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OXIDATIVE DIMERIZATION OF 1,1-DIMETHYL-4-PHENYLSEMICARBAZIDE WITH LEAD TETRAACETATE: A NOVEL ROUTE TO THE HEXAHYDROTETRAZINE RING SYSTEM

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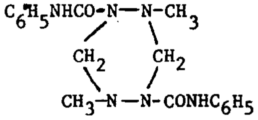
The finding that 1-benzyloxy-3-phenylureas undergo oxidative ring closures with lead tetraacetate in chloroform to 1-benzyloxybenzimidazolones in nearly quantitative yields (1) caused us to extend the study to other systems containing a readily oxidizable group situated γ with respect to an aromatic ring. Our first effort with phenoxyethanol was moderately successful and a 15% yield of benzodioxane* product was obtained. At this time Starnes (2) reported ring closed products from the lead tetraacetate oxidation of 3,3,3-triphenyl-1-propanol. Because of this report our attention was turned to the oxidation of other systems.

Of several related structures studied malonic anilide, phenoxyacetoneoxime (3) and 1,2,4-triphenylsemicarbazide underwent oxidation but did not give ring closed products. Quite a different sort of oxidative ring closure was observed with 1,1-dimethyl-4-phenylsemicarbazide [I], which was prepared from 1,1-dimethylhydrazine and phenyl isocyanate. Oxidation of I with one equivalent of lead tetraacetate in chloroform at room temperature for one hour resulted in formation of an oil which slowly changed to a white solid (75%), mp 242.5-243.5 from acetone-water mixture, identified as 1,4-dimethyl-2,5-di(phenylcarbamyl)hexahydrotetrazine [II] by elemental analysis and spectral properties: ir (Nujol) 1670 cm^{-1} (C=O); nmr ($CDCl_3$) singlet 2.79 ppm (6H) doublet 4.59 ppm (2H) j=13 cps, doublet 4.99 ppm (2H) j=13 cps, multiplet 6.99-7.60 (10H), broad singlet 8.44 ppm (2H).

$C_6H_5NHCONHN(CH_3)_2$

I



II

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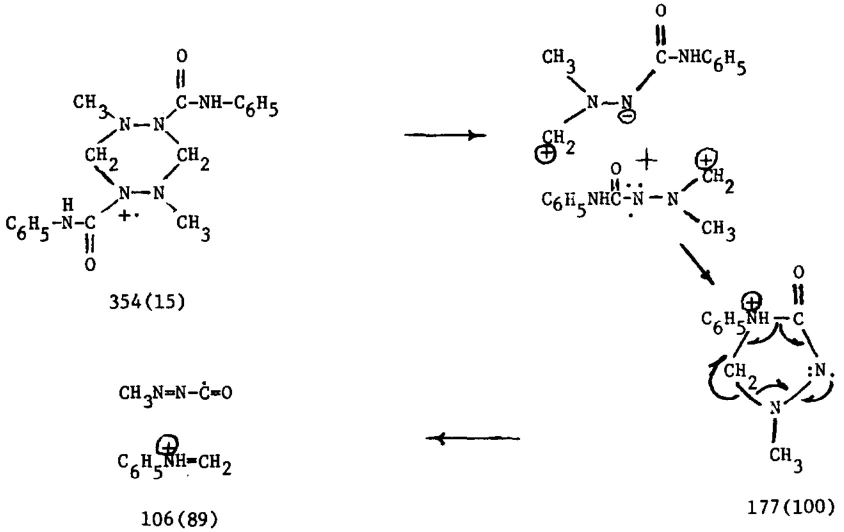
* This experiment was carried out by S. W. Jeppeson in this laboratory.

The two doublets in the nmr were considered to arise from the equatorial and axial hydrogen of the methylenes, and at 150° in bromoform these two doublets collapsed to a broad singlet only to reappear upon cooling. Major species in the mass spectrum at 70 ev are shown with an interpretation based on the known decomposition pathways of related molecules (5) in Chart 1, m/e (relative intensities).

Metastable peaks at 88.6 and 63.4 show the precursor-daughter relationship of each of these species.



In the oxidation of these systems we are observing three important types of behavior; 1,5-oxidative ring closure from 1-benzyloxy-3-phenylurea, 1,3-oxidation and dimerization from [I], and 1,2-oxidative elimination with formation of azobenzene and phenyl isocyanate from 1,2,4-triphenylsemicarbazide. These initial studies are illustrative of important oxidative pathways of organic nitrogen compounds.

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