TABLE I

CHARACTERISTICS OF 2-BROMO-SUBSTITUTED DIPHENYLPROPANE-1,3-DIONES

No.	R	R′	Yield, % from Sodium salt	Yield, % from Copper salt	M.P.	Color	Formula	Halogen, % Found	Halogen, % Calcd.
1[a]	Phenyl	Phenyl	60	79	93	Colorless	$C_{15}H_{11}BrO_2$	26.01	26.40
2	*p*-Bromophenyl	Phenyl	70	81	114	Colorless	$C_{15}H_{10}Br_2O_2$	41.25	41.80
3	*p*-Chlorophenyl	Phenyl	68	80	118	Colorless	$C_{15}H_{10}BrClO_2$	34.84	34.22
4	Anisyl	Phenyl	54	79	128	Colorless	$C_{16}H_{13}BrO_3$	24.40	24.02
5	*p*-Tolyl	Phenyl	62	80	110	Colorless	$C_{16}H_{13}BrO_2$	25.15	25.22
6	Anisyl	Anisyl		81	97	Colorless	$C_{17}H_{15}BrO_4$	21.94	22.03

[a] Ref. (1).

TABLE II

CHARACTERISTICS OF 4-BROMOPYRAZOLES

No.	R	R′	Yield, %	M.P.	Color	Formula	Halogen, % Found	Halogen, % Calcd.
1[b]	Phenyl	Phenyl	72	198	Colorless	$C_{15}H_{11}BrN_2$	26.31	26.75
2	Phenyl	*p*-Bromophenyl	67	223	Colorless	$C_{13}H_{10}Br_2N_2$	42.11	42.32
3	Phenyl	*p*-Chlorophenyl	68	221	Dirty white	$C_{15}H_{10}BrCIN_2$	34.22	34.63
4	Phenyl	Anisyl	63	178	Colorless	$C_{16}H_{12}BrN_2O$	24.20	28.31
5	Phenyl	*p*-Methylphenyl	65	172	Dirty white	$C_{16}H_{13}BrN_2$	25.35	25.55
6	Anisyl	Anisyl	64	228	Colorless	$C_{17}H_{15}BrN_2O_2$	22.11	22.28

[a] Ref. (12).

under reflux for about an hour. On cooling shining crystals separated. These were recrystallized from alcohol.

The different pyrazole derivatives prepared are summarized in Table II.

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Reaction of *t*-Alkylazomethines with Ketene

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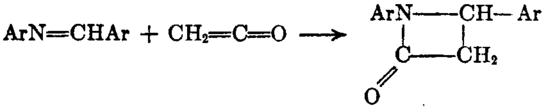
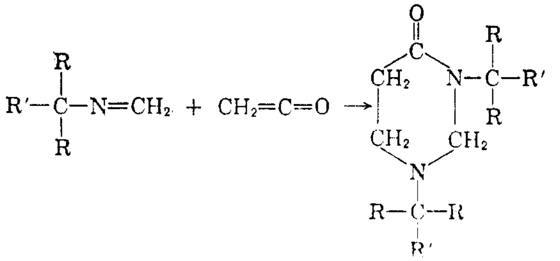
Staudinger[1] and more recently Pfleger and Jager[2] have examined the reaction of ketene with a variety of substituted benzal anilines. Invariably they found that the reaction proceeded to give β-lactams of the type I, this being analogous to the formation of β-lactones from ketene and aldehydes.



I

The present work describes the zinc chloride catalyzed reaction of *N*-*t*-butyl-and *N*-*t*-octylazomethines with ketene.

No reaction was observed between the azomethines IIa and IIb and ketene at temperatures in excess of 100°. However, when a catalytic amount of zinc chloride was used, both IIa and IIb reacted exothermally with ketene at room temperature. The viscous oily products of these reactions were not the expected β-lactams but rather had empirical formulas corresponding to a combination of two moles of the azomethine, IIa or IIb, with one mole of ketene.



IIa. $R = R' = -CH_3$ IIIa. $R = R' = -CH_3$
IIb. $R = -CH_3$ IIIb. $R = -CH_3$
$R' = -CH_2-C(CH_3)_3$ $R' = -CH_2-C(CH_3)_3$

The postulated structure, IIIa, was proved by the following experiments. With 2,4-dinitrophenylhydrazine reagent IIIa gave cleanly a 70% yield of formaldehyde dinitrophenylhydrazone which is in agreement with the methylene diamine structure for IIIa. Acid hydrolysis of IIIa yielded the crystalline β-*t*-butylamino-*N*-*t*-butylpropionamide(IV), the structure of which was established by synthesis from *t*-butylamine and *N*-*t*-butylacrylamide.

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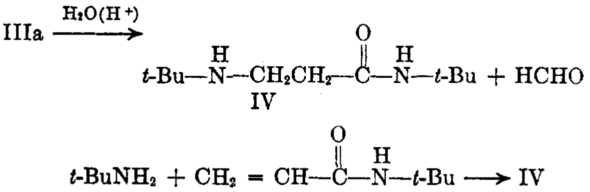
(1) H. Staudinger, *Ber.*, 50, 1035 (1917).
(2) R. Pfleger and A. Jager, *Ber.*, 90, 2460 (1957).

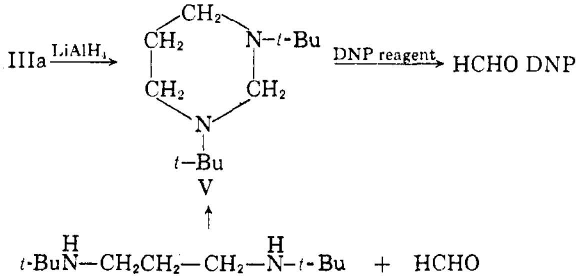


$$\text{IIIa} \xrightarrow{H_2O(H^+)} t\text{-Bu}-\overset{H}{N}-CH_2CH_2-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-t\text{-Bu} + HCHO$$

IV

$$t\text{-BuNH}_2 + CH_2 = CH-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-t\text{-Bu} \longrightarrow \text{IV}$$

(IIIb was also hydrolysed to β-*t*-octylamino-*N*-*t*-octylpropionamide.) Lithium aluminum hydride reduction of IIIa under forcing conditions produced the cyclic diazine, V, whose structure was proved by independent synthesis from *N*,*N'*-di-*t*-butyltrimethylenediamine and formaldehyde. V was also shown to yield formaldehyde dinitrophenylhydrazone on treatment with 2,4-dinitrophenylhydrazine reagent.



A reaction was also found to take place between ketene and *N*-methyl-, *N*-butyl-, and *N*-cyclohexylazomethine trimers; however, the reaction products were complex and were not characterized.

EXPERIMENTAL

N,N'-Di-t-butyl-1,3-diazine-4-one (IIIa). *t*-Butyl azomethine (106.5 g., 1.25 moles) was placed in a 4-cm. diameter gas absorption tube fitted with an inlet running to the bottom of the tube and an outlet protected by a drying tube. A solution of 1.25 g. of zinc chloride in about 20 cc. of ether was added and ketene bubbled through at a rate of 0.35 mole/hr. for 5 hr. During this time the reaction was occasionally cooled in ice to keep it at or slightly above room temperature. The viscous reaction mixture was distilled through a short Vigreux column to give 71 g. (53%) of *N*,*N'*-di-*t*-butyl-1,3-diazine-4-one (IIIa), b.p. 118–120° (2 mm.), n_D^{25} 1.4679.

Anal. Calcd. for $C_{12}H_{24}N_2O$: C, 67.87; H, 11.39; N, 13.20. Found: C, 67.96; H, 11.31; N, 13.02.

N,N'-Di-t-octyl-1,3-diazine-4-one (IIIb). *t*-Octylazomethine (141 g., 1 mole) was placed in a 4-cm. diameter gas absorption tube fitted with an inlet running to the bottom of the tube and an outlet protected by a drying tube. A solution of 1 g. of zinc chloride in about 20 cc. of ether was added and ketene passed through at a rate of 0.5 mole/hr. for 2.75 hr. During this time some cooling in ice was necessary to keep the reaction near room temperature. The very viscous product was distilled through a short Vigreux column to yield 56 g. of crude product, b.p. 180–183° (1.5–2 mm.). This was redistilled to yield 42.9 g. (27%) of *N*,*N'*-di-*t*-octyl-1,3-diazine-4-one (IIIb) b.p. 167–169° (0.25 mm.), n_D^{25} 1.4751.

Anal. Calcd. for $C_{20}H_{40}N_2O$: C, 74.01; H, 12.43; N, 8.63. Found: C, 73.76; H, 12.64; N, 8.72.

β-t-Butylamino-N-t-butylpropionamide (IV). A 10-g. sample of *N*,*N'*-di-*t*-butyl-1,3-diazine-4-one (IIIa), 30 ml. of water and 5 ml. of concd. hydrochloric acid were mixed and heated under reflux for 2 hr. After standing overnight the mixture was made basic with 20% sodium hydroxide solution and extracted with methylene chloride. The organic layer was dried over magnesium sulfate, the methylene chloride blown off under a stream of air on the steam bath, and the residual oil distilled through a short Vigreux column to yield 5.4 g. (57.5%) of β-*t*-butylamino-*N*-*t*-butylpropionamide, b.p. 80–95° (0.15 mm.). After recrystallization from petroleum ether (b.p. 60–90°) it melted at 61–63°.

Anal. Calcd. for $C_{11}H_{24}N_2O$: C, 65.95; H, 12.08; N, 13.99; neut. equiv., 200.32. Found: C, 66.08; H, 12.28; N, 13.91; neut. equiv.,[3] 200.2.

β-t-Octylamino-N-t-octylpropionamide. A 10-g. sample of *N*,*N'*-di-*t*-octyl-1,3-diazine-4-one (IIIb), 30 cc. of water and 4 cc. of concd. hydrochloric acid were heated under reflux 4 hr. The mixture was made basic with 20% sodium hydroxide solution and extracted with methylene chloride. The methylene chloride was boiled off on the steam bath and the residual oil distilled through a short Vigreux column to give 5.5 g. (57%) of β-*t*-octylamino-*N*-*t*-octylpropionamide, b.p. 143–145° (0.15 mm.), n_D^{25} 1.4679.

Anal. Calcd. for $C_{19}H_{40}N_2O$: C, 73.01; H, 12.90; N, 8.97. Found: C, 72.82; H, 12.77; N, 8.68.

Formaldehyde dinitrophenylhydrazone from N,N'-di-t-butyl-1,3-diazine-4-one (IIIa). A 5-g. sample of *N*,*N'*-di-*t*-butyl-1,3-diazine-4-one (IIIa) was dissolved in 50 ml. of alcohol and 150 ml. of dinitrophenylhydrazine solution[4] added, followed by 20 ml. of water. The mixture was heated on the steam bath for 10 min. and then cooled in ice. There crystallized 3.5 g. (70%) of formaldehyde dinitrophenylhydrazone. After recrystallization from alcohol it melted at 164–166° and gave no depression on admixture and melting with an authentic sample.

β-t-Butylamino-N-t-butylpropionamide (IV) *from N-t-butylacrylamide and t-butylamine.* A mixture of 25.4 g. (0.2 mole) of *N*-*t*-butylacrylamide, 146 g. (2 moles) of *t*-butylamine and a pinch of hydroquinone were sealed in a steel bomb and heated between 180 and 200° for 20 hr. The product was stripped and distilled to give 32 g. (80%) of β-*t*-butylamino-*N*-*t*-butylpropionamide, m.p. 60–62°. No depression was observed on admixture and melting with β-*t*-butylamino-*N*-*t*-butylpropionamide (IV) obtained by hydrolysis of *N*,*N'*-di-*t*-butyl-1,3-diazine-4-one (IIIa).

N,N'-Di-t-butyl-1,3-diazine (V) *from N,N'-di-t-butyl-1,3-diazine-4-one* (IIIa). A mixture of 15 g. of *N*,*N'*-di-*t*-butyl-1,3-diazine-4-one, 5.70 g. of lithium aluminum hydride and 150 ml. of tetrahydrofuran were refluxed for 12 hr. The excess of lithium aluminum hydride was decomposed by the cautious addition of 6.0 ml. of water and then 7.95 ml. of water, 9.00 ml. of 10% potassium hydroxide solution and 13.35 ml. of water added in that order. The precipitated solid was filtered off and washed with 100 ml. of tetrahydrofuran. The tetrahydrofuran was distilled under reduced pressure and the residual oil dissolved in methylene chloride and dried over magnesium sulfate. Distillation yielded 8.4 g. (60%) of *N*,*N'*-di-*t*-butyl-1,3-diazine (V), b.p. 54–56° (0.2 mm.), n_D^{25} 1.4601.

Anal. Calcd. for $C_{\ 2}H_{26}N_2$: C, 72.66; H, 13.21; N, 14.13; neut. equiv., 99.2. Found: C, 72.50; H, 13.34; N, 14.02; neut. equiv.,[3] 99.5.

Formaldehyde 2,4-dinitrophenylhydrazone from N,N'-di-t-butyl-1,3-diazine (V). To a solution of 0.44 g. of *N*,*N'*-di-*t*-butyl-1,3-diazine (V) in 15 cc. of 95% ethanol was added 2,4-dinitrophenylhydrazine reagent[4] prepared from 0.8 g. of 2,4-dinitrophenylhydrazine and the mixture warmed on the steam bath for 15 min. and then allowed to stand at room temperature for 24 hr. The precipitated formaldehyde dinitrophenylhydrazone was isolated by filtration and

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(3) The neutralization equivalent was determined by potentiometeric titration with 0.1*N* perchloric acid in glacial acetic acid solution.

(4) *The Systematic Identification of Organic Compounds*, R. Shriner, R. Fuson, and D. Curtin, Fourth Ed., John Wiley and Sons, Inc., New York, 1956, p. 219.

washed with 10 ml. of 50% ethanol. It weighed 4.0 g. and melted at 155–159°. After recrystallization from ethanol it melted at 162–165° and gave no depression on admixture and melting with authentic formaldehyde 2,4-dinitrophenylhydrazone.

N,N'-Di-t-butyl-1,3-diazine (V) *from N,N'-di-t-butyltrimethylenediamine.* To 3.44 g. of *N,N'*-di-*t*-butyltrimethylenediamine was added 1.6 g. of 37% aqueous formaldehyde and the mixture stirred for 16 hr. at room temperature. Water (5 ml.) was added and the mixture extracted with methylene chloride. The organic layer was dried over anhydrous magnesium sulfate and distilled to yield 2.8 g. of *N,N'*-di-*t*-butyl-1,3-diazine (V), b.p. 55–56° (0.2 mm.), n_D^{25} 1.4609. The infrared spectrum of this material was identical with that *N,N'*-di-*t*-butyl-1,3-diazine (V) prepared by lithium aluminum hydride reduction of *N,N'*-di-*t*-butyl-1,3-diazine-4-one (IIIa).

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Reaction of Phenyl Isocyanate with Phenyl Glycidyl Ether

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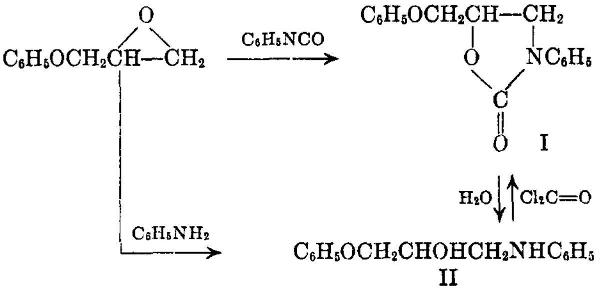
Under forcing conditions and in the presence of a catalytic quantity of benzyldimethylamine, phenyl glycidyl ether reacts with phenyl isocyanate to form the 1:1 cyclic adduct, 5-phenoxymethyl-3-phenyloxazolidin-2-one (I) in a 45% yield. The assignment of structure I to the product is based on the hydrolysis of the latter to an amino alcohol (II) which proved to be identical with that obtained by the reaction of phenyl glycidyl ether with aniline. The amino alcohol (II) has not previously been characterized nor is it firmly characterized in the present work; however, in view of the known greater susceptibility of terminal epoxides to nucleophilic attack at the primary rather than the secondary carbon atom,[2] it seems reasonable that II is 1-anilino-3-phenoxypropanol-2 rather than the isomeric 2-anilino-3-phenoxypropanol-1.

The hydrolysis of the oxazolidinone (I) was accompanied by the evolution of carbon dioxide in the amount required by structure I, and the resultant amino alcohol (II) could be converted back to I in a 49% yield by treatment with phosgene, thus further substantiating structure I.

When the duration of the reaction between the epoxide and the isocyanate was shortened from sixteen hours to one and one-half hours, the yield of I was markedly reduced and part of the isocyanate was recovered in the form of its trimer, triphenyl isocyanurate (III). None of the trimer III could be isolated after the more extended reaction time. A separate experiment established the fact that catalytic quantities of benzyldimethylamine and phenyl glycidyl ether, used in combination, caused a relatively rapid and almost quantitative trimerization of phenyl isocyanate to III. These results suggest that the actual course of the oxazolidinone-forming reaction involves a relatively rapid, reversible trimerization of phenyl isocyanate to III accompanied by a slower reaction between phenyl glycidyl ether and phenyl isocyanate. While the isocyanurate structure III is commonly held to be relatively stable and has not been previously reported as subject to dissociation, in the present work it has been found that III, when treated with a stoichiometric amount of phenyl glycidyl ether in the presence of benzyldimethylamine, forms the oxazolidinone I in yields corresponding to those obtained from phenyl glycidyl ether and phenyl isocyanate. Further evidence for the dissociation of III was furnished by the isolation of *n*-butylphenylurethan in a 73% yield from the reaction of III with *n*-butyl alcohol in the presence of the co-catalysts, benzyldimethylamine and phenyl glycidyl ether.



The reaction of phenyl isocyanate with one other epoxide has been briefly studied. Under reaction conditions that were similar to those used in the reaction with phenyl glycidyl ether, benzylethylene oxide provided a 12% yield of a compound that had the correct analysis for 5-benzyl-3-phenyloxazolidin-2-one (IV). In addition, a 36% yield of the trimer III was isolated along with a 50% recovery of unconsumed benzylethylene oxide. A more extended reaction time resulted in an increase in the yield of IV to 34%. Only 6% of unchanged epoxide was recovered and none of the trimer III could be isolated. The decreased degree of reactivity of benzylethylene oxide as compared to phenyl glycidyl ether in this reaction is consistent with the reported order of reactivity of substituted ethylene oxides to nucleophilic attack.[3]

EXPERIMENTAL[4]

5-Phenoxymethyl-3-phenyloxazolidin-2-one (I). A mixture of 11.9 g. (0.1 mole) of phenyl isocyanate, 15.0 g. (0.1 mole) of redistilled phenyl glycidyl ether, and 0.1 g. of benzyldimethylamine was heated in a sealed tube at 160° for 17 hr. The semicrystalline reaction mass was repeatedly recrystallized from benzene to yield 12.1 g. (45%) of 5-phen-

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[1] Kordite Company, Macedon, N. Y.

[2] R. C. Elderfield, *Heterocyclic Compounds,* Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1950, p. 32.

[3] L. Shechter, J. Wynstra, and R. Kurkjy, *Ind. Eng. Chem.,* 49, 1107 (1957).

[4] All melting points are uncorrected.