

phase (both temperatures in absolute degrees).

This equation is valid over the entire range of temperature and composition from the freezing point of the pure component to the eutectic temperature, if the solution is ideal and Q is constant. According to this equation the plot of $\log X$ against $1/T$ will be a straight line. When the data recorded in Table I were plotted in this manner, it was found that only in the system diphenylamine-phenoxathiin did straight lines result when both components were considered as solvents. In the system diphenylamine-dibenzofuran, a straight line resulted when dibenzofuran was taken as solvent. In all other cases the curves deviated in varying degrees from a straight line particularly at the higher concentration of solute, that is, near the eutectic concentrations.

From the data obtained in these experiments the freezing point constants—that is, the freezing point lowering, in degrees centigrade, per mole of solute dissolved in 1000 g. of the solvent—were calculated for the six compounds worked with. The values obtained were: diphenylamine 6.55, phenoxathiin 7.7, *p*-nitrophenetole 5.7, 1-nitro-

naphthalene 6.5, dibenzofuran 7.3 and phenothiazine 12.0. The eutectic temperatures and compositions are presented in Table II.

TABLE II
EUTECTIC COMPOSITIONS AND TEMPERATURES FOR BINARY SYSTEMS CONTAINING DIPHENYLAMINE

Other compound	Mole, %	Eutectic temp., °C.
Phenoxathiin	49.5	26.4
<i>p</i> -Nitrophenetole	44.6	24.3
1-Nitronaphthalene	49.8	23.7
Dibenzofuran	35.2	34.6
Phenothiazine	7.5	49.3

Summary

The crystallization temperatures, eutectic composition, and eutectic temperatures have been determined for the binary systems diphenylamine and phenoxathiin, diphenylamine and *p*-nitrophenetole, diphenylamine and 1-nitronaphthalene, diphenylamine and dibenzofuran, and diphenylamine and phenothiazine. From the data obtained the freezing point constants were calculated for the six compounds investigated.

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[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Ketene Acetals. IX. Ketene Dialkylacetals

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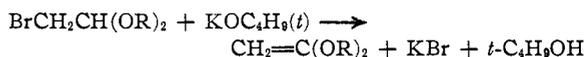
The preparation of ketene diethylacetal by two distinctly different procedures¹ and the properties which this compound was found to possess have shown, beyond all doubt, that the claims of Scheibler and associates² to have isolated this substance from the reaction of sodium and/or sodium ethoxide with ethyl acetate are spurious. In spite of this fact it seemed worth while to prepare and record the correct properties of certain homologs of ketene diethylacetal which have been reported³ from Scheibler's laboratory. One of these homologs, methylketene diethylacetal, $\text{CH}_3\text{CH}=\text{C}(\text{OC}_2\text{H}_5)_2$, has been described in the paper that dealt with the preparation of ketene acetals by the action of sodium on α -bromo-orthoesters.^{1c}

(1) (a) Beyerstedt and McElvain, *THIS JOURNAL*, **58**, 529 (1936); (b) Johnson, Barnes and McElvain, *ibid.*, **62**, 968 (1940); (c) Walters and McElvain, *ibid.*, **62**, 1482 (1940).

(2) Scheibler *et al.*, *Ber.*, **55**, 801 (1922); *Ann.*, **458**, 15 (1927); *THIS JOURNAL*, **55**, 425 (1933).

(3) Scheibler, Marhenkel and Nikolic, *Ann.*, **458**, 21 (1927).

The present paper reports the preparation and properties of ketene di-*n*-propyl-, di-isobutyl- and di-isoamylacetal. Each of these compounds was prepared by the elimination of hydrogen bromide from the corresponding dialkylbromoacetal by means of potassium *t*-butoxide according to the procedure reported in an earlier paper,^{1b} thus



The boiling points of these homologous ketene acetals and of the corresponding esters of which the ketene acetals are the enol ethers are summarized in Table I. The boiling points of the ketene acetals as reported³ by Scheibler and his collaborators are also included in this table. For comparison the corresponding values for ketene diethylacetal and methylketene diethylacetal which were reported earlier^{1c} are given. It may be seen from these data that there is not only the marked

difference between the boiling points of the ketene acetals and the corresponding esters that was noted in a previous paper,⁴ but that this difference increases, as would be expected, when the size of the acetalalkyl group increases. In this connection it should be noted that the boiling points which Scheibler has reported for these ketene acetals are practically the same as, or even lower than, those of the corresponding esters.

TABLE I
BOILING POINTS OF KETENE ACETALS, R'CH=C(OR)₂,
AND THE CORRESPONDING ESTERS, R'CH₂COOR

R' is	R is	B. p., °C.	B. p., of ester	Diff.	B. p. rep. by Scheibler, <i>et al.</i>
H	<i>n</i> -Propyl	153-154	101	53	105
H	<i>i</i> -Butyl	180-181	116	65	111
H	<i>i</i> -Amyl	210-211	142	69	132
H	Ethyl	122-124	77	47	78
CH ₃	Ethyl	133-134	98	36	80

Nissen.⁵ These acetals boiled at 146-148°, 170-172° and 209-212°, respectively, and in general, their physical properties corresponded with those reported for these compounds by Hinton and Nieuwland.⁶

Bromo-dialkylacetals.—These compounds were prepared by two different procedures, (a) the direct bromination of the acetal according to the method of Hartung and Adkins for the preparation of bromo-diethylacetal⁷ and (b) by the addition of bromine to vinyl acetate in solution in the alcohol corresponding to the acetal. Procedure (b) is an adaptation of the method described by Filachione⁸ for the preparation of bromo-diethylacetal and from the standpoint of convenience, is preferable to procedure (a). The yields when procedure (a) was used were 40-66% while those from procedure (b) were 50-60% of the theoretical.

Ketene Dialkylacetals.—These ketene acetals were prepared by the action of potassium *t*-butoxide in *t*-butyl alcohol on the bromoacetals according to the procedure for the preparation of ketene diethylacetal.^{1b} The properties and analyses of these compounds are summarized in Table III.

TABLE II
BROMO-DIALKYLACETALS, BrCH₂CH(OR)₂

R is	B. p., °C. (mm.)	<i>n</i> _D ²⁰	<i>d</i> ₄ ²⁰	Formula	Analyses, % Br	
					Calcd.	Found
<i>n</i> -Propyl ^a	94-95 (19)	1.4406	1.199
<i>i</i> -Butyl	109-110 (19)	1.4390	1.129	C ₁₀ H ₂₁ O ₂ Br	31.56	31.82
<i>i</i> -Amyl	137-139 (20)	1.4440	1.102	C ₁₂ H ₂₅ O ₂ Br	28.41	28.73

^a This acetal has been described previously by Rotbart, *Ann. Chim.*, [11] 1, 507 (1934).

TABLE III
KETENE DIALKYLACETALS, CH₂=C(OR)₂

R is	Yield, %	B. p., °C. (mm.) ^a	<i>n</i> _D ²⁰	<i>d</i> ₄ ²⁰	Formula	Analyses, %			
						Carbon		Hydrogen	
						Calcd.	Found	Calcd.	Found
<i>n</i> -Propyl	52	58-59 (16)	1.4200	0.879	C ₈ H ₁₆ O ₂	66.62	66.45	11.19	11.06
<i>i</i> -Butyl	47	76-77 (17)	1.4212	.875	C ₁₀ H ₂₀ O ₂	69.72	69.49	11.70	11.64
<i>i</i> -Amyl	51	105-106 (17)	1.4300	.856	C ₁₂ H ₂₄ O ₂	71.95	71.80	12.08	12.08

^a The boiling points of these acetals at atmospheric pressure are given in Table I.

Other properties together with the analyses of the new ketene dialkylacetals are listed in Table III.

One other substituted ketene diethylacetal, ethoxyketene diethylacetal (triethoxyethylene), has been reported³ from Scheibler's laboratory. Unsuccessful attempts to prepare this compound will be described in a later paper.

Experimental

Dialkylacetals.—Di-*n*-propyl-, di-*i*-isobutyl- and di-*i*-isoamylacetal were prepared by the method of Adkins and

(4) Beyerstedt and McElvain, *THIS JOURNAL*, **59**, 2266 (1937).

Summary

The preparation of ketene di-*n*-propyl-, di-*i*-isobutyl- and di-*i*-isoamylacetal is described. The properties which these acetals are found to possess completely invalidate the claims of Scheibler to have prepared this type of compound by the action of sodium or sodium ethoxide on an ester.

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(5) "Organic Syntheses," Coll., Vol. I, 1 (1932).

(6) Hinton and Nieuwland, *THIS JOURNAL*, **52**, 2893 (1930).

(7) Hartung and Adkins, *ibid.*, **49**, 2520 (1927).

(8) Filachione, *ibid.*, **61**, 1705 (1939).