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An Adduct (1:2) from Diphenylcyclopropenone Oxime and Phenyl Isocyanate

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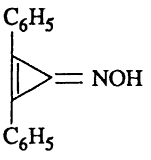
Diphenylcyclopropenone oxime combined with phenyl isocyanate to give 1,2,7-triphenyl-4-[(phenylamino)carbonyl]-5-oxa-4,7-diazaspiro-[2.4]hept-1-en-6-one.

In the course of an investigation on straightforward reactions of diphenylcyclopropenone oxime **1** to give hydroxylaminodiphenylcyclopropenylium tricyanomethanide (**2**) and the energetic trinitromethanide salt **3** from additions with tricyanomethane and trinitromethane, 1) a reexamination of the adduct obtained from a combination of two moles of an isocyanate with the ketoxime **1** was undertaken. The experimental procedure previously described was followed to give an adduct from phenyl isocyanate. 2,3) It was erroneously identified as 1,2,4-triphenyl-6-[(phenylamino)carbonyloxy]-4,6-diazaspiro[2.3]hex-1-en-5-one (**4**) and has been reassigned the structure of 1,2,7-triphenyl-4-[(phenylamino)carbonyl]-5-oxa-4,7-diazaspiro-[2.4]hept-1-en-6-one (**5**). Identification of the product as a derivative of the 1,2,4-oxadiazolidin-5-one heterocycle was supported by its physical properties and spectroscopy and confirmed by X-ray crystallography. 4,5)

An initial electrophilic attack by phenyl isocyanate at the nitrogen atom of the oxime moiety with simultaneous or subsequent tautomerization of the hydroxylamine derivative **6** was proposed to give the nitrone **7** as an intermediate adduct (1:1). An analogous formation of hydroxylamines **2**,**3** tended to support the intermediacy of the hydroxylamine **6**. This addition of an isocyanate differed from related reactions of simpler oximes where the formation of oxime carbamate esters, $R_2C=NOCONHR$, predominated and isomeric nitrones, $R_2C=N^+(O^-)CONHR$, were not detected. 3) A 1,3-dipolar addition between the nitrone **7**



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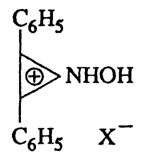
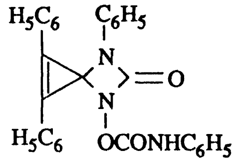


2 $X = C(CN)_3$
3 $X = C(NO_2)_3$



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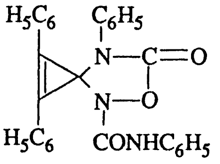

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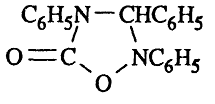

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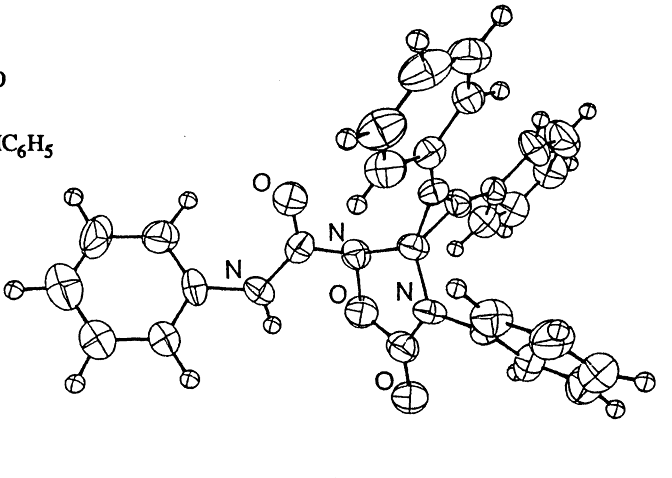
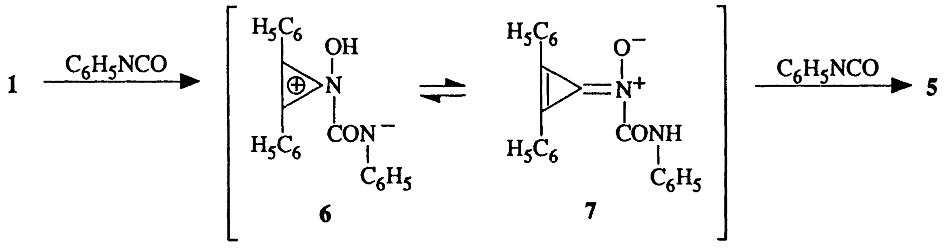


Fig. 1. 5 Ortep plot.



and a second molecule of phenyl isocyanate presumably accounted for the formation of the oxadiazaspiro[2.4]heptenone **5** with no trace of the isomeric diazaspiro[2.3]hexenone structure **4**. Similar 1,3-dipolar additions between nitrones and isocyanates were known, e.g., 2,3,4-triphenyl-1,2,4-oxadiazolidin-5-one (**8**) was obtained from phenyl isocyanate and C,N-diphenylnitrone.[6)]

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References

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4) Compound **5**: colorless needles (ether/petroleum ether) mp 141–142 °C (lit [3)] mp 142–145 °C); IR (KBr): ν 1771 [3)] (lit [6,7)] ν 1740 to 1785 for C=O in a 1,2,4-oxadiazolidin-5-one); ^{13}C NMR ($CDCl_3$): δ 67.8, 117.8, 120.0, 124.5, 125.6, 127.3, 128.2, 129.1, 129.3, 129.5, 130.4, 130.7, 132.9, 136.9, 154.2, 156.4.

5) Crystal data for **5**: $C_{29}H_{21}N_3O_3$, M_r = 459.51, triclinic, space group P$\bar{1}$, a = 9.973(7) Å, b = 10.774(4) Å, c = 12.412(8) Å, α = 74.28(3)°, β = 67.39(7)°, γ = 88.97(4)°, V = 1179.5(10) Å^3, Z = 2, D_{calc} = 1.294 g cm^{-3}, λ(Mo Kα) = 0.71073 Å, μ = 0.795 cm^{-1}, F(000) = 960, T = 293 K, R = 0.0285, R_w = 0.0312 for 900 observed reflections ($I > 3\sigma_I$). A total of 1615 intensities were measured with an Enraf-Nonius CAD4 diffractometer using the ω-2θ scan mode. The structure was solved by direct methods and refined by full-matrix least squares techniques. C, N, and O atoms were refined anisotropically and H atom positions were refined with fixed isotropic temperature factors. The molecular structure is depicted in Fig. 1. Full details of the structure will be published elsewhere.

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