



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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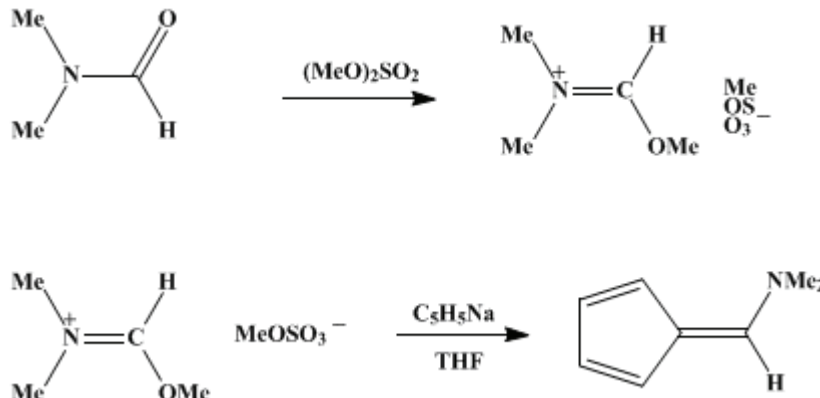
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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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 **cyclopentadienylsodium**² 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. Bredereck, 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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