



A Publication  
of Reliable Methods  
for the Preparation  
of Organic Compounds

## Working with Hazardous Chemicals

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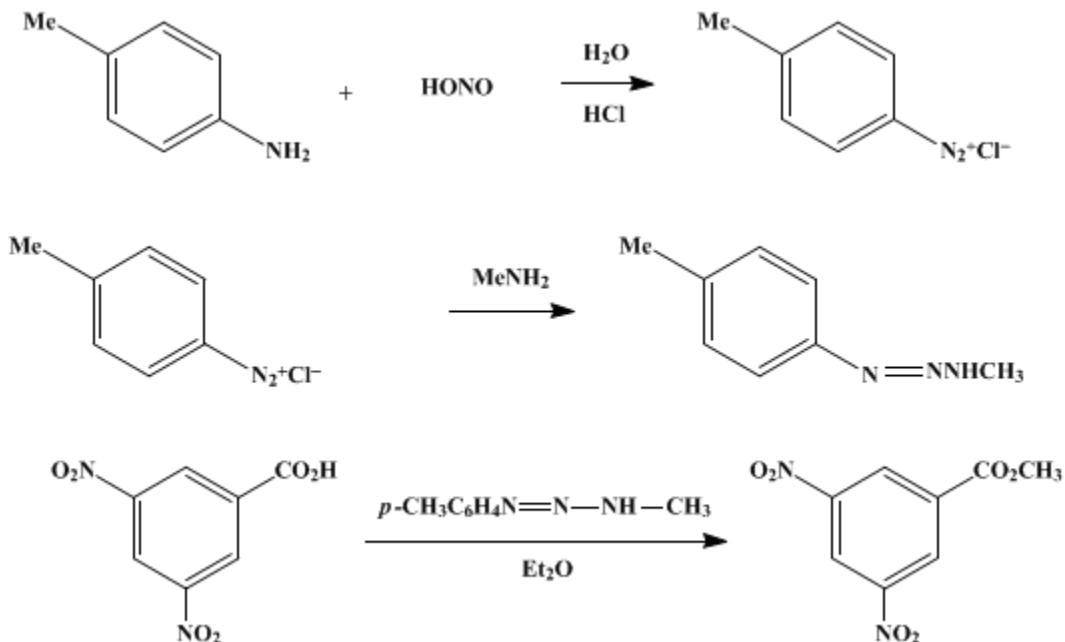
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

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## 1-METHYL-3-*p*-TOLYLTRIAZENE AND ITS USE IN THE ESTERIFICATION OF ACIDS

### [Triazene, 1-methyl-3-*p*-tolyl-]



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Checked by I. Katz and R. Breslow.

### 1. Procedure

A. *1-Methyl-3-p-tolyltriazenes*. *p*-Toluidine (50.2 g., 0.47 mole) is added to a 2-l. flask equipped with a 200-ml. dropping funnel and an efficient stirrer, and the flask is immersed in an ice-salt bath at *ca.*  $-10^{\circ}$ . A solution of 46.8 g. (0.55 mole) of potassium nitrite in 150 ml. of water is placed in the dropping funnel, and a mixture of 250 g. of crushed ice and 140 ml. of concentrated hydrochloric acid is added to the *p*-toluidine with stirring. The potassium nitrite solution is slowly added with continued stirring during 1–2 hours until a positive starch-potassium iodide test is obtained (Note 1), and the mixture is stirred for an additional hour to ensure the reaction of all the toluidine.

The solution of *p*-toluenediazonium chloride is then brought to pH 6.8–7.2 at  $0^{\circ}$  with cold, concentrated, aqueous sodium carbonate, whereupon the solution becomes red to orange in color and a small amount of red material settles out. The cold, neutral solution is transferred to a dropping funnel and added slowly to a vigorously stirred mixture of 150 g. of sodium carbonate, 300 ml. of 30–35% aqueous methylamine (Note 2), and 100 g. of crushed ice in a 3-l. flask. The reaction mixture is kept at *ca.*  $-10^{\circ}$  during the addition, which requires about 45 minutes (Note 3). The solution is extracted with three 1-l. portions of ether. The ethereal extracts are dried with anhydrous sodium sulfate and evaporated on a rotary evaporator at room temperature to give 65 g. of crude 1-methyl-3-*p*-tolyltriazenes (Note 4). This is placed in a water-cooled sublimer, and the triazene is sublimed at  $50^{\circ}$  (1 mm.) (Caution! See (Note 5)); 43.3 g. (0.29 mole, 62%) of a yellow, crystalline sublimate, m.p.  $77-80^{\circ}$ , is obtained (Note 6). The sublimate can be recrystallized from hexane to give the triazene as white needles, m.p.  $80.5-81.5^{\circ}$ . More conveniently, it is dissolved in the minimum amount of ether, and the solution is diluted with 2 volumes of hexane and cooled to  $0^{\circ}$  to give flat plates with a slightly yellow cast; m.p.  $79-81^{\circ}$ . The yield of pure triazene is 33–37 g. (47–53%) (Note 7).

B. *Esterification of 3,5-dinitrobenzoic acid with 1-methyl-3-p-tolyltriazenes* (Note 8). A solution of

1-methyl-3-*p*-tolyltriazene (1.05 g., 7.0 mmoles) in 10 ml. of ether is placed in a 100-ml. flask equipped with a 100-ml. dropping funnel (Note 9). A solution of 1.50 g. (7.1 mmoles) of 3,5-dinitrobenzoic acid in 25 ml. of ether is placed in the dropping funnel and is slowly added to the triazene solution; the contents of the flask are gently swirled from time to time. During the addition, nitrogen is evolved, and the solution becomes red in color. After the nitrogen evolution has ceased (*ca.* 1 hour), the ethereal solution is transferred to a separatory funnel and washed with 5*N* hydrochloric acid to remove toluidine (Note 10). It is then washed with 5% aqueous sodium carbonate and dried over anhydrous sodium sulfate. Evaporation of the ether yields methyl 3,5-dinitrobenzoate (1.11–1.42 g., 70–90%) as light tan crystals, m.p. 106–107.5° (Note 11). Recrystallization from ether yields small, flat plates, m.p. 107–107.5°.

## 2. Notes

1. The individual tests with starch-potassium iodide paper should be made 1–2 minutes after the addition of potassium nitrite has been stopped.
2. The checkers used 40% aqueous methylamine supplied by Matheson, Coleman and Bell.
3. The reaction is over when a drop of solution no longer gives a red color with a solution of  $\beta$ -naphthol in aqueous sodium carbonate.
4. The chief impurity is 1,5-di-*p*-tolyl-3-methyl-1,4-pentazadiene (m.p. 148°). This can be removed by fractional crystallization, but it is easier to sublime the triazene from the reaction mixture.
5. Care should be exercised during the sublimation, which should be conducted behind an appropriate shield. During the sublimation of an analog of 1-methyl-3-*p*-tolyltriazene, 1-benzyl-3-*p*-tolyltriazene, a violent explosion has occurred. In order to achieve effective sublimation, a temperature of 90–100° was required, and this elevated temperature may have been a factor in causing the explosion (private communication from D. W. Hutchinson).
6. The sublimate contains a trace of 1,3-di-*p*-tolyltriazene, as shown by thin-layer chromatography. Recrystallization yields the pure 1-methyl-3-*p*-tolyltriazene.
7. This procedure works well only with water-soluble amines. A procedure has been given elsewhere for the preparation of triazenes of water-insoluble amines.<sup>2</sup>
8. The ethyl, propyl, butyl, and other esters may be prepared similarly from the corresponding triazenes.
9. Many solvents may be used for this reaction; the reaction rate, however, is greater in nonpolar solvents. Less color develops in the reaction mixture if the system is flushed with nitrogen at this point.
10. The triazenes of secondary carbinamines also yield some N-alkyltoluidine.<sup>3</sup> Colored impurities normally enter the aqueous phase at this point in the work-up.
11. The infrared spectrum of this material is essentially identical with that of the pure, recrystallized ester.

## 3. Discussion

1-Methyl-3-*p*-tolyltriazene has been prepared by the reaction of methylmagnesium bromide with *p*-tolyl azide,<sup>4</sup> and, in unspecified yield, by the addition of methylamine to *p*-toluenediazonium chloride.<sup>5</sup>

## 4. Merits of the Preparation

This procedure represents the most convenient synthesis of 1-methyl-3-*p*-tolyltriazene. Triazenes with more complex alkyl groups may be prepared from the corresponding amine<sup>2</sup> or Grignard reagent.<sup>4</sup>

The alkylation of acids with triazenes is superior to alkylation with diazomethane and other diazoalkanes in that the triazenes are crystalline, stable materials which are easy to prepare and store. Alkylations with triazenes are unlikely to be accompanied by side reactions, such as addition to strained or conjugated double bonds, which are frequently observed in alkylations with diazoalkanes.

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## References and Notes

1. Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218.
2. E. H. White and H. Scherrer, *Tetrahedron Lett.*, 758 (1961).

3. E. H. White, H. Maskill, D. J. Woodcock, and M. A. Schroeder, *Tetrahedron Lett.*, 1713 (1969).
  4. O. Dimroth, M. Eble, and W. Gruhl, *Ber.*, **40**, 2390 (1907).
  5. C. S. Rondestvedt, Jr., and S. J. Davis, *J. Org. Chem.*, **22**, 200 (1957).
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**Appendix**  
**Chemical Abstracts Nomenclature (Collective Index Number);**  
**(Registry Number)**

ester

1-methyl-3-p-tolyltriazenes

hydrochloric acid (7647-01-0)

ether (60-29-7)

sodium carbonate (497-19-8)

sodium sulfate (7757-82-6)

nitrogen (7727-37-9)

β-naphthol (135-19-3)

methylamine (74-89-5)

potassium nitrite (7758-09-0)

Diazomethane (334-88-3)

methylmagnesium bromide (75-16-1)

3,5-Dinitrobenzoic acid (99-34-3)

toluidine,  
p-toluidine (106-49-0)

hexane (110-54-3)

triazenes

1-Methyl-3-p-tolyltriazenes,  
Triazene, 1-methyl-3-p-tolyl- (21124-13-0)

Methyl 3,5-dinitrobenzoate (2702-58-1)

p-toluenediazonium chloride

1,5-di-p-tolyl-3-methyl-1,4-pentazadiene (41798-81-6)

1-benzyl-3-p-tolyltriazene

1,3-di-p-tolyltriazene

p-tolyl azide (2101-86-2)