[2] di-*p*-tolylcarbodiimide,[3] phenyl isocyanate,[3-6] phenyl isothiocyanate,[3,4] and ketene.[7] Generally, these reactions could be described as follows.

$$>\mathrm{Si}{-}\mathrm{N}< + \mathrm{A}{=}\mathrm{B} \rightleftharpoons\ >\mathrm{Si}{-}\mathrm{A}{-}\mathrm{B}{-}\mathrm{N}< \qquad (1)$$

However, no studies have been performed with cyclic compounds. In this paper, the ring-opening reaction of β-propiolactone with trimethylsilyldialkylamines is reported.

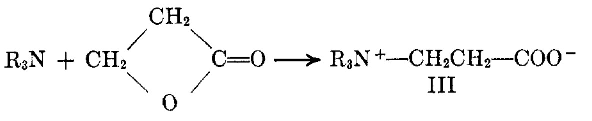
Results and Discussion

There are two possible modes of ring-opening reactions for β-propiolactone, alkyl oxygen bond (I *via* a) and acyl oxygen bond (II *via* b) fission, respectively.



(2)

In the case of tertiary amines, betaines (III) were obtained with the alkyl oxygen bond breakage of β-propiolactone as in eq 3.[8] However, both modes of ring opening were observed with primary or secondary amines.



(3)

$$\mathrm{R_3N} + \mathrm{CH_2CH_2C(=O)O} \longrightarrow \mathrm{R_3N^+{-}CH_2CH_2{-}COO^-} \qquad (3)$$

The reaction between β-propiolactone and trimethylsilyldialkylamines was performed by adding β-propiolactone (10 mmoles) to trimethylsilyldialkylamine (12 mmoles) dissolved in ethylene dichloride (2 ml), allowing the mixture to stand for 24 hr at 80°, and distilling the product under reduced pressure.

The reaction products show a strong infrared absorption at 1720 cm^{-1} which could be assigned as the stretching frequency of the carbonyl group. A strong absorption band at 1725 cm^{-1} was observed by Okawara, *et al.*,[9] in the infrared spectrum of trimethylsilyl acetate. No absorption was observed between 1600 and 1700 cm^{-1} which could be ascribed to amide absorption of β-trimethylsiloxypropion-N,N-dialkylamides (II).

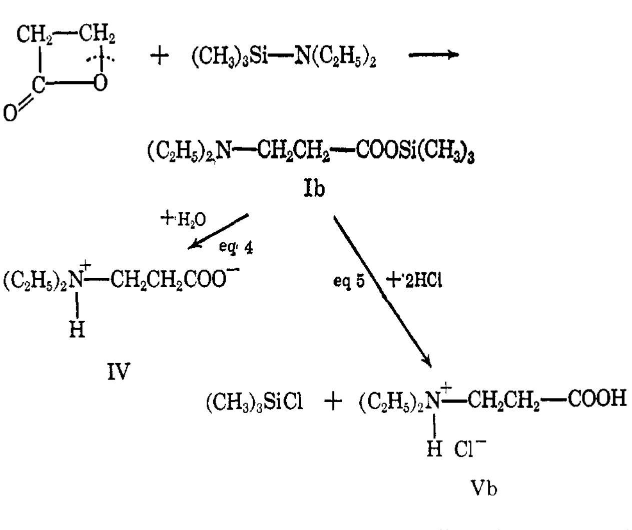
A singlet methyl proton signal of trimethylsilyl group in the adduct with trimethylsilyldiethylamine (Ib) appeared at τ 9.74 in the nmr spectrum and it could be well compared with that in trimethylsilyl acetate at 9.73.

However, in the case of trimethylethoxysilane, this signal showed a sharp singlet at τ 10.01. Although the methylene proton in trimethylethoxysilane showed a quartet at τ 6.77, no signal was observed below 7.0 in Ib.

The above-mentioned infrared and nmr results suggest that the reaction product were not β-trimethylsiloxypropion-N,N-dialkylamides (II) but the trimethylsilyl esters of N,N-dialkyl-β-alanine (I). Therefore, it is apparent that β-propiolactone is cleaved selectively at the alkyl oxygen bond through the reaction course a of eq 2.

From the cryoscopic molecular weight determination in benzene, Ib was shown to exist as a monomer and no association was indicated.

The trimethylsilyl ester of N,N-diethyl-β-alanine (Ib) was extremely sensitive to moisture and was hydrolyzed easily to the zwitterion of N,N-diethyl-β-alanine (IV) (eq 4).



Vigorous reaction occurred between I and 2 equiv of hydrogen chloride dissolved in dry ether, giving trimethylchlorosilane and corresponding N,N-dialkyl-β-

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(1) H. Breederveld, *Rec. Trav. Chim.*, **81**, 276 (1962).

(2) H. Breederveld, *ibid.*, **79**, 1126 (1960).

(3) A. G. Davies and Y. Ishii, to be published.

(4) J. F. Klebe, J. B. Bush, Jr., and J. E. Lyons, *J. Am. Chem. Soc.*, **86**, 4400 (1964).

(5) W. Fink, *Chem. Ber.*, **97**, 1433 (1964).

(6) D. Y. Zhinkin, M. M. Morgunova, K. K. Popkov, and K. A. Andrianov, *Dokl. Akad. Nauk SSSR*, **158**, 641 (1964).

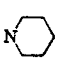
(7) W. W. Limburg and H. W. Post, *Rec. Trav. Chim.*, **81**, 430 (1962).

(8) T. L. Gresham, J. E. Jansen, F. W. Shaver, R. A. Bankert, and F. T. Fiedorek, *J. Am. Chem. Soc.*, **73**, 3168 (1951).

(9) R. Okawara, D. E. Webster, and E. G. Rochow, *ibid.*, **82**, 3287 (1960).

TABLE I

TRIMETHYLSILYL ESTERS OF N,N-DIALKYL-β-ALANINE (I), $XCH_2CH_2COOSi(CH_3)_3$, AND CORRESPONDING HYDROCHLORIDES (V), $XCH_2CH_2COOH \cdot HCl$

Run	X	Bp, °C (mm)	Yield, %	Mp of V, °C	Found, %[a] C	Found, %[a] H	Found, %[a] N	Calcd, %[a] C	Calcd, %[a] H	Calcd, %[a] N
a	$N(CH_3)_2$	84.0–85.0 (31)	64	186.5–187.5	39.17	7.87	9.18	39.10	7.89	9.12
b	$N(C_2H_5)_2$	54.0–54.1 (1.0)	88	136.0–147.0	46.33	8.88	7.96	47.28	8.88	7.71
c	$N(C_3H_7)_2$	76.2–77.2 (2.0)	84	81.0–83.0	51.87	9.35	6.60	51.53	9.63	6.68
d		59.0–60.0 (1.0)	80	165.0–166.0	46.67	7.91	7.70	46.79	7.87	7.80
e		80.0–80.5 (2.0)	83	218.0–218.8	49.90	8.59	7.22	49.60	8.34	7.23
f		98.0–99.0 (3.0)	64	218.0–219.0	42.60	7.40	7.86	42.97	7.23	7.16

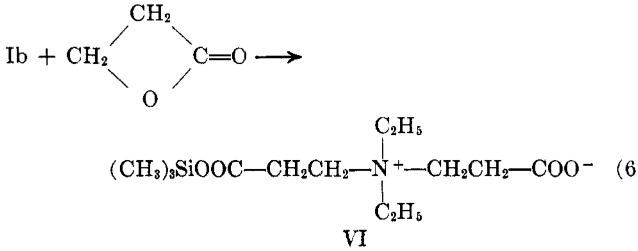
[a] Analytical data for V.

alanine hydrochlorides (Va–f) (eq 5). The results obtained for six trimethylsilyldialkylamines are summarized in Table I.

This chemical behavior of I would also support the proposed structure.

It was found that Ib could react with further moles of β-propiolactone in few minutes at 70°. The reaction product showed characteristic infrared absorptions at 1610 and 1395 cm^{-1}, which could be assigned as the stretching frequencies of the carboxylate anion.

Since Ib is a tertiary amine, the following reaction with β-propiolactone might be possible in a analogous way as eq 3.



$$(CH_3)_3SiOOC\text{—}CH_2CH_2\text{—}\overset{C_2H_5}{\underset{C_2H_5}{N^+}}\text{—}CH_2CH_2\text{—}COO^- \quad (6)$$

VI

Although the isolation of betain VI was unsuccessful because of the further addition of β-propiolactone to the carboxylate anion of VI as will be cited later, the existence of the carboxylate anion would be explained by eq 6.

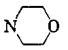
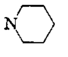
Recently Kagiya, *et al.*,[10] reported that a betain was the first product for the reaction of β-propiolactone and triethylamine; however, considerable addition to the carboxylate anion of the betain occurred and gave poly-β-propiolactone. Also in our case, the infrared spectrum of this reaction product showed a strong and broad absorption at 1740 cm^{-1}. Therefore, additions of β-propiolactone to VI appeared to occur.

In order to find the behavior of this addition reaction, polymerization studies of β-propiolactone catalyzed by several trimethylsilyldialkylamines were performed. The results were shown in Table II.

The poly-β-propiolactones obtained were white powders which had melting points at 91–93°. Molecular weights were estimated with Kagiya's equation[11] and found to increase with the conversions to polymers as indicated in Figure 1. This fact shows a typical behavior of the stepwise polymerization.[10,11]

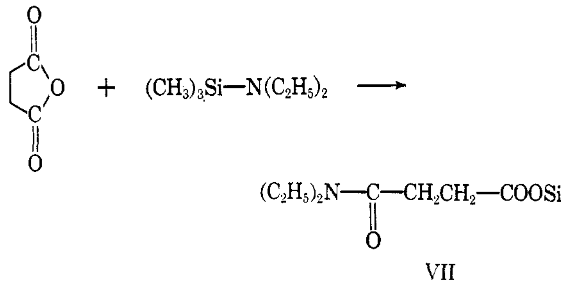
TABLE II

POLYMERIZATION OF β-PROPIOLACTONE BY TRIMETHYLSILYLDIALKYLAMINES, $(CH_3)_3SiX$ AT 30°[a]

X	Conversion, %	M_p/C[b]	η[c]	Mol wt × 10^3[d]	pK_a (25°)
	17	102	0.056	1.3	8.36[e]
$N(CH_3)_2$	31	186	0.079	2.1	10.64[f]
$N(C_2H_5)_2$	39	224	0.095	2.7	10.98[f]
$N(C_3H_7)_2$	42	252	0.094	2.7	11.00[g]
	47	282	0.099	2.8	11.22[h]
	47	282	0.10	2.9	11.27[h]

[a] β-Propiolactone (60 mmoles) and trimethylsilyldialkylamine (0.1 mmole) were allowed to react for 110 hr. [b] M_p, β-propiolactone converted to polymer; C, catalysis concentration. [c] Determined in chloroform at 35°. [d] Estimated molecular weight using the eq 9 proposed by T. Kagiya, T. Sano, and K. Fukui, *J. Chem. Soc. Japan Ind., Chem. Sect.*, **68**, 1144 (1965). [e] H. K. Hall, Jr., *J. Am. Chem. Soc.*, **78**, 2570 (1956). [f] N. F. Hall and M. R. Sprinkle, *ibid.*, **54**, 3469 (1932). [g] G. Girault-Veplearschi, *Bull. Soc. Chim. France*, 577 (1956). [h] S. Searles, M. Lamres, F. Block, and L. A. Quarterman, *J. Am. Chem. Soc.*, **78**, 4917 (1956).

The possibility of the insertion of β-propiolactone between the silicon and oxygen bond in I or betain VI was excluded, because the trimethylsilyl ester of mono-(N,N-diethylamido)succinic acid (VII), prepared from succinic anhydride and trimethylsilyldiethylamine as in eq 7, did not react with β-propiolactone under the same condition.



(7)

$$(C_2H_5)_2N\text{—}\underset{\underset{O}{\|}}{C}\text{—}CH_2CH_2\text{—}COOSi(CH_3)_3$$

VII

Therefore the stepwise additions of β-propiolactone to betain (VI) would probably occur with the carboxylate anion in the following manner, giving poly-β-propiolactone.

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(10) T. Kagiya, T. Sano, and K. Fukui, *J. Chem. Soc. Japan Ind. Chem. Sect.*, **68**, 1144 (1965).

(11) T. Kagiya, *et al.*, footnote *d* of Table II.

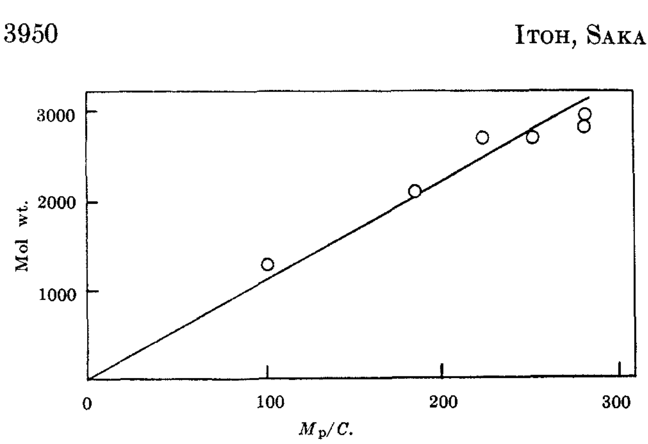
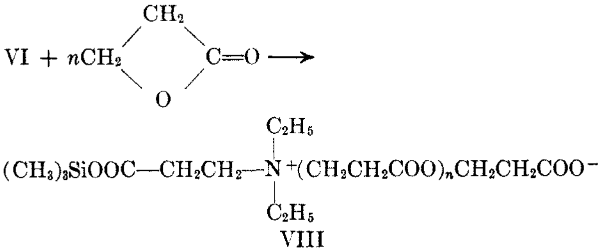


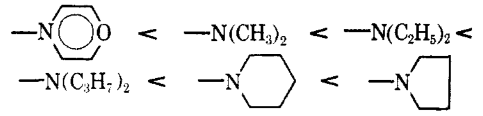
Figure 1.—The correlation between the molecular weight of poly-β-propiolactones and the conversions of β-propiolactone at 30°: $[\beta\text{-propiolactone}]_0$ = 60 mmoles; $[\text{N,N-dialkylaminotrimethylsilane}]_0$ = 0.1 mmole; time = 110 hr.



$$(CH_3)_3SiOOC—CH_2CH_2—\overset{C_2H_5}{\underset{C_2H_5}{N^+}}(CH_2CH_2COO)_nCH_2CH_2COO^- \quad (8)$$

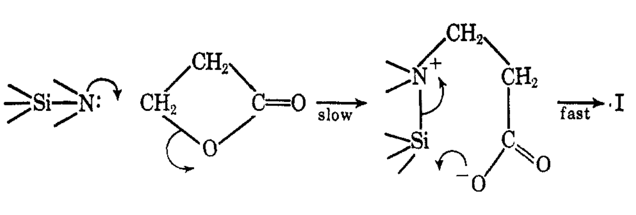
VIII

The yields of poly-β-propiolactone (VIII) increased with the basicities of trimethylsilyldialylamines which was presumed from the pK_a values of corresponding secondary amines,[12–15] the order was as follows.



This order would reflect the rates of the ring-opening reactions between β-propiolactone and trimethylsilyldialylamines and show that the nucleophilic attack of the nitrogen atom upon β-propiolactone is the rate-determining step of this reaction. This view would agree with the observation of Swain and Scott[16] that the reaction rates of β-propiolactone with several nucleophiles[17] correlated linearly with the corresponding nucleophilic constants (n).

The above interpretations and the fact that the bond breakage of β-propiolactone by trimethylsilyldialkylamines occurred at the same position as by tertiary amines, giving betain (III) as in eq 3, might suggest the following mechanism which passing through a betain intermediate (IX).



IX

Since no infrared absorption expected from the carboxylate anion in IX was observed in progress of the reaction, the first step would be slower than the second one.

Kinetic studies for this reaction will be reported in the near future.

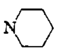
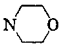
Experimental Section[18]

Materials.—The β-propiolactone was a commercial extra pure reagent and was distilled before use under reduced pressure [bp 71.0° (33 mm)]. Ethylene dichloride was purified by treating with concentrated sulfuric acid and phosphorus pentaoxide, distilling, and drying over calcium hydride.

Preparations of Trimethylsilyldialkylamines.—Secondary amines (0.1 mole) were added dropwise to the same amounts of ethylmagnesium bromide in 100 ml of ether and allowed to stand for 1 hr at room temperature. The above solution was added to trimethylchlorosilane (0.1 mole) dissolved in 50 ml of dry ether with vigorous stirring for 30 min. The reaction mixture was refluxed for 2 hr and kept overnight at room temperature. After the removal of magnesium halides and solvent, trimethylsilyldialkylamine was distilled. All procedures above were done under an atmosphere of argon or nitrogen. The products showed a symmetric deformation infrared frequency of trimethylsilyl group at 1245 cm^{-1}. The yields and the boiling points were shown in Table III.

TABLE III

TRIMETHYLSILYLDIALKYLAMINES, $(CH_3)_3SiX$

X	Bp, °C (mm) [lit. bp]	Yield, %
$N(CH_3)_2$[a]	85–86 (760) [86.2,[b] 85[c]]	65
$N(C_2H_5)_2$	125–126 (760) [126.8–127.1 (738)[d]]	72
$N(C_3H_7)_2$[e]	67.0 (26)	75
	141–142 (760) [142 (760)[f]]	55
	162 (760) [161 (760)[f]]	63
 [a,g]	57–60 (20)	38

[a] Prepared according to the method of R. C. Osthoff and S. W. Kantor, *Inorg. Syn.*, **5**, 59 (1957). [b] E. A. V. Ebsworth and H. J. Emeléus, *J. Chem. Soc.*, 2150 (1958). [c] J. Goubeau and J. Jiménez-Barberá, *Z. Anorg. Allgem. Chem.*, **303**, 218 (1960). [d] S. H. Langer, S. Connell, and I. Wender, *J. Org. Chem.*, **23**, 50 (1958). [e] *Anal.* Calcd for $C_9H_{23}NSi$: N, 8.08. Found: N, 8.05. [f] L. Birkofer and A. Ritter, *Angew. Chem.*, **77**, 416 (1965). [g] *Anal.* Calcd for $C_7H_{17}NOSi$: C, 52.76; H, 10.78. Found: C, 52.20; H, 10.71.

Trimethylsilyl Ester of N,N-Diethyl-β-alanine (Ib).—Trimethylsilyldiethylamine (12 mmoles) was dissolved in ethylene dichloride (2 ml). β-Propiolactone (10 mmoles) was added to the above solution under an atmosphere of argon. The reaction mixture was kept overnight at 80°. Solvent and the excess amounts of trimethylsilyldiethylamine were distilled off and the product (Ib) was distilled at reduced pressure [54.0–54.1° (1.0 mm)]. The colorless liquid was obtained in 83% yield. Molecular weight was determined by the cryoscopic method in benzene. *Anal.* Calcd for $C_{10}H_{23}NO_2Si$: mol wt, 217. Found: mol wt, 211. The infrared spectrum of Ib showed a strong carbonyl stretching frequency at 1720 cm^{-1} in carbon tetrachloride. The nmr spectrum of Ib (chloroform) showed a trimethylsilylmethyl proton at τ 9.74 as a sharp singlet, and the signals ascribed to three methylene protons as complex multiplets between 7.25 and 7.80 were observed.

The reaction of β-propiolactone with five other trimethylsilyldialkylamines was performed in the same manner as Ib and the results were summarized in Table I.

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(12) See Table II, footnote *e*.

(13) See Table II, footnote *f*.

(14) See Table II, footnote *g*.

(15) See Table II, footnote *h*.

(16) C. G. Swain and C. B. Scott, *J. Am. Chem. Soc.*, **75**, 141 (1953).

(17) P. D. Bartlett and G. Small, Jr., *ibid.*, **72**, 4867 (1950).

(18) Melting points were determined using the Yanagimoto MP-S1 melting point apparatus which was corrected. The infrared and nmr spectra were obtained, respectively, with a Nippon Bunko IR-S and a Japan Electron Optics C-60 spectrometer.

N,N-Diethyl-β-alanine Hydrochloride (Vb).—To Ib (5.0 mmoles), hydrogen chloride dissolved in dry ether was added gradually with swirling. A violently exothermic reaction occurred and the white precipitates of Vb appeared. The solvent and trimethylchlorosilane formed were removed and dried at reduced pressure. This reaction proceeded quantitatively. The recrystallization was performed with dry ethanol. N,N-Dialkyl-β-alanine hydrochlorides from Ia,c–f were obtained in the same manner as Ib. Melting points and analytical data were shown in Table I.

Hydrolysis of the Trimethylsilyl Ester of N,N-Diethyl-β-alanine (Ib).—Four millimoles of water was added to Ib (4.0 mmoles). The reaction was slightly exothermic and a white precipitate was formed. The product, the zwitterion of N,N-diethyl-β-alanine (IV), was washed with dry ether and dried under reduced pressure. Yield was 82%, mp 75.5–76.0° (lit.[19] mp 74–75°), $\nu_{C=O}$ 1601 and 1395 cm^{-1}. *Anal.* Calcd for $C_7H_{15}NO_2$: H, 10.58; N, 9.73. Found: H, 10.96; N, 9.52.

The Reaction of Ib and β-Propiolactone.—β-Propiolactone (2.7 mmoles) was added dropwise to Ib (3.3 mmoles) at 70°. The reaction was completely finished in a few minutes. The infrared spectrum of this reaction mixture showed strong and broad absorptions at 1740, 1610, and 1395 cm^{-1}.

Trimethylsilyl Ester of Mono(N,N-diethylamido)succinic Acid (VII).—Succinic anhydride (10 mmoles) was added to the same amounts of trimethylsilyldiethylamine. An exothermic reaction was occurred, characteristic infrared absorptions ascribed to succinic anhydride vanished, and two strong absorptions of carbonyl stretching frequencies at 1720 and 1645 cm^{-1} appeared. The former was ascribed to the trimethylsilyl ester and the latter to the N,N-diethylamide. Distillation of VII was performed [bp 130.0–130.6° (4 mm)] and the viscous, oily liquid product was obtained in 62% yield. The methanolysis of VII was done by adding the excess amounts of dry methanol, distilling off methanol and trimethylmethoxysilane, obtaining a white crystal of succinic acid mono-N,N-diethylamide, and reprecipitating from acetone and petroleum ether (bp 30–70°) mp 85.0–86.0°. *Anal.* Calcd for $C_8H_{15}NO_3$: C, 55.47; H, 8.75; N, 8.09. Found: C, 55.54; H, 8.83; N, 8.10.

Polymerization of β-Propiolactone.—Polymerization studies were carried out in glass ampoules filled with dry nitrogen. After β-propiolactone (4.32 g) was added, 0.1 mole of trimethylsilyldialkylamine was introduced and sealed. The ampoules were set in a water bath controlled at 30.0 ± 0.1° for 110 hr. The white powder of poly-β-propiolactone precipitated gradually. Reaction mixtures were dissolved in small amounts of chloroform and precipitated by adding the solution to 60 ml of dry ether. Solvents and unreacted β-propiolactone were separated and polymers were washed with dry ether. Polymers were dried at 50° (1 mm). Intrinsic viscosity of polymers was determined in chloroform at 35.0°. The molecular weights were estimated with eq 9 proposed by Kagiya, *et al.*[11]

$$[\eta] = 2.74 \times 10^{-4} M^{0.74} \qquad (9)$$

The results were summarized in Table II.

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[19] K. Morsch, *Monatsh. Chem.*, **63**, 220 (1933).

The Action of Bromine in Acetic Acid on 4,5-Diphenyl-2-imidazolone

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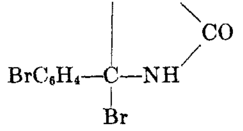
Received May 9, 1966

The action of bromine in acetic acid on 4,5-diphenyl-2-imidazolone leading to 4,4′-dibromobenzil and 4,5-di(p-bromophenyl)glycoluril has been reexamined, and the reaction has been studied in the presence of varying amounts of water, of sodium acetate as a buffer, and of urea. Under suitable conditions, 4,5-diacetoxy-4,5-diphenyl-2-imidazolidinone could be isolated and this substance, as well as the corresponding glycol, appears to be a labile intermediate during the oxidation of the imidazolone to benzil. Biltz isolated an intermediate compound in the reaction which he regarded as 4,5-dibromo-4,5-di(p-bromophenyl)-2-imidazolidinone, for which we propose a different structure. A reaction sequence for the oxidation leading to the various products is proposed. A number of phenyl-substituted imidazolones were also oxidized under different conditions.

Biltz[1] found that when 4,5-diphenyl-2-imidazolone was refluxed with bromine in acetic acid, 4,4′-dibromobenzil and 3a,6a-di(*p*-bromophenyl)glycoluril were formed; we have investigated this reaction in order to identify any intermediates and to apply the reaction to the synthesis of benzils.

Biltz had found that the sparingly soluble 4,5-di(*p*-bromophenyl)-2-imidazolone dissolved readily when bromine was added to a suspension of the compound in acetic acid; from this solution a solid separated to which he assigned the structure I. We have reexamined this compound and found that it contains two acetate groups and two active bromine atoms, and elemental analysis indicated the formula $C_{19}H_{17}Br_5N_2O_5$; we propose structure IV for it. When the compound was heated or an aqueous suspension of it was treated with a reducing agent or it was allowed to stand with glacial acetic acid containing anhydrous sodium acetate, a diacetate was obtained. This diacetate was also formed when 4,5-di(*p*-bromophenyl)-2-imidazolone was treated with glacial acetic acid containing bromine and anhydrous sodium acetate; it was hydrolyzed by cold, aqueous acetic acid to the known 4,5-dihydroxy-4,5-di(*p*-bromophenyl)-2-imidazolidinone[2] (II). Spectral evidence and elemental analysis suggested the structure III for the diacetate.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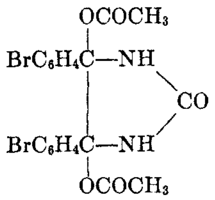
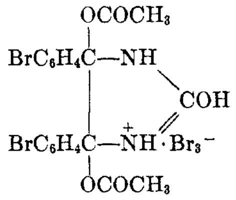

III


IV

Scheme I following is proposed for the oxidation of 4,5-di(*p*-bromophenyl)-2-imidazolone (V) and for the formation of the various intermediates which are mentioned.

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[1] H. Biltz, *Ber.*, **41**, 1754 (1908).

[2] H. Greenberg and T. van Es, *J. Org. Chem.*, **30**, 3937 (1965).