sodium salt was then obtained by precipitation with alkali.

For the preparation of sodium perbutyrate, perbutyric acid was prepared from butyric acid and 90% hydrogen peroxide[6] and the salt was prepared as in the case of sodium peracetate.

The salts so obtained were found to contain one atom of active oxygen which could be analyzed iodometrically.

In the analysis of the active oxygen content, it was found that on treating with acidified potassium iodide solution, in neither case was liberation of iodine instantaneous; thus in the case of sodium peracetate, iodine liberation was complete only after 30 min. at room temperature and in the absence of light while sodium perbutyrate required 75 min. under the same conditions.

Sodium peracetate decomposes at 55° leaving a residue which contains no active oxygen. On standing at room temperature for 3 days in a moist atmosphere, a sample of sodium peracetate lost all of its active oxygen content and when a sample was stored *in vacuo* at room temperature, the active oxygen content had decreased by 66% after 24 hr. and by 93% after 7 days.

EXPERIMENTAL

Note: The use of a safety shield is recommended in carrying out the following reactions.

Sodium Peracetate. A saturated solution of sodium carbonate was added with constant stirring to "Becco" peracetic acid[3] (50 ml.) at 8–10° until a *p*H of 8.0 was obtained as indicated by a *p*H meter. The resulting mixture was extracted with ether (5 × 50 ml.) and the extracts dried over magnesium sulfate. Analysis of an aliquot showed that the combined extracts contained 5.94 g., of peracetic acid. To the ethereal solution was added at 0°, sodium hydroxide (3.13 g.) dissolved in water (5 ml.) and 95% ethanol (70 ml.), causing an immediate precipitate. It was allowed to stand for 15 min. The salt was separated by filtration, washed with ethanol, then with ether and dried *in vacuo* at room temperature.

The sodium peracetate was analyzed for active oxygen iodometrically and for sodium gravimetrically as the sulfate.[7] Found: active O, 16.42; Na, 24.31% CH_3CO_3Na requires: active O, 16.32; Na, 23.46%.

Sodium perbutyrate. To an aqueous solution of perbutyric acid at 0° was added a saturated solution of sodium carbonate until a *p*H of 8.0 was obtained as indicated by a *p*H meter. To the pure peracid (2.7 gm.) in ethyl acetate was added at 0°, sodium hydroxide (1.05 gm.) dissolved in 95% alcohol. On standing at 0° for 2 hr., sodium perbutyrate precipitated. It was filtered off, washed and dried *in vacuo* at room temperature and analyzed for active oxygen iodometrically. Found: active O, 12.80% $C_4H_7O_3Na$ requires: active O, 12.68%.

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[6] J. D'Ans and W. Frey, *Ber.*, **45**, 1845 (1912).

[7] A similar preparation of several grams of dry sodium peracetate exploded violently, while sitting in a flask at room temperature. Caution is recommended in handling this compound.

A New Technique in Preparing 2,4-Dinitrophenylhydrazones. III. Two Examples of Hitherto Unobtainable Simple Derivatives: Diacetone Alcohol and Methyl Vinyl Ketone

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Recently[1] the convenient use of diglyme (dimethylether of diethylene glycol) solutions of 2,4-dinitrophenylhydrazine for preparing 2,4-dinitrophenylhydrazones was described. It was suggested at that time that the new technique might be usable for preparing 2,4-dinitrophenylhydrazones of sensitive compounds. This suggestion has now been found to be valid, and in view of the interest that has been shown in the earlier publication[1a] we are prompted to illustrate the further usefulness of the new technique with two examples. We have been able to prepare for the first time the true derivative of diacetone alcohol and the derivative of methyl vinyl ketone.

Diacetone alcohol. The 2,4-dinitrophenylhydrazone, melting point 203°, that is everywhere listed as the derivative of diacetone alcohol, is really the derivative of mesityl oxide. The conventional methods of preparation[1a] of the 2,4-dinitrophenylhydrazone cause the acid-catalyzed dehydration of the ketol to mesityl oxide.

If a solution of diacetone alcohol in a diglyme solution of 2,4-dinitrophenylhydrazine is acidified with acetic acid, however, the orange derivative, I, formed is that of diacetone alcohol and has a melting point of 157–159°. If, instead of acetic acid, hydrochloric acid is used, or if I is dissolved in ethanol and acidified with hydrochloric acid, the dark red derivative of mesityl oxide is obtained.

Methyl Vinyl Ketone. The only report of the reaction of 2,4-dinitrophenylhydrazine with this simple ketone is that of I. N. Nazarov and co-workers.[2] These authors report a compound with a melting point of 217°, the carbon analysis of which was 2.3% low for the expected derivative. They do not appear to have accepted their derivative as authentic. We have prepared the authentic derivative of this ketone; it has a melting point of 139.5–140.5°. It was prepared first in these laboratories by the diglyme technique using hydrochloric acid for catalysis. If attempts were made to prepare this derivative by conventional methods, using ethanol as solvent, the derivative was not obtained, but one of the products obtained was the derivative of 4-ethoxybutanone-2, melting point 92–93°. If methanol were used as a solvent, the derivative of 4-methoxybutanone-2 was obtained,

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[1] (a) H. J. Shine, *J. Org. Chem.*, **24**, 252 (1959); (b) H. J. Shine, *J. Chem. Ed.*, **36**, 575 (1959).

[2] I. N. Nazarov, L. A. Kazitsyna and I. I. Zaretskaya, *Zhur. Obshchei Khim.*, **27**, 606 (1957).

melting point 88–90°. Thus, it is apparent that the solvent used is important in determining the final products of reaction. We found, indeed, that the derivative of methyl vinyl ketone can also be obtained if tetrahydrofuran and *tert*-butyl alcohol are used as solvents. In the latter case the derivative precipitates quickly and addition of the alcohol to the double bond does not take place. In the former case, as in the diglyme solutions, the solvent cannot react with the ketone or its derivative. Our work with methyl vinyl ketone has led us to begin investigating in some detail the products that are formed from the derivative of methyl vinyl ketone and of the alkoxybutanones in acidic solutions. We shall report on this investigation at a later date. It is quite apparent to us at this stage that attempts to make the derivatives of these ketones by conventional methods very often lead to products that are not the expected derivatives.

EXPERIMENTAL

Diacetone alcohol 2,4-dinitrophenylhydrazone. One milliliter of vacuum distilled diacetone alcohol was added to 20 ml. of a diglyme solution containing 0.8 g. of 2,4-dinitrophenylhydrazine. To this was added 3 ml. of acetic acid. The solution was allowed to stand at room temperature for 2 hr. and was then placed in the refrigerator for 24 hr. Water was added to the cold solution until it became turbid and the solution was again refrigerated until crystallization occurred. The orange product, m.p. 137–147°, was recrystallized twice from ethanol and then twice from benzene, giving glistening orange plates, m.p. 157–9°; λ_{max} ($CHCl_3$): 370 mmμ; λ_{max} (ligroin): 351 mmμ; ϵ_{max} ($CHCl_3$): 23,250.

Anal. Calcd. for $C_{12}H_{16}N_4O_5$: C, 48.65; H, 5.44; N, 18.9. Found[3]: C, 48.59; H, 5.36; N, 18.69.

A small amount of the derivative was dissolved in ethanol and acidified with concentrated hydrochloric acid. A red precipitate formed overnight. Crystallization from diglyme gave m.p. 203°. The melting point of the derivative of mesityl oxide was 203°.

Methyl vinyl ketone 2,4-dinitrophenylhydrazone. To a solution of 0.2 ml. of methyl vinyl ketone (Matheson, Coleman and Bell, technical, used without purification) in 10 ml. of the diglyme reagent solution was added 3 drops of concentrated hydrochloric acid. The solution stood overnight at room temperature. Addition of water gave an orange product, m.p. 137–8°. Several recrystallizations from ethanol gave long orange needles, m.p. 139.5–140.5°; λ_{max} ($CHCl_3$): 370 mmμ; λ_{max} (ligroin): 352 mmμ; ϵ_{max} ($CHCl_3$): 24,670.

Anal. Calcd. for $C_{10}H_{10}N_4O_4$: C, 48.00; H, 4.03; N, 22.38. Found[3]: C, 48.07; H, 4.24; N, 22.62.

4-Ethoxybutanone-2 2,4-dinitrophenylhydrazone. This was obtained first when attempting to make the 217° product from methyl vinyl ketone by the described[2] procedure. A solution was made by boiling 1 g. of 2,4-dinitrophenylhydrazine in a mixture of 45 ml. of ethanol, 5 ml. of dioxane (freshly purified) and 1 ml. of concentrated hydrochloric acid. The cool solution was filtered from solid that had crystallized and was added to a solution of 1 ml. of methyl vinyl ketone in 2 ml. of ethanol. A small amount of an orange yellow solid precipitated, m.p. 202–8°. Dilution of the filtrate with water gave a flocculent yellow precipitate, m.p. 84–87°. Several crystallizations from ethanol gave light orange crystals, m.p. 92–3°; (literature: 89–90°[4]; 100–1°[5]); λ_{max} ($CHCl_3$): 362 mmμ; λ_{max} (ligroin): 344 mmμ; ϵ_{max} ($CHCl_3$): 21, 570.

Anal. Calcd. for $C_{12}H_{16}N_4O_5$: C, 48.65; H, 5.44; N, 18.90. Found[6]: C, 48.38; H, 5.30; N, 18.80.

4-Methoxybutanone-2 2,4-dinitrophenylhydrazone. The procedure described above was used. Again, the solution precipitated a yellow orange solid, m.p. 208–210°. Treatment of the filtrate as above gave a yellow product, m.p. 97–100°. Several crystallizations from methanol gave blunt, dark yellow needles, m.p. 88–90°; (literature[5]: 85–86°) λ_{max} ($CHCl_3$): 364 mmμ; λ_{max} (ligroin): 345 mmμ; ϵ_{max} ($CHCl_3$): 21,520.

Anal. Calcd. for $C_{11}H_{14}N_4O_5$: C, 46.81; H, 5.00; N, 19.84. Found:[4] C, 46.64; H, 4.89; N, 19.70.

Ultraviolet spectra. A Beckman DK-2 instrument was used. The ligroin used was Eastman Kodak's permanganate purified, b.p. 66–75°. Because of the unexpectedly high values of λ_{max} of the diacetone alcohol derivative the corresponding λ_{max} of mesityl oxide were determined. They were 383 mmμ ($CHCl_3$) and 365 mmμ (ligroin). The λ_{max} (isooctane) given[2] for mesityl oxide was 364 mmμ; while the λ_{max} (isooctane) calculated[2] for methyl vinyl ketone was 354 mmμ.

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(3) Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

(4) N. A. Milas, et al., *J. Am. Chem. Soc.*, **70**, 1597 (1948).

(5) I. N. Nazarov, S. G. Matsoyan, and V. N. Zhamagortsyan, *Zhur. Obshchei Khim.*, **23**, 1986 (1953).

(6) Geller Laboratories, Bardonia, N. Y.

Isomeric Bis(trimethylsilyl)xylylenes

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In a recent article[1] we described the synthesis of *m*- and *p*-bis(trimethylsilyl)xylylenes from coupling the respective xylylene dihalides and trimethylchlorosilane with magnesium in tetrahydrofuran. We wish to report the successful preparation of the remaining isomer, bis(trimethylsilyl)-*o*-xylylene, to complete the series and an additional dichloro-derivative of the *p*-isomer, bis(dimethylchlorosilyl)-*p*-xylylene. The physical properties of the three isomeric compounds are summarized in Table I and the infrared absorption spectrum of the *o*-isomer is reproduced in Fig. 1.

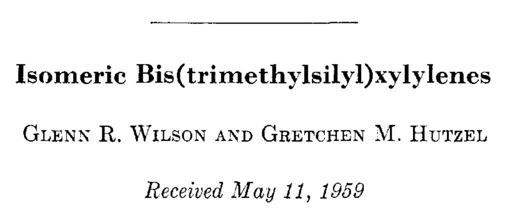

Fig. 1. Bis(trimethylsilyl)-*o*-xylylene

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(1) G. R. Wilson, G. M. Hutzel, and A. G. Smith, *J. Org. Chem.*, **24**, 381 (1959).