CYCLOADDITION REACTIONS OF DIPHENYLKETENE WITH 1-AZA-1,3-DIENE AND CONJUGATED SULFILIMINES

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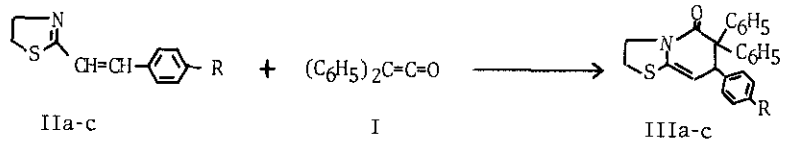
The cycloaddition reactions of diphenylketene (I) with several azadienes have been examined. 2-Styryl-thiazoline (IIa-c) and I generally underwent a 4+2 cycloaddition to give thiazolo[3,2-a]pyridines (IIIa-c). On the other hand, reaction of I with 2-styrylquinoline and 2-styrylpyridine gave rise to a 2+2+2 cycloaddition products (Va, b), respectively. Similar reaction of I with 6-styrylphenanthridine gave pyrido[1,2-f]phenanthridine (VII) and a lactone (Vc).

The orientation of the addition products of I with sulfilimines (VIII, XI, XII) which we reported in our previous paper was the error and the reverse.

During the last several years, the cycloaddition reactions of ketenes with various azadienes such as 1-aza-1,3-diene[1], 1,2-diaza-1,3-diene[2], 1,3-diaza-1,3-diene[3], 1,4-diaza-1,3-diene[4], 2,3-diaza-1,3-diene[5], and other heterodienes[6] have been extensively investigated. The cycloaddition reactions of ketenes with these heterodienes generally give 1,2- or 1,4-cycloadducts and/or 2:1-molar cycloadducts. During the course of our studies concerning cycloaddition reactions of diphenylketene (I), these publications have prompted us to investigate the reaction of I with azadienes having -N=C-C=C- or -N=C-N=S- double bond systems in which the carbon-nitrogen double bond of azadiene is a part of the heterocyclic system.

The reaction of I with azadienes (IIa-c) was carried out in the following manner: a mixture of I (2 mmol) and IIa-c (2 mmol) in dry xylene was refluxed for 10 hr followed by evaporation *in vacuo* to give a crystalline substance, which was purified by recrystallization giving the 1,4-cycloadducts (IIIa-c).



IIa-c I IIIa-c

a : R=H
b : R=Cl
c : R=NO_2

The proposed structures of these adducts were confirmed by elemental analyses and spectral data to be the thiazolo[3,2-a]-pyridine (IIIa-c) (Table I).

In contrast to the above, the reaction of I with 2-styryl-quinoline (IVa) afforded the 2:1-molar adduct (Va) in 51% yield. The ir spectrum of Va exhibited strong absorptions at 1765 and 1655 cm^{-1} ascribable to a vinyl ester moiety ($-CO_2CH=CH-$) and

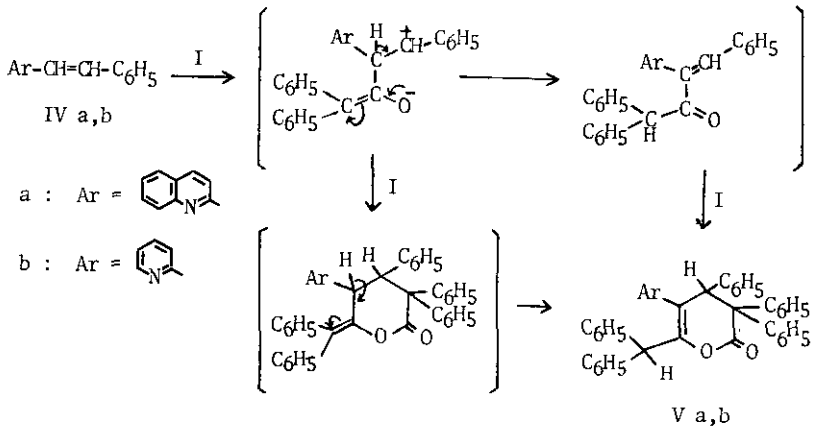
Table I. Physical properties of 1,4-Cycloadducts[a], IIIa-c

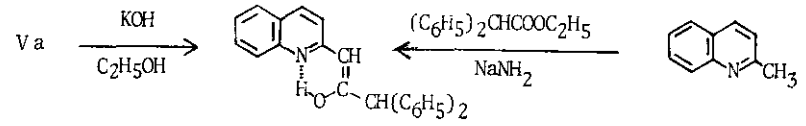
Compd. No.	mp(°C)	Yield (%)	IR(KBr) cm^{-1} C=O	PMR ($CDCl_3$) ppm $-S-CH_2CH_2-N-$	$-CH-Ar$	$-C=CH-$	CMR ($CDCl_3$) ppm $-N-C-$ (O)
IIIa	186-188	39	1663	3.05, 4.16 (each t, J=7.5)	4.16 (d, J=6)	5.43 (d, J=6)	
IIIb	185-187	48	1665	3.08, 4.15 (each t, J=7.5)	4.16 (d, J=6)	5.41 (d, J=6)	
IIIc	208-210	78	1663	3.13, 4.22 (each t, J=7.5)	4.33 (d, J=6)	5.46 (d, J=6)	168.3

a) Satisfactory elemental analyses were obtained for all compounds.

its pmr spectrum showed characteristic signals at 5.37 (s) and 5.26 (s) ppm, assignable to methine protons. The cmr spectrum showed a signal at 168.8 ppm due to an ester carbonyl carbon. These data suggested that the product was a 2:1-molar adduct (Va). The reaction of I with 2-styrylpyridine (IVb) also afforded a

2:1-molar adduct (Vb) in 34% yield. The ir spectrum of Vb suggested the existence of a vinyl ester with absorptions at 1761 and 1676 cm^{-1}. The pmr spectrum showed signals at 5.28 (s) and 5.10 (s) ppm due to methine protons. Furthermore the cmr spectrum also showed a signal at 168.5 ppm due to an ester carbonyl carbon. Treatment of Va with potassium hydroxide in ethanol afforded 2-(2-hydroxy-2-diphenylmethyl)ethenylquinoline (VIa) [mp 159-160°; mass m/e 337(M^+); pmr δ($CDCl_3$) 5.12 (1H, s, -CH-C-), 5.43 (1H, s, =CH-), 14.63 (1H, br, -OH); ir(KBr) 1630 cm^{-1} (C=C)], which was also obtained by the reaction[7] of quinaldine with ethyl diphenylacetate in the presence of sodium amide. The structure assignment of VIa was based on elemental analysis and spectral properties[8].



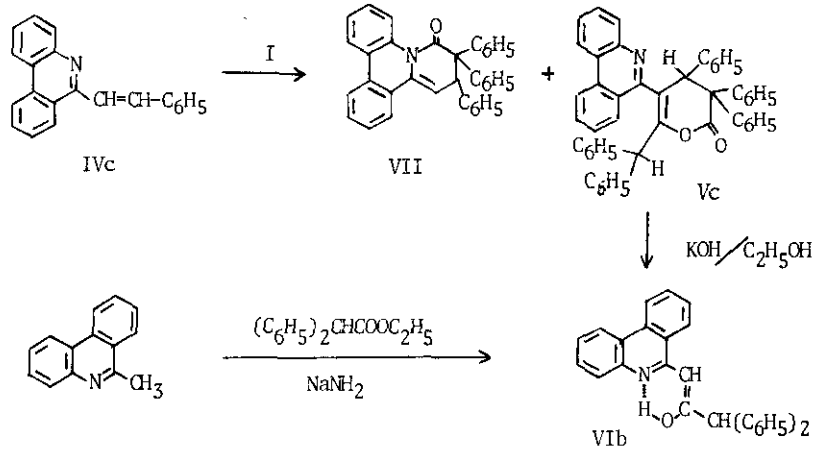


VIa

On the other hand, the reaction of I with 6-styrylphenanthridine (IVc) afforded the 1,4-cycloadduct (VII) [mp 233-234°; mass m/e 475 (M^+); pmr δ($CDCl_3$) 4.30 (1H, d, J=8.0, -CH-C_6H_5), 6.46 (1H, d, J=8.0, -C=CH-); cmr δ($CDCl_3$) 171.3 (-N-C-); ir(KBr) 1681 cm^{-1} (C=O)] in 23% yield from IVc and a lactone (Vc) [mp 230-232°; mass m/e 669 (M^+); pmr δ($CDCl_3$) 4.52 (1H, s), 5.02 (1H, s); cmr δ($CDCl_3$) 169.0 (-C-O-); ir(KBr) 1762 cm^{-1} (C=O)] in

47% yield from IVc. Treatment of Vc with potassium hydroxide in ethanol afforded 6-(2-hydroxy-2-diphenylmethyl)ethenylphenanthridine (VIb) [mp 184-185°; mass m/e 387 (M^+); pmr δ($CDCl_3$) 5.22 (1H, s, -CH-C-), 6.13 (1H, s, =CH-), 14.68 (1H, br, -OH); ir(KBr) 1610 cm^{-1} (C=C)], which was also obtained by the reaction[7] of 6-methylphenanthridine with ethyl diphenylacetate in the presence of sodium amide.

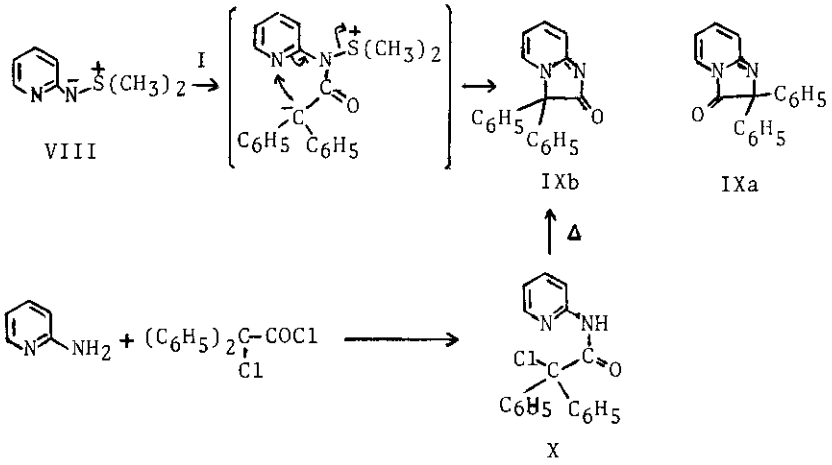
However, I failed to react with 2-(p-methoxystyryl)benzoxazole or 2-(p-methoxystyryl)benzothiazole and only starting materials were recovered.

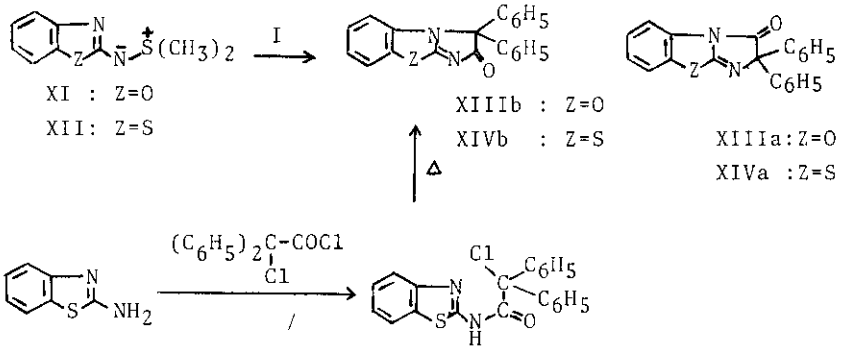


In a previous paper[9], we reported that the structure of the reaction products of I with N-pyridin-2-yl-S,S-dimethylsulfilimine (VIII), N-benzoxazol-2-yl-S,S-dimethylsulfilimine (XI), and N-benzothiazol-2-yl-S,S-dimethylsulfilimine (XII) were 2,3-dihydro-3-keto-2,2-diphenylimidazo[1,2-a]pyridine (IXa), 2,3-dihydro-3-keto-2,2-diphenylimidazo[2,1-b]benzoxazole (XIIIa) and 2,3-dihydro-3-keto-2,2-diphenylimidazo[2,1-b]benzothiazole (XIVa), respectively. However, from the results of our reinvestigation, it has been revealed that the orientation of the addition of I to sulfilimines (VIII, XI, and XII) is reversed, that is, the structure of these respective adducts is 2,3-dihydro-2-keto-3,3-diphenylimidazo[1,2-a]pyridine (IXb), 2,3-dihydro-2-keto-3,3-diphenylimidazo[2,1-b]benzoxazole (XIIIb), and 2,3-dihydro-2-keto-3,3-diphenylimidazo[2,1-b]benzothiazole (XIVb). It can be presumed that this erroneous conclusion may be

attributed to the presence of small quantities of impurities contained in the product from the previously described alternative synthesis[9] of IXb, and to the fact that the structures of XIIIa and XIVa were inferred by analogy with that of IXa without further rigid experimental studies.

So we recently carried out a reexamination of the synthesis of IXb employing a slightly modified procedure. This time, unlike previous experimints, we succeeded in isolating the intermediate, 2-chlorodiphenylacetamido pyridine (X). 2-Aminopyridine and chlorodiphenylacetyl chloride in dry ether containing a small amount of dry pyridine was stirred in an ice-salt bath at -2° for 1.5 hr. X was obtained as a yellow viscous oil, which yielded colorless crystals, mp 82-85°, when treated with n-hexane. This intermediate (X) was heated directly in an oil bath at 120° for 11 hr. After neutralization of the reaction mixture with $NaHCO_3$, extraction with $CHCl_3$ and evaporation of the solvent, the product was recrystallized from acetone, yielding colorless crystalls (IXb), mp 210-214°. XIVb was prepared in the same manner as IXb and the product had mp 250-252°. It has been shown by mixed melting point tests and spectral data that these products, IXb and XIVb, are identical to the adducts obtained from the reaction of I with VIII and XII, respectively. Attempts to obtain XIIIb in the same way have





been unsuccesful.

Further work on the reaction of I with azadienes is in progress.

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