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REACTIONS OF 2,6-DIMETHYLPHENYLISONITRILE WITH SOME SMALL RING KETONES

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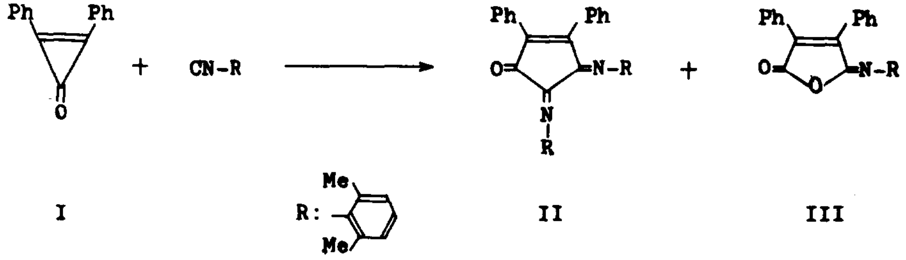
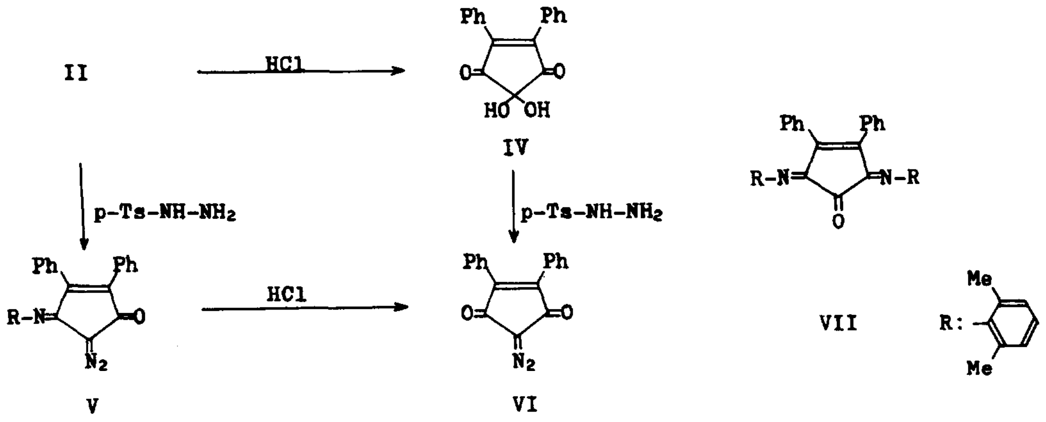
Although it has been known that isonitriles do not react normally with ketones(1), we have observed that 2,6-dimethylphenylisonitrile reacts with some conjugated small ring ketones in refluxing benzene to afford ring expanded products.

Thus the reflux of three equivalents of 2,6-dimethylphenylisonitrile(2) with diphenylcyclopropenone (I) in benzene for 4 hours under nitrogen stream resulted in the formation of 4,5-bis(2,6-dimethylphenylimino)-2,3-diphenylcyclopenten-1-one (II), mp 184°, in 76 % yield, and a trace amount(3) of N-(2,6-dimethylphenyl)diphenylisomaleimide (III), mp 172-173°. The structure of II was established by the elemental analysis, the molecular weight determination(4) and the following spectral observations: characteristic IR peaks at 1640 cm^{-1} ($\nu_{C=N}$) and 1710 cm^{-1} ($\nu_{C=O}$) ; UV maxima in ethanol at 240 mμ (ε 25,200) and 330 mμ (ε 15,400) ; NMR signals at $2.4\text{-}2.9_\tau$ (m, 10 H), $3.1\text{-}3.4\,\tau$ (m, 6 H), $7.95\,\tau$ (s, 6 H), and 8.25_τ (s, 6 H). The structure was confirmed further by following chemical transformations.



The compound II was hydrolyzed by dilute hydrochloric acid to give 2,2-dihydroxy-4,5-diphenylcyclopentene-1,3-dione (IV), and 2,6-dimethylaniline in quantitative yields. This enedione IV showed quite similar patterns in its IR and UV spectrum to those of cyclopentene-1,3-dione reported by DePuy and Wells(5).

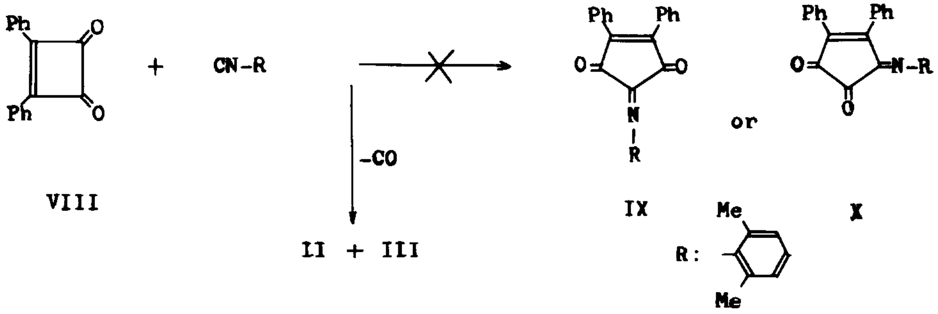
When II was treated with p-toluenesulfonylhydrazine in benzene, there was obtained 5-diazo-4-(2,6-dimethylphenylimino)-2,3-diphenylcyclopenten-1-one (V), mp 132-133°, in 76 % yield. Under a similar treatment, IV also gave the diazo derivative VI, which was found to be identical to the material obtained by the hydrolysis of V. The identity of two samples was established by mmp and comparisons of their IR and UV spectra. Thus the structure of II should not be symmetrical 2,5-bis(2,6-dimethylphenylimino)-3,4-diphenylcyclopenten-1-one (VII) but it is the structure as shown in the figure.



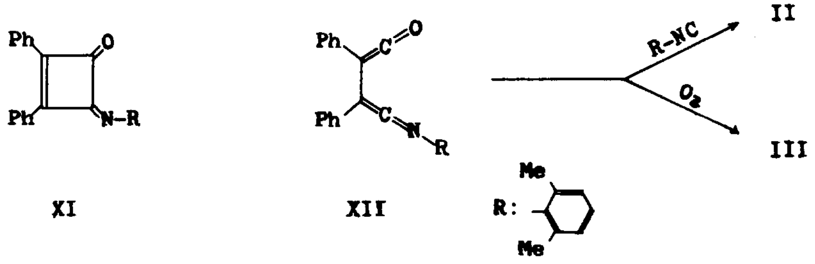
The product III might be produced in the reaction with oxygen which was present as impurity at an intermediate stage, since when the reaction was carried out without nitrogen purge, its yield raised up to 2.3 %. The elemental analysis and NMR indicated that this compound should have only one imino group and its IR and UV was very similar to those of N-substituted isomaleimide(6).

Its transformation into the maleimide was accomplished by a treatment of III with a catalytic amount of hydrochloric acid in methanol. The resulting N-(2,6-dimethylphenyl)diphenylmaleimide, mp 191-192°, was characterized by the comparison with an authentic specimen prepared by the reaction of diphenylmaleic anhydride(7) with 2,6-dimethylaniline.

Now, the reaction of 3,4-diphenylcyclobutenedione (VIII) with the isonitrile under the presence of air also resulted in the formation of II,66 %, and III, 1.7 %. Apparently, there must be a loss of carbon monoxide in the reaction. There was actually observed a considerable evolution of gas during the reaction and it could be the carbon monoxide. Since a reflux of the diketone alone in benzene for a prolonged period resulted in the recovery of the starting diketone in a quantitative amount, the loss of carbon monoxide, i.e. the formation of diphenylcyclopropenone, did not evidently take place prior to the reaction.



Although the formation of II and III from I can be considered to be the insertion of the isonitrile to a strained C-C bond via a primary insertion product, i.e. monoimine of cyclobutenedione intermediate (XI), we believe that the reaction is taking a route of the intermittent formation of bis(phenylketene)-monoimine (XII). Because the reaction of VIII gives the product II but not IX or X which is strictly expected to be produced by an insertion of isonitrile to VIII, and also because monotosylhydrazone(8) of VIII which has a similar structure with



XI does not react with isonitrile under the same condition(9). In a separate experiment we have observed that bis-ketenimine, which has been prepared by the reaction of dimethyl acethylenedicarboxylate with 4-bromo-2,6-dimethylphenylisonitrile, reacts with the isonitrile further to afford cyclopentenetriimine derivatives under a mild condition(10).

References

(1) Hexafluoroacetone has been known to react with alkyl isonitrile under a mild condition. W. J. Middleton, D. C. England and C. G. Krespan, J. Org. Chem., 32, 948 (1967).

(2) The reaction of diphenylcyclopropenone (I) with cyclohexyl- or p-toly-isonitrile gave only the polymeric materials.

(3) When the reaction was carried out in nitrogen atomosphere and freshly distilled dry benzene and materials degased in vacuo were used, III could not be obtained.

(4) All compounds reported hereafter showed satisfactory results on elemental analysis and molecular weight determination. Melting points are uncorrect.

(5) C. H. DePuy and P. R. Well, J. Am. Chem. Soc., 82, 2909 (1960).

(6) R. J. Cotter, C. K. Snares and J. M. Whelan, J. Org. Chem., 26, 10 (1961).

(7) C. L. Reimer, Ber., 13, 741 (1880).

(8) A. T. Blomquist and E. A. LaLancette, J. Am. Chem. Soc., 83, 1387 (1961).

(9) N. Obata and T. Takizawa, unpublished results. It seems this result indicates that XII cannot be a tautomer of XI.

(10) T. Takizawa, N. Obata, Y. Suzuki and T. Yanagida, Tetrahedron Letters, 3407 (1969).