Tetrahedron Letters, Vol. 33, No. 16, pp. 2231-2234, 1992
Printed in Great Britain

0040-4039/92 $5.00 + .00
Pergamon Press Ltd

2-(1,2-Dihydro-3-oxo-4,5-diphenyl-3*H*-pyrrol-2-ylidene)-1,2-dihydro-4,5-diphenyl-3*H*-pyrrol-3-one: A New Pyrrole-based Indigotin Analogue

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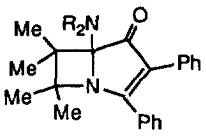
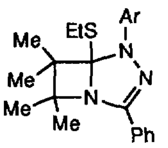
Key Words: 1-Azetines; diphenylcyclopropenone; X-ray crystal structure.

Abstract. Thermolysis, in boiling o-dichlorobenzene, of the cycloadducts 5 and 10a,b of diphenylcyclopropenone and 2-(alkylthio)azetines 4 and 9a,b yield the title compound 8.

Heimgartner[1] has shown that 2-(dialkylamino)-1-azetines yield 1:1 cycloadducts **1** with diphenylcyclopropenone. More recently, we have isolated the 1,3-dipolar cycloadducts from nitrile oxides, nitrile ylides,[2] and nitrilimines[3] with 2-alkoxy- and 2-alkylthio-1-azetines. Of particular interest are the nitrilimine adducts **2**, which on heating undergo loss of the alkylthio-group and cleavage of the fused four-membered ring to yield butenyl-triazoles **3**.[3]



1



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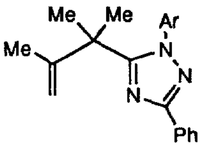


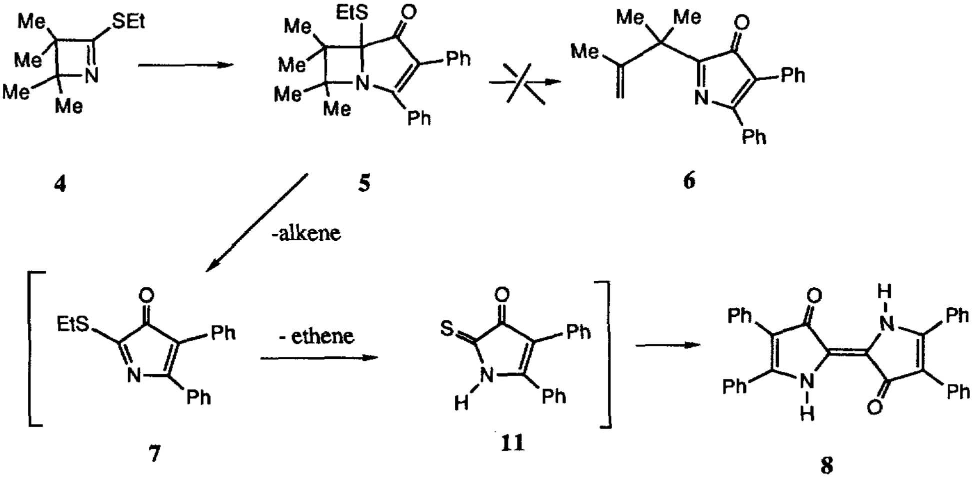
3

We were intrigued by the possibility that cycloadducts **5** of alkylthio-azetines (e.g. **4**) with diphenylcyclo-propenone would undergo analogous thermal fragmentation to provide examples of the little known[4,5] 3-azacyclopentadienone system **6**.

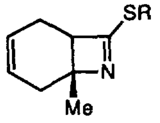
Addition of 2-(ethylthio)-1-azetine **4**[2] to diphenylcyclopropenone was achieved in acetonitrile at room temperature (72 h) and gave cycloadduct (**5**; 87%, m.p. 162-3°).[6] This bicycle was stable in boiling toluene and in boiling xylene, but under reflux in *o*-dichlorobenzene (b.p. 179-80°) furnished a complex mixture (by t.l.c.) from which the major product (38%), a deep-purple high melting solid (m.p. 309-12°), was isolated by flash chromatography on silica. The structure of this product, which was not apparent from the usual (i.r., ^{1}H n.m.r. and mass) spectral data,[7] was assigned on the basis of an X-ray crystal analysis[8] (Figure) as the indigotin-like structure **8**.

The identical product (32% yield) was also formed on thermolysis of the cycloadduct (**10a**; m.p. 118-24°, 65% yield), obtained by reaction of diphenylcyclopropenone with bicyclic azetine (**9a**; oil; 60%).[9]

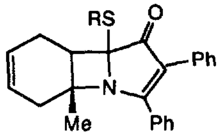
The mode of formation of this novel[10] bi-pyrrolinone derivative is not yet clear. It is tempting to suggest that formation is by a (2 + 2) cycloreversion of the adducts (**5** or **10a**), followed by loss of ethene by a thermal McClafferty type rearrangement. Dimerisation and desulphurisation of the resulting thioamide **11** would then yield the product. However, the methylthio-compound (**10b**; m.p. 119-23°), prepared (84% yield) from diphenylcyclopropenone and the (methylthio) azetine (**9b**; oil), in which loss of the methyl group by a McClafferty process is prohibited, on heating, also affords the purple bi-pyrrolinone derivative **8** in 29% yield.



4 **5** **6** **7** **11** **8**



9 a) R = Et
b) R = Me



10 a) R = Et
b) R = Me

1-Methyl-1,4-cyclohexadiene has been trapped, as the azetidinone (albeit in low yield ~ 7%) by chlorosulphonyl-isocyanate, during the thermolysis of **10a**. However, all attempts so far to trap the azacyclopentadienone **7**, or the dienone tautomer of **11** as a diene[4] or as a dienophile have failed. Further work is in progress to determine the origin of this novel product.

We thank Roussel Scientific Institute U.K. Ltd. and SERC for a CASE award to K.H.

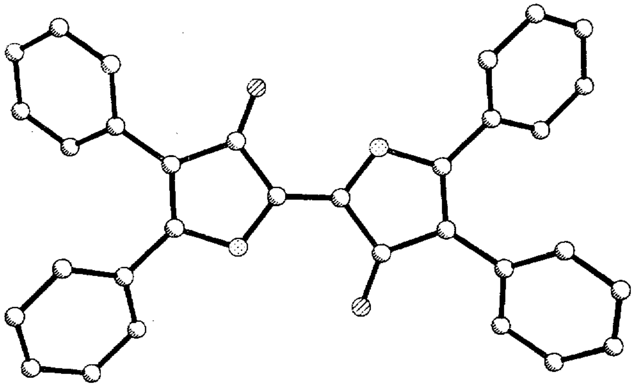


FIGURE - **Molecular Structure of 2-(1,2-Dihydro-3-oxo-4,5-diphenyl-3*H*-pyrrol-2-ylidene)-1,2-dihydro-4,5-diphenyl-3*H*-pyrrol-3-one**

References and Notes

1. H. Heimgartner, F. Stierli, R. Prewo, and J.H. Bieri, *Helv. Chim. Acta*, 1983, **66**, 1366.
2. A-B.N. Luheshi, R.K. Smalley, P.D. Kennewell and R. Westwood, *Tetrahedron Lett.*, 1990, **31**, 123.
3. A-B.N. Luheshi, R.K. Smalley, P.D. Kennewell, and R. Westwood, *Tetrahedron Lett.*, 1990, **31**, 127.
4. T. Eicher, F. Abdesakan, G. Franke, and J.L. Weber, *Tetrahedron Lett.*, 1975, 3915: T. Eicher and G. Franke, *Justus Liebigs Ann. Chem.*, 1981, 1337.
5. H. Preut, T. Eicher, G. Franke, and C. Krüger, *Acta Crystallog.*, 1982, **B38** 1368: K-H. Klaska, O. Jarchow, T. Eicher, H. Preut, *Acta Crystallog.*, 1979, **B35**, 2788.
6. All new compounds have been fully characterised by i.r., ^{1}H n.m.r. and elemental/or mass spectroscopic analysis.

7. F.t.i.r. (nujol) 3393 (NH), 1739 cm^{-1} (C=O). δ_H (300 MHz, $CDCl_3$) 7.22-7.59 (8H, m, Ar), 8.99 (1H, bs, NH): δ_C (CCl_3), 112.6, 121.0, 126.8, 128.1, 128.4, 129.0, 129.3, 130.2, 130.7, 131.6, 162.0, 189.0.
8. **Crystal Data** for $C_{32}H_{22}N_2O_2$: M = 466.5, triclinic, spacegroup $P\bar{1}$, a = 10.696(3), b = 10.738(3), c = 11.353(3) Å, α = 98.15(2)°, β = 108.50(2)°, γ = 107.49(2)°, U = 1138.1(5) Å^3, D_c = 1.361 g cm^{-3}, Z = 2, F(000) = 488, M_o-K_α X-radiation (graphite monochromator) λ = 0.71073 Å, μ (M_o-K_α = 0.080 mm^{-1}. A dark purple irregular block of dimensions 0.8 x 0.5 x 0.3 mm was used for measurement at 230°K. Intensity data in the range $3^\circ < 2\ni < 50^\circ$ were collected using a $\ni$ - $2\ni$ scan technique on a Siemans R3m/V diffractometer. The intensities of 3 reflections measured periodically showed a negligible decrease. A total of 4268 reflections was collected of which 4033 (R_{int} = 0.032) were independent and 1519 ($I > 3\sigma$ (I)) were used in the refinement. The structure was solved by direct methods and refined by full matrix least squares methods. The asymmetric unit consists of two half moleules from which the full molecules are generated by crystallographic centres of symmetry. All hydrogen s atom were found from difference Fourier maps and were then placed in calculated positions and refined riding upon their respective parent atoms. At convergence R - 0.050 and wR - 0.056 where w = [σ^2(F) + 0.0008F^2]. The largest features in the final difference map were + 0.20 and -0.23 eÅ^3 respectively. All calculations performed using the SHELXTL-PLUS program suit on a MICROVAX II.
9. Bicyclic azetine **9a** is prepared by thionation (Lawessons reagent) of the corresponding azetidinone (L.A. Paquette, J.F. Hansen, and J.C. Philips, *J. Amer. Chem. Soc.*, 1971, **93**, 152) and alkylation of the resulting thione (93%: m.p. 124-6°C) with triethyloxonium tetrafluoroborate.
10. Alkyl- and cycloalkyl-derivatives of the bipyrrolinone system are known: G. Pfeiffer and H. Bauer, *Justus Liebigs Ann. Chem.*, 1980, 564.

(Received in UK 24 January 1992)