



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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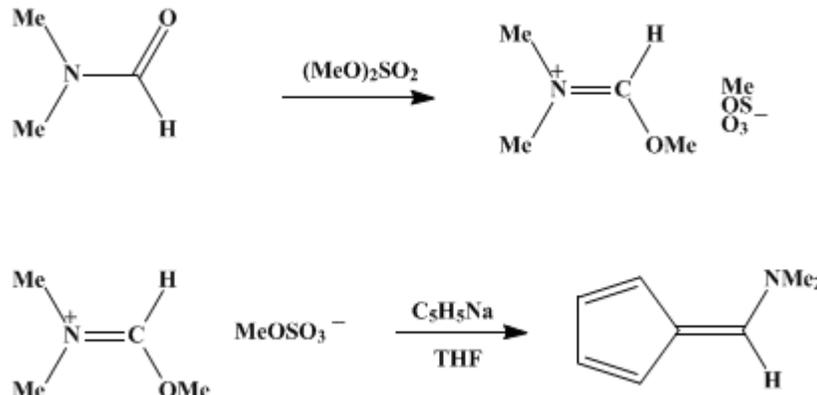
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 5, p.431 (1973); Vol. 47, p.52 (1967).

6-(DIMETHYLAMINO)FULVENE



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Checked by S. S. Olin and Ronald Breslow.

1. Procedure

A. *N,N*-Dimethylformamide-dimethyl sulfate complex. In a 500-ml. four-necked flask equipped with mechanical stirrer, reflux condenser with calcium chloride drying tube, dropping funnel, and thermometer is placed 73 g. (1.0 mole) of dimethylformamide, and 126 g. (1.0 mole) of dimethyl sulfate is added dropwise with stirring at 50–60° (Note 1). After the addition is complete, the mixture is heated for another 2 hours at 70–80°. The dimethylformamide complex forms as a viscous, colorless or pale yellow ether-insoluble oil.

B. *6*-(Dimethylamino)fulvene. A 1-l. four-necked flask is equipped with mechanical stirrer, dropping funnel with calcium chloride drying tube, thermometer, and nitrogen delivery apparatus (Note 2). The flask is flushed with dry nitrogen, and in it is placed 1.0 mole of cyclopentadienylsodium² in 700 ml. of tetrahydrofuran (Note 3). The dimethylformamide-dimethyl sulfate complex prepared above is transferred to the dropping funnel and added slowly with stirring under nitrogen to the cyclopentadienylsodium at –10° (ice-salt bath). During the addition the temperature is kept below –5°. After the addition is complete, the mixture is stirred at 20° for 2 hours. The solution is filtered (with suction) from the precipitated sodium methyl sulfate, which is washed with another 200 ml. of tetrahydrofuran, and the combined tetrahydrofuran solutions are concentrated under reduced pressure. The residue is a dark brown oil which solidifies on cooling.

The crude product is crystallized after treatment with activated carbon from ca. 1.5 l. of petroleum ether (b.p. 60–80°) or 800 ml. of cyclohexane. From the orange-yellow solution 84 g. (69%) of *6*-(dimethylamino)fulvene separates in yellow leaflets, m.p. 67–68° (Note 4). Concentration of the filtrate and further recrystallization of the residue from petroleum ether or cyclohexane gives an additional 8 g. of product. The combined yield is 92 g. (76%).

2. Notes

1. Dimethylformamide and dimethyl sulfate must be purified by distillation in the absence of moisture.
2. The nitrogen delivery apparatus has been completely described.²
3. Air and moisture must be carefully excluded from the reactants during the course of this preparation.
4. *6*-(Dimethylamino)fulvene is light-sensitive and is stored in brown bottles.

3. Discussion

N,N-Dimethylaminoethoxymethylum fluoborate³ can be used instead of *N,N*-dimethylaminomethoxymethylum methyl sulfate⁴ to prepare *6*-(dimethylamino)fulvene.⁵ The same

fulvene is also obtained from the condensation of [cyclopentadiene](#) with [diethoxy\(dimethylamino\) methane](#).⁶

4. Merits of the Preparation

This procedure illustrates formylation by N,N-dimethylaminomethoxymethylmethyl sulfate, a compound which can be produced readily by reaction of easily available materials. [6-\(Dimethylamino\) fulvene](#) is a useful intermediate for the synthesis of various fused-ring nonbenzenoid aromatic compounds.

References and Notes

1. Institute for Organic Chemistry, University of Munich, Munich, Germany.
 2. [K. Hafner and H. Kaiser, this volume, p. 1088.](#)
 3. H. Meerwein, P. Borner, O. Fuchs, H. J. Sasse, H. Schrodt, and J. Spille, *Ber.*, **89**, 2060 (1956).
 4. H. Brederbeck, F. Effenberger, and G. Simchen, *Ber.*, **96**, 1350 (1963).
 5. K. Hafner, K. H. Vöpel, G. Ploss, and C. König, *Ann.*, **661**, 52 (1963).
 6. H. Meerwein, W. Florian, N. Schön, and G. Stopp, *Ann.*, **641**, 1 (1961).
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

petroleum ether

N,N-Dimethylformamide-dimethyl sulfate complex

dimethylformamide-dimethyl sulfate complex

N,N-dimethylaminomethoxymethylmethyl sulfate

[nitrogen \(7727-37-9\)](#)

[dimethyl sulfate \(77-78-1\)](#)

[sodium methyl sulfate \(512-42-5\)](#)

[cyclohexane \(110-82-7\)](#)

[carbon \(7782-42-5\)](#)

[Tetrahydrofuran \(109-99-9\)](#)

[dimethylformamide \(68-12-2\)](#)

[CYCLOPENTADIENE \(542-92-7\)](#)

[6-\(Dimethylamino\)fulvene \(696-68-4\)](#)

[cyclopentadienylsodium](#)

N,N-Dimethylaminoethoxymethylum fluoborate
diethoxy(dimethylamino) methane (1188-33-6)

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