[Contribution from the Baker Laboratory of Chemistry at Cornell University]

# THE STRUCTURE OF WEDEKIND'S KETENIUM COMPOUNDS*

LEON L. MILLER and JOHN R. JOHNSON

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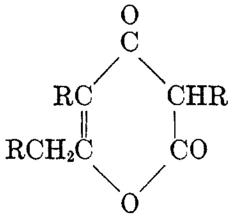
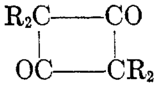
About thirty years ago Wedekind[1] and his collaborators investigated the action of aliphatic tertiary amines on the acid chlorides of mono- and di-substituted acetic acids. Their studies led to the generalization that typical acid chlorides of the form $RCH_2-COCl$ give rise to 2,4-pyronones (I), and those of the form $R_2CH-COCl$ to 1,3-cyclobutanediones (II). The ketenes (III) were assumed to be intermediate products but were not isolated by Wedekind.



I



II

$RCH{=}C{=}O$

$R_2C{=}C{=}O$

III

From isobutyryl chloride and triethylamine they obtained the crystalline dimethylketene dimer[2] (mp. 115–116°) in 18–20 per cent. yields, along with a small quantity of a colorless liquid (b.p. 192–193°). They concluded that this accessory product was composed of one molecule of dimethylketene and one of triethylamine, although their analytical data did not agree accurately with this composition. The compound was named dimethylketene-triethylium[3] and two structures (IV and V) were suggested for it.†

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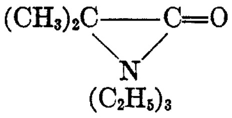
* This article is an abstract of a portion of a doctoral dissertation submitted to the Faculty of the Graduate School of Cornell University by Leon L. Miller.

[1] Wedekind *et al.*, *Ann.*, **323**, 246 (1902); **378**, 264 (1910).

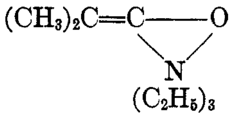
[2] Wedekind and Weiswange, *Ber.*, **39**, 1631 (1906).

[3] Wedekind and Miller, *Ber.*, **42**, 1269 (1909).

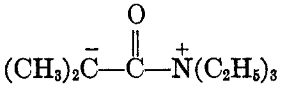
† A meaningless coördination formula, $(CH_3)_2C = CO \cdots N(C_2H_5)_3$, was proposed subsequently by Wedekind and Weinand, *Ber.*, **55**, 64 (1922).



IV

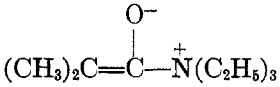


V



$(CH_3)_2\overset{-}{C}-\overset{\overset{O}{\|}}{C}-\overset{+}{N}(C_2H_5)_3$

VI



$(CH_3)_2C=\overset{\overset{O^-}{|}}{C}-\overset{+}{N}(C_2H_5)_3$

VII

Dimethylketene-triethylium was the first of a series of five similar substances which were obtained by Wedekind and were regarded as a new class of ketene derivatives.[4] These were given the general name ketenium compounds, to distinguish them from Staudinger's ketene bases,[4] formed by combination of two molecules of a ketene and one of a pyridine base. The latter differ very markedly from the ketenium compounds in their chemical behavior.

It is now recognized that nitrogen cannot exceed a covalence of four, and the modern equivalents of Wedekind's original formulæ would be electromeric (resonating) forms (VI and VII) of an addition complex. Since these systems are structurally analogous to enolate anions they should be extremely reactive, but actually the ketenium compounds are remarkably inert. Wedekind observed that dimethylketene-triethylium is unaffected by strong aqueous alkalies and is hydrolyzed only by prolonged heating with concentrated hydrochloric acid. He reported the formation of isobutyric acid and triethylamine hydrochloride by hydrolysis, and obtained isobutyraldehyde and triethylamine by catalytic reduction. The stability of the ketenium compounds cannot be reconciled with the structures VI and VII, which probably represent the labile intermediate products that are responsible for the catalytic effect of tertiary amines in certain ketene reactions. Furthermore, Staudinger[4] observed that the ketenium compound is not formed by direct combination of dimethyl ketene and triethylamine, and the present investigation disclosed the fact that it is not formed by heating dimethylketene dimer and triethylamine for 150 hours at 140°.

Since the ketenium compounds cannot be formulated upon any rational basis,* it seemed of interest to investigate their properties more fully. Repetition of Wedekind's procedure, with slight modifications, increased

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[4] *Cf.* STAUDINGER, "Die Ketene," **1912**, pp. 19, 87; STEWART, "Recent Advances in Organic Chemistry," **1927**, I, p. 95.

* The rational formula, $(CH_3)_2C = C(OC_2H_5)N(C_2H_5)_2$, appears to be excluded by the chemical behavior of the compound.

the yield of dimethyl ketene dimer to 60 per cent. of the theoretical; nevertheless, there was obtained a small quantity (3–5 per cent. yield) of the ketenium compound, which agreed in physical and chemical properties with that of Wedekind. However, the basic product resulting from its hydrolysis proved to be diethylamine instead of triethylamine (as reported by Wedekind). This result suggested that the alleged dimethylketene-triethylium is merely the diethylamide of isobutyric acid. This conclusion was confirmed by the fact that an authentic specimen of this amide (synthesized from diethylamine and isobutyric anhydride) was found to be identical in all respects with the supposed ketenium compound.

TABLE

PHYSICAL CONSTANTS OF DIETHYLAMIDES COMPARED WITH THOSE OF WEDEKIND'S KETENIUM COMPOUNDS

| ACID CHLORIDES R–CO–Cl | PHYSICAL CONSTANT | TRIETHYLIUM[a] COMPOUNDS | DIETHYLAMIDES R–CO–N$(C_2H_5)_2$ |
|---|---|---|---|
| $(CH_3)_2CH-$ | $n_D^{20}$<br>sp.gr.<br>b.p. | 1.440<br>0.892 (18°)<br>192–193°/740 mm. | 1.4382<br>0.891 (24°)<br>192–193°/740 mm. |
| $C_6H_5CHCl-$ | b.p.<br>m.p. | 150–155°/0.5 mm.<br>51° | 156–158°/4 mm.<br>51–51.5° |
| $ClCH_2-$ | b.p. | 120–125°/10 mm. | 109–110°/9 mm. |
| $Cl_2CH-$ | b.p. | 142–145°/18 mm. | 124–126°/19 mm.[b] |
| $BrCH_2-$ | b.p. | 128–129.5°/18 mm. | 114–117°/9 mm. |

[a] Physical constants in this column are those of Wedekind and Miller.[3]

[b] This specimen contained some of the monochloro compound.

Specimens of the appropriate diethylamides were synthesized for comparison with the four other ketenium compounds reported by Wedekind, and the results are shown in the table. The diethylamide of phenylchloroacetic acid was found to melt at 51–51.5°, in close agreement with the value 51° reported for the supposed ketenium compound. In general, the boiling-points of the authentic diethylamides are lower than the values reported for the ketenium compounds; these discrepancies are due to the fact that Wedekind's determinations were made with exceedingly small specimens. There can be no doubt that dimethylketene- and phenylchloroketene-triethylium are identical with the diethylamides of the corresponding acids, and it is extremely probable that the same is true for the remainder of the list.

The diethylamides appear to arise from the presence of small quantities of diethylamine as an impurity in the triethylamine. Owing to the use of a considerable excess of the latter, a quantity of only 1–3 per cent. of secondary amine would account for the observed results. It is unlikely that the diethylamides arise by the interaction of triethylamine with the acid chloride; a reaction of this type has been found to occur with trimethylamine and benzene sulfonyl chloride but not with benzoyl chloride.[5]

$$(CH_3)_2CH\text{—}COCl + 2\ N(C_2H_5)_3 \rightarrow (CH_3)_2CH\text{—}CO\text{—}N(C_2H_5)_2 + N(C_2H_5)_4Cl$$

This possibility appears to be excluded in the present instance, since an examination of the amine salt produced in the reaction failed to reveal any tetraethylammonium chloride.

## EXPERIMENTAL

*Isobutyryl chloride and triethylamine.*—(a) A solution of 100 g. (0.94 mole) of pure isobutyryl chloride in 100 cc. of pure, dry carbon disulfide was added dropwise with shaking, but without external cooling, to 97 g. (0.96 mole) of dry triethylamine (Kahlbaum) in 200 cc. of carbon disulfide. The reaction mixture was warmed gently for several hours, and after standing overnight the precipitate of amine hydrochloride was removed by suction filtration. The procedure of Wedekind was followed except that the reaction was not carried out in a constant stream of dry hydrogen. The products obtained were: 113 g. of triethylamine hydrochloride (86% of the theoretical), 22 g. of dimethylketene dimer (33% yield), and 4 g. of a light-yellow liquid (b.p. 192–194; $n_D^{20}$ 1.443) corresponding to Wedekind's dimethyl ketenetriethylium (b.p. 192–194°, $n_D^{20}$ 1.440). The supposed triethylium compound had a disagreeable odor and gave a positive test for sulfur. From a similar experiment Wedekind obtained 123 g. of triethylamine hydrochloride (95% yield), 12 g. of dimethyl ketene dimer (18% yield) and 17 g. of crude triethylium compound.

(b) Since Staudinger[6] has shown that dimethyl ketene combines with carbon disulfide in the presence of tertiary amines it is evident that this solvent is inappropriate. Wedekind had observed that anhydrous ether was superior but failed to note that carbon disulfide actually reacted with the ketenes. Our experiments showed that the yields of dimethylketene dimer were increased threefold by using anhydrous ether or ligroïn (60–80°) as solvent and effecting the reaction at room temperature. In a typical preparation, 53 g. (0.5 mole) of isobutyryl chloride in 100 cc. of anhydrous ether was added to 86 g. (0.85 mole) of triethylamine in 150 cc. of the same solvent, and the reaction mixture was allowed to stand at 20–25° for 10–15 days. The products were 65 g. (95% of the theoretical) of triethylamine hydrochloride, 20 g. (57% yield) of dimethylketene dimer, and about 2 g. of a *colorless* liquid, b.p. 192–194°, $n_D^{20}$ 1.438. This product had a pleasant terpene-like odor, instead of the disagreeable odor of the specimens obtained from carbon disulfide solutions.

Wedekind and Miller[3] state that their specimen gave a 95% yield of triethylamine

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[5] JONES AND WHALEY, *J. Am. Chem. Soc.*, **47**, 1343 (1925).

[6] STAUDINGER, *Helv. Chim. Acta*, **8**, 320 (1925).

hydrochloride, m.p. 253°, upon hydrolysis with concentrated hydrochloric acid in a sealed tube. The identity of the amine was not confirmed by further tests. Our specimen of the liquid boiling at 192–193° gave a 60% yield of diethylamine hydrochloride, m.p. 214–217°. No melting-point depression was observed when this salt was mixed with authentic diethylamine hydrochloride, m.p. 218–219°. The free amine from our specimen gave an acid-oxalate, m.p. 207–210°, which showed no melting-point depression on mixture with authentic diethylamine acid-oxalate, m.p. 208–210°.

*Authentic diethylamides.*—(a) Isobutyrodiethylamide was prepared by treating 25 g. (0.16 mole) of isobutyric anhydride with 10 g. (0.14 mole) of diethylamine, and refluxing gently for one-half hour. Fractionation of the mixture gave 17.5 g. (90% yield) of the diethylamide; b.p. 192–194°/740 mm., $n_D^{20}$ 1.4382, sp. gr. (24°) 0.892.

*Anal.* Calc'd for $C_8H_{17}NO$: N, 9.78. Found: N, 9.61, 9.68.

(b) Phenylchloracetodiethylamide was obtained in 40% yield by adding a solution of 4 g. (0.02 mole) of phenylchloroacetyl chloride in ligroïn (60–80°) to 3 g. (0.04 mole) of diethylamine in the same solvent. The general method of Jacobs and Heidelberger[7] gave a similar yield. A cold aqueous solution of 17 g. (0.16 mole) of diethylamine hydrochloride, containing 0.33 mole of sodium hydroxide, was treated with 25 g. (0.13 mole) of phenylchloroacetyl chloride. There was obtained 12 g. of the diethylamide; colorless, viscous liquid, b.p. 156–158°/4 mm. On cooling and scratching the oil solidified, and after crystallization from methyl alcohol melted at 51–51.5°.

*Anal.* Calc'd for $C_{12}H_6ClNO$: Cl, 15.72. Found: Cl, 15.68, 15.70.

(c) Chloroacetodiethylamide has been described by Jacobs and Heidelberger[7] who reported its boiling point as 125.5–130.5° (mainly 126.5–128.5°)/21–22 mm. Our specimen, prepared from chloroacetyl chloride according to their directions, distilled at 109–110°/9 mm.

(d) Dichloroacetodiethylamide was prepared from the middle fraction (b.p. 84–85°/9 mm.) of a commercial specimen of "pure" dichloroacetic acid, by conversion to the acid chloride and treatment with diethylamine according to the general method of Jacobs and Heidelberger. The diethylamide (50% yield) distilled at 124–126°/19 mm., but chlorine analyses indicated that this product contained about 90% of the desired amide and 10% of the monochloro compound.

*Anal.* Calc'd for $C_6H_{11}Cl_2NO$: Cl, 38.53. Found: Cl, 36.92, 36.80, 36.99.
Calc'd for $C_6H_{12}ClNO$: Cl, 23.72.

As we were interested merely in knowing roughly the boiling-point of this amide, the preparation was not repeated with pure dichloroacetic acid. It is evident that the diethylamides of chloroacetic and dichloroacetic acids (like the free acids and acid chlorides) have almost exactly the same boiling-points and cannot be separated by ordinary fractional distillation methods.

(e) Bromoacetodiethylamide was obtained in 20% yield by treating 14 g. of diethylamine, in aqueous alkaline solution, with 38 g. of bromoacetyl bromide. This amide is a colorless liquid, b.p. 114–117°/9 mm., possessing powerful lachrymatory and sternutative properties.

*Anal.* Calc'd for $C_6H_{12}BrNO$: Br, 41.38. Found: Br, 41.45, 41.80, 41.87.

A preliminary attempt to obtain this amide from bromoacetic acid by way of bromoacetyl chloride, gave an impure product containing an appreciable amount of the chloro amide.

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[7] Jacobs and Heidelberger, *J. Biol. Chem.*, **21**, 148 (1915).

## SUMMARY

The reaction between isobutyryl chloride and triethylamine, in the presence of organic solvents, has been investigated. The principal product was found to be dimethylketene dimer, which can be isolated in 60 per cent. yield by slight modifications of Wedekind's procedure.

It has been shown that Wedekind's ketenium compounds, such as dimethylketene- and phenylchloroketene-triethylium, are merely dialkylamides of the corresponding acids and are not to be regarded as a general class of ketene derivatives. Apparently these amides owe their origin to the presence of a small amount of secondary amine as an impurity in the usual samples of aliphatic tertiary amines.