HETEROCYCLES, Vol.12, No.4, 1979

THE PREPARATION OF 1,4-DIARYL-1,4-BIS(DIETHYLPHOSPHONOMETHYL)-AZINEMETHYLENE AND ITS REACTION WITH ARYLALDEHYDES[1]

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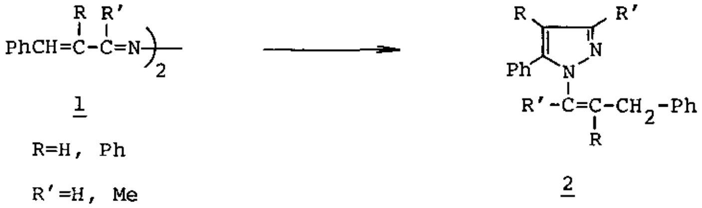
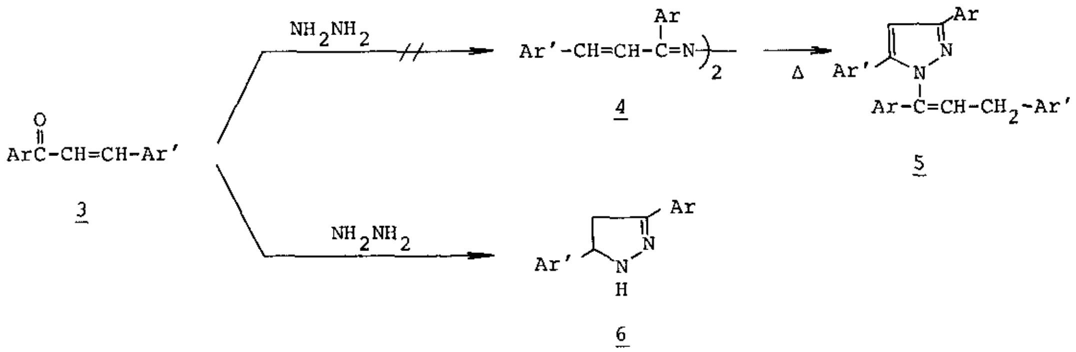
Abstract — The title compounds, 1,4-diphenyl- (11a) and 1,4-di-*p*-tolyl-1,4-bis(diethylphosphonomethyl)azinemethylene (11b) were prepared by the reaction of the corresponding 1,4-bis(bromomethyl)-1,4-diphenyl- (10a) and 1,4-bis(bromomethyl)-1,4-di-*p*-tolylazinemethylene (10b) with triethylphosphate. It was found in the reaction of 11 with arylaldehydes such as benzaldehyde (8a) and *p*-tolualdehyde (8b) that 1-(1,3-diarylpropen-1-yl)-3,5-diarylpyrazoles (5) were obtained as main product but not expected styryl aryl ketone azines (4).

It has been previously reported that[2-7] azines were thermally decomposed by a free-radical process, giving the corresponding Piloty-Robinson's reaction products as the main product in many cases.

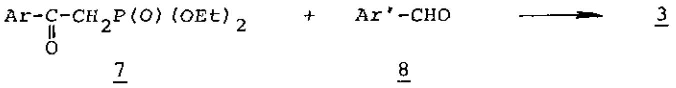
On the other hand, Stern and Krause[8,9] reported on the formation of N-substituted pyrazoles (2) from the pyrolysis of certain α,β-unsaturated azines (1).



The results suggest that the pyrolysis of styryl aryl ketazines (4) seems afford the corresponding N-substituted 3,5-diarylpyrazoles (5). However, the compound 4 has been not yet prepared since the reaction of styryl aryl ketones (3) with hydrazine afforded easily the corresponding 3,5-diaryl-Δ^2-pyrazolizines (6)[10] but not 4.



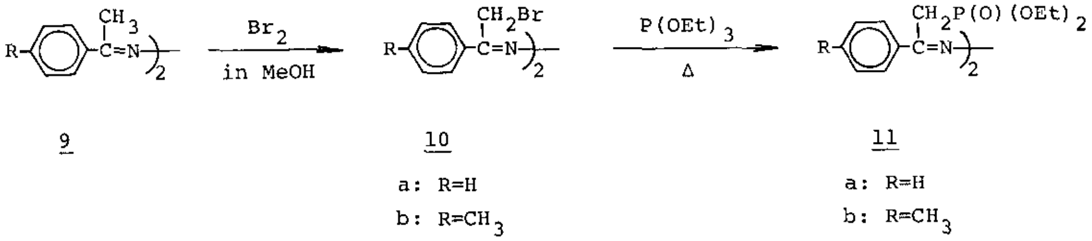
It was known that[11] 3 was prepared by the reaction of diethyl phenacylphosphonate (7) with arylaldehydes (8).



$$\underset{7}{\text{Ar-}\underset{\text{O}}{\overset{}{\text{C}}}\text{-CH}_2\text{P(O)(OEt)}_2} + \underset{8}{\text{Ar'-CHO}} \longrightarrow 3$$

This result suggests that the reaction of 1,4-diaryl-1,4-bis(diethylphosphonomethyl)azinemethylene (11) with 8 might give the corresponding 4.

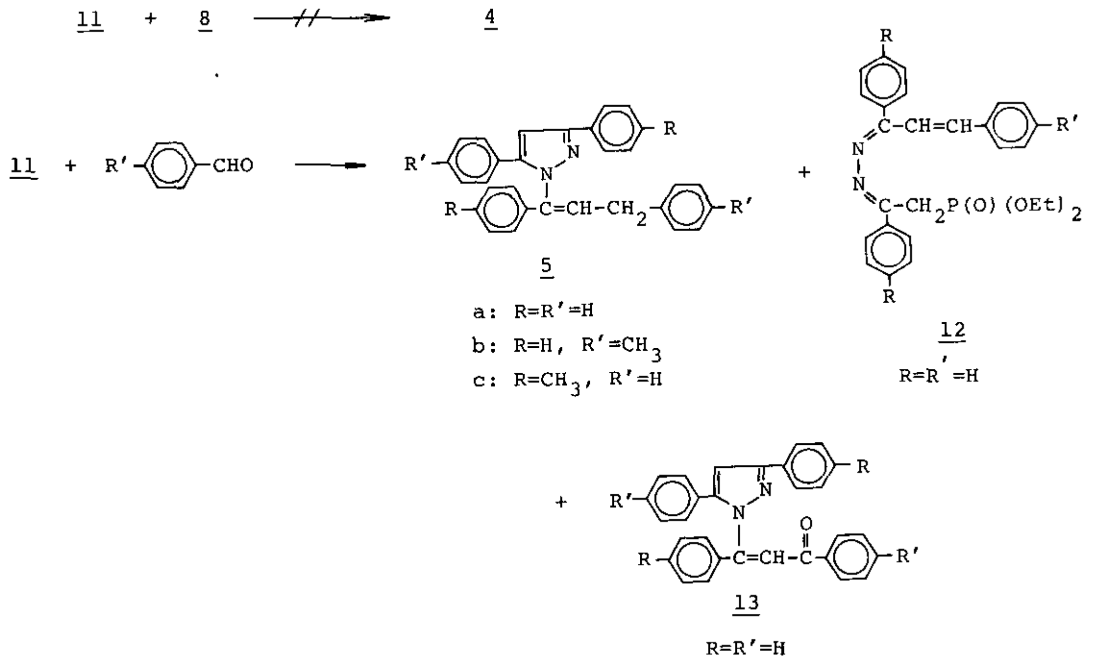
We now wish to report on the preparation of 10 and its reaction with 8.



When 1,4-bis(bromomethyl)-1,4-diphenyl- (10a)[12] and 1,4-bis(bromomethyl)-1,4-di-*p*-tolylazinemethylene (10b)[13] were treated with triethyl phosphonate at 140° for 15 min, the corresponding 1,4-diphenyl- (11a; pale yellow needles, mp 75°C) and 1,4-di-*p*-tolyl-1,4-bis(diethylphosphonomethyl)azine methylene (11b; yellow needles, mp 105-107°C) were obtained in almost quantitative yields, respectively.

The reaction of 11 with benzaldehyde (8a) and *p*-tolualdehyde (8b) was carried out under various conditions, and the results are summarized in Table 1.

It should be noted in the reaction of 11a with 8a that the unexpected 5a (colorless needles, mp 117-118°C) was obtained together with formation of byproducts such as 12 and 13 but not the expected 4. Based on its spectral data and elemental analysis, the main product 5a was determined as 1-(1,3-diphenylpropen-



5

a: R=R'=H
b: R=H, R'=CH$_3$
c: R=CH$_3$, R'=H

12

R=R'=H

13

R=R'=H

1-yl)-3,5-diphenylpyrazole which seemed to be an expected prodtct in the pyrolysis of the corresponding 4 as described above.

Table 1. Reaction of 11 with 8 in the Presence of NaOCH$_3$ [a)]

Run	11	8	Solvent	Temp.(°C)	Time(h)	Product (%)
1 [b,c)]	a	a	DMF	18	3	5a(6),12(35),13(4)
2	a	a	DMF	50	1	5a(22),12(8),13(12)
3 [c)]	a	a	DMF	50	8	5a(26),12(5),13(24)
4 [c)]	a	a	DMF	95	8	5a(61),12(+),13(2)
5 [d)]	a	a	DMF	95	8	5a(48)
6 [e)]	a	a	MeOH	reflux	8	5a(28),13(+)
7	a	a	Benzene	reflux	8	5a(80),13(5)
8	a	b	Benzene	reflux	8	5b(85)
9	b	a	Benzene	reflux	8	5c(75)

a) A mixture of 5 mmole of 11, 10 mmole of 8 and 20 mmole of NaOMe in 50 ml of solvent was stirred at the indicated temperature for the desired time, unless otherwise stated.

b) The molar ratio of 11 and 8: 1 mole/1 mole.

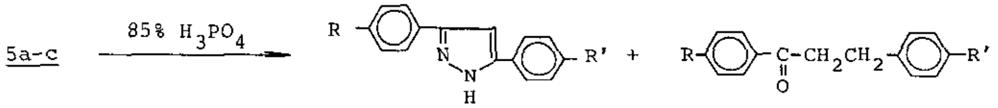
c) Small amount of an unidentified compound ($C_{30}H_{24}N_2$, colorless needles, mp 117-118°C) was also obtained.

d) The molar ratio of 11 and 8: 1 mole/6 mole.

e) Small amount of an unidentified compound ($C_{30}H_{24}N_2$, colorless needles, mp 151-153°C) was also obtained.

When change of solvent from DMF or MeOH to benzene, the yield of 5a increased to 80%. In the same condition, 1-(3-*p*-tolyl-1-phenylpropen-1-yl)-3-phenyl-5-*p*-tolyl- (5b; colorless prisms, mp 141-143°C) and 1-(3-phenyl-1-*p*-tolylpropen-1-yl)-3-*p*-tolyl-5-phenylpyrazole (5c; colorless prisms, mp 148-149°C) were also obtained from the corresponding 11 and 8 in good yields, respectively.

The hydrolysis of 5 with 85% H_3PO_4 afforded 3,5-diarylpyrazoles (14) and 1,3-diarylpropan-1-ones (15). The yields of the products are summarized in Table 2.



14

a: R=R'=H

b: R=CH_3, R'=H

15

a: R=R'=H

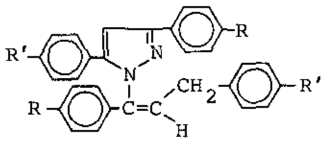
b: R=H, R'=CH_3

c: R=CH_3, R'=H

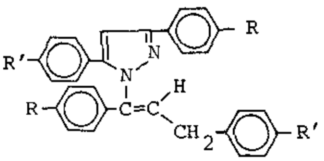
Table 2. The Hydrolysis of 5 with 85% H_3PO_4 at 185°C for 5 h.

5	Product (%)
a	14a(80), 15a(90)
b	14b(77), 15b(67)
c	14b(68), 15c(67)

The above results support strongly the proposed structure of 5, however, its geometrical structure (5-1 or 5-2) could not be confirmed by available data.

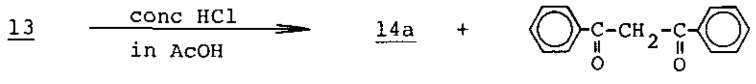


5-1



5-2

The compound 13 (pale yellow prisms, mp 160.5-162.5°C) was hydrolized with conc HCl in acetic acid to give 14a and dibenzoylmethane (16) in 80% and 85% yields, respectively. Based on the above results and its spectral data the structure of 13 might be proposed as 1-(1-phenyl-2-benzoylethylen-1-yl)-3,5-diphenylpyrazole.



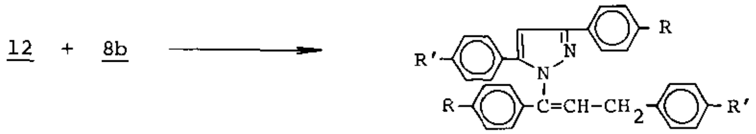
16

The compound 12 (orange yellow viscous oil) seems to be 1,4-diphenyl-1-benzylidenemethyl-4-(diethylphosphonomethyl)azinemethylene from its spectral data and to be an intermediate in the formation of 5a and 13.

Indeed, the reaction of 12 with 8a afforded 5a and 13 together with 14a.

$$\underline{12} + \underline{8a} \xrightarrow{\text{NaOMe}} \underline{5a} + \underline{13} + \underline{14a}$$

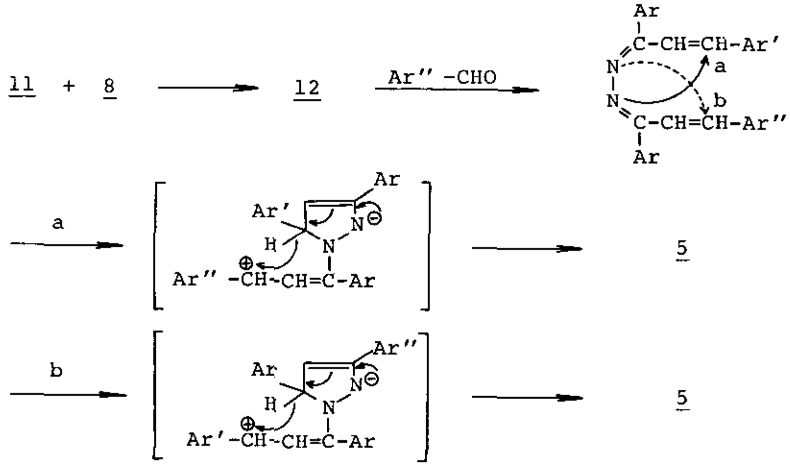
It was also found that the reaction of 12 with 8b afforded a mixture of 17a and 17b together with other by-products.



17

a: R=H, R'=CH_3
b: R=CH_3, R'=H

Although the expected 4 could not be isolated in these reactions, 4 seems to be an intermediate in the formation of 5. The following scheme shows the reaction routes of formation of 5.



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13. This compound was prepared by same manner as previous work (see literature 12); orange needles (from $CHCl_3$), mp 183-183.5°C.

Received, 20th December, 1978