TABLE III

ANALYSES

Expt.	Alkylbenzene	% C		% H		Mol. wt.	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
23	i-C_8H_{17}	88.4	88.6	11.6	11.0	190	182
24	i-$C_{12}H_{25}$	87.6	88.0	12.3	12.2	246	243

found possible to recover boron fluoride, as the dihydrate, from the acid layers by addition of the calculated amount of water and distillation.[6] Boron fluoride was thus recovered as $BF_3 \cdot 2H_2O$, b. p. 91° at 25 mm., from Expt. 35 in 95% yield.

Further work is in progress.

Summary

1. Certain acidic dehydrating agents assist boron fluoride as a condensing agent in the alkylation of benzene with primary alcohols.
2. Data are given for thirty-eight experiments, showing the influence of conditions upon yields of products.
3. Normal and secondary alcohols give secondary alkylbenzenes. Iso and tertiary butyl alcohol gave t-butylbenzene. Dialkylation proceeds mainly para.
4. Alcohols as high as dodecyl have been used successfully.

NOTRE DAME, INDIANA RECEIVED FEBRUARY 23, 1940

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Chlorination and the Structure of Acetylketene

BY CHARLES D. HURD AND J. L. ABERNETHY

The recent paper[1] by Boese on "diketene" mentions that this substance "rapidly absorbs chlorine at low temperatures to yield γ-chloroacetoacetyl chloride" and states that it is "stable only at low temperatures and cannot be purified by distillation." Since no details were listed, this note is submitted in view of our similar work on the same compound.

Chlorine was passed into an ice-cold, vigorously-stirred solution of 7 cc. of acetylketene in 20 cc. of carbon tetrachloride until there was a 6-g. increase in weight. The mixture was slightly yellow in color. Distillation of the solvent with a steam-bath left an orange-colored residue of chloroacetoacetyl chloride, $ClCH_2COCH_2COCl$, which was vacuum distilled. Extensive decomposition occurred, but 1.5 cc. of the acid chloride was obtained at 93–96° (8 mm.), or 117–119° (17 mm.). The distillate was orange colored and fumed in moist air. A black tar remained in the distilling flask. These physical constants were obtained for the chloroacetoacetyl chloride: $d^{20}{}_4$ 1.4397; $n^{20}{}_D$ 1.4860; mol. rotation, calcd. 30.77, found 30.89.

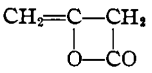
Anal. Calcd. for $C_4H_4O_2Cl_2$: Cl, 45.7. Found: Cl, 45.2, 45.1.

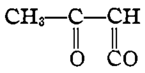
Chloroacetoacetyl chloride was converted to ethyl chloroacetoacetate, $ClCH_2COCH_2COOC_2H_5$, as follows. Five cc. of acetylketene in 30 cc. of carbon tetrachloride was treated with chlorine until 4.5 g. had been absorbed. Then, without distillation, the solution was poured slowly into an excess of absolute alcohol at 0°. On distillation, 6 cc. of the ethyl ester was collected at 117–119° (17 mm.). This ester has been made in other ways by several investigators.[2]

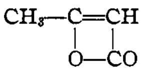
Chloroacetoacetanilide, $ClCH_2COCH_2CONHC_6H_5$, was obtained by mixing pure chloroacetoacetyl chloride with an equivalent amount of aniline in benzene. The aniline hydrochloride was removed by washing with water. Then the benzene was distilled off and the resulting anilide was crystallized from ether. The melting point was 140–141°.

Anal. Calcd. for $C_{10}H_{10}O_2NCl$: N, 6.61. Found: N, 6.75, 6.71.

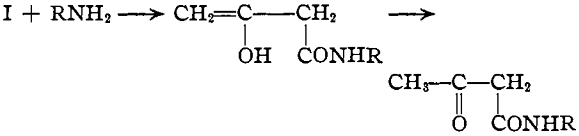
Boese adopts vinylaceto-β-lactone (I) as a preferred structure for ketene dimer. With


I


II


III

(I) addition reactions with alcohols or amines may be explained by assuming reaction at the lactone position, followed by tautomerization



$$\mathrm{I} + RNH_2 \longrightarrow \underset{\displaystyle OH\quad CONHR}{CH_2{=}C{-}{-}CH_2} \longrightarrow \underset{\displaystyle O\qquad CONHR}{CH_3{-}\overset{}{C}{-}CH_2}$$

Hydrogenation to butyro-β-lactone must involve addition at the double bond. Neither of these reactions are critical for purposes of structure

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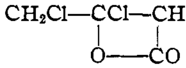
(1) Boese, *Ind. Eng. Chem.*, **32**, 20 (1940).

(2) Lespieau, *Compt. rend.*, **138**, 422 (1904); Picha, Doht and Weisl, *Monatsh.*, **27**, 1247 (1906); Schlotterbeck, *Ber.*, **42**, 2570 (1909); Alexandrow, *ibid.*, **46**, 1022 (1913).

proof because they may be explained also from acetylketene (II) or its resonance isomer crotono-β-lactone (III).

When the dimer is halogenated, chlorine presumably adds to the double bond. If structure II is selected then a subsequent rearrangement is involved to explain the formation of chloroacetoacetyl chloride which is actually produced. Since ethyl acetobromoacetate, $CH_3COCHBrCOOC_2H_5$, is known[3] to rearrange to ethyl bromoacetoacetate, $CH_2BrCOCH_2COOC_2H_5$, such a rearrangement for the corresponding acid chloride also seems plausible. Indeed it may be assumed that the COCl or COBr groups promote a more rapid rearrangement than the $COOC_2H_5$ group.

Formula I, in the halogenation reaction, also calls for rearrangement because 

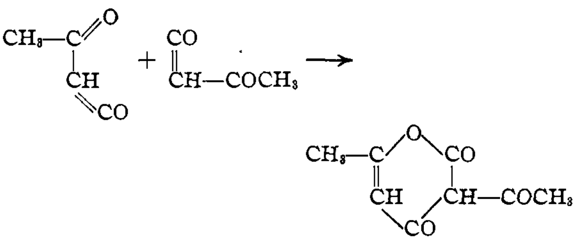
$$\begin{array}{llll} CH_2Cl— & CCl & — & CH_2 \\ & | & & | \\ & O & — & CO \end{array}$$

would represent the initial addition product at the double bond. Less readjustment is necessary than with II, however, because chlorine alone is involved, instead of hydrogen and chlorine. This seems to be the strongest evidence in favor of I. Unfortunately for its case, halogenation evidence is unreliable so frequently that one hesitates to trust it unless it is supported by other and better evidence.

An example in point is furfuryl chloride. By rules of metathesis, one would expect it to yield furylacetonitrile in its reaction with sodium cyanide. Instead, the substance obtained[4] is 5-methyl-2-furonitrile. Again, isobutylene and chlorine[5] yield chiefly methallyl chloride instead of isobutylene dichloride. Many other instances of irregularity with halogens might be cited.

The recently determined[6] value for the parachor of ketene dimer is more favorable to the equilibrium mixture of II $\rightleftarrows$ III than to I, II or III taken individually. The observed parachor at 25° is 188.0. The calculated parachors for I, II and III, respectively, are 182.4, 197.2, and 182.4.

Polymerization of ketene dimer to dehydroacetic acid (ketene tetramer) is far more simply explained from II than from I. From II, it is but an addition of the Diels-Alder type



From I, it is necessary to assume an initial condensation of the Claisen type, followed by several tautomeric shifts, and finally ring-closure.

One of the most powerful tools for structural proof is ozonolysis. By this approach, compound I should give rise to malonic acid, II to pyruvic aldehyde or acetic acid, III to pyruvic aldehyde or acetic acid. In the actual ozonolysis,[7] ketene dimer gave rise to pyruvic aldehyde and acetic acid. Malonic acid was sought for but not found.

This accumulation of critical evidence favors II and III as the correct structure for ketene dimer, and discredits formula I.

Summary

Evidence is reviewed for the structure of ketene dimer. An equilibrium mixture of the resonance isomers acetylketene and crotono-β-lactone best fits the evidence. Vinylaceto-β-lactone, which has been proposed recently, fails to explain the behavior on ozonolysis. Also, this structure does not satisfy the parachor, nor does it lend itself to a simple explanation of the polymerization to dehydroacetic acid.

Chlorine and acetylketene give rise to chloroacetoacetyl chloride. The latter reacts with alcohol and aniline to yield the ester and anilide, respectively.

EVANSTON, ILLINOIS RECEIVED MARCH 4, 1940

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(3) Hantzsch, *Ber.*, **27**, 355, 3168 (1894).

(4) Runde, Scott and Johnson, THIS JOURNAL, **52**, 1284 (1930); Reichstein, *Ber.*, **63**, 749 (1930).

(5) Burgin, Engs and Hearne, *Ind. Eng. Chem.*, **31**, 1413 (1939).

(6) Hurd and Roe, THIS JOURNAL, **61**, 3358 (1939).

(7) Hurd and Williams, *ibid.*, **58**, 964, 968 (1936).