The mono-semicarbazone formed long colorless needles (from dilute alcohol) melting at 203–204°.

Anal. Calcd. for $C_{18}H_{19}O_2N_3$: C, 69.9; H, 6.2; N, 13.6. Found: C, 69.9; H, 6.4; N, 13.6.

The Action of Mesitylmagnesium Bromide on Mesitylglyoxal.—Seventeen and six-tenths grams (0.1 mole) of mesitylglyoxal was added, over a period of six hours, to a solution of mesitylmagnesium bromide containing approximately 0.1 mole of reagent and no unchanged magnesium metal. The reaction mixture was decomposed with ice and hydrochloric acid and extracted with ether. Evaporation of the ether solution left an oil from which, on cooling, colorless crystals separated. Further cooling of the mother liquor gave a small amount of bright yellow crystals. The yellow solid was shown by the method of mixed melting points to be dimesityl diketone.

1,2-Di-(β-isoduryloyl)-ethylene Glycol.—The colorless product obtained from the above procedure melted at 160.5–161.5° (from alcohol).

Anal. Calcd. for $C_{22}H_{26}O_4$: C, 74.5; H, 7.4; mol. wt., 354. Found: C, 74.7; H, 7.7; mol. wt., 368.

The glycol was also prepared by the method of Gomberg and Bachmann.[4] To the reducing mixture prepared from 2.5 g. of magnesium and 7 g. of iodine in 17 cc. of dry ether and 25 cc. of dry benzene was added 8.8 g. of mesitylglyoxal dissolved in 8 cc. of benzene. The mixture was shaken and cooled frequently under the tap. At the end of forty-five minutes it was poured into water. By this method 39% of the theoretical amount of glycol was obtained.

Attempts to oxidize the glycol with nitric acid were unsuccessful. Also, the cömpound did not rearrange when treated according to the method of Gomberg and Bachmann.[4]

Diacetate of 1,2-Di-(β-isoduryloyl)-ethylene Glycol.—Two-tenths of a gram of the glycol was boiled with acetyl chloride for one hour. A colorless solid separated when water was added. The compound was recrystallized from alcohol; melting point 185.0–185.5°. The yield was nearly quantitative.

Anal. Calcd. for $C_{26}H_{30}O_6$: C, 71.2; H, 6.9. Found: C, 71.2; H, 7.0.

1,2-Di-(β-isoduryloyl)-ethane.—A mixture of 25 cc. of glacial acetic acid, 0.5 g. of red phosphorus, 0.5 g. of iodine and 0.5 cc. of water was heated for a few minutes and to the resulting solution was added 1.5 g. of the 1,2-di-(β-isoduryloyl)-ethylene glycol. The solution was boiled for two hours, filtered while hot and poured into 250 cc. of water containing 2 g. of sodium bisulfite. The reduction product when recrystallized from alcohol melted at 138–139°. According to Conant and Lutz[3] 1,2-di-(β-isoduryloyl)-ethane melts at 138.5°.

Summary

Mesitylglyoxal has been prepared by the oxidation of acetomesitylene with selenium dioxide.

In contact with alkalies mesitylglyoxal rearranges to mesitylglycolic acid.

Grignard reagents reduce the keto-aldehyde to the 1,2-di-(β-isoduryloyl)-ethylene glycol. It seems probable that the reducing agent is the bromomagnesium alcoholate. This suggestion is supported by the fact that an α-diketone is formed in the reaction.

URBANA, ILLINOIS RECEIVED DECEMBER 26, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY]

The Thermal Decomposition of Organic Compounds from the Standpoint of Free Radicals. VII. The Ethylidene Radical

BY F. O. RICE AND A. L. GLASEBROOK[1]

Staudinger and Kupfer[2] have shown that when carbon monoxide is passed through an ethereal solution of diazomethane, $CH_2{=}N{\equiv}N$, and the resulting gaseous mixture is led through a quartz tube heated in the range 400–500°, ketene $CH_2{=}CO$, which may easily be identified either by its odor or by combining it with aniline, is formed. They concluded that the CO combines directly with the nascent CH_2. It occurred to us therefore that a repetition of this experiment using diazoethane $CH_3CH{=}N{\equiv}N$ instead of diazomethane should give us some evidence concerning the existence of the ethylidene radical CH_3CH. When we repeated the original experiment we confirmed Staudinger's results, obtaining more than a gram of acetanilide from 0.8 g. of diazomethane; however, a second run, using diazoethane, yielded not a trace of methylketene, $CH_3CH{=}CO$; the gases leaving the hot tube had no characteristic odor, and a small quantity of aniline through which the gases were passed was recovered unchanged.

We next determined to test for the Paneth effect[3] with metallic mirrors during the decomposition of diazoethane. To this end we purified some diazoethane by distilling it at diminished pressure through a vacuum jacketed column, since our crude material contained some lower

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[1] General Motors Co. Fellow, 1930–1934.

[2] Staudinger and Kupfer, *Ber.*, **45**, 508 (1912).

[3] Paneth and Hofeditz, *ibid.*, **62**, 1335 (1929),

boiling constituent (possibly diazomethane), as well as various higher boiling materials used in the preparation. The pure substance was preserved in solution in dibutyl phthalate (which had also previously been partly distilled in a vacuum to remove any traces of volatile impurities). This solution could be preserved for several weeks at −80° and served as a convenient reservoir of pure diazoethane. When this pure diazoethane passed through a quartz tube heated in the range 600–650° at a pressure of about 0.5 mm. according to a technique previously described,[4] it had no effect whatsoever on an antimony mirror, although using diazomethane[5] under similar conditions, the mirror was removed almost instantaneously. Using diazoethane we found no effect, even on the thinnest mirrors, at furnace temperatures up to 1000°. Furthermore, no effect was observed when tellurium or zinc mirrors were substituted for those of antimony.

In connection with the foregoing work it is only necessary to go into experimental details concerning the preparation and preservation of the diazoethane. This was prepared in a 100-cc. round-bottomed Pyrex flask with a side arm.[6] The neck of the flask was fitted with a dropping funnel and the side arm was bent in order to conduct the vapors into a Pyrex tube containing 20 cc. of dibutyl phthalate immersed partly in liquid air. The generating flask contained 40 cc. of dibutyl phthalate and 5 cc. of nitrosoethyl urethan; 5 cc. of saturated potash in pure methanol was added from the dropping funnel without heating. A deep yellow color developed immediately and by means of a vacuum the diazoethane vapor was drawn over into the liquid air trap. On warming to −80° or a little higher and shaking, the diazoethane dissolved in the dibutyl phthalate.

This solution required further purification, which was accomplished by distillation at about 60 mm. through a vacuum-jacketed still head. The first and last portions of the distillate were rejected and the middle fraction preserved in a solution of dibutyl phthalate which had previously been heated in a high vacuum to remove any volatile impurities.

Using this method we had no explosions although it is perhaps a wise precaution to conduct all the operations behind a screen. It seems to be necessary to keep the vapors of the diazo compounds away from organic matter of any kind; consequently from the bottom of the column to the receiver containing the dibutyl phthalate we used only glass connections. The yield by this method is about 30%. Diazomethane in dibutyl phthalate solution may be obtained in a similar manner.

The mixtures of diazomethane or diazoethane with carbon monoxide are not explosive when ether is not present if the carbon monoxide is always kept greatly in excess of the diazo compound.

Since the ethylidene radical may presumably undergo the reactions represented by the equations,[7] the decomposition products were tested with

	ΔH (cal.)
$CH_3CH \longrightarrow CH\equiv CH + H_2$	− 20
$2CH_3CH \longrightarrow CH_3CH=CHCH_3$	−148
$CH_3CH \longrightarrow CH_2=CH_2$	− 65

ammoniacal cuprous chloride, but the test showed the complete absence of acetylene. We then passed diazoethane slowly through a quartz tube at 650° and 2–3 mm., under which conditions complete decomposition occurs. The products were passed through a liquid air trap and the molecular weight of the condensed material, determined by weighing the sample and then measuring the pressure in a vessel of known volume at a fixed temperature, was found to be 28.2 (ethylene = 28). We next added slightly less than the theoretical quantity of chlorine and proved that the resulting liquid was 1,2-dichloroethane by determining its molecular weight and boiling point. It seems probable, therefore, assuming that the ethylidene radical separates from the molecule, that the reaction $CH_3CH \longrightarrow C_2H_4$ occurs with a very small energy of activation and to the practical exclusion of other reactions.

It may be mentioned in this connection that Curtius and Zinkeisen[8] prepared acetaldazine, $CH_3CH=N-N=CHCH_3$, and examined the products formed when it is thermally decomposed. This substance is a liquid and is only slightly affected by eight hours heating at 180°. However, when it was passed through a combustion tube heated to a higher temperature, practically complete decomposition occurred. Curtius and Zinkeisen tested for the products to be expected according to the equation

$$CH_3CH=N-N=CHCH_3 \longrightarrow CH_3CH=CHCH_3 + N_2$$

They found substantially the theoretical amount of nitrogen (accompanied by a very small quantity of hydrocyanic acid) but no butylene was formed. After making these observations they apparently did not examine the matter further.

We decided then to repeat this experiment with the object of finding the nature of the hydrocarbon formed in the decomposition. Accordingly we prepared a quantity of the acetaldazine and de-

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(4) Rice, Johnston and Evering, THIS JOURNAL, 54, 3529 (1932).

(5) Rice and Glasebrook, *ibid.*, 55, 4329 (1933).

(6) See von Pechmann, *Ber.*, 31, 2643 (1898).

(7) The values of ΔH were estimated from the values 102, 100, 82.5, 148 and 200 cal. for the H–H, C–H, C–C, C=C and C≡C bonds, respectively.

(8) Curtius and Zinkeisen, *J. prakt. Chem.*, 58, 315 (1898).

composed it by passing it rapidly at about 7 mm. pressure through a quartz tube heated to approximately 750°. We also performed some experiments in which we heated the material in a quartz bulb at about 700 mm. pressure and 450° for ninety minutes. No butylene was found in any of these experiments. About 60% of the material appeared to decompose according to the equation

$$CH_3CH{=}N{-}N{=}CHCH_3 \longrightarrow N_2 + 2C_2H_4$$

presumably by rupture of the carbon–nitrogen double bonds followed by the rearrangement of the ethylidene fragments. The remaining 40% decomposed to give chiefly a non-volatile oil whose composition was not determined, and some hydrocyanic acid and probably methane. This seems to result from rupture of the N–N bond, followed by decomposition of the CH_3CHN groups into hydrogen cyanide and free methyl groups.

When acetaldazine is heated above 700° in a rapid stream at low pressures, it shows the Paneth effect with antimony mirrors, which fact we attribute to the presence of methyl groups in the second method of decomposition.

Products from thermal decomposition of acetaldazine. A number of experiments were performed using acetaldazine, some by a flowing method at pressures of 5–10 mm. and some by a static method at pressures near atmospheric. In Table I we give the results obtained in a typical low pressure experiment. The decomposition products were passed through a liquid air trap and at the end of the experiment the trap was brought to −80° and connected with a Toepler pump. The gases evolved (Fraction 1) were collected and weighed and the mol. wt. determined by measuring the pressure, temperature and volume. Fraction 2 was obtained in a similar manner by raising the temperature of the trap to 0°. This fraction smelled strongly of hydrogen cyanide. A residue remained, only part of which could be pumped out on heating the trap to 100°.

TABLE I

Temp. of furnace, °C.	750
Press., mm.	9
Wt. of acetaldazine, g.	0.95
Time of experiment, min.	25
Wt. of fraction 1 (−80°), g.	0.158
Mol. wt. fraction 1	29.06
Wt. of fraction 2 (0°), g.	0.30
Mol. wt. fraction 2	28.7

If acetaldazine decomposes according to the equation

$$CH_3CH{=}N{-}N{=}CHCH_3 \longrightarrow N_2 + 2C_2H_4$$

0.95 g. should yield 0.63 g. of C_2H_4 whereas we obtained only 0.46 g. of condensable gas, part of which was hydrogen cyanide.

Table II gives the results obtained in a typical static experiment.

TABLE II

DECOMPOSITION OF ACETALDAZINE AT HIGHER PRESSURES

Static method, quartz bulb, cc.	850
Temp. of furnace, °C.	470
In. press., mm.	740
Wt. of acetaldazine, g.	0.388
Time of experiment, min.	120
Vol. of permanent gas, cc.	96.6
Mol. wt. of permanent gas	25.3
Liquid air condensate, g.	0.30
Wt. of fraction 1, g.	0.122
Mol. wt. of fraction 1	28.8
Wt. of fraction 1 after KOH	0.096
Mol. wt. fraction 1 after KOH	28.06

At the end of the run, the contents of the quartz bulb were pumped out slowly through a small liquid air trap by means of a Toepler pump. The permanent gas was collected, measured and its molecular weight determined. Fraction 1 was obtained as before by pumping off the gases from the trap at −80°. After weighing and determining the molecular weight, the gases were treated with a small quantity of solid potash. This removed hydrogen cyanide and also any small amounts of carbon dioxide present.

It seems clear that the permanent gas was not pure nitrogen as was assumed by Curtius and Zinkeisen. The measured molecular weight corresponds to a 75:25% nitrogen–methane mixture; hydrogen is the only other gas that could have been present.

Summary

Our experiments seem to indicate that, if the ethylidene radical is formed in the thermal decomposition of diazoethane $CH_3CH{=}N{\equiv}N$, it is a radical of exceedingly short life, since in contrast with the behavior of diazomethane $CH_2{=}N{\equiv}N$, the Paneth effect with metallic mirrors is not shown. Furthermore, no methylketene can be detected when the decomposition is carried out in an atmosphere of carbon monoxide. Further, since ethylene is the only condensable gas formed during this decomposition, in particular since neither acetylene nor butene-2 is formed, it seems likely that the ethylidene radical rearranges very easily according to the equation $CH_3CH \longrightarrow CH_2{=}CH_2$.

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