

indicated to be different from aldehyde 1 were combined and rechromatographed on an alumina (acid-washed) column packed in petroleum ether and eluted with various mixtures of petroleum ether and methylene chloride. The first component to be eluted was recrystallized from ethyl acetate to give yellow crystals of 10-methyl-9-anthraldehyde, mp 170–172° (lit.<sup>13</sup> mp 170–171.4°).

*Anal.* Calcd for C<sub>16</sub>H<sub>12</sub>O: C, 87.2; H, 5.5. Found: C, 86.9; H, 5.2.

The nmr spectrum (deuteriochloroform) showed absorption at  $\tau$  -1.28 (CHO), 1.08–1.31, 1.70–1.95, 2.34–2.82 (ArH), and 7.04 (CH<sub>3</sub>) with relative peak areas of 1:2:2:4:3; the mass spectrum exhibited a peak corresponding to the molecular ion.

The second component to be eluted was aldehyde 1.

A vapor phase chromatographic analysis (2-ft SE-30 silicone rubber on Diatoport W column at 235°) of a similar reaction mixture indicated that 16% aldehyde 1 and 23% aldehyde 4 were formed.

Reaction times of 8 and 65 hr were also tried; in the former case the reaction had not proceeded far enough, and in the latter case a tarry mass was obtained.

**Reaction of 1,4-Bis(chloromethyl)benzene with Dimethyl Sulfoxide.**—A solution of 25.0 g (0.14 mole) of 1,4-bis(chloromethyl)benzene in 100 ml of dimethyl sulfoxide (dried over calcium hydride) was heated on a steam bath for 100 hr. White material sublimed to the top of the flask and was shown by infrared and elemental analyses to be paraformaldehyde.

*Anal.* Calcd for (CH<sub>2</sub>O)<sub>x</sub>: C, 40.0; H, 6.7. Found: C, 39.6; H, 6.8; S, <1; Cl, <1.

The reaction mixture was poured into ice-water and extracted with methylene chloride. The solvent was removed and the residue was shown by vapor phase chromatography to contain, at most, a trace of *p*-tolualdehyde in addition to a number of other products.

(13) L. F. Fieser and J. E. Jones, *J. Am. Chem. Soc.* **64**, 1666 (1942).

**Tetramethylterephthaldialdehyde.**—To 42 g (0.182 mole) of 3,6-bis(chloromethyl)durene in 1 l. of dimethyl sulfoxide at room temperature (20–25°) under nitrogen was added slowly (30 min) a solution prepared by adding 60 g (0.68 mole) of 2-nitropropane to a solution of 10 g (0.44 g-atom) of sodium in 600 ml of ethanol. The reaction mixture gradually became homogeneous and then heterogeneous as it was stirred for 6 hr at room temperature. Then the reaction mixture was added to ca. 6 l. of ice-water and allowed to stand overnight. The precipitate was removed by filtration and dissolved in methylene chloride. This solution was extracted with dilute hydrochloric acid and sodium bicarbonate solution, dried with sodium sulfate, and concentrated to dryness to give 30.5 g, mp 180–185°, of off-white product. Recrystallization from benzene-cyclohexane gave 25.5 g (74%), mp 181–185°, of white product (lit.<sup>14,15</sup> mp 165°, 187°).

*Anal.* Calcd for C<sub>12</sub>H<sub>14</sub>O<sub>2</sub>: C, 75.8; H, 7.4. Found: C, 75.5; H, 7.6.

**2,5-Dimethylterephthaldialdehyde.**—By using the same procedure as for tetramethylterephthaldialdehyde, the product was obtained in 56% yield, mp 96–101°.

*Anal.* Calcd for C<sub>10</sub>H<sub>10</sub>O<sub>2</sub>: C, 74.1; H, 6.2. Found: C, 74.0; H, 6.1.

**1,5-Naphthalenedicarboxaldehyde.**—By using the same procedure as for tetramethylterephthaldialdehyde, the product was obtained in 65% yield, mp 192–194° (lit.<sup>16</sup> mp 192°).

**Acknowledgment.**—The author wishes to thank Mr. W. C. Perkins for technical assistance, Dr. T. H. Regan for nmr spectra, and Mr. G. P. Happ and Mr. D. P. Maier for mass spectra.

(14) L. A. Mikeska and D. F. Koenecke, U. S. Patent 2,806,883 (1957).

(15) R. J. Leary, U. S. Patent 3,081,347 (1963).

(16) W. Ried, H. Bodem, U. Ludwig, and H. Neidhardt, *Chem. Ber.*, **91**, 2479 (1958).

## The Base-Catalyzed Reaction of Pinacolone with Formaldehyde<sup>1</sup>

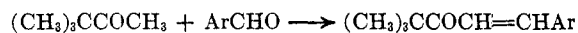
DONALD R. MOORE AND ANDREW OROSLAN

*J. P. Stevens and Company, Inc., Central Research Laboratory, Garfield, New Jersey*

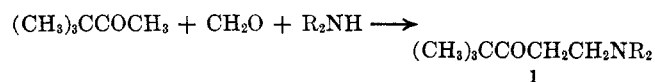
Received February 9, 1966

The aldol reaction of pinacolone with formaldehyde has been carried out in water-dioxane and in methanol, giving products resulting from the addition of 2 moles of formaldehyde. Acetylation of the products gives the acetates which are shown to saponify in alkaline mercaptan solution without consuming mercaptan. This unexpected result is interpreted as a consequence of the molecular stereochemistry of these hindered compounds.

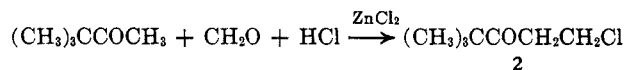
Although the aldol reaction of ketones with aldehydes forms an extensive body of knowledge<sup>2</sup> the specific reactions of pinacolone (methyl *t*-butyl ketone) have received scant attention. Base-catalyzed condensations of pinacolone with furfural<sup>3</sup> and piperonal<sup>4</sup> give the expected benzylidene derivatives. Pinacolone also undergoes a Mannich reaction with para-



formaldehyde and piperidine<sup>5</sup> or dimethylamine<sup>6</sup> giving the normal base 1. Colonge<sup>7</sup> has recorded the chloro-



methylation of pinacolone with paraformaldehyde, hydrogen chloride, and zinc chloride giving 1-chloro-4,4-dimethyl-3-pentanone 2. No simple ketol has



been reported from a reaction of formaldehyde with pinacolone. Dubois<sup>2</sup> was unable to isolate an identifiable ketol when pinacolone was treated with alcoholic formaldehyde catalyzed by sodium carbonate. In a kinetic study, Kangas<sup>8</sup> demonstrated that pinacolone gives no reaction with aqueous alcoholic formaldehyde catalyzed with lithium hydroxide in 24 hr at 25° or 5 hr at 35°. It is the purpose of this paper to report the successful reaction of pinacolone with formaldehyde and to record some interesting observations regarding the reactivities of the products obtained.

Pinacolone fails to react with excess, 37% aqueous formaldehyde at pH 1 or 9 even after heating under reflux for 50 hr. It has been found that reaction at pH 12 under reflux for 40 hr affords a crystalline

(1) Presented at First Middle Atlantic Regional Meeting of the American Chemical Society, Philadelphia, Pa., Feb 1966.

(2) For an excellent study, see J. E. Dubois, *Ann. Chim. (Paris)*, **6**, 406 (1951).

(3) H. Midorakawa, *Bull. Chem. Soc. Japan*, **27**, 143 (1954).

(4) A. A. Boon and F. J. Wilson, *J. Chem. Soc.*, 1751 (1910).

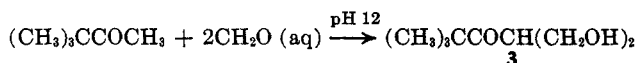
(5) C. Mannich and W. Hof, *Arch. Pharm.*, **265**, 589 (1927).

(6) C. G. Overberger and A. M. Schiller, *J. Polymer Sci.*, **54**, S30 (1961).

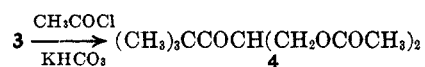
(7) J. Colonge, *Bull. Soc. Chim. France*, **3**, 2116 (1936).

(8) L. R. Kangas, Ph.D. Thesis, University of Delaware, Newark, Del., 1954; *Dissertation Abstr.*, **22**, 4198 (1962).

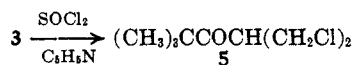
product, mp 72–73°, isolated by distillation and obtained in 8–10% conversion.<sup>9</sup> Based on its infrared spectrum, elemental analysis, and reactions described below, this crystalline product is formulated as 1-hydroxy-2-hydroxymethyl-4,4-dimethyl-3-pentanone (**3**)



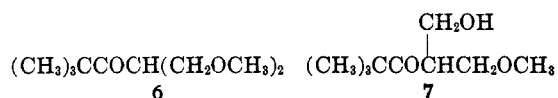
arising from the addition of 2 moles of formaldehyde to pinacolone. The presence of two hydroxyl groups in diol **3** was demonstrated by two reactions. Acetylation of diol **3** with acetyl chloride in ethyl acetate, using suspended potassium bicarbonate as the acid acceptor, afforded diacetate **4** in 75% yield. Chlorination of



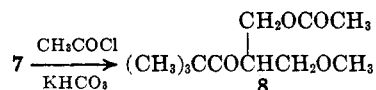
diol **3** with thionyl chloride–pyridine gave the dichloride **5** in 61% yield.



An analogous addition of formaldehyde to pinacolone was carried out in methanol adjusted to pH 12 by the addition of sodium methoxide. Two products, separable by distillation, were obtained: a dimethyl ether **6**, isolated in 5% conversion, and an unsymmetrical methoxy alcohol **7**, isolated in 20% conversion. Com-



ound **7** was further characterized by reaction with acetyl chloride to form methoxy acetate **8**.

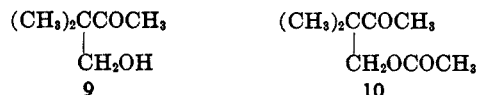


The structures assigned the new compounds **3–8** are fully supported by the analytical data and infrared spectra of these products (see Experimental Section). Worthy of note is the position of the carbonyl-stretching infrared absorption found for the two hydroxy ketones, **3** and **2**,  $\lambda_{\text{max}}^{\text{CHCl}_3}$  5.93 and 5.92  $\mu$ , respectively. The shift to longer wavelength from the "normal" position (5.80–5.87  $\mu$ )<sup>10</sup> is attributable to the internal hydrogen bonding possible in these compounds. Examination of Fisher–Hirshfelder–Taylor models of **3** and **7** shows no steric restrictions to the formation of a six-membered, hydrogen-bonding ring between one of the alcohol functions and the carbonyl group. The remaining hydroxymethyl (or methoxymethyl) group is free to rotate and may assume a conformation minimizing interactions of the two C–O dipoles. The new compounds lacking a  $\beta$ -hydroxyl function show normal positions for the carbonyl-stretching maxima (see Experimental Section).

(9) "Yields" of the products isolated from the formaldehyde reactions are reported as conversions and have not been increased by corrections for recovered pinacolone.

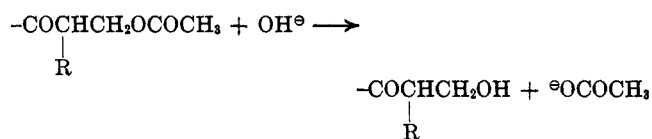
(10) L. J. Bellamy, "The Infra-Red Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, pp 134–136 and references therein.

4-Hydroxy-3,3-dimethylbutanone<sup>11</sup> **9** and its acetate **10** were synthesized as model compounds and found to show the same effect,  $\lambda_{\text{max}}^{\text{CHCl}_3}$  (C=O) 5.91 and 5.85  $\mu$ , respectively.

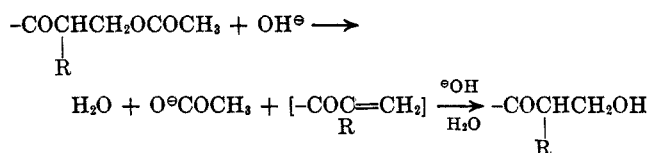


During the course of our investigations with these compounds, an abnormal reaction was found which is attributable to a steric effect. Diacetate **4** and monoacetate **8** give normal saponification analyses with aqueous sodium hydroxide, presumably forming the parent hydroxy compounds, **3** and **7**, respectively. If the saponification is conducted in the presence of *n*-dodecyl mercaptan, no reduction in the mercaptan content of the solution is observed. A consideration of the mechanism of this saponification affords two possibilities: direct and elimination–addition paths.

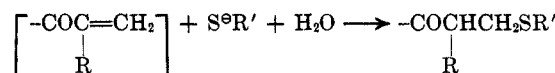
Direct



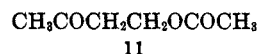
Elimination–addition



If direct hydrolysis occurs, involving either alkyl-oxygen or acyl-oxygen scission, no mercaptan disappearance would be expected. If, alternatively, the elimination–addition course obtains, mercaptide ion would be expected to compete favorably with hydroxide ion for the unsaturated intermediate.



We have observed this latter course of saponification with mercaptan consumption in a wide variety of situations.<sup>12</sup> Specific to the present case, 4-acetoxybutanone<sup>13</sup> **11** consumed 0.9 moles of mercaptan, but



acetate **10**, lacking the requisite activated hydrogen atom, consumed no mercaptan. The failure of diacetate **4** and monoacetate **8** to consume mercaptan during saponification in spite of possessing the formal requirements for the elimination–addition reaction may be understood by examination of models of this crowded system.

The methine hydrogen adjacent to the carbonyl is shielded by the *t*-butyl group (Newman's Rule of Six),<sup>14</sup> and attack by base at this position to initiate elimination would be expected to be hindered. Another

(11) J. Decombes, *Compt. Rend.*, **203**, 1077 (1936).

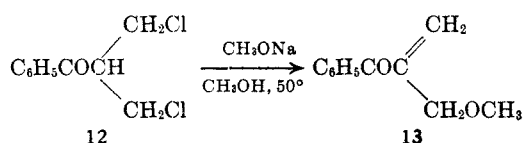
(12) Papers describing (a) our investigations in the addition of mercaptans to "activated" vinyl groups and (b) the elimination reaction with concomitant mercaptan disappearance are in preparation.

(13) R. F. Fisher and C. W. Smith (to Shell Development Co.), U. S. Patent 2,857,422 (Oct 21, 1958).

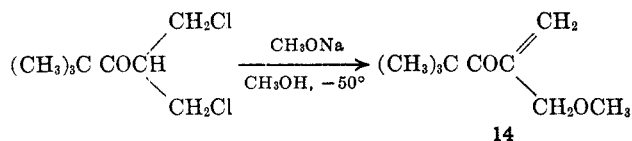
(14) M. S. Newman, *J. Am. Chem. Soc.*, **72**, 4783 (1950).

over-all, conformational factor may be operative in this instance. Diacetate **4** may assume two limiting conformations of crescent shape: in the first, the methine hydrogen is severely obstructed on the concave face, while the five oxygen atoms are studded on the convex surface; in the second, the methine hydrogen is on the convex face, shielded only by the *t*-butyl group, but the five oxygen atoms are crowded together on the concave face. In polar media, diacetate **4** would be expected to assume an intermediate conformation which favors the first limiting conformation in order to facilitate hydrogen bonding to the oxygen atoms. In such a situation, access to the methine hydrogen is effectively blocked.

In order to establish that mercaptan could add to the double bond if it were present, we sought to prepare a suitable unsaturated model for the reaction. In 1955, Beets and Heeringa<sup>15</sup> described the conversion of dichloride **12** to the allyl ether **13** by treatment with



sodium methoxide at 50°. When treated similarly, dichloride **5** gave only the diether **6**; however, by conducting the reaction at -50°, and employing a slight deficiency of sodium methoxide, we obtained the allyl ether **14**.



A model of **14** shows no steric factor to inhibit mercaptide ion attack at the methylene terminus of the double bond. In the experiment, a sample of **14**, purified by gas chromatography, was found to consume 1.3 moles of mercaptan in alkaline solution. The consumption of over 1 mole of mercaptan is attributed to competing allylic displacement: the phenyl analog **13** consumes 2.0 moles of mercaptan under the same conditions.

The importance of the observation that **14** adds mercaptan may be assessed by the following considerations. Compound **14** is the product of the elimination of the elements of acetic acid from monoacetate **8**, and as such, is the intermediate expected if **8** saponifies by an elimination-addition path. Because **8** has been found not to add mercaptan under these conditions, while the intermediate **14** does, the elimination-addition pathway during saponification is clearly contra-indicated for monoacetate **8**. Since diacetate **4** differs little from monoacetate **8** in steric environment about the critical methine hydrogen, and also fails to add mercaptan, we conclude that both diacetate **4** and monoacetate **8** saponify by the direct path for steric reasons.

### Experimental Section

Microanalyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y., and Micro-Analysis, Inc.,

(15) M. G. J. Beets and L. G. Heeringa, *Rec. Trav. Chim.*, **74**, 1085 (1955).

Wilmington, Del. Melting points were taken on a Fisher-Johns melting point block; all melting points and boiling points are uncorrected. Infrared spectra were run in chloroform solution on a Beckman IR-8 spectrophotometer. Gas-liquid partition chromatograms were run on a Burrell Kromo-Tog Model K-D instrument, using helium carrier gas (120 cc/min), a thermal conductivity detector, and column temperature programming.

**Reaction of Pinacolone with Formaldehyde in Water. 1-Hydroxy-2-hydroxymethyl-4,4-dimethyl-3-pentanone (Diol 3).**—Pinacolone (500 g, 5.0 moles) was combined with 37% aqueous formaldehyde solution (840 g, 10.4 moles) in a mixture of 500 ml of water and 1500 ml of *p*-dioxane. The pH of the reaction mixture was adjusted to 12 (moistened indicating paper) with 50% aqueous sodium hydroxide. The reaction mixture was stirred and heated daily over a 7-day period (total reflux time 40 hr), with periodic readjustment of the pH to 12. The reaction mixture was extracted with chloroform and the dried extracts were stripped of solvents and volatile material to a pot temperature of 75° (35 mm). Distillation of this residue afforded three cuts: (a) bp 45–126° (4–5 mm), 31 g; (b) bp 122–124° (0.9–1.0 mm), 116 g which solidified; and (c) bp 127–128° (1.6–1.9 mm), 11.5 g. There was decomposition evident at the end of the distillation, and a residue of 52 g was obtained.

The solid diol **3** (fraction b) was recrystallized from chloroform-hexane (1:2) and obtained as needles, mp 71–73°, wt 80.5 g (10% conversion). Compound **3** is soluble in common organic solvents except hexane, and will dissolve in an equal weight of water. An analytical sample prepared by a further recrystallization from chloroform-hexane melted at 70–72° and showed infrared absorption at 2.75 (sharp, weak), 2.91 (broad, strong), 5.93 (strong), 9.63  $\mu$  (strong).

*Anal.* Calcd for  $\text{C}_8\text{H}_{16}\text{O}_3$ : C, 59.97; H, 10.11. Found: C, 60.05, 59.82; H, 10.14, 10.04.

**1-Acetoxy-2-acetoxymethyl-4,4-dimethyl-3-pentanone (Diacetate 4).**—Diol **3** (10.0 g, 0.063 mole) and anhydrous potassium bicarbonate (18.6 g, 0.186 mole) were combined with 100 ml of ethyl acetate. Acetyl chloride (14.6 g, 0.186 mole) was added slowly to the stirred mixture at room temperature. The internal temperature rose slowly to 40°. After the addition was over, the reaction was stirred briefly and permitted to stand at room temperature for 60 hr. The mixture was filtered, and the filtrate was dried over anhydrous magnesium sulfate and refiltered.

Distillation afforded the diacetate **4** (9.4 g, 62% yield) as a colorless, pleasant smelling liquid, bp 92–93° (0.2 mm),  $n_D^{20}$  1.4389. The infrared spectrum had maxima at 5.74 (strong) and 5.84  $\mu$  (strong). The equivalent weight was determined by saponification.

*Anal.* Calcd for  $\text{C}_{12}\text{H}_{20}\text{O}_5$ : C, 59.00; H, 8.25; equiv wt, 122. Found: C, 58.39; H, 8.10; equiv wt, 118.5.

**1-Chloro-2-chloromethyl-4,4-dimethyl-3-pentanone (Dichloride 5).**—Diol **3** (10.0 g, 0.063 mole) was dissolved in pyridine (12.5 g, 0.158 mole) and the flask was flushed with nitrogen. Thionyl chloride (18.9 g, 0.158 mole) was added dropwise under nitrogen with occasional cooling to moderate the vigorous exothermic reaction. When addition had been completed, the reaction mixture was heated to 90° for 1 hr under nitrogen, then permitted to cool and stand overnight.

The mixture was poured cautiously onto ice and the whole was extracted thoroughly with chloroform. The dried extracts were distilled to obtain the colorless dichloride **5**, bp 94–96° (15 mm) (6.3 g, 61% yield),  $n_D^{20}$  1.4637. The infrared spectrum showed no hydroxyl absorption, and had a strong carbonyl band at 5.86  $\mu$ .

*Anal.* Calcd for  $\text{C}_8\text{H}_{14}\text{Cl}_2\text{O}$ : C, 48.74; H, 7.15; Cl, 35.98. Found: C, 48.82; H, 7.61; Cl, 36.5.

**Reaction of Pinacolone with Formaldehyde in Methanol.**—The reaction of pinacolone with formaldehyde in methanol was carried out similarly to the reaction in water-dioxane described above. Sodium methoxide in methanol was employed as the catalyst. Fractional distillation of the product mixture and gas-liquid partition chromatographic analysis (2% diethylene-glycol succinate on Gas Chrom P) of the distillation fractions showed the presence of two main products.

**A. 1-Methoxy-2-methoxymethyl-4,4-dimethyl-3-pentanone (dimethyl ether 6),** bp 85° (2.0 mm),  $n_D^{20}$  1.4286, was isolated in 5% conversion. The sample showed strong infrared bands at 5.88 and 9.05  $\mu$ .

*Anal.* Calcd for  $\text{C}_{10}\text{H}_{20}\text{O}_3$ : C, 63.79; H, 10.71. Found: C, 63.32; H, 10.65.

**B. 1-Hydroxy-2-methoxymethyl-4,4-dimethyl-3-pentanone (methoxy alcohol 7)**, bp 97–98° (2.0 mm),  $n_D^{20}$  1.4403, was isolated in 12% conversion. The sample showed infrared absorption bands at 2.87 (medium), 5.92 (strong), and 9.04  $\mu$  (strong).

Gas-liquid partition chromatographic analysis showed the presence of 10–20% of dimethyl ether 6 which could not be separated by fractional distillation. 7 was therefore characterized by conversion to 1-acetoxy-2-methoxymethyl-4,4-dimethyl-3-pentanone(methoxyacetate 8) employing the procedure described above for diacetate 4. Compound 8 was obtained in 86% yield, bp 80° (0.4 mm),  $n_D^{20}$  1.4327. This sample showed strong infrared absorption bands at 5.73, 5.85, and 9.02  $\mu$ .

*Anal.* Calcd for  $C_{12}H_{20}O_5$ : C, 61.11; H, 9.26. Found: C, 61.08; H, 9.38.

**4-Hydroxy-3,3-dimethylbutanone (9)**.—This compound was prepared by the reaction of methyl isopropyl ketone with formaldehyde described by Decombes,<sup>11</sup> 9 boiled 94–96° (24 mm) and had infrared absorption bands at 2.85 (medium) and 5.91  $\mu$  (strong).

The alcohol was acetylated following the procedure described above for diacetate 4 to produce 4-acetoxy-3,3-dimethylbutanone 10, bp 108–111° (32 mm). The infrared absorption band for the ketone carbonyl was found to be 5.85  $\mu$ .

**2-Benzoyl-3-methoxy-1-propene (13)**.—This compound was prepared by the method of Beets and Heeringa,<sup>15</sup> and boiled at 88–89° (0.1 mm),  $n_D^{20}$  1.5312.

**2-Methoxymethyl-4,4-dimethyl-1-penten-3-one (14)**.—Dichloride 5 (40.6 g, 0.205 mole) was dissolved in 200 ml of methanol and the solution chilled to –50° with an acetone–Dry Ice bath. A solution of sodium methoxide (freshly prepared from sodium (8.74 g, 0.38 mole) and 100 ml of anhydrous methanol) was added slowly over 1 hr while maintaining the reaction mixture at –50°. The mixture was stirred 2 hr at –50°, then permitted to warm to room temperature, and stand overnight.

Precipitated sodium chloride (21.9 g, 0.374 mole) was removed by filtration, and the filtrate was distilled to give a fraction, bp 86–89° (30 mm, 23.0 g). Gas-liquid partition chromatography (2% diethylene glycol succinate on Gas Chrom P) showed this fraction to be principally the desired 14. Purification was effected by redistillation and collection from the gas chromatograph. Pure material showed  $n_D^{20}$  1.4360 and infrared absorption bands at 5.96 (strong) and 6.02  $\mu$  (strong, shoulder).

*Anal.* Calcd for  $C_9H_{16}O_2$ : C, 69.19; H, 10.32. Found: C, 69.07; H, 10.22.

**Vinyl Analyses.**<sup>12</sup> **A. Activated Vinyl Compounds.**—The analytical method used is that described by American Cyanamid Co. for acrylonitrile using *n*-dodecyl mercaptan,<sup>16</sup> with the exception that reaction times in the alkaline mercaptan medium were extended to 0.5 hr. Under these conditions, mercaptan consumptions were measured: 13, 2.0 moles; and 14, 1.3 moles.

**B. "Latent" Vinyl Compounds.**—The elimination reaction in the presence of mercaptan is conducted similarly, except that more base (0.5 *N* potassium hydroxide in ethanol) is added to compensate for that consumed by the acid formed on elimination, and to maintain alkaline conditions during the analysis. In this analysis, mercaptan consumptions were measured: 4, none; 8, none; 10, none; and 11, 0.9 moles. Under similar conditions, base consumptions were measured: 4, 2.04; 8, 1.1; 10, 1.1; and 11, 1.05 moles.

**Acknowledgments.**—We wish to thank Dr. G. C. Tesoro for helpful discussion and advice during this work, Mr. Frank Draugelis for assistance with the experiments, and Mr. Chester Becker for running the infrared spectra and gas chromatograms.

(16) *The Chemistry of Acrylonitrile*, 2nd ed, American Cyanamid Co., New York, N. Y., 1959, pp. 61–63.

## The Reaction of Formates and Formamides with Base<sup>1</sup>

JAMES C. POWERS, READ SEIDNER,<sup>2</sup> THOMAS G. PARSONS, AND HARVEY J. BERWIN<sup>3</sup>

*Contribution No. 1965 from the Department of Chemistry, University of California at Los Angeles, Los Angeles, California 90024*

*Received March 1, 1966*

Formates react with strong bases such as sodium hydride, potassium *t*-butoxide, and triphenylmethylsodium to produce alkoxides and carbon monoxide. Formamides undergo a similar transformation with sodium hydride. The usefulness of these reactions in synthesis and attempts to trap possible intermediate carbanions is discussed.

The reaction of alkoxides with carbon monoxide under pressure to yield formates is a well-documented process.<sup>4</sup> This reaction is reversible and formates can be decomposed into alcohols and carbon monoxide by alkali alkoxides.<sup>5,6</sup> The exact course of formate, decompositions has been clouded by several unexplainable observations. Adkins, for example, found that sodium reacted with formates with evolution of only 66% of the theoretical amount of carbon monoxide.<sup>7</sup> Scheibler in a series of papers describes the

isolation of "carbonite ions" from the reaction of formates with bases.<sup>8</sup> Adickes later showed that these so called "carbonite ions" were in fact either alkoxides or products from the addition of alkoxides to formates.<sup>9</sup>

**Formates.**—Ethyl formate reacts rapidly with sodium hydride at room temperature with the evolution of carbon monoxide and hydrogen. We first noticed this reaction while performing some condensation reactions using sodium hydride as a base and ethyl formate as the solvent. Since this reaction seemed quite interesting and potentially useful if carbanionic intermediated could be trapped, we decided to investigate this process further. In order to simplify isolation and purification of products, most of our subsequent work was carried out with *n*-butyl formate.

Butyl formate reacted rapidly with sodium hydride in diethyl ether with the evolution of gas. Upon work-up of the reaction mixture, a 68% yield of 1-butanol was obtained. When the reaction was car-

(1) A preliminary account of some of the investigations reported in this paper has appeared: J. C. Powers, R. Seidner, and T. G. Parsons, *Tetrahedron Letters*, 1713 (1965).

(2) National Science Foundation summer undergraduate research participant, 1964.

(3) National Science Foundation summer undergraduate research participant, 1965.

(4) B. S. Lacy, R. G. Dunning, and H. H. Storch, *J. Am. Chem. Soc.*, **52**, 926 (1930); A. Staher, *Ber.*, **47**, 580 (1914); J. C. Gjaldback, *Acta Chem. Scand.*, **2**, 683 (1948).

(5) (a) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 311; (b) J. Hine, "Divalent Carbon," Ronald Press Co., New York, N. Y., 1964, p 79.

(6) H. J. Ringold [*J. Am. Chem. Soc.*, **78**, 816 (1956)] reports that a steroidal formate is decomposed by aluminium isopropoxide under conditions of the Oppenauer oxidation.

(7) (a) H. E. Carswell and H. Adkins, *ibid.*, **50**, 235 (1928); (b) G. J. Pfeiffer and H. Adkins, *ibid.*, **53**, 1043 (1931).

(8) H. Scheibler, *Ber.*, **59B**, 1022 (1926); **60B**, 554 (1927); **67B**, 312, 314 (1934).

(9) F. Adickes, *ibid.*, **60B**, 272 (1927); **63**, 3016, 3022 (1930); F. Adickes and P. P. Peckelhoff, *ibid.*, **68B**, 1138 (1935).