drying and evaporation of solvent left the crude product as an oil. It was converted to the picric acid complex by dissolving it in 10 ml. of methanol containing 2.68 g. of picric acid. There was obtained 2.64 g. (51%) of red-brown complex, m.p. 129–132° (dec.) (lit.[1] 131–133°). Decomposition of a sample of the complex gave II, identified by m.p. and mixed m.p. Its ultraviolet absorption spectrum exhibited λ_{max} 229 mμ and 300 mμ, log ε 4.75 and 3.80, respectively (alcohol).

Cyclohepta[de]naphthalene. A suspension of 5.00 g. (0.0274 mole) of I and 13.52 g. (0.0548 mole) of recrystallized chloranil in 85 ml. of xylene was refluxed in a nitrogen atmosphere for 20 hr. The reaction mixture was transferred to a separatory funnel by repeated rinsing with petroleum ether (60–66°) and 10% aqueous sodium hydroxide and diluted with 700 ml. of water. After extracting the aqueous phase with several portions of ether, the combined organic solution was washed twice with dilute sodium hydroxide and then repeatedly with water. The dry (sodium sulfate) solution was distilled through a 2 ft. bead-packed column using a steam bath.

The residual oil was then dissolved in a minimum volume of petroleum ether (60–66°) and charged to a column of acid-washed alumina (1 × 18 in.). The first eluate, containing I and II, appeared colorless in white light and blue in ultraviolet light. The red band (black in ultraviolet) contained III. The red eluate was concentrated using the bead column and the chromatography repeated. A third chromatogram afforded 0.454 g. of red liquid which was then dissolved in 20 ml. of ethanol and treated with 20 ml. of saturated alcoholic picric acid solution. The mixture was warmed until homogeneous, cooled, and filtered to yield 0.64 g. of brown-black complex, m.p. 186° (dec.) (7.5% based on unrecovered I). Repeated recrystallization from ethanol gave pure picric acid complex of III, m.p. 206–208° (dec.).

Anal. Calc'd for $C_{20}H_{13}N_3O_7$: C, 58.96; H, 3.21. Found: C, 58.54; H, 3.09.

A sample (0.196 g.) of the complex was decomposed by washing an ethereal solution several times with aqueous sodium hydrogen carbonate. Isolation in the usual manner gave 0.084 g. of red solid (III), m.p. 88.5–90° (with sintering at 86°). The sample for analysis was prepared by sublimation at 0.3 mm.

Anal. Calc'd for $C_{14}H_{12}$: C, 94.34; H, 5.66. Found: C, 94.20; H, 5.62.

A mixed melting point with material prepared by the other route[5,10] was not depressed. Catalytic hydrogenation of a 2.8 mg. sample gave I. The ultraviolet absorption spectrum of III was virtually identical with that reported.[5]

The colorless eluates from all of the above chromatograms were combined and concentrated as before. To the residual oil thus obtained was added a solution of 5.0 g. of picric acid in 50 ml. of ethanol. Fractional crystallization gave a total of 4.82 g. (56% based on unrecovered I) of light red complex of II, m.p. 127–130° (dec.) (lit.[1] 131–133°). Further recrystallization gave material melting 130–132° (dec.). The bronze color previously reported for this complex was found to be due to a slight contamination by black solid. The pure hydrocarbon (II) was isolated and identified as described above, m.p. 44.5–46° (lit.[1] 43–45°).

The mother liquor of the above picric acid complex was concentrated and cooled whereupon 2.63 g. (23%) of orange complex of I crystallized, m.p. 113–114°, characterized in the usual way.

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(10) Kindly provided by Prof. V. Boekelheide.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Reactions of Atoms and Free Radicals in Solution. XXXIX. The Reaction of Diacetyl Peroxide with *sec*-Butyl Nitrite and 3-Amyl Nitrite

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The thermal decomposition of diacetyl peroxide in *sec*-butyl nitrite and 3-amyl nitrite results in the formation of a white solid of empirical formula CH_3NO. Cryoscopic molecular weight determination in benzene indicates that the material is a "dimer" $(CH_3NO)_2$. The Rast method (in camphor) indicated a molecular weight of 55. Upon hydrogenation of the "dimer" $(CH_3NO)_2$ a quantitative yield of methylamine was obtained. The "dimer" $(CH_3NO)_2$ forms a hydrochloride of the empirical formula $(CH_3NO.HCl)$.

It was shown in previous publications that nitroso compounds[2] and nitrite esters[3] are excellent inhibitors in the free radical bromination of aliphatic hydrocarbons. In the hope of elucidating the mechanism whereby nitrite esters act as inhibitors, the reactions of diacetyl peroxide with 3-amyl nitrite and *sec*-butyl nitrite, respectively, were investigated.

When diacetyl peroxide, dissolved in *sec*-butyl nitrite, was slowly added to *sec*-butyl nitrite, maintained at 73°, a reaction resulted (as indicated by an evolution of gas). Upon cooling the reaction mixture, a white solid, *A*, separated, and no additional amounts of this material were found on concentrating the filtrate. It was also established by conventional chemical methods that the filtrate contained

(1) The material presented in this paper formed part of a dissertation submitted in 1948 by Theodore H. Meltzer to the Graduate School of the University of Chicago in partial fulfillment of the requirements for the Ph.D. degree.

(2) Kharasch, White, and Mayo, *J. Org. Chem.*, **3**, 33 (1938).

(3) Kharasch, Hered, and Mayo, *J. Org. Chem.*, **6**, 818 (1941).

methyl ethyl ketone, *sec*-butyl alcohol, and methyl acetate.[4]

If we assume that the decomposition of diacetyl peroxide proceeds in part in the manner indicated below:

$$CH_3COOOCOCH_3 \xrightarrow{\Delta} CH_3\cdot + CO_2 + CH_3COO\cdot$$

$$CH_3CH_2\underset{\underset{ONO}{|}}{C}HCH_3 + CH_3\cdot \longrightarrow CH_3CH_2\underset{\underset{O\cdot}{|}}{C}HCH_3 + (CH_3NO)$$

B

$$2(CH_3NO) \longrightarrow (CH_3NO)_2 \quad A$$

$$2B \longrightarrow \text{ketone} + \text{alcohol}$$

then the yield of the white solid *A* is about 45% of the amount calculated on this basis.

The analyses of the white solid *A* (m.p. 122°) indicated that it has the empirical formula CH_3NO. Cryoscopic molecular weight determination in benzene indicated that it was a "dimer" $(CH_3NO)_2$ in that solvent. Subsequent to completion of this work, Coe and Doumani[5] described the "preparation of nitrosomethane dimer (m.p. 122°) by the photochemical decomposition of *tert*-butyl nitrite in the vapor-phase at 25° and at pressures of about 50 mm. using a quartz mercury vapor lamp."[6]

Toward some reagents, the dimer $(CH_3NO)_2$ behaves in a manner similar to that of the "monomer" $(CH_2{=}NOH)$.[7] Toward other reagents its behavior is quite different. Thus, both the "monomer" $(CH_2{=}NOH)$ and the "dimer" $(CH_2NO)_2$ reduce Tollen's reagent and Fehling's solution. When heated in the presence of acetic acid, both give tests for formaldehyde. They differ, however, in that the "monomer" forms a crystalline acetyl (and benzoyl) derivative, whereas we have been unable to form an acetyl (or a benzoyl) derivative of the "dimer" $(CH_3NO)_2$. Furthermore, whereas the "monomer" $(CH_2{=}NOH)$ forms salts of the empirical formula $(CH_2{=}NOH)_3{\cdot}HCl$, the "dimer" $(CH_3NO)_2$ forms salts of the empirical formula[8] $(CH_3NO){\cdot}HCl$. Also, an aqueous solution of formaldoxime monomer shows continuous absorption in the ultraviolet, whereas an aqueous solution of the "dimer" exhibits a maximum at 276 mμ.

Hydrogenation of the "dimer" $(CH_3NO)_2$ in the presence of PtO_2 gave about 98% of the calculated amount of methylamine. Dunstan and Bossi[7] claim that when formaldoxime "monomer" is reduced by a metal and an acid or a metal in basic solution, all of the nitrogen appears as ammonia, but when the acetyl derivative is similarly reduced, two atoms of nitrogen appear as ammonia and the third as methylamine.

Many unsuccessful attempts were made by us to convert the "monomer" $(CH_2{=}NOH)$ to the "dimer" $(CH_3NO)_2$, and the "dimer" to the "monomer." It would appear that the "monomer" and the "dimer" are distinct entities, and that in some solvents at least they do not exist in a tautomeric equilibrium. The conclusion that nitrosoalkanes isomerization to oximes is not instantaneous has also been reached by Chilton and Gowenlock[9] and Müller and Metzger.[10]

EXPERIMENTAL

The diacetyl peroxide was prepared by the procedure previously described.[11] The *sec*-butyl and the 3-amyl nitrite were prepared by the procedure described in "Organic Syntheses."[12] The alcohols and the nitrite esters used in this study had the following physical constants: *sec*-butyl alcohol (b.p. 98–99°, n_D^{20} 1.3972); *sec*-butyl nitrite (b.p. 67–68°, n_D^{20} 1.3727); 3-amyl alcohol (b.p. 114–115°, n_D^{20} 1.4079); 3-amyl nitrite (97–98°, n_D^{20} 1.3867).

The apparatus and procedure used in the decomposition of diacetyl peroxide have been described in a previous publication.[11]

Decomposition of diacetyl peroxide in sec-butyl nitrite. Diacetyl peroxide (32.5 g. of 95% material = 0.26 mole), dissolved in *sec*-butyl nitrite, was slowly added to *sec*-butyl nitrite maintained at 73°. It took 2 hr. for the introduction of the peroxide (the ratio of nitrite to peroxide was 6:1). At the end of that time, the mixture was heated for an additional 10 hr. The gases (CO_2 and CH_4) were collected in the usual way.

The reaction mixture was then cooled to −80°, and the white solid *A* which separated (7 g.) was collected on a filter. Unsuccessful attempts were made to obtain additional amounts of the solid by removal of some of the nitrite ester at reduced pressure.

Crystallization of the white solid *A* (7 g.) from carbon tetrachloride gave a material (6.5 g.) which melted at 122°, and a material (0.5 g.) which was very little soluble in carbon

(4) At the time this work was done, no satisfactory methods for the quantitative estimation of the methyl ethyl ketone, *sec*-butyl alcohol, and methyl acetate in the *sec*-butyl nitrite (used as a solvent) were available, although there was no difficulty in demonstrating (qualitatively) the presence of these materials. The gases evolved were: carbon dioxide (0.38 mole) and methane (2275 ml. at 25° and 737 mm.) per 0.26 mole of diacetyl peroxide. The gas contained less than 5% of nitric oxide.

(5) Coe and Doumani, *J. Am. Chem. Soc.*, **70**, 1516 (1948).

(6) For other papers dealing with the formation of monomeric and dimeric aliphatic nitroso compounds by pyrolysis of dialkyl mercury compounds in the presence of nitric oxide, see Chilton and Gowenlock, *J. Chem. Soc.*, 3232 (1953); 3174 (1954); see also recent work by Müller and Metzger, *Ber.*, **88**, 165 (1955), on dimers of nitroso alkanes and the recent work of Gowenlock and Trotman, *J. Chem. Soc.*, 4190 (1955). Note also that F_3CNO exists as a monomer [Jander and Haszeldine, *J. Chem. Soc.*, 912 (1954)].

(7) The "monomer" $(CH_2{=}NOH)$ was first isolated by Dunstan and Bossi, *J. Chem. Soc.*, **73**, 353 (1898). It is a liquid which boils at 83–85°.

(8) Unfortunately, through an oversight we have not demonstrated whether or not the "dimer" can be regenerated from its salts. Neither have Dunstan and Bossi[7] demonstrated that formaldoxime "monomer" can be recovered from its salts. The addition of nitrosoalkane dimers to conjugated dienes is under investigation in this laboratory.

(9) Chilton and Gowenlock, *J. Chem. Soc.*, 3177 (1954).

(10) Müller and Metzger, *Ber.*, **88**, 165 (1955).

(11) Kharasch, Jensen, and Urry, *J. Org. Chem.*, **10**, 390 (1945).

(12) Noyes, *Org. Syntheses*, **Coll. Vol. 2**, 108 (1943).

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 CH_3NO: 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 Weinberger[14] 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°.

Anal. Calc'd for $(CH_3NO.HCl)$: 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 PtO_2 at room temperature. The amount of hydrogen absorbed corresponded to 1.97 moles per mole of CH_3NO. 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 H_2PtCl_6 (5%). The weight of the precipitate $(CH_3NH_2)_2 \cdot H_2PtCl_6$ 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 *sec*-butyl nitrite.

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

[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 Bösler[5] is usually employed in converting this aldehyde to anisoin. It involves reflux-

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(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.