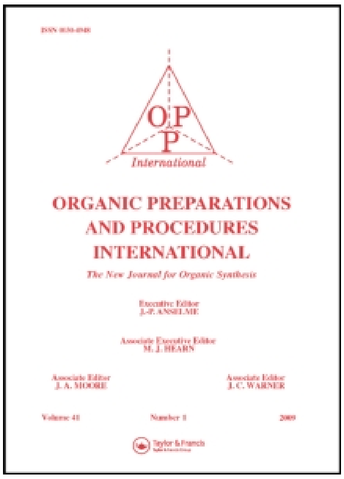


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

2-ACETYL-3,5-DIMETHYLFURAN (3,5-Dimethyl-2-furyl methyl ketone)

A. T. Balaban[a][b]
[a] Institute of Atomic Physics, Bucharest, Romania [b] International Atomic Energy Agency, Vienna, Austria

To cite this Article Balaban, A. T.(1969) '2-ACETYL-3,5-DIMETHYLFURAN (3,5-Dimethyl-2-furyl methyl ketone)', Organic Preparations and Procedures International, 1: 1, 63 — 66

To link to this Article: DOI: 10.1080/00304946909458351

URL: http://dx.doi.org/10.1080/00304946909458351

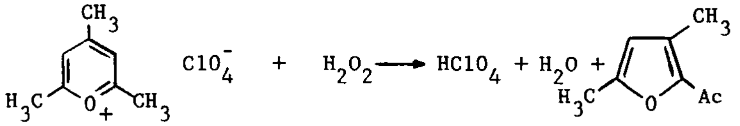
ORGANIC PREPARATIONS AND PROCEDURES 1(1), 63-66 (1969)

2-ACETYL-3,5-DIMETHYLFURAN

(3,5-Dimethyl-2-furyl methyl ketone)

A. T. Balaban

Institute of Atomic Physics, Bucharest, Romania
(Present address: International Atomic Energy Agency, Vienna, Austria)



The reaction between symmetrically alkyl-substituted pyrylium salts (i.e. with identical substituents in both alpha, or both beta, positions) and hydrogen peroxide proceeds by ring contraction affording 2-acylfurans[1]. A similar contraction has recently been observed in the oxidation of other six-membered heteroaromatic cations by manganese dioxide[2], or in the oxidation of flavylium salts by hydrogen peroxide affording benzofuran derivatives[3]. Interestingly, 2-acylfurans undergo ring expansion reverting to six-membered heterocyclic systems on catalytic hydrogenation[4,5] or on treatment with ammonia[6]. No other method for preparing 2-acetyl-3,5-dimethylfuran has as yet been reported.

EXPERIMENTAL

In a 1-l long-necked round-bottomed flask are placed 111.3 g (0.5 mole) 2,4,6-trimethylpyrylium perchlorate (Note 1), 91 ml 30% hydrogen peroxide (0.8 mole), 500 ml water and 1 ml 70% perchloric acid. The flask is set for steam distillation using a two-bore rubber stopper, large-bore glass tubing (8-10 mm) and an efficient downward condenser (about 10 mm bore and 1 m length). Steam is introduced into the flask until the mixture is heated to boiling temperature, when the perchlorate dissolves and the reaction begins. The distillation is carried cautiously at first (Note 2), then as rapidly as the condenser allows. A total amount of 400 ml distillate is collected: the lower yellowish layer is separated, the aqueous layer is extracted once with 50 ml ether. The combined organic layers are washed with 50 ml cold 10% sodium hydroxide solution (Note 3) then twice with 30 ml water, dried over anhydrous sodium sulfate, and transferred into a 100 ml Claisen flask. The ether is evaporated at reduced pressure and after a few drops forerun, the product is collected at 124°/75 mm, 130°/100 mm, as a colourless refringent liquid with characteristic odour (Note 4) (b.p. $_{760}$ 195°, m.p. 18°, n_D^{20} 1.4962, d_4^{20} 1.0427*). It amounts to 31-35 g (45-50% yield) (Notes 5-8).

*) Data not reported previously.

Notes

1. Trimethylpyrylium perchlorate is prepared after ref. 7. As stated previously,[8] the dry perchlorate is harmless in the absence of shock or heat.

2. The initial vigorous reaction may cause the mixture to boil violently and to be carried in the condenser.

3. On washing with hydroxide, the upper ethereal layer becomes colourless and the aqueous layer yellow. If the yellowish colour persists in the organic layer, a second washing with 20 ml 10% NaOH and then with 50 ml 10% $FeSO_4$ solution must be effected.

4. The reaction yields acetyl-dimethyl-furan as the only volatile, water-insoluble compound, therefore the product distils practically

constantly, with insignificant amounts of forerun and leaves practically no residue.

5. The sensitivity to acids of the furan nucleus makes it necessary to remove the product from the acid reaction mixture as soon as it is formed. A more complicated device for effecting this is the use of a reflux condenser and an adapter for recycling the (lower!) aqueous layer (owing to its high surface tension, the product, although heavier than water, remains on top).

A small amount of product is however resinified in both cases, remaining in the flask as a dark-coloured oil which hardens on cooling (to be discarded when still warm).

6. The amount of hydrogen peroxide employed is critical for the course of the reaction. With larger amounts, the initial reaction becomes more violent and difficult to control, and the yield is lowered owing to the formation of water-soluble acid by-products (mostly formic, along with acetic and other acids, cf. ref. 9); the solution in the distilling flask remains light-coloured and clear, and tar formation is suppressed. With lower amounts of hydrogen peroxide the reaction does not go to completion and larger amounts of tar are formed, which again lower the yield.

7. The reaction may be applied to other symmetrically alkyl-substituted pyrylium salts,[1,10] which are easily prepared through bisacylation of olefins.[11,12]

8. The oxidation of 2-acetylfuran derivatives to 2-furoic acids by sodium hypochlorite or hypobromite is described in ref. 1. Observations of steric hindrance in 2-acylfurans are recorded in ref. 13.

REFERENCES

1. A. T. Balaban and C. D. Nenitzescu, Chem. Ber., 93, 599 (1960).
2. I. Degani and R. Fochi, Ann. Chim. (Roma), 58, 251 (1968).
3. L. Jurd, J. Org. Chem., 29, 2602 (1964).
4. N. I. Shuikin, I. F. Belskii, A. T. Balaban and C. D. Nenitzescu, Izv. Akad. Nauk S.S.S.R., Otdel. khim. Nauk, 491 (1962).
5. N. I. Shuikin, I. F. Belskii and G. K. Wasiliewskaja, Z. Chem., 2, 359 (1962); I. F. Belskii and N. I. Shuikin, Usp. khim., 32, 707 (1963).
6. L. D. Smirnov, K. M. Dyumaev, N. I. Shuikin and I. F. Belskii, Izv. Akad. Nauk S.S.S.R., Otdel. khim. Nauk, 2246 (1962).
7. A. T. Balaban and C. D. Nenitzescu, Org. Synth., 44, 98 (1964).
8. A. Barabas, E. Gard, A. Vasilescu and A. T. Balaban, J. Labelled Comp., 2, 359 (1966).
9. A. P. Salchinkin, Zh. prikl. khim., 32, 1605 (1959).
10. K. Dimroth and W. Mach, Angew. Chem., 80, 489 (1968).
11. A. T. Balaban, Tetrahedron Letters (in press), Pyrylium salts formed by diacylation of olefins, Part XVIII, and previous papers in the series.
12. A. T. Balaban, W. Schroth and G. Fischer, "Advances in Heterocyclic Chemistry", Vol. 10 (A.R. Katritzky and A. J. Boulton, editors), Academic Press, New York 1968.
13. A. T. Balaban, P. T. Frangopol and M. Keplinger, Spectrochim. Acta, 19, 367 (1963).

(Received September 13, 1968)