[Contribution from the Laboratory of Organic Chemistry of the University of Wisconsin]

Nitrogen Analogs of the Ketene Acetals

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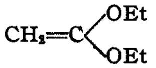
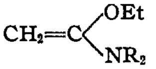
Since the high additive reactivity of the carbon to carbon double bond of ketene diethylacetal (I) is attributed to a hetero-enoid system in which *two* hetero-atoms (oxygen) activate the methylene carbon, it seemed of interest to prepare and study analogous compounds (II and III) in which one or both of the oxygens of ketene acetal are replaced by the more effective hetero-atom, nitrogen.



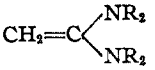
$CH_2{=}C(OEt)_2$

I



$CH_2{=}C(OEt)(NR_2)$

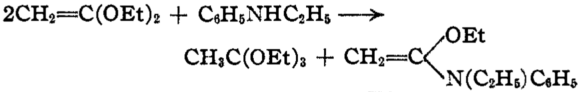
II



$CH_2{=}C(NR_2)_2$

III

A compound of type II, N-ethyl-N-(α-ethoxyvinyl)-aniline (1-ethoxy-1-ethylphenylaminoethylene, IV), was reported[1] in the fifth paper of a series on the ketene acetals. It was prepared by the action of ethylaniline on ketene acetal.



$$2CH_2{=}C(OEt)_2 + C_6H_5NHC_2H_5 \longrightarrow CH_3C(OEt)_3 + CH_2{=}C(OEt)N(C_2H_5)C_6H_5$$

IV

The compound IV was converted by hydrolysis into ethylaniline, alcohol and acetic acid; all attempts to stop the hydrolysis at the intermediate N-ethylacetanilide stage were unsuccessful. A compound of type III, 1,1-bis-(diethylamino)-2-chloroethylene [$ClCH{=}C(N(C_2H_5)_2)_2$], was recently reported[2] as the product of the reaction of dichloroacetylene with diethylamine. This diaminoethylene, in contrast to IV, was converted by hydrolysis in the presence of diethylamine into N,N-diethyl-diethylaminoacetamide.

A 1,1-disubstituted ethylene, 1,1-bis-(p-dimethylaminophenyl)-ethylene, which may be considered a vinylog of III, has been described.[3] Recently Gates[4] reported the reaction of this highly polar ethylene with certain quinones and noted that it was considerably more reactive than the analogous 1,1-dianisylethylene which may be looked on as a vinylog of ketene acetal (I).

While ethylaniline reacts with ketene acetal to give the 1,1-disubstituted ethylene IV, piperidine reacts with the acetal to form 1,1,1-tripiperidinoethane[1] (V). It was thought that a structure corresponding to III might be obtained from the pyrolysis of the tripiperidinoethane or from a quaternary base derived from it. The tripiperidinoethane V is quite stable to heat—it boils at 255–258° without decomposition—but when it was refluxed in a bath at 290–300° for nine hours, approximately 89% of the theoretical quantity of piperidine slowly distilled from it. However, the remaining product was polymeric, indicating either that the loss of piperidine was intermolecular or that the 1,1-dipiperidinoethylene, resulting from the intramolecular loss of piperidine, was polymerized during the long period of pyrolysis.

$$\underset{\text{V}}{nCH_3C(NC_5H_{10})_3} \longrightarrow CH_3C(NC_5H_{10})_2(CH_2C(NC_5H_{10})_2)_{n-2}CH_2C(NC_5H_{10})_3 + (n-1)C_5H_{10}NH$$

The dipiperidinoethylene corresponding to III could not be obtained by the pyrolysis of a quaternary base derived from V. Two methiodides were obtained when equivalent amounts of methyl iodide and V were allowed to react; one of these was an oily monomethiodide and the other, m. p. 157–162°, had an iodine content corresponding to a double salt of the mono- and dimethiodides. An excess of methyl iodide with V gave a third methiodide, m. p. 334–335°, which appeared to be a double salt of the di- and trimethiodides. Pyrolysis of the quaternary hydroxide from the monomethiodide yielded acetylpiperidine (53%); pyrolysis of the mixed t-butoxides from the double salt, m. p. 157–162°, returned the original tripiperidinoethane (V) in 85% yield.

The fact that ethylaniline reacts with ketene acetal to form the ethylene IV while piperidine yields the ethane V suggested the study of the action of other secondary amines on the acetal. Diethylamine and di-n-butylamine were chosen for this purpose and it was found that they behaved quite differently from the previously studied secondary amines. Both the 1-ethoxy-1-dialkylaminoethylene (II) and 1,1-bis-(dialkylamino)-ethylene (III) were obtained when either of these dialkylamines was heated with ketene acetal at 120–130°. The yields of III were 34–41% and of II 13–16% of the theoretical. The amounts of ethyl orthoacetate obtained along with the amino compounds showed that the following ratios of reactants were required

$$2CH_2{=}C(OEt)_2 + R_2NH \longrightarrow CH_3C(OEt)_3 + CH_2{=}C(OEt)NR_2 \quad \text{(II)}$$

$$3CH_2{=}C(OEt)_2 + 2R_2NH \longrightarrow 2CH_3C(OEt)_3 + CH_2{=}C(NR_2)_2 \quad \text{(III)}$$

It seems probable that the first step in the formation of II is the addition of the amine to ketene acetal followed by the loss of alcohol from the addition product (VI); the addition of another amine molecule to II and the subsequent loss of alcohol produces III. It is apparent from the above ratios of reactants that the rate at which the amine adds to the acetal is much lower than that at which alcohol adds to form the orthoester

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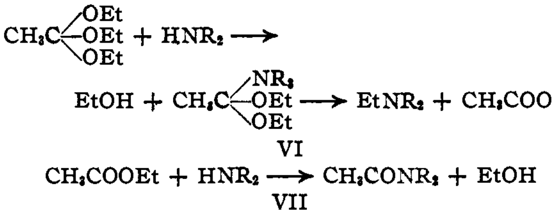
[1] Barnes, Kundiger and McElvain, This Journal, 62, 1281 (1940).

[2] Ott, Dittus and Weissenburger, *Ber.*, 76, 86 (1943).

[3] Pfeiffer and Wizinger, *Ann.*, 461, 132 (1928).

[4] Gates, This Journal, 66, 124 (1944).

Evidence for a mechanism involving the addition of the amine to ketene acetal was obtained when the preparation of II and III by the aminolysis of ethyl orthoacetate was attempted. This reaction did not occur in the temperature range (120–130°) used for the reaction of ketene acetal and the amine, but required 200–220° for about twelve hours to consume the orthoester completely. Under these conditions the orthoester was quantitatively converted to the N,N-dialkylacetamide (VII). The fact that the tertiary amine, $EtNR_2$, also was formed in this reaction indicates that an initial aminolysis product (VI) decomposed at this reaction temperature entirely into ethyl acetate instead of the ethoxyaminoethylene (II) which is formed at the lower temperature with ketene acetal. Further aminolysis of the normal ester then produced the amide.



$$CH_3C(OEt)_3 + HNR_2 \longrightarrow$$

$$EtOH + CH_3C(NR_2)(OEt)_2 \longrightarrow EtNR_2 + CH_3COOEt$$

VI

$$CH_3COOEt + HNR_2 \longrightarrow CH_3CONR_2 + EtOH$$

VII

Although none of the tertiary amine, $EtNR_2$, could be isolated from the reaction of ketene acetal and the secondary amines, small amounts of the amides (VII) were found, indicating that some decomposition of the intermediate addition product (VI) into ethyl acetate occurred at the lower temperatures that were used for this reaction.

The ethoxyaminoethylenes (II) as well as the diaminoethylenes (III) are basic and dissolve in dilute (5%) aqueous acids. The diaminoethylenes are hydrolyzed to the corresponding amide and the secondary amine. Alcoholysis of the diamino compounds gives a mixture of the ethoxyaminoethylenes (II) and the amides. N-Ethyl-N-(α-ethoxyvinyl)-aniline (IV) dissolves exothermically in alcohol but distillation of the solution returns this ethylene unchanged. This behavior, together with the fact that the ethylenes of type II (R is ethyl and *n*-butyl) result from the alcoholysis of those of type III in the presence of a large excess of alcohol, suggests that the addition product VI readily reverts to the ethoxyaminoethylene on heating. Both the ethoxyaminoethylenes and diaminoethylenes (II and III) show considerable tendency to polymerize during distillation.

An attempt was made to hydrogenate 1,1-bis-(diethylamino)-ethylene (III, R is ethyl) to the corresponding ethane. Under the mildest conditions (Raney nickel and 2100 pounds of hydrogen pressure at 60°) of hydrogen absorption, hydrogenolysis occurred and a mixture of diethylamine and triethylamine was obtained.

Further work on the reactions of these nitrogen analogs of ketene acetal has been suspended temporarily. It is hoped that a fuller account of their properties and reactions may be reported at a later date.

Experimental

Pyrolysis of 1,1,1-Tripiperidinoethane.—In a 50-ml. flask was placed 18.5 g. (0.07 mole) of 1,1,1-tripiperidinoethane.[1] The flask was attached to an 8-cm. Widmer column and heated in a Wood's metal bath at 290–300° for nine hours. At the end of this time 5.1 g. (89%) of piperidine had distilled from the flask. Distillation of the remaining material gave 3.32 g. of an oily liquid boiling at 75–160° (1 mm.), and an undistillable residue of 7.8 g.

The tripiperidinoethane was quite stable at its boiling point for short periods of time and could be distilled at atmospheric pressure. At 740 mm. it distilled at 255–258° as a pale yellow oil, $n^{20}D$ 1.5060.

Methiodides of 1,1,1-Tripiperidinoethane.—To 35.1 g. (0.13 mole) of 1,1,1-tripiperidinoethane in 100 ml. of dry benzene was added 17.9 g. (0.13 mole) of methyl iodide in 50 ml. of benzene. This solution was allowed to stand twelve hours. On cooling the oil which had formed partially crystallized. The solid was collected on a filter and after two recrystallizations from acetone weighed 5.3 g. and melted at 157–162°. Evaporation of the mother liquors from this recrystallization gave 9.27 g. of material melting at 144–155°. The product melting at 157–162°, from the following analysis, appeared to be the double salt of the mono- and dimethiodides.

Anal. Calcd. for $C_{18}H_{36}N_3I \cdot C_{19}H_{39}N_3I_2$: I, 37.7. Found: I, 36.8.

Evaporation of the benzene from the oil in the filtrate after the first separation of crystals gave 21.2 g. (43%) of the oily monomethiodide. After several washings with absolute ether and drying in a vacuum desiccator, this oil was analyzed.

Anal. Calcd. for $C_{18}H_{36}N_3I$: I, 30.2. Found: I, 31.2.

The double salt of the di- and trimethiodide was prepared as follows: To a solution of 20.4 g. (0.14 mole) of methyl iodide in 40 ml. of absolute alcohol was added a solution of 10.0 g. (0.04 mole) of 1,1,1-tripiperidinoethane in 20 ml. of absolute alcohol and the resulting alcoholic solution refluxed an hour. The crystals which appeared on cooling were collected on a filter. After one recrystallization from absolute alcohol the product weighed 9.13 g. and melted at 334–335°

Anal. Calcd. for $C_{19}H_{39}N_3I_2 \cdot C_{20}H_{42}N_3I_3$: I, 52.8. Found: I, 52.2.

Preparation and Pyrolysis of the Methyl Quaternary Hydroxide of 1,1,1-Tripiperidinoethane.—A solution of potassium *t*-butoxide was prepared by dissolving 1.85 g. (0.05 atom) of potassium in 125 ml. of dry *t*-butyl alcohol. To this was added 0.9 g. (0.05 mole) of water and then 19.7 g. (0.05 mole) of the oily monomethiodide. The precipitated potassium iodide (7.7 g. or 99.5% of the theoretical amount) was filtered off and the *t*-butyl alcohol was evaporated with a water pump. The residue on distillation, gave 3.23 g. (53%) of acetylpiperidine, b. p. 69–70° (0.3 mm.).

Preparation and Pyrolysis of the Double Methyl Quaternary *t*-Butoxide of 1,1,1-Tripiperidinoethane.—To a solution of 3 g. (0.08 atom) of potassium in 100 ml. of dry *t*-butyl alcohol was added 25 g. (0.025 mole) of the double salt of the mono- and di-methiodide of 1,1,1-tripiperidinoethane in 50 ml. of *t*-butyl alcohol. The alcohol then was removed by distillation at atmospheric pressure. The remaining material, on distillation, yielded 12.03 g. (85%) of 1,1,1-tripiperidinoethane, b. p. 85–95° (1 mm.).

1,1-Bis-(diethylamino)-ethylene.—To 46 g. (0.64 mole) of diethylamine was added 111 g. (0.95 mole) of ketene acetal. This mixture was allowed to stand twelve hours and was then heated in a bomb at 120° for five and one-half hours. The bomb was cooled, emptied and washed with 50 ml. of dry ether. The washings were combined with the main product and distilled. After removal of the ether, the material was fractionated through a 10-plate Fenske column packed with glass helices. Fraction (a), 20.8 g.,

b. p. 50–72°, consisted of diethylamine, and a small amount of alcohol; fraction (b), 75.5 g., b. p. 65–73° (40 mm.) was chiefly ethyl orthoacetate; fraction (c), 10.8 g., b. p. 73–89° (40 mm.) was chiefly 1-ethoxy-1-diethylaminoethylene; fraction (d), b. p. 89–93° (40 mm.) amounted to 22 g. (41%) of pure 1,1-bis-(diethylamino)-ethylene, n^{20}_{D} 1.4520, d^{20}_{4} 0.8226.

Anal. Calcd. for $C_{10}H_{22}N_2$: N, 16.5. Found: N, 16.8.

1,1-Bis-(di-*n*-butylamino)-ethylene.—To 176 g. (1.35 moles) of di-*n*-butylamine was added 116 g. (1 mole) of ketene acetal. This mixture was heated at 130° for thirteen hours. Then the excess amine and the ethyl orthoacetate were removed by fractionation through a 13-cm. Widmer column. The residue on distillation gave (a) 9.9 g. of material boiling at 55–61° (0.3 mm.), (b) 21.7 g. boiling at 61–100° (0.4 mm.) and (c) 32.3 g. (34.5%) of 1,1-bis-(di-*n*-butylamino)-ethylene, b. p. 105–109° (0.7 mm.); n^{20}_{D} 1.4582; d^{20}_{4} 0.8326. Refractionation of fractions (a) and (b) gave 13.2 g. (13%) of 1-ethoxy-1-di-*n*-butylaminoethylene, b. p. 68–77° (0.7 mm.), and 12.77 g. (15%) of N,N-di-*n*-butylacetamide, b. p. 77–85° (0.8 mm.).

Anal. Calcd. for $C_{18}H_{38}N_2$: N, 9.93; M_D, 92.39. Found: N, 9.99; M_D, 92.46.

Reaction of Ethyl Orthoacetate with Di-*n*-butylamine.—To 26 g. (0.16 mole) of ethyl orthoacetate was added 80 g. (0.6 mole) of dl-*n*-butylamine and the mixture heated in a bomb at 200–220° for twelve hours. At the end of this time, the bomb was cooled and emptied, and washed with a small amount of ether. The reaction mixture and washings were distilled. Fraction (a) 13 g., b. p. 70–80°, consisted of alcohol and some ether; fraction (b), 53 g., b. p. 52–116° (11 mm.), was a mixture of di-*n*-butylamine and ethyl-di-*n*-butylamine; fraction (c), b. p. 116–120° (11 mm.), was N,N-di-*n*-butylacetamide and amounted to 27 g. (99%). The amine mixture (fraction b) together with 300 ml. of 10% sodium hydroxide solution was placed in a 3-necked, round-bottom 500-ml. flask, provided with a stirrer, reflux condenser and a dropping funnel, and 73 g. (0.52 mole) of benzoyl chloride was added slowly from the funnel while the mixture was stirred. The resulting mixture was heated and stirred for an hour at 100°. After removal of the aqueous solution, the insoluble organic layer was distilled and 5.5 g. (22%) of the tertiary amine, ethyl di-*n*-butylamine,[5] b. p. 173–185°, was collected before the N,N-di-*n*-butylacetamide began to distil.

Hydrolysis of 1,1-Bis-(di-*n*-butylamino)-ethylene.—To 5.6 g. (0.02 mole) of the diaminoethylene was added 5 g. (0.28 mole) of water containing a drop of dilute hydrochloric acid. No apparent reaction took place, so the mixture was heated on the steam-bath for one hour. After cooling, the mixture was extracted with ether, the extract dried over anhydrous sodium sulfate, and the ether removed. On distillation of the residue the following fractions were obtained: (a) 0.98 g. (38%) of di-*n*-butylamine, b. p. 50–56° (17 mm.); n^{20}_{D} 1.4161; (b) 0.05 g. of a mixture of amine and the amide, b. p. 56–126° (17 mm.) and (c) 1.49 g. (47%) of N,N-di-*n*-butylacetamide, b. p. 126–131° (17 mm.), n^{20}_{D} 1.4427. A residue of 1.0 g. remained in the flask.

Hydrogenation of 1,1-Bis-(diethylamino)-ethylene.—A solution of 13.3 g. (0.08 mole) of the diaminoethylene in 50 ml. of ether was placed in a hydrogenation bomb with 0.5 g. of Raney nickel catalyst and shaken at 40° with a hydrogen pressure of 2100 pounds for four hours. No pressure drop was noted, and the temperature was raised to 60°. After three hours at 60°, the catalyst was removed and the ether distilled. Most of the diethylamine present was carried off in the ether. The second fraction (7.2 g.), at 48–87°, was a mixture of diethyl- and triethylamines. The diethylamine was removed from this mixture with benzenesulfonyl chloride and the remaining triethylamine identified as the picrate, m. p. 172.5–173°; a mixed melting point with an authentic sample of the picrate of triethylamine was 172–173°.

Alcoholysis of 1,1-Bis-(diethylamino)-ethylene: 1-Ethoxy-1-Diethylaminoethylene.—A solution of 55.8 g. (0.33 mole) of the diaminoethylene in 85.0 g. of absolute alcohol was refluxed for four hours and then the alcohol and diethylamine was distilled off. The remainder was fractionated through a 10-plate Fenske column. The first fraction boiling at 74–75° (40 mm.) was 1-ethoxy-1-diethylaminoethylene and amounted to 29.0 g. (62%); n^{20}_{D} 1.4382; d^{20}_{4} 0.8441. The second fraction was 11.8 g. (31%) of N,N-diethylacetamide, b. p. 93–100° (40 mm.); n^{20}_{D} 1.4310.

Anal. Calcd. for $C_8H_{17}ON$: N, 9.79; OC_2H_5, 31.5; M_D, 44.54. Found: N, 9.75; OC_2H_5, 31.5; M_D 44.08.

1-Ethoxy-1-(di-*n*-butylamino)-ethylene.—A solution of 29.6 g. (0.11 mole) of 1,1-bis-(di-*n*-butylamino)-ethylene in 80 ml. of absolute alcohol was refluxed five hours and then distilled. Fraction (a) 74 g., consisted of alcohol, b. p. 75–79°; fraction (b) 13.3 g., was di-*n*-butylamine, b. p. 40–65° (25 mm.). The remainder of the liquid was fractionated through a 10-plate Fenske column. Fraction (c), 2.64 g., b. p. 55–109° (15 mm.), was a mixture of di-*n*-butylamine and the ethoxy-aminoethylene; fraction (d) was pure 1-ethoxy-1-di-*n*-butylaminoethylene, b. p. 109–110° (15 mm.), n^{20}_{D} 1.4460; d^{20}_{4} 0.8512, and amounted to 5.62 g. (27%); fraction (e), b. p. 109–126° (15 mm.), was N,N-di-*n*-butylacetamide and weighed 4.54 g. (25%); a residue of 6.1 g. could not be distilled.

Anal. Calcd. for $C_{12}H_{25}ON$: N, 7.03; OC_2H_5, 22.6; M_D, 62.56. Found: N, 6.96; OC_2H_5, 21.1; M_D, 62.41.

Reaction of N-Ethyl-N-(α-ethoxyvinyl)-aniline[1] (1-Ethoxy-1-ethylphenylamino-ethylene) with Alcohol.—To 5.43 g. (0.028 mole) of this ethylene was added 1.31 g. (0.028 mole) of absolute alcohol. The mixture became hot and after standing for several hours it was distilled. After the alcohol distilled out 3.7 g. (68%) of the original ethylene, b. p. 128–130° (22 mm.), was recovered.

Summary

In contrast to ethylaniline and piperidine, which yield, respectively, 1-ethoxy-1-ethylphenylamino-ethylene and 1,1,1-tripiperidinoethane when caused to react with ketene diethylacetal, diethylamine and di-*n*-butylamine convert this acetal to 1,1-bis-(dialkylamino)-ethylenes ($CH_2{=}C(NR_2)_2$) and 1-ethoxy-1-dialkylamino-ethylenes ($CH_2{=}C(OEt)NR_2$).

1,1,1-Tripiperidinoethane loses piperidine on pyrolysis but polymeric material and not the dipiperidinoethylene is the product of this decomposition. Pyrolysis of quaternary bases derived from 1,1,1-tripiperidinoethane also fails to produce 1,1-dipiperidinoethylene.

Ethyl orthoacetate is quantitatively converted to N,N-dialkylacetamides by diethylamine and di-*n*-butylamine. The tertiary amine, $EtNR_2$, also is formed in this aminolysis.

Some of the properties of the 1,1-bis-(dialkylamino)-ethylenes and the 1-ethoxy-1-dialkylamino-ethylenes, which may be considered as nitrogen analogs of the ketene acetals, are discussed.

Madison, Wisconsin

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[5] German Patent 611,283; *Chem. Abs.*, **29**, 4022 (1935).