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Observations on the Nature of McAlpine's "Stable" and "Unstable" Xanthates

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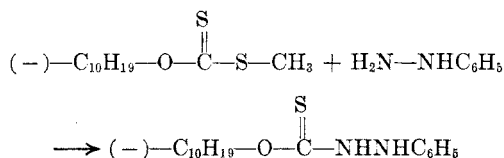
Evidence is presented which shows that the "stable" form of (-)-menthyl methyl xanthate, first reported by McAlpine,¹ is formed by the removal of peroxide impurities from the "unstable" form. The stable form can be converted back to the unstable form by the addition of benzoyl peroxide. The two forms are identical structurally.

In studies on the pyrolysis of various xanthates, McAlpine¹ reported the curious behavior of the methyl xanthates of (-)-menthol and (-)-borneol, which under certain conditions were stable to vacuum distillation. This behavior is contrary to that usually exhibited by xanthates, which on heating readily decompose to give olefins in high yield in the well known Chugaev reaction.²

McAlpine¹ found that the "stable" methyl xanthate of (-)-menthol could be obtained in several ways. Distillation under reduced pressure of (-)-menthyl methyl xanthate prepared according to Chugaev³ resulted in 50% decomposition to a menthene mixture, and the remainder of the distillate was the stable xanthate, which could be distilled repeatedly without further decomposition. When the "unstable" xanthate was heated in 1-butanol it was also converted to the stable form.

McAlpine¹ was unable to detect any difference in physical properties between the stable and unstable xanthates. The two compounds had identical melting points, which showed no depression on admixture, had identical optical rotations, and gave the same results on analysis.

McAlpine's work has been repeated and confirmed in this laboratory. Further evidence that the two compounds are identical has also been obtained. The stable and unstable xanthate were converted to the phenylhydrazine derivatives, according to the procedure of Mann.⁴ The derivatives had identical melting points and no depression was observed on admixture, indicating that the xanthate linkage was intact in both compounds.



The infrared spectra of the stable and unstable xanthates were superposable. Finally, both xanthates had identical rates of decomposition when pyrolyzed at 150° at atmospheric pressure. The

menthene mixtures obtained from large scale pyrolyses of both xanthates were analyzed by the racemization technique of Barton, Head, and Williams.⁵ The unstable xanthate gave 24% Δ²-menthene, and the stable gave 27% Δ²-menthene. Hückel, Tappe, and Legutke⁶ obtained a value of 28% Δ²-menthene in the mixture obtained by reduced pressure distillation.⁷ Within experimental error, these values are identical, and thus the two forms of the xanthate give the same ratio of Δ²- to Δ³-menthene on pyrolysis.

The evidence points to the conclusion that the two compounds have identical structures, and that the stable xanthate was produced by the removal from the unstable xanthate of an impurity, present in quantities too small to be detected by the above tests.

The methods used by McAlpine¹ to produce the stable xanthate suggested that a peroxide was the most likely impurity. Tarbell and Harnish⁸ suggested that the xanthate was decomposing by a chain process, and that the stable form was produced when the chain initiator was removed by sufficient purification.

To test the peroxide hypothesis, a solution of the unstable xanthate in benzene was shaken with an aqueous solution of ferrous ammonium sulfate. Subsequent distillation under reduced pressure gave an 84% yield of the stable xanthate.

Further evidence that the difference in behavior was due to the presence of peroxides was obtained by adding a trace of benzoyl peroxide to a benzene solution of the stable xanthate. Subsequent distillation under reduced pressure resulted in complete decomposition of the xanthate. Substitution of benzoic acid for the benzoyl peroxide had no effect on the stability of the xanthate.

When a sample of the stable xanthate was irradiated with ultraviolet light for several days, the sample slowly liquefied, lost weight, darkened in color, and the odor of methyl mercaptan was evi-

(5) D. H. R. Barton, A. J. Head, and R. J. Williams, *J. Chem. Soc.*, 453 (1952).

(6) W. Hückel, W. Tappe, and G. Legutke, *Ann.* **543**, 191 (1940).

(7) Their menthyl methyl xanthate was prepared in the same manner as Chugaev's and McAlpine's, and would thus correspond to the unstable form.

(8) D. S. Tarbell and D. P. Harnish, *Chem. Revs.*, **49**, 61 (1951).

(1) I. M. McAlpine, *J. Chem. Soc.*, 1114 (1931); 906 (1932).

(2) Cf. G. L. O'Connor and H. R. Nace, *J. Am. Chem. Soc.*, **74**, 5454 (1952) for discussion and further references.

(3) L. Chugaev, *Ber.*, **32**, 3332 (1899).

(4) F. G. Mann, *J. Chem. Soc.*, 666 (1945).

dent. No attempt was made to identify the other products of the decomposition.

The results reported here, together with those obtained by McAlpine,¹ indicate that (–)-menthyl methyl xanthate (and probably (–)-bornyl methyl xanthate¹) is rendered unstable towards heat by the presence of traces of peroxides. It therefore appears likely that an additional mode of decomposition, probably proceeding by a free radical path, is possible in the pyrolysis of xanthates. Although both forms gave products indicating preference for *cis*-elimination, this need not imply that the free-radical decomposition proceeds through a cyclic intermediate² involving a *cis*-hydrogen. The 4-hydrogen of the menthane ring is tertiary while the 2-hydrogen is secondary, and it is well known that tertiary hydrogens are attacked more readily than secondary ones by free radicals.⁹

It is interesting to note that treatment of β -cholestanyl methyl xanthate with ferrous ammonium sulfate had no effect on the rate of pyrolysis.² Elucidation of the generality and mechanism of the peroxide-induced instability awaits further investigation.

EXPERIMENTAL

(–)-Menthyl methyl xanthate. The procedure of Chugaev^{3,10} was used. The (–)-menthol had m.p. 43–43.5°; $[\alpha]_D -45^\circ$ (1% in CHCl₃), -51° (1% in 95% EtOH). Reported¹¹ m.p. 43°, $[\alpha]_D -49^\circ$. The (–)-menthyl methyl xanthate had m.p. 39–39.5°, 39.9–40.3° (corr.); $[\alpha]_D -80^\circ$ (1% in CHCl₃) after 1 recrystallization from dilute ethanol. Reported^{3,10} for unstable xanthate, m.p. 39°; $[\alpha]_D -81.7^\circ$ (4.5% in CHCl₃).

Conversion of the unstable xanthate to the stable xanthate. A. by treatment with ferrous ammonium sulfate. A solution of 2.5 g. of unstable xanthate in 35 ml. of benzene (Merck & Co., Inc., thiophene-free grade) was washed with six 25-ml. portions of freshly prepared ferrous ammonium sulfate solution, then with water, and finally dried over anhydrous magnesium sulfate. The benzene was removed by distillation under reduced pressure (bath temperature 25°), and the residue was distilled in a modified Claisen flask with a 3-in. Vigreux side arm to give 2.1 g. (84%) of the stable xanthate, b.p. 110–121° (11 mm.); m.p. 38.5–39°. Several repetitions of the experiment gave comparable results.

B. by distillation under reduced pressure. The results obtained by McAlpine¹ were confirmed. The stable xanthate obtained from the initial distillation had b.p. 130–140° (10 mm.) on redistillation; m.p. 39–39.5°; mixture melting point with unstable xanthate, 38.5–39.5°; yield 40–50%.

C. by heating in 1-butanol. A solution of 15 g. of unstable xanthate in 100 ml. of 1-butanol was heated under reflux for 14 hr. Then the solvent was removed under reduced pressure and the residue was distilled from a Claisen flask to give 10.4 g. (71%) of stable xanthate, b.p. 92–101° (0.5 mm.); m.p. 39.5–40.5°; m.p. of unstable xanthate taken at same time, 39.5–40.5°; mixture m.p. 39.5–40.5°; $[\alpha]_D -78^\circ$ (1% in CHCl₃).

Pyrolysis of unstable xanthate. A 10-g. (0.041 mole) sample

of unstable xanthate was heated at 145–155° for 6 hr. under reflux. Distillation of the residue through an efficient semi-micro column¹² gave a 57% yield of menthenes, b.p. 64.5–65° (22 mm.); $n_D^{25} 1.4500$; $[\alpha]_D +117^\circ$ (1% in CHCl₃). A sample was racemized⁸ and then had $[\alpha]_D +32^\circ$ (1% in CHCl₃) which corresponds to 24% of Δ^2 -menthene in the original mixture.

Pyrolysis of stable xanthate. An 8.0-g. (0.0325 mole) sample of the stable xanthate was pyrolyzed in the same fashion, and 2.30 g. (51% yield) of menthenes was obtained, b.p. 61–64° (20–22 mm.); $n_D^{25} 1.4500$; $[\alpha]_D +36^\circ$ (1% in CHCl₃); after racemization, $+35^\circ$, which corresponds to 26.5% of Δ^2 -menthene in the original mixture.

Phenylhydrazine derivatives of stable and unstable xanthates. The same procedure was used for the stable and unstable xanthate. A solution of 2.0 g. of the xanthate and 0.72 g. of phenylhydrazine in 40 ml. of ethanol was heated under reflux for 6 hr. The solvent was evaporated and the residue allowed to stand in a refrigerator until (10 days) it solidified. The crystals were triturated with cold ligroin and recrystallized from 95% ethanol. The derivative of the stable xanthate had m.p. 150–151°; of the unstable xanthate, 148.5–149.5°; mixture m.p. 147–149°.

Comparison of infrared spectra of stable and unstable xanthate. The spectra of 2% solutions in carbon tetrachloride of unstable and stable (prepared by the butanol method) were superimposable (20 identical peaks between 3.30 and 11.15 μ). Samples of the two in Nujol mulls also gave identical spectra (16 identical peaks between 3.28 and 12.0 μ). The spectra were determined with a sodium chloride prism.

Rate of decomposition of the stable and unstable xanthates. The rate of decomposition was measured by placing weighed samples of the xanthates in test tubes in a bath held at 149.5–150°. Periodically the tubes were removed, the reaction quenched by cooling in cold benzene, and the tubes weighed. From the weight loss the per cent decomposition was calculated. Plots of log per cent decomposed *versus* time gave straight lines with slope = 2.75, 2.12 for the unstable; 2.47, 2.24 for the stable (prepared by the butyl alcohol method).

Treatment of the stable xanthate with benzoyl peroxide. To a solution of 3.0 g. (0.012 mole) of stable xanthate (prepared by the butyl alcohol method) in 15 ml. of anhydrous benzene (Merck & Co., Inc., thiophene-free grade) was added a few crystals of benzoyl peroxide. The resulting solution was allowed to stand overnight in a refrigerator and then the solvent was removed under reduced pressure at 25°. The residue was distilled through a Claisen flask with a 3-in. Vigreux side arm and 1.32 g. (79%) of menthene was obtained, b.p. 68–70° (50 mm.); $n_D^{25} 1.4516$.

The above experiment was repeated but the solution was distilled immediately after the addition of the benzoyl peroxide. An 85% yield of menthenes was obtained, b.p. 68–70° (50 mm.); $n_D^{25} 1.4497$.

The experiment was then repeated but with a few crystals of benzoic acid in place of the benzoyl peroxide. The stable xanthate was recovered in 91% yield, b.p. 110–116° (11 mm.); m.p. 39–39.5°.

Chromatography on alumina of the unstable xanthate. A solution of 2 g. of the unstable xanthate in heptane was passed over a column of alumina (Merck & Co., Inc., suitable for chromatographic absorption) and 1.82 g. was recovered on removal of the solvent. The residue distilled completely at 17 mm. pressure and the distillate solidified, m.p. 38.5–39°; mixture melting point with unstable xanthate, 38.5–39°.

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