REACTIONS OF DIPHENYLCYCLOPROPENONE WITH HYDRAZINE DERIVATIVES: FORMATION OF PYRAZOLONE DERIVATIVES VIA 3-AMINOCINNAMOHYDRAZIDES[1]

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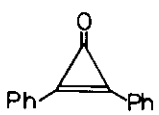
Abstract —— Reactions of diphenylcyclopropenone (1) with hydrazine or phenylhydrazine gave ring opening products (4,5-diphenylpyrazolones, 3) via 3-aminocinnamohydrazide derivatives (4). However, hydrazones (2) were obtained, in general, with 1 and hydrazine derivatives which possess electron accepting substituents under acidic conditions. Mechanism of the above reactions is discussed.

Cyclopropenones are the smallest member of nonbenzenoid aromatic compound family possessing cross-conjugate carbonyl group. Several reactions with nucleophilic reagents have been investigated.[2,3] Although modes of the reactions are different by each nucleophile, almost all cases of these reactions cause ring opening of the cyclopropenone system, especially, under basic conditions.[2,3] With ketonic reagents, Kitahara[4] and Eicher[5] reported formation of the oxime and the hydrazone derivatives (2) by reactions of 2,3-diphenylcyclopropenone (1) with hydroxylamine and with arylhydrazine derivatives, respectively. On the other hand, deoxybenzoin oxime and 4,5-diphenylisoxazolone were obtained with hydroxylamine under the basic conditions by Breslow and his co-workers.[6] Interestingly, Kitahara's reaction conditions seem to be basic.[4] Ketonic character of 1 is the most fundamental chemical nature. Therefore, we decided to reinvestigate the reactions of 1 with several ketonic reagents under different conditions. As the results, we found by the reactions of 1 with hydrazines that 1 gave an intermediate (derivatives of 3-amino-2-phenylcinnamohydrazide, 4) before the formation of pyrazolone derivatives (3). Phenylhydrazone hydrochloride (2a) of 1 was obtained in 80% yield by the reaction with phenylhydrazine hydrochloride (acidic conditions) as reported by Eicher.[5]

However, when 1 was treated with phenylhydrazine (basic conditions), new products (3a, mp 282 °C, dec., 9%, and 4a, mp 181 °C, dec., 50%) were obtained. The former was identified as 1,4,5-triphenylpyrazol-3-one.[7] Molecular formula of 4a is $C_{21}H_{19}ON_3$. It shows amino (3440 and 3250 cm^{-1}) and amide carbonyl (1630 and 1595 cm^{-1}) absorptions in the ir spectrum, and does not show any saturated CH peaks in its nmr spectrum. Treatment of 4a with acidic ethanol afforded 3a in a good yield with loss of ammonia. The structure of 4a was deduced to be 3-amino-2,N'-diphenylcinnamohydrazide from the result of the above acid treatment and from its spectral data. The same type product (4b) was obtained with hydrazine hydrate in THF.



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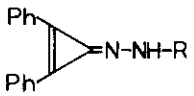

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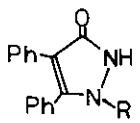

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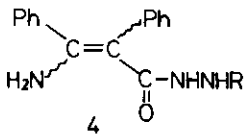

4

a:R=Ph; b:R=H; c:R=Me; d:R=p-MeC_6H_4; e:R=p-ClC_6H_4;
f:R=p-$NO_2C_6H_4$; g:R=2,4-$(NO_2)_2C_6H_3$

Methyl-, p-tolyl-, and p-chlorophenylhydrazines gave the corresponding pyrazolone derivatives (3c-3e) under basic conditions. Arylhydrazones (2e-2f) were obtained by the reactions of 1 with p-chloro-, p-nitro-, and 2,4-dinitrophenylhydrazines, respectively, under acidic conditions. Interestingly, p-tolylhydrazine hydrochloride gave the pyrazolone 3d, but p-nitro- and 2,4-dinitrophenylhydrazines yielded only hydrazone derivatives (2f and 2g) under both acidic and basic conditions. The results obtained were presented in the Table.

The above facts indicate that the reaction modes are controlled by the basicity of the hydrazines. Mechanism of the ring opening reaction can be explained as follows. Attack at 2- or 3-position of the cyclopropenone nuclei takes place first and yields cyclopropanone derivatives as unstable intermediates (5). The second reaction of another hydrazines on 5 and elimination of anilines (or ammonia) via (6) give the ring opening products --- aminocinnamohydrazides 4. Ring-chain tautomerization of 4 to 4' followed by elimination of ammonia give the final products --- pyrazolones 3.[8] Although the formation of 5 could not be confirmed, the above explanation is reasonable, because cyclopropanone system is very strained and reactive entity.

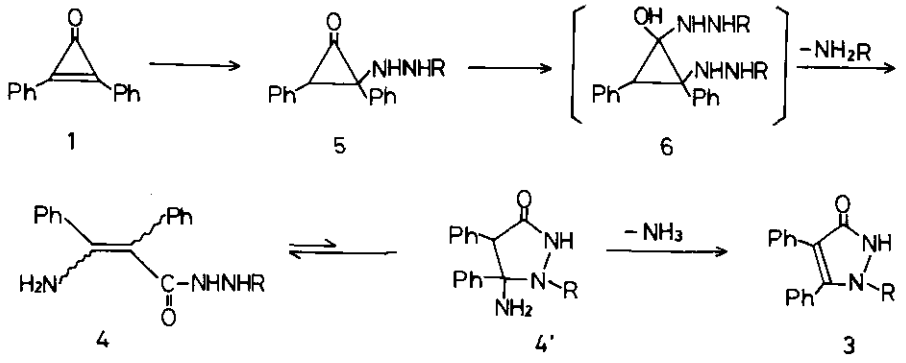

Table. Reactions of 2,3-Diphenylcyclopropenone with $RNHNH_2$

R[a]	conditions[b]	products (yield, %)[c]
Ph	acidic	2a (80)[d]
Ph	basic	3a (9), 4a (50)
H	basic	3b (30)
H	basic[e]	4b (10)
Me	basic	3c (26)
p-tolyl	acidic	3d (15)
p-tolyl	basic	3d (10)
p-chlorophenyl	acidic	2e (58)[d]
p-chlorophenyl	basic	3e (13)
p-nitrophenyl	acidic	2f (quant)[d]
p-nitrophenyl	basic	2f (67)
2,4-dinitrophenyl	acidic	2g (94)[d]
2,4-dinitrophenyl	basic[f]	2g (79)

a) 1-2 moles of the reagent were used.

b) The reactions were carried out in EtOH at room temperature otherwise stated. Acidic means that the reagent was used as HCl salt and also, basic means that the free hydrazine or their HCl salt with sodium hydroxide was used.

c) Isolated yield.

d) Isolated as HCl salt.

e) The reaction was carried out in THF.

f) The reaction was carried out under reflux.

Intermediary of cyclopropanones is well known in several reactions such as Favorskii rearrangement. Amination on sp^2 carbon next to carbonyl group in conjugate systems by reactions with hydrazines is rather rare. To our knowledge, 2-aminotropone derivatives formation from tropone and its derivatives with hydrazine is the only example in non-benzenoid aromatic ketones.[9] Present example and the 2-aminotropone formation suggest that this type of sp^2 carbon amination of vinylogous cyclic ketones would be general reaction patterns. So that, the reactions of annulenones (both $(4n+2)\pi$ and 4π systems) with hydrazines are interesting and worthy to investigate. Further studies of these reactions of 1 with ketonic reagents is now in progress.

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