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A NOVEL CYCLOADDITION REACTION OF 4-BROMO-2,6-DIMETHYL-PHENYLISONITRILE WITH ACETYLENE DERIVATIVES

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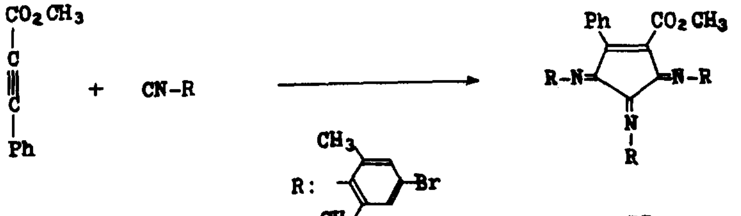
In the preceeding communication we described the reaction of diphenylcyclopropenone or diphenylcyclobutenedione with 2,6-dimethylphenylisonitrile to give 4,5-bis(2,6-dimethylphenylimino)-2,3-diphenylcyclopenten-1-one via monoimine of bisketene intermediate(1). In this communication we wish to report the formation of cyclopentenetriimine derivatives from 4-bromo-2,6-dimethylphenylisonitrile and acetylene derivatives.

The reflux of 4-bromo-2,6-dimethylphenylisonitrile with two equivalent of methyl phenylpropiolate (I) in benzene for 11 hours gave 4-carbomethoxy-5-phenylcyclopentene-1,2,3-tri(N-2,6-dimethylphenyl)imine (II) as deep violet crystals, mp 210-211°, in 41 % yield.

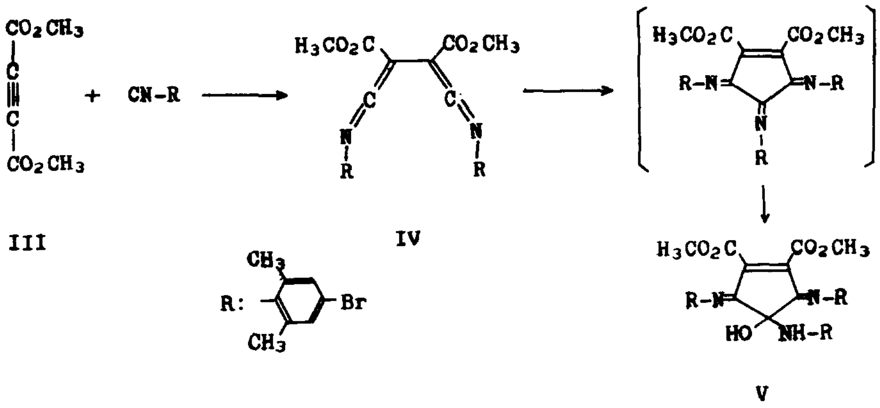


I

II

The elemental analysis and molecular weight determination indicated that the compound II should have the composition of one molecule of acetylene I and three molecules of isonitrile. In the IR region, II exhibited the characteristic absorptions at 1742 cm^{-1} and at 1638 cm^{-1} which were due to the ester group and the imino group, respectively. The characteristic peak at 2280 cm^{-1} attributable to the triple bond in the starting material disappeared in the product. Compound II showed also characteristic UV and NMR spectrum: UV maxima in ethanol at 250mμ (log ε 4.56), 252 mμ (4.58) and 310 mμ (4.26); NMR signals at 2.20-3.05 τ (m, 11 H), 6.92τ (s, 3 H), 7.95τ (s, 6 H), 8.15τ (s, 6 H) and 8.20τ (s, 6 H). These results all indicate that II should be the structure as shown in the figure.

On the other hand, the reaction of the isonitrile with two equivalent dimethyl acetylenedicarboxylate (III) proceeded in benzene at room temperature for 24 hours.(2) Subsequent removal of the solvent <u>in vacuo</u> at room temperature and separation by means of silicagel chromatography gave numbers of product(3), one of which was found to be 2-hydroxy-2-N-(4-bromo-2,6-dimethylphenyl)amino-4,5-dicarbomethoxycyclopentene-1,3-di(N-4-bromo-2,6-dimethylphenyl)imine(V), mp 169-170°, in 3 % yield.



Compound V showed satisfactory results on elemental analysis and molecular weight determination as that expected from $C_{33}H_{32}N_3O_5Br_3$. V showed characteristic IR peaks at 3470 cm⁻¹ (ν_{OH}), 3250 cm⁻¹ (ν_{NH}), 1745 cm⁻¹ ($\nu_{C=O}$)and 1675 cm⁻¹ ($\nu_{C=N}$), UV maxima in ethanol at 253 mμ (log ε 4.49), and 370 mμ (4.08), and NMR signals at 2.8-3.1 τ (m, 7 H), 6.4 τ (s, 6 H), 6.6 τ (s, 1 H), 7.6 τ (s, 3 H), 7.7 τ (s, 3 H), 8.2τ (s, 9 H) and 8.5τ (s, 3 H). Thus the structure of V was formulated as the mono hydrate of cyclopentenetriimine(1,4).

When the reaction was carried out at 0-5° to trap the intermediate of this reaction, interestingly bis [(N-2,6-dimethyl-4-bromophenyl)carbomethoxyketenimine] (IV), mp 180-181°, was isolated in 3 % yield in addition to compound V. The yield of IV raised up to 9.2 % in the reaction of acetylene III with two equivalent of isonitrile. The elemental analysis, molecular weight determination and NMR indicated that this compound IV should have the molecular formula $C_{24}H_{22}N_2O_4Br_2$. In its IR region, IV exhibited the characteristic absorptions at 2090 cm^{-1} and at 2060 cm^{-1} which were due to the heterocumulated double bond(5) and the absorption at 1710 cm^{-1} ($\nu_{C=O}$) attributable to the ester group. The NMR spectrum of IV exhibited a singlet(4 H) at 2.70τ , a singlet (6 H) at 6.25τ and a singlet (12 H) at 7.60τ . Therefore, it is clear that two ester groups and two N-4-bromo-2,6-dimethylphenyl ketenimine groups are present in this compound. The structure of IV was confirmed further by acidic hydrolysis to give the corresponding bis-amide.

Bis-ketenimine IV reacted further with isonitrile at room temperature to give the hydrate of cyclopentenetriimine V in reasonable yield after working up by silicagel chromatography.

Consequently, bis-ketenimine is actually the intermediate in the reaction of isonitrile with acetylene derivatives to give cyclopentenetriimine II or V. The formation of bis-ketenimine might be taking a route of isonitrile attack to a 1:1 adduct, i.e. iminocyclopropene intermediate(6). Because diphenylcyclopropenone reacts with isonitrile in the similar fashion(1)

References

(1) N. Obata and T. Takizawa, "Reaction of 2,6-dimethylphenylisonitrile with some small ring ketones" accompanying communication, Tetrahedron Letters, 3403,(1969).

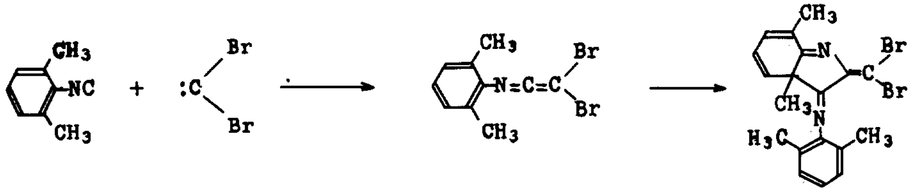
(2) E. Winterfeld reported the similar reaction in the review, however, they gave no details for this reaction. E. Winterfeld, Angew. Chem. internat. edit., **6**, 423 (1967).

(3) The structure of other complex compounds is now under investigation by means of chemical reactions and X-ray analysis.

(4) It is considered that the position of hydrate is at the center carbon of three imino groups because of analogy in cyclopentenetrione(1).

(5) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules", John-Wiley and Sons, Inc., New York, 1958. See also: C. L. Stevens and J. C. French, *J. Am. Chem. Soc.*, **75**, 657 (1953).

(6) Another interesting possibility for the formation of bis-ketenimine is that the isonitrile reacts with bis-carbene which has been considered to be isoelectronic to acetylene triple bond(7). In a separate experiment, we have observed the reaction of 2,6-dimethylphenylisonitrile with dibromocarbene to yield indolenine derivatives via a ketenimine intermediate. These results will be published near future.



(7) E. Winterfeld and G. Giesler, *Angew. Chem.*, **78**,588 (1966); E. LeGoff and R. B. LaCount, *Tetrahedron Letters*, 2333 (1967).