tetrachloride and which melted at 132°.¹³ The latter material was the formaldoxime polymer, since no depression in melting point was noted upon admixture with an authentic sample of the polymer of formaldoxime.

Anal. Calc'd for CH₃NO: C, 26.64; H, 6.73; N, 31.11; Mol. wt., 45. Found: C, 26.88; H, 6.69; N, 31.16; Mol. wt. (in benzene), 90.

The molecular weight in benzene thus indicates that the compound is a "dimer" $(CH_3NO)_2$. The molecular weight of the material as determined by the Rast method (in camphor) was 55.

An aqueous solution of the white solid (m.p. 122°) reduced Tollen's reagent and Fehling's solution upon heating. When boiled with acetic acid, formaldehyde was liberated, as evidenced by the formation of a methone derivative which melted at 189°. The melting point of this material was not depressed by admixture with a known sample of the methone derivative of formaldehyde (m.p. 189°). The procedure used in carrying out the methone test is described by Weinberger¹⁴ and by Vorlander.¹⁵

Preparation of hydrochloride of $(CH_3NO)_2$. One gram of the material $(CH_3NO)_2$ was dissolved in 150 ml. of dry ether, the whole cooled to 0°, and dry hydrogen chloride was passed into the solution. A white crystalline material separated. The crystals were collected on a Büchner funnel and washed repeatedly with dry ether. The crystals melted (with sublimation) at 140°.

(13) The melting point of formaldoxime polymer must be taken in a sealed capillary to avoid sublimation. Depending upon the rate of heating, m.p. varies from 132° to 138°.

(14) Weinberger, Ind. Eng. Chem., Anal. Ed., 3, 357
(1931).
(15) Verlanden Z. Angl. Chem. 57, 241 (1990).

(15) Vorlander, Z. Anal. Chem., 77, 241 (1929).

Anal. Calc'd for (CH₈NO.HCl): N, 17.17; Cl, 43.50. Found: N, 17.20; Cl, 43.60.

When prepared under rigorously anhydrous conditions, the hydrochloride is stable. However, it hydrolyzes rapidly in the presence of water with evolution of a gas.

Hydrogenation of $(CH_3NO)_2$. The compound $(CH_3NO)_2$ (0.2772 g.) was dissolved in glacial acetic acid (25 ml.), and hydrogenated over PtO₂ at room temperature. The amount of hydrogen absorbed corresponded to 1.97 moles per mole of CH₃NO. The catalyst was collected on a filter, and the filtrate made up to 50 ml. with absolute alcohol. An aliquot (15 ml.) was treated with 6 ml. of an alcoholic solution of H₂PtCl₆ (5%). The weight of the precipitate (CH₃NH₂)₂.-H₂PtCl₆ was 98% of the calculated value. The melting point of the chloroplatinate was 223–225°, and it was not depressed by admixture of the chloroplatinate of an authentic sample of methylamine.

Anal. Calc'd for $(CH_3NH_2)_2H_2PtCl_6$: Pt, 41.4. Found: Pt, 41.5.

The methylamine was further identified by the conversion to N-methylbenzamide. The melting point of this material was 81°, and the melting point was not depressed by admixture with an authentic sample of N-methylbenzamide.

The reaction of diacetyl peroxide with 3-amyl nitrite. Except for minor modifications in procedure, the decomposition of diacetyl peroxide in 3-amyl nitrite maintained at 90°, proceeded in a manner similar to that described in the case of sec-butyl nitrite. The yield of the white solid was somewhat lower. It melted at 122°, and no depression in the melting point was noted upon admixture with the white solid obtained in the decomposition of diacetyl peroxide in secbutyl nitrite.

CHICAGO 37, ILL.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF J. T. BAKER CHEMICAL COMPANY]

Benzoin Condensation of Anisaldehyde

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The benzoin condensation of anisaldehyde is shown to be reversible in an ethanol-water reaction medium. Since irreversible side reactions of anisaldehyde lower the yield of anisoin, and it is generally believed that the benzoin condensation is irreversible in the absence of water, attempts have been made to increase the yield of anisoin from anisaldehyde by carrying out the condensation in a nonaqueous medium. The data from a series of such runs indicate that anisoin decomposes even in a nonaqueous medium and suggest that the benzoin condensation of anisaldehyde is reversible even in the absence of water.

Though the benzoin condensation takes place rapidly and goes nearly to completion with benzaldehyde,² it is slower and the yields are lower with many substituted benzaldehydes.³ The reversibility of this reaction in the case of benzaldehyde has been intensively investigated by various authors.⁴ Various irreversible side reactions occur (such as destruction of the aldehyde by the Cannizzaro reaction) which reduce the yield of benzoin if the heating period is unduly prolonged. In the case of slower-reacting substituted benzaldehydes a prolonged heating period is usually unavoidable.

In the course of preparative work on anisoin we have investigated the extent of the reversibility of the benzoin condensation of anisaldehyde. The procedure of Bösler⁵ is usually employed in converting this aldehyde to anisoin. It involves reflux-

⁽¹⁾ Present address: Southern Regional Research Laboratory, U. S. Department of Agriculture, New Orleans, La.

⁽²⁾ R. Adams and C. S. Marvel, Org. Syntheses, Coll. Vol. 1, 2nd ed., 94 (1941).

⁽³⁾ W. S. Ide and J. S. Buck, Org. Reactions, 4, 269 (1948).

⁽⁴⁾ See references cited in Reference 3. In particular, see (a) E. Anderson and R. A. Jacobson, J. Am. Chem. Soc., 45, 836 (1923); and (b) A. Lachman, J. Am. Chem. Soc., 46, 708 (1924).

⁽⁵⁾ M. Bösler, Ber., 14, 327 (1881). For a modification giving improved yields see J. Dewar and J. Read, J. Soc. Chem. Ind., 347 (1936). This procedure in our hands gave 40-45% yields in the first crop and 10-15% in the second.

ing a mixture of potassium cyanide⁶ and anisaldehyde in aqueous ethanol for several hours. The data from a series of runs carried out by a slight modification (see EXPERIMENTAL) of the Bösler procedure are presented in Table I. These data show an increasing yield and quality of anisoin for 4–5 hr., followed by a decrease in both yield and quality (as indicated by melting points).

TABLE I

YIELDS OF ANISOIN USING POTASSIUM CYANIDE AND ETHANOL-WATER

Reflux Time, hours,	Yield, %	M.P. of Product, °C.
2	24	103-110
3	34	106 - 110
4	41	108-111
5	44	105 - 110
6	40	103-110
10	23	100-110

As a check on the amount of anisoin which might be decomposed during the heating period, a run was carried out employing an equal weight of anisoin in place of the anisaldehyde. After a 4-hr. reflux period there was recovered only 67% of the anisoin along with a 10% yield of anisaldehyde, a small amount of anisic acid and other by-products which were not identified. This evidence, combined with the data in Table I, suggests that a major factor in the low yield of anisoin from anisaldehyde is probably the destruction of the aldehyde by competing side reactions, since the decomposition of anisoin, though quite appreciable, is not complete enough in a 4-hr. heating period to account for the low yields of anisoin tabulated. However, any effect which reduces the decomposition of the anisoin after it is formed should increase the yield.

It is well known⁷ that the benzoin condensation proceeds readily in the absence of water, and is generally believed that the presence of water is necessary for the reversal of this reaction.⁸ Though the evidence for this belief is small,⁹ there appears to be

no evidence or statement to the contrary in the literature. Thus, a series of runs have been carried out under essentially anhydrous conditions (see EXPERIMENTAL) using sodium cyanide as a catalyst and the dimethyl ether of ethylene glycol as a solvent. The data are tabulated in Table II. It is quite obvious that anisoin is decomposed on continued heating in this anhydrous medium, since the yield increases to a maximum and then declines in a manner somewhat parallel to that shown in Table I.¹⁰ Though we cannot state positively that the anisoin reverts to anisaldehyde under the conditions of these experiments, the similarity of these results to those obtained from both anisaldehyde and benzaldehyde in ethanol water, in which it is established that the benzoin reverts to the aldehyde, strongly suggests that the benzoin condensation, at least for anisaldehyde, is reversible in the absence of water.

TABLE II

Yields of Anisoin Using Sodium Cyanide and Ethylene Glycol Dimethyl Ether

Reflux Time, Min.	Yield, %	M.P. of Product, °C.
$\begin{array}{c} 30 \\ 60 \\ 90 \\ 120 \\ 180 \\ 360 \end{array}$	16 25 35 27 15 None	108–111 109–111 108–111 105–110 90–105

EXPERIMENTAL

The starting materials. The anisaldehyde was a commercial material which was freshly distilled before use. The potassium and sodium cyanides were reagent grade materials reported to assay 99.8% and 97.2%, respectively. For the anhydrous experiments the latter was dried overnight at 110°. The loss in weight indicated that the only significant "impurity" was moisture. The ethylene glycol dimethyl ether was a commercial material which was dried over sodium before use.

Procedure for the data in Table I. To a mixture of 11.2 g. of potassium cyanide, 45 ml. of water and 75 ml. of 95% ethanol was added by pipet 50 ml. (56 g.) of anisaldehyde. A series of such runs were heated under reflux for varying times as indicated in Table I. After the heating period the reaction mixtures were cooled with seeding and shaking until crystallization was well under way. Then the mixtures were maintained at 0° overnight before filtering. The yields are tabulated, along with the melting points, which indicate the quality of anisoin obtained (lit.¹¹ m.p. 113°).

⁽⁶⁾ During the current work it was noted that the reaction mixture was homogeneous at the start of the heating period, but soon separated into two phases. It was also noted that when an equivalent amount of sodium cyanide was used in place of the potassium salt all of the material remained in one phase throughout the reflux period and the yield of anisoin was considerably reduced, suggesting that the separation into two phases helps prevent the decomposition of the anisoin formed in the reaction. Similarly, the use of methanol water in the place of ethanol water gave one phase throughout the heating period, and a reduced yield of anisoin even with potassium cyanide.

⁽⁷⁾ See ref. 3, p. 274.

⁽⁸⁾ See ref. 3, p. 277.

⁽⁹⁾ The principal evidence seems to be the report of Lachman (see ref. 4b) that no decomposition of benzoin occurs in the presence of sodium or potassium cyanide in anhydrous pyridine. However, neither of these cyanides is appreciably soluble in pyridine. The results of A. A. Morton

and J. R. Stevens, J. Am. Chem. Soc., 52, 2031 (1930) indicate no detectable reversibility during the first few hours when benzaldehyde is subjected to a benzoin condensation with sodium cyanide in anhydrous petroleum ether. However, this aldehyde goes to the benzoin in yields of over 90% (see also refs. 2 and 3), so little effect could be expected from the reverse reaction during the earlier stages.

⁽¹⁰⁾ Also see Table I of Reference 4b for similar behavior with benzaldehyde.

⁽¹¹⁾ Heilbron, Dictionary of Organic Compounds, rev. ed., Oxford University Press, New York, 1953, Vol. I.

The decomposition of anisoin. A mixture of 56 g. of anisoin (m.p. 112-113°), 11.2 g. of potassium cyanide, 75 ml. of 95% ethanol, and 45 ml. of water was heated under reflux for 4 hr. It was then cooled with shaking until crystallization was well under way and then left at 0° overnight. There was recovered 37.5 g. (67%) of material of m.p. 105-111°. The mother liquor was diluted with water and extracted with ether. The ether extract was stirred with saturated sodium bisulfite solution, and from the aqueous phase was recovered 5.8 g. (10%) of anisaldehyde by the addition of sodium carbonate to the bisulfite solution. Removal of the ether from the organic phase left 6.0 g. of viscous red oily material.¹² Acidification of the original

(12) No attempt was made to determine the nature of this material. J. C. Irvine, J. Chem. Soc., 79, 668 (1901) has reported the recovery of a similar by-product of complex nature from the benzoin condensation of ortho-methoxy-benzaldehyde. For the by-products of the benzoin condensation of benzaldehyde see ref. 3, p. 277.

aqueous phase yielded 3.5 g. of a solid of m.p. $181-183^{\circ}$ which gave no depression when mixed with anisic acid (lit.¹¹ m.p. 184°). On another similar run which was refluxed for 24 hr., cooling yielded no crystalline anisoin, but a 10% yield of anisaldehyde was recovered.

The "anhydrous" runs. These runs were carried out under conditions similar to those for the Grignard and similar reactions. The glassware was dried overnight at 125° before use. Dry nitrogen was used to eliminate moisture from the atmosphere. To the system, being flushed with nitrogen, was added 2 g. of sodium cyanide (dried at 110°), 25 ml. (28 g.) of anisaldehyde, and 40 ml. of anhydrous ethylene glycol dimethyl ether. The runs were heated under reflux for the times indicated in Table II, then stoppered, and maintained at 0° overnight. The anisoin was filtered and washed first with the cold solvent, and then with water to remove sodium cyanide. The yields and melting points are tabulated in Table II.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

Phosphinemethylenes.¹ II. Triphenylphosphineacylmethylenes

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The preparation and some properties of triphenylphosphinebenzoylmethylene (III) and triphenylphosphineacetylmethylene (IV) are reported. Previous formulations of these compounds are rejected.

The properties of the phosphinemethylenes³ $(R_3P=CXY \leftrightarrow R_3P^+-C^-XY)$, such as their color, their stability, and their ability to react with aldehydes and ketones,⁴ seem to be closely related to the distribution of the negative charge in the molecule.

$$R_{a}P = CXY + H_{2}O \longrightarrow R_{2}(YXHC)PO + RH \text{ or } R_{a}PO + CH_{2}XY$$
$$R_{a}P = CXY + R'R''CO \longrightarrow R_{a}PO + R'R''C = CXY$$

During an investigation⁵ into the structure and properties of the phosphinemethylenes we have ex-

amined two types, I and II, which owe their remarkable stability to the incorporation of the negative charge in a nonbenzenoid (I) and a benzenoid (II) aromatic system. The observed dipole moment of triphenylphosphoniumcyclopentadienylide (I)¹ (7.0 D) is consistent with its representation as a resonance hybrid to which pentacovalent (Ia) and tetracovalent (Ib) phosphorus structures make roughly equal contributions. I was stable toward concentrated alkali and unreactive toward carbonyl functions. II could be hydrolyzed to triphenylphos-



⁽¹⁾ A convenient way of naming the compounds herein discussed is based on the name "phosphinemethylene" for the parent formulation $H_3P=CH_2$ (cf. ref. 3 and Collected Formula Index of Chem. Abs.). Thus, $(C_6H_5)_3P=CH_2$ would be triphenylphosphinemethylene, $(C_6H_5)_3P=CH_-C_5H_5$, triphenylphosphinebenzoylmethylene. The compounds could be named as derivatives of phosphorane, PH₅ [cf. Chem. Eng. News, **30**, 4515 (1952)]. Thus, $(C_6H_5)_3P=CH_-CO_6H_5$ would be triphenylphonebenzoylbe triphenylphosphorane, PH₅ [cf. Chem. Eng. News, **30**, 4515 (1952)]. Thus, $(C_6H_5)_3P=CH_-CO_6H_5$ would be triphenylphonebenzoylbe triphenylbe triphenylphonebenzoylbe triphenylbe triphenyl

⁽²⁾ From part of the Ph.D. thesis of S. Dershowitz.

⁽³⁾ G. M. Kosolapoff, Organophosphorus Compounds, John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 28, 355.

⁽⁴⁾ For references see G. Wittig, *Experientia*, 12, 41 (1956); and ref. 5 of this paper.

^{(5) (}a) F. Ramirez and S. Levy, J. Am. Chem. Soc., 79, 67 (1957); (b) F. Ramirez and S. Dershowitz, J. Am. Chem. Soc., 78, 5614 (1956).