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BASE CATALYZED CONDENSATION OF DIMEDONE WITH β-NITROSTYRENE

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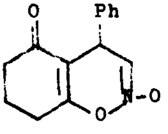
The initial report[1] of the base-catalyzed condensation of 1,3-cyclohexanedione with β-nitrostyrene proposed structure 1 for the product. Two revised structures were reported subsequently in independent investigations: Nielsen and Archibald[2] suggested structure 2; and 3 was suggested by Larson, *et al.*[3] We have been working on the related dimethyl system and find that an X-ray crystal structure determination leads to structure 4.



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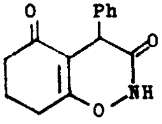

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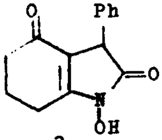

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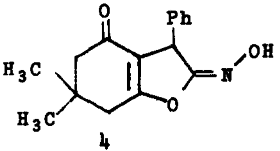

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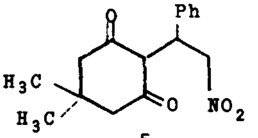
Nielsen and Archibald[2] reported that the initial adduct 5 obtained from dimedone and β-nitrostyrene could not be cyclized; in our hands 5 was smoothly dehydrated to 4 under a variety of conditions (trace of $NaOCH_3$ in warm CH_3OH; trace of Et_3N in THF). In addition, treatment of dimedone and β-nitrostyrene in ether with triethylamine led directly to 40% yields of 4.



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Compound 4, $C_{16}H_{17}NO_3$, mp 170-173° dec. (variable), gave satisfactory combustion analyses and molecular weight (mass spectra). Its spectral properties leave no doubt that it differs only by the presence of the methyl groups from the 1,3-cyclohexanedione-β-nitrostyrene product: λ_{EtOH} 217 nm (sh, 10,800), 272 nm (11,000); λ_{EtOH,OH^-} 218 nm (sh, 9400), 282 nm (7800; ν^{KBr} 3260, 1700, 1625 cm^{-1}; δ_{CDCl_3} 1.10 (singlet, 6H), 2.10 (singlet, 2H), 2.53 (doublet, J=2.5 mHz, 2H), 5.08 (triplet, J=2.5 mHz, 1H), 7.25 (broad singlet, 5H), 9.70 (singlet, 1H, exchanges with D_2O).

The compound crystallizes from methanol in the centrosymmetric space group, $P2_1/n$, with four molecules in a unit cell having the dimensions: a=13.158 ±0.002 Å, b=8.657 ±0.002, c=12.205 ±0.002, β=98.84 ±0.01°. The density observed by flotation is 1.317 g/cm^3; the calculated density for $C_{16}H_{17}NO_3$ is 1.316 g/cm^3.

The structure was solved by iterative application of the Sayre equation,[4] in a manner similar to the symbolic addition procedure of Karle and Karle.[5] The E map calculated from the solution with the most self-consistent set of phases clearly showed all atoms except hydrogen. The structure was refined by the least-squares method to an R factor of 0.042, with all hydrogen atoms having isotropic temperature factors and all other atoms anisotropic.

The oxime, as shown in structure 4, is exclusively *anti* with respect to the oxygen of the heterocyclic ring, and in the crystalline state is hydrogen bonded to the carbonyl oxygen of an adjacent molecule. Complete details of the structure will be published elsewhere.

Plausible mechanisms can be drawn for the conversion of 5 to 4 and for the degradation of 4 (with hydrogen in place of methyl) to the observed[1,3] products. In agreement with Larson, *et al.*,[3] we find that the acetyl derivative of 4 is not an N-acetyl derivative (ν^{Nujol} 1750 cm^{-1}), but gross spectral changes indicate that additional rearrangement has occurred.

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