

Novel One Step Syntheses of Two Substituted *s*-Triazines

G. R. Hansen (1) and F. D. Blake (2)

Department of Chemistry, University of Idaho

Sir:

Though the reaction described herein does not appear to be general, its novelty and simplicity prompt us to report the synthesis of two substituted *s*-triazines from neutral pseudothiourcas.

Heating *S*-methyl-*N,N'*-diphenylpseudothiourea (I) at 140° in the absence of solvent for two days caused the evolution of methyl mercaptan and resulted in a 31% yield of 1,3,5-triphenyl-2,4,6-triphenyliminohexahydro-*s*-triazine (II); ir (Nujol) 1640 cm<sup>-1</sup> (C=N); nmr (deuteriochloroform-TMS internal standard, δ = 0) δ 6.25-7.15 (m, aromatic H); mass spectrum *m/e* 582 (M<sup>+</sup>), 388 (M<sup>+</sup> - 194, loss of diphenylcarbodiimide, C<sub>13</sub>H<sub>10</sub>N<sub>2</sub>) and 194 (diphenylcarbodiimide, C<sub>13</sub>H<sub>10</sub>N<sub>2</sub>). The elemental analysis was consistent with the molecular formula C<sub>39</sub>H<sub>30</sub>N<sub>6</sub>.

The early literature reports the preparation of several materials having the same molecular formula as II by polymerization of diphenylcarbodiimide. The materials are characterized as trimers and described as amorphous solids melting at 145.5-158° (3);, 158-160° (4) and 168-170° (5); they differ greatly from II which is crystalline and melts sharply at 196.5-197.5° (absolute ethanol).

Polymerization of diphenylcarbodiimide in our laboratory yielded a powdery solid melting at 170-175° and insoluble in boiling absolute ethanol; the solid was not identical with II.

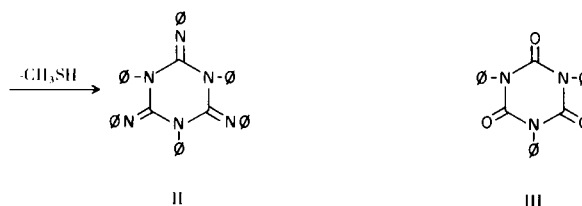
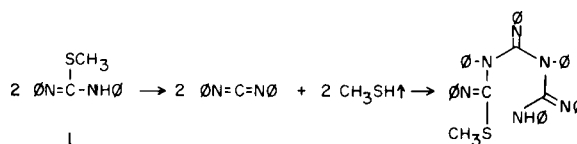
Acid hydrolysis of II failed to yield the desired known 1,3,5-triphenylisocyanurate (III) which would have served as an absolute structure confirmation. Hydrolysis of II with concentrated sulfuric acid and concentrated hydrochloric acid gave *N,N',N''*-triphenylguanidine in 61% and 50% yields, respectively.

Two attempts to independently synthesize II from III failed. In the first attempt, III was to have been reacted with phosphorus pentachloride and the product with aniline; the second required the reaction of III with phosphorus pentasulfide and the product with aniline in the presence of lead carbonate. In both cases, the initial reaction failed.

Urea has been reacted with ammonia, ammonium chloride and aluminum sulfate at high temperature to produce guanidine hydrochloride (6). The attempt to bring

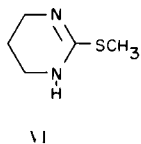
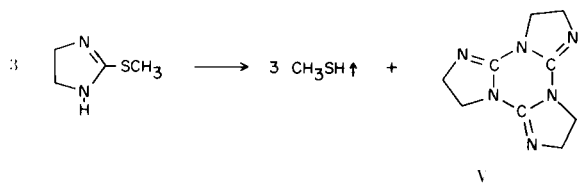
about an analogous reaction between III, aniline, aniline hydrochloride and aluminum chloride failed to give II.

Since polymerization of diphenylcarbodiimide does not yield II, it is suspected that the mechanism of the reaction involves the attack of a basic nitrogen on a carbon atom holding a methylthio group. One possible mechanism would involve the formation of diphenylcarbodiimide, its reaction in two to one ratio with I and subsequent closure with loss of methyl mercaptan.



Heating 2-methylthio-2-imidazoline (IV) at 100-140° in the absence of solvent for three hours caused evolution of methyl mercaptan and resulted in a 69% yield of perviously known 2,3,6,7,10,11-hexahydrotriimidazo (1,2-*a*; 1',2'-*c*; 1'',2''-*e*)-*s*-triazine (V); ir (Nujol) 1660 cm<sup>-1</sup> (C=N); nmr (deuteriochloroform-TMS internal standard, δ = 0) δ 3.90 (s, all imidazoline ring H); mass spectrum *m/e* 204 (M<sup>+</sup>). The melting point (320-321°) was in agreement with a previously reported value, 322-324° (7).

As linearity of the N-C-N linkage in the imidazoline is not possible, a carbodiimide intermediate is also impossible and it is assumed that the mechanism involves attack of the NH nitrogen of IV on the carbon holding the methylthio group, again with subsequent loss of methyl mercaptan.



This reaction is not general. Heating 2-methylthio-1,4,5,6-tetrahydropyrimidine (VI) at its melting point for one

week in the absence of solvent yielded none of the corresponding *s*-triazine.

#### REFERENCES

- (1) Inquiries should be directed to G. R. Hansen. Present address: Monsanto Co., 800 N. Lindbergh Blvd., St. Louis, Missouri 63166.
- (2) Present address: 3M Company, 3M Center - St. Paul, Minnesota 55101.
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Moscow, Idaho