The Cycloaddition of Nitrilimines with 1,2-Dibenzoylethylenes

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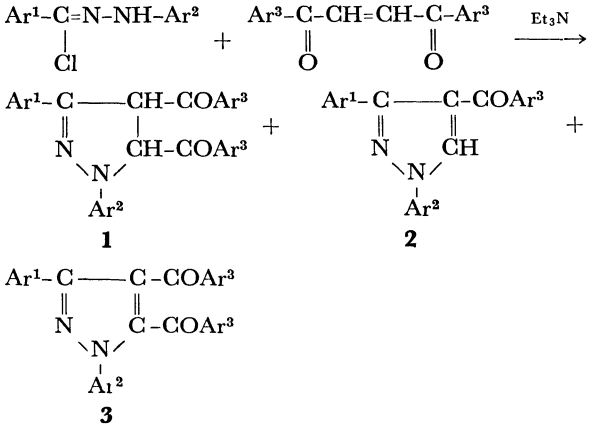
The cycloaddition of nitrilimines with 1,2-dibenzoylethylenes gave an unexpected 1,3-diaryl-4-benzoylpyrazole and benzoic acid, along with an expected cycloadduct, 1,3-diaryl-4,5-dibenzoyl-2-pyrazoline, and its dehydrogenated product, 1,3-diaryl-4,5-dibenzoylpyrazole. The elimination of the benzoyl group from the pyrazoline followed by dehydrogenation was shown to be the course of the unusual reaction.

The 1,3-dipolar cycloaddition of diarylnitrilimines with olefins is a versatile method for the stereoselective and regioselective synthesis of 2-pyrazolines or pyrazoles.[1-4] Diarylnitrilimines for the cycloaddition with dipolarophiles are usually prepared *in situ* by the dehydrochlorination of hydrazonoyl chlorides with triethylamine[4] and by the other method.[5,6] 1,2-Dibenzoylethylenes, with particular reference to their geometrical isomerism, have been intensively investigated by Lutz and his collaborator;[7] the ethylenes are good dipolarophiles for the investigation of the stereochemistry of the cycloaddition.[8]

This paper will report that the cycloaddition of nitrilimines with 1,2-dibenzoylethylenes gave 4-benzoylpyrazoles in high yields, along with the expected products. For example, the reaction of *cis*-1,2-dibenzoylethylene with *N*-(*p*-nitrophenyl)-*C*-phenylnitrilimine gave the unexpected 4-benzoyl-1-(*p*-nitrophenyl)-3-phenylpyrazole as the sole isolable product in a 48% yield, with the elimination of a benzoic acid, probably from the 4,5-dibenzoyl-2-pyrazoline. There is no precedent for the oxidative elimination of benzoic acid from 4,5-dibenzoyl-2-pyrazoline. We now wish to propose a scheme in which the nucleophilic attack of water on the 5-carbonyl carbon of the pyrazoline followed by the elimination of benzoic acid yielded the 4-benzoylpyrazoline, which then eliminated hydrogen of afford the unexpected pyrazole.



Scheme 1.

TABLE 1. THE REACTION OF DIARYLNITRILIMINES WITH 1,2-DIBENZOYLETHYLENES[a]

Nitrilimine		Dibenzoylethylene	Products yield/%		
Ar^1	Ar^2	$A^3=C_6H_5$	**1**	**2**	**3**
C_6H_5	*p*-$NO_2C_6H_4$	*trans*	21	47	10
C_6H_5	*p*-$NO_2C_6H_4$	*cis*	—	48	trace
p-Tolyl	*p*-Tolyl	*trans*	—	91	—

a) The reaction was carried out by Procedure A (see Experimental).

Results and Discussion

The cycloaddition between *trans*-1,2-dibenzoylethylenes and diarylnitrilimines prepared from hydrazonoyl chlorides in the presence of an excess of triethylamine was carried out in benzene at 80 °C for 5 h. The reaction products from the reaction mixture were shown to be *trans*-1,3-diaryl-4,5-dibenzoyl-2-pyrazolines (**1**), 1,3-diaryl-4,5-dibenzoylpyrazoles (**3**), and unexpected 1,3-diaryl-4-benzoylpyrazoles (**2**) (Scheme 1, Table 1. See Tables 2—4 for the notation of Ar^1, Ar^2, and Ar^3).

It is well-known that the reaction of nitrilimines with *cis*- and *trans*-olefins gives 2-pyrazolines stereospecifically in high yields.[4] With some *cis*-olefins in the presence of a base, however, two possible *cis*- and *trans*-pyrazolines can be formed by the base-catalyzed isomerization of the *cis*-product to the *trans*.[8,9] The pyrazole (**2a**) was isolated in a 48% yield from the reaction mixture of *N*-(*p*-nitrophenyl)-*C*-phenylnitrilimine and *cis*-1,2-dibenzoylethylene, while neither *cis*- nor *trans*-pyrazoline (*cis*- or *trans*-**1a**) was detected. The expected *cis*-pyrazoline (*cis*-**1a**) may be directly decomposed to **2a**, because some of the *trans*-pyrazoline (*trans*-**1a**) would remain in the reaction mixture under the conditions if the base-catalyzed isomerization product, *trans*-pyrazoline (*trans*-**1a**) were an intermediate to **2a**.

The NMR spectroscopy is a convenient method for establishing the stereochemistry of the adduct (**1**), since the coupling constants between 4- and 5-protons indicate whether the adduct is *trans* (J=6 Hz) or *cis* (J=12 Hz),[10] although some exceptions are known.[11] Thus, the *trans* structure of the expected 1,3-dipolar cycloadducts, (**1**) was confirmed on the basis of elemental analyses and NMR ($J_{4,5}$=6 Hz) and IR spectra.

2-Pyrazolines can be easily aromatized by autoxidation or thermal dehydrogenation, even in the absence of oxygen, or by some reagents such as a hydrogenation

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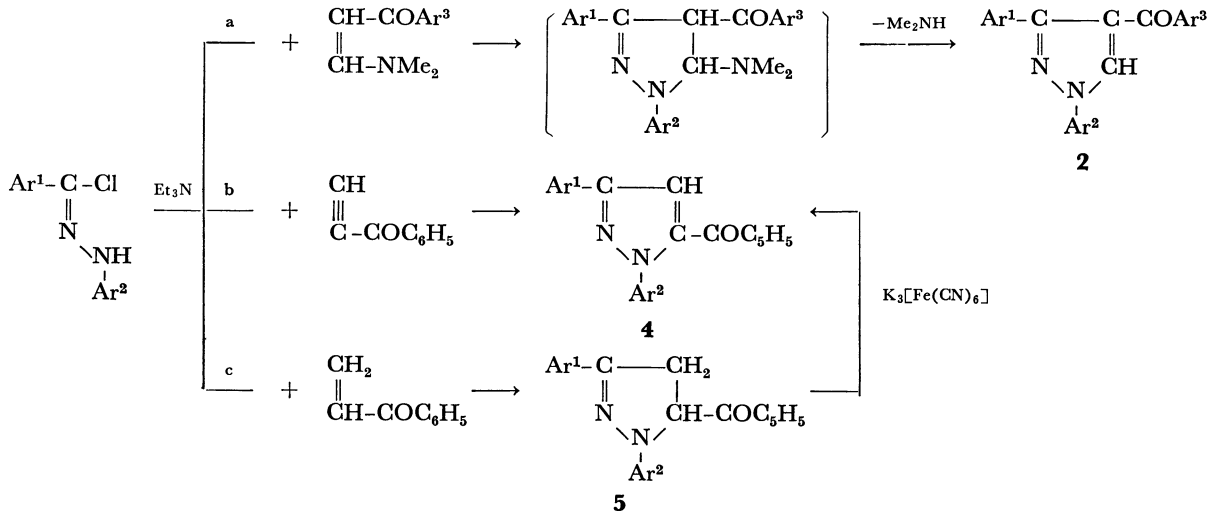
catalyst, although little is known about these mechanisms[4,12] and only a small amount of hydrogen was identified.[18] The pyrazoles (**3**) were shown to be products dehydrogenated from **1** by the following experiment: the treatment of **1a** in a refluxing toluene solution with a suspension of active alumina gave **3a** in a 54% yield.

The structure of the pyrazole (**2b**) was established by elemental analysis ($C_{23}H_{20}N_2O$), NMR (two tolyl methyl at δ 2.34, H-5 at δ 8.19) and IR ($\nu_{C=O}$ 1635 cm^{-1}) spectra, and comparison with an authentic sample described below. Enamine is a regioselective dipolarophile,[13] and the reaction of nitrilimines with 3-dimethylamino-1-phenylpropen-1-one gave unstable intermediate pyrazolines, which eliminated dimethylamine to afford pyrazoles (**2**).[14,15] The regioselective cycloaddition of nitrilimines with ethynyl phenyl ketone[2,16,17] and phenyl vinyl ketone[13] gave pyrazoles (**4**) and pyrazolines (**5**) respectively. The alkaline–potassium hexacyanoferrate(III) oxidation of **5** also gave pyrazole (**4**), a regioisomer of the pyrazole (**2a**)[12] (Scheme 2). We could not find any trace amount of **4** in the reaction mixture of the *N*-(*p*-nitrophenyl)-*C*-phenylnitrilimine with dibenzoylethylenes.

If the reaction of the nitrilimines with *trans*-dibenzoylethylene was carried out at room temperature under nitrogen by the careful exclution of moisture and work-up below 30 °C the expected 1,3-dipolar cycloadducts **1** were isolated in high yields (Table 2). The isolated pure 4,5-dibenzoyl-2-pyrazolines (**1**) are



Scheme 2.

Table 2. Preparation of 2-pyrazoline (**1**)[a]

	Ar^1	Ar^2	Ar^3	Yield[c] %	Mp °C	IR (KBr) $\nu_{C=O}/cm^{-1}$	NMR($CDCl_3$) δ/ppm 4-H	5-H	$J_{4,5}$/Hz
1a	C_6H_5	*p*-$NO_2C_6H_4$	C_6H_5	77	160—162	1700 1675	5.38	5.97	6
1c	C_6H_5	*p*-$NO_2C_6H_4$	*p*-Tolyl	70	188—198	1699 1676	5.29	5.86	6
1d	C_6H_5	*p*-$NO_2C_6H_4$	*p*-ClC_6H_4	84	185—194	1708 1682	5.29	5.82	6
1e	C_6H_5	*p*-$NO_2C_6H_4$	Mesityl	74	210—220	1713 1709	4.99	5.92	3
1f	C_6H_5	C_6H_5	C_6H_5	58	201—202	1695 1681	5.26	5.75	7
1g	C_6H_5	C_6H_5	*p*-Tolyl	19[b]	178—183	1695 1680	5.23	5.72	7
1h	C_6H_5	*p*-Tolyl	C_6H_5	27[b]	161—166	1691 1685	5.26	5.72	7
1i	*p*-Tolyl	*p*-Tolyl	Mesityl	81	202—204	1708	4.89	5.67	3
1j	C_6H_5	*p*-ClC_6H_4	C_6H_5	75	160—165	1698 1680	5.26	5.73	6
1k	C_6H_5	*p*-ClC_6H_4	*p*-Tolyl	38	190—197	1693 1684	5.24	5.69	7
1l	*p*-$NO_2C_6H_4$	C_6H_5	C_6H_5	3[b]	147—150	1699 1680	5.24	5.89	6

a) The preparation was carried out by Procedure B (Experimental). b) Some of the pyrazolines (**1**) were decomposed to **2** or intractable compounds under the conditions. c) Isolated yields shown were not optimized.

Table 3. Decomposition of **1** to **2**

	Ar^1	Ar^2	Ar^3	Yield/%			Pyrazole **2**		
				2	Recovered **1**	Ar^3COOH	Mp/°C	IR (KBr) $\nu_{C=O}$/cm^{-1}	NMR ($CDCl_3$) δ 5-H/ppm
2a	C_6H_5	*p*-$NO_2C_6H_4$	C_6H_5	65	0	60	213—214	1645	8.39
2b[a]	*p*-Tolyl	*p*-Tolyl	C_6H_5				130—131	1635	8.19
2c	C_6H_5	*p*-$NO_2C_6H_4$	*p*-Tolyl	65	0	60	198—200	1636	8.32
2d	C_6H_5	*p*-$NO_2C_6H_4$	*p*-ClC_6H_4	55	0	50	188—190	1635	8.40
2e	C_6H_5	*p*-$NO_2C_6H_4$	Mesityl	75	0	65	180—183	1667	8.09
2f	C_6H_5	C_6H_5	C_6H_5	30	1	20	138—141	1635	8.24
2g	C_6H_5	C_6H_5	*p*-Tolyl	50	10	—	151—155	1640	8.24
2i	C_6H_5	*p*-Tolyl	C_6H_5	40	55	—	149—151	1639	8.21
2f	*p*-Tolyl	*p*-Tolyl	Mesityl	55	40	30	152—165	1648	7.90
2j	C_6H_5	*p*-ClC_6H_4	C_6H_5	10	60	—	171—172	1630	8.20
2k	C_6H_5	*p*-ClC_6H_4	*p*-Tolyl	2	98	—	183—188	1640	8.20
2l	*p*-$NO_2C_6H_5$	C_6H_5	C_6H_5	60	0	—	171—172	1643	8.30

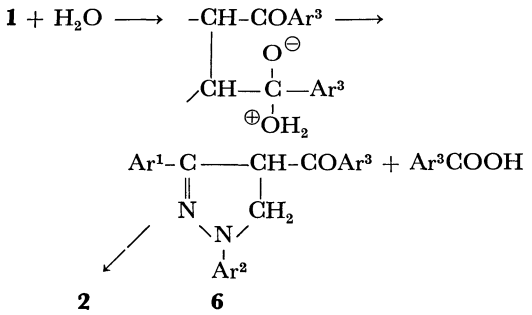
a) Pure **1c** could not be isolated.

thermally stable up to about 150 °C. However, the pyrolysis of **1** about 150 °C or the treatment of **1** with a base (and moisture) at about 80 °C gave **2** with appreciable rate.

To our knowledge, no pyrolysis of 4- or 5- (or 4,5-di-)benzoylpyrazolines which eliminates a benzoyl group to pyrazoles has yet been reported. The cycloadducts of the dibenzoylethylenes with nitrones[8a] and diazomethane[8b] are rather thermally stable. The pyrolysis of the pyrazolines (**1**) at 180 °C really gave the pyrazoles (**2**) and benzoic acid. We tried to decompose several *trans*-2-pyrazolines (**1**) to **2** (3—75% yields) at 200 °C for 10 min (Table 3), although the reaction conditions used were not strictly the same.

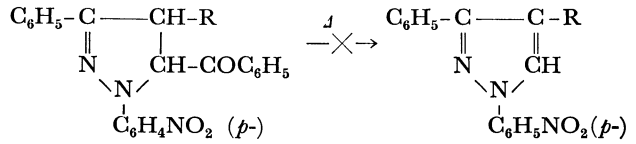
One can easily postulate the thermal elimination of benzaldehyde from **1** followed by the autoxidation of the benzaldehyde to produce the benzoic acid. However, all attempts to detect benzaldehyde, for example, by VPC, NMR, IR, and MS (the MS of **1a** was superimposable with that of an equimolar mixture of the **2a**, pyrazole, and benzoic acid), failed except for the one case to be described below. The careful exclusion of oxygen and moisture from the pyrolysis system under nitrogen decreased the yield of benzoic acid down to 35% along with a small amount of benzaldehyde (up to 10% yield), while the only decomposition products observed were the pyrazoles (**2**) and benzoic acid under usual conditions under nitrogen without strict drying over P_2O_5.

Benzaldehyde has been shown to react easily with aniline (or butylamine) to yield *N*-benzylideneaniline (or *N*-benzylidenebutylamine). No formation of any benzylideneamines in the pyrolysis products of **1a** in aniline (or butylamine) ruled out the formation of benzaldehyde as an intermediate. On the other hand, *N*-butylbenzamide (53% yield) and **2a** (62% yield) were isolated from the reaction mixture of **1a** in butylamine at 80 °C for 5 h, while benzoic acid is stable under the conditions. Furthermore, moisture and base enhanced the decomposition of **1** to **2**. The rate ratio of the decomposition of wet **1a** to that of dry **1a** was about 2. The decomposition of **1** to **2** in the presence of a small amount of water and triethyamine gave the pyrazole (**2**) in excellent yields (for example, **2a** in an 86% yield from **1a**) than the results shown in Table 3. Pyrazoline and pyrazole have some basic character; thus, the decomposition of **1** to **2** may be promoted by self-catalysis. Taking the results in butylamine into consideration, the acceleration of the pyrolysis rate by water can be explained if we assume that a reasonable first step involved the initial nucleophilic attack of water on 5-carbonyl carbon followed by the cleavage of the carbon-carbon bond to give 4-benzoylpyrazoline (**6**) (Scheme 3). Several attempts to prepare an authentic specimen of the intermediate, **6**, or to isolate it from the reaction mixture were fruitless; therefore, **6** may be thermally unstable and may undergo dehydrogenation to **2**. However, only a trace amount of hydrogen was detected in the pyrolysis products of **1a** by VPC (activated charcoal 5 m at 50 °C, carrier gas argon) and so far the fate of the hydrogen can not be identified.



Scheme 3.

Importance of two benzoyl groups at both 4- and 5-positions for the facile decomposition of **1** to **2** was shown by comparison with a series of 2-pyrazolines, where only the 5-position has a benzoyl group (Scheme 4). None of the compounds (**7a**—**c**) has a tendency to decompose thermally up to 250 °C under conditions where the pyrolysis of **1** occurs very easily. We have so far been able to find any definite explanations of the importance of the two benzoyl groups



7a, R=H
b, R=C_6H_5 (*trans*)
c, R=*p*-Tolyl (*trans*)

Scheme 4.

on **1** in the facile transformation of **1** into **2**. One possible explanation is that the carbonyl-carbonyl interactions between the two benzoyl groups, along with steric hindrance, would facilitate the reactivity of the carbonyl carbon toward nucleophiles.

Experimental

All the melting points are uncorrected. The IR spectra were obtained on a Hitachi 215A Infrared Spectrophotometer. The ^{1}H-NMR spectra were measured of a Varian T-60A instrument in $CDCl_3$ unless otherwise stated, with TMS as an internal standerd. The column chromatography was carried over silica gel eluted with $CHCl_3$. All the new compounds reported here gave satisfactory elemental analyses.

Materials. The *N*-arylarenehydrazonoyl chlorides were prepared by the method of Huisgen *et al.*[4,9] The *trans*- and *cis*-1,2-dibenzoylethylenes were prepared by the method of Lutz et al.[7] The phenyl vinyl ketone and ethynyl phenyl ketone are commercially available (Nakarai Chem. Co.) and were used without further purification.

Reactions of Diarylnitrilimines with 1,2-Dibenzoylethylenes. General Procedure A: *N*-(*p*-Nitrophenyl)benzohydrazonoyl chloride (2.6 g, 9.5 mmol) as a precursor of the *N*-(*p*-nitrophenyl)-*C*-phenylnitrilimine was added, in small portions to a stirred solution of *trans*-1,2-dibenzoylethylene (2.3 g, 9.5 mmol) and triethylamine (2 ml) in benzene (50 ml) at 80 °C over a period of 30 min. The mixture was then stirred at 80 °C for 5 h. The precipitated triethylamine hydrochloride was filtered off, and the filtrate was evaporated *in vacuo*. The residue was crystallized from benzene to give the 2-pyrazoline (*trans*-**1a**; 0.96 g, 21%). The filtrate from the crystallization was chromatographed to give the pyrazole **2a** (1.6 g, 47%) and **3a** (0.45 g, 10%). The results are shown in Table 1. **1a**. Found: C, 73.48; H, 4.59; N, 8.58%. Calcd for $C_{29}H_{21}N_3O_4$: C, 73.25; H, 4.45; N, 8.84%. **2a**. Found: C, 71.89; H, 4.23; N, 11.11%. Calcd for $C_{22}H_{15}N_3O_3$: C, 71.53; H, 4.09; N, 11.38%. **3a**. Found: C, 73.47; H, 4.22; N, 8.91%. Calcd for $C_{29}H_{19}N_3O_4$: C, 73.56; H, 4.05; N, 8.88%.

General Procedure B: A solution of *N*-(*p*-nitrophenyl)benzohydrazonoyl chloride (1.1 g 4.0 mmol), *trans*-1,2-dibenzoylethylene (0.95 g, 4.0 mmol), and triethylamine (0.7 ml) in dry benzene (50 ml) was stirred at room temperature under nitrogen for 2 d. The triethylamine hydrochloride thus precipitated was filtered off, and the filtrate was evaporated *in vacuo* at below 30 °C. The residue was triturated with cold benzene to give the 2-pyrazoline (*trans*-**1a**, 1.5 g, 77%). **1** were recrystallized from DMF–H_2O without heating. The results are shown in Table 2.

Decomposition of 2-Pyrazolines (1). General Procedure: **1a** (0.57 g, 1.2 mmol) was heated in a sublimation apparatus at 200 °C for 10 min under reduced pressure (*ca.* 30 mmHg). Benzoic acid was thus isolated (0.088 g, 60%) as a sublimate. The residue was chromatographed to give **2a** (0.29 g, 65%) (and the recovered **1**). The results are shown in Table 3.

Detection of Benzaldehyde in the Pyrolysis products of 1a.

a) By NMR: **1a** was deccmposed at 180 °C for 10 min in an NMR sample tube under N_2. The peak of benzaldehyde (δ 9.9, -CHO) was not detected, but the peak of benzoic acid (δ 12.7, -OH) was detected.

b) By MS: The strong peak of benzoic acid (m/e=122) appeared, while that of benzaldehyde (m/e=106) appeared very weak in the mass spectrum of **1a**.

c) By IR: A KBr pellet containing **1a** was heated at 180 °C for 10 min under N_2. The characteristic absorption of benzaldehyde (ν=2770 cm^{-1}) was not detected.

d) By VPC: When **1a** was analyzed by VPC (injection temperature 200—250 °C), only a trace amount of benzaldehyde was detected.

e) Decomposition of 1a after Thorough Drying: **1a** (0.81 g, 1.7 mmol) was dried over P_2O_5 under reduced pressure (2 mmHg) for 2 d; then the **1a** was decomposed at 200 °C for 10 min under 2 mmHg in a sealed vessel to give the sublimated benzoic acid (0.072 g, 35%) and the benzaldehyde (*ca.* 0.02 g, less then 10%). The residue was crystallized from $CHCl_3$–EtOH to give **2a** (0.33 g, 53%).

Decomposition of 1a in Aniline. A solution of **1a** (0.22 g, 0.46 mmol) and hydroquinone (0.1 g) in aniline (5 ml, distilled over KOH) was refluxed for 10 min under N_2. The reaction mixture was then poured into aq $NaHCO_3$ and extracted with benzene. The benzene layer was washed with aq $NaHCO_3$ several times. The water layer was separated, acidified with aq HCl, and extracted with ether. The ether was evaporated to give the benzoic acid (0.028 g, 50%). The benzene layer was washed with aq HCl several times and evaporated *in vacuo*. The residue was crystallized from $CHCl_3$–EtOH to give **2a** (0.14 g, 65%). Neither benzylideneaniline nor *N*-phenylbenzamide was detected in the reaction products by TLC.

Decomposition of 1a in butylamine. A solution of **1a** (0.52 g, 1.1 mmol) in butylamine (50 ml, distilled over CaH_2) was refluxed for 5 h under N_2. After the amine was evaporated under nitrogen and reduced pressure, the residue was distilled to give *N*-butylbenzamide (140—170 °C/0.1 mmHg, 0.10 g, 53%). The residue of the distillation was crystallized from $CHCl_3$–EtOH to give **2a** (0.23 g, 62%). Neither benzoic acid nor *N*-benzylidenebutylamine was detected in the reaction products by TLC.

Preparation of Pyrazole (2) from Enamine (Scheme 2a). General Procedure: A solution of *N*-(*p*-nitrophenyl)benzohy-

Table 4. Pyrazole (3)

	Ar^1	Ar^2	Ar^3	Yield %	Mp °C	IR (KBr) $\nu_{C=O}$/cm^{-1}
3a	C_6H_5	*p*-$NO_2C_6H_4$	C_6H_5	54	137—139	1671
3c	C_6H_5	*p*-$NO_2C_6H_4$	*p*-Tolyl	51	143—148	1665
3e	C_6H_5	*p*-$NO_2C_6H_4$	Mesityl	38	150—155	1641
3f	C_6H_5	C_6H_5	C_6H_5	48	135—136	1668

drazonoyl chloride (1.4 g, 5.1 mmol), 3-dimethylamino-1-phenyl-2-propen-1-one (0.90 g, 5.2 mmol), and triethylamine (2 ml) in benzene (30 ml) was refluxed for 6 h. After a usual work-up, **2a** was recrystallized from $CHCl_3$–EtOH or DMF–H_2O in about a 30% yield.

*Preparation of Pyrazole (**3**) from Pyrazoline (**1**). General Procedure*: A solution of **1a** (0.44 g, 0.95 mmol) in toluene (50 ml) was refluxed with neutral aluminum oxide (5 g) until the solution was discolored (for about 5 h). The mixture was then filtered, and the filtrate was evaporated. The residue was crystallized from EtOH to give **3a** (0.23 g, 54%), which was then recrystallized from EtOH. The results are shown in Table 4.

*Preparation of 2-Pyrazoline (**7**). General Procedure*: A solution of *N*-(*p*-nitrophenyl)benzohydrazonoyl chloride (1.0 g, 3.7 mmol), phenyl vinyl ketone (0.57 g, 4.3 mmol), and triethylamine (2 ml) was stirred at room temperature for 2 d to give **7a** in a 88% yield; mp 242 °C (from EtOH). IR (KBr): 1698 cm^{-1} (C=O); NMR (DMSO-d_6) δ: 3.41 (dd, J=6 and 18 Hz, 1H, H-4), 4.17 (dd, J=12 and 18 Hz, 1H, H-4), 6.42 (dd, J=6 and 12 Hz, 1H, H-5). **7b** from *trans*-1,3-diphenyl-2-propen-1-one, 60% yield; mp 134—141 °C (from EtOH). IR (KBr): 1694 cm^{-1} (C=O); NMR ($CDCl_3$) δ: 4.66 (d, J=4 Hz, 1H, H-4), 5.71 (d, J=4 Hz, 1H, H-5). **7c** from *trans*-1-phenyl-3-*p*-tolyl-2-propen-1-one, 53% yield; mp 204—205 °C (from EtOH). IR (KBr): 1684 cm^{-1} (C=O); NMR ($CDCl_3$) δ: 4.61 (d, J=4 Hz, 1H, H-4), 5.67 (d, J=4 Hz, 1H, H-5).

*Preparation of 5-Benzoyl-1-(p-nitrophenyl)-3-phenylpyrazole (**4**). Method A (Scheme 2b)*: A solution of *N*-(*p*-nitrophenyl)-benzohydrazonoyl chloride (0.69 g, 2.5 mmol), ethynyl phenyl ketone (0.33 g, 2.5 mmol), and triethylamine (1 ml) in benzene (50 ml) was stirred at room temperature for 20 h. After a usual work-up, the pyrazole was isolated in less than a 10% yield.

Method B (Scheme 2c): A solution of **7a** (0.26 g, 0.70 mmol) in EtOH (20 ml) was added to a solution of $K_3[Fe(CN)_6]$ (0.53 g, 1.6 mmol), and KOH (0.2 g) in aqueous EtOH (50 ml) at room temperature. The mixture was then stirred at room temperature for 10 h, poured into 200 ml of water, and extracted with benzene. The benzene layer was washed with water several times and concentrated. The residue was crystallized from EtOH to give the pyrazole (**4**) in a 28% yield; mp 164 °C (from EtOH). IR (KBr): 1670 cm^{-1} (C=O); NMR ($CDCl_3$); δ: 7.13 (s, 1H, 4-H). Found: C, 71.30; H, 4.04; N, 11.33%. Calcd for $C_{22}H_{15}N_3O_3$: C, 71.53; H, 4.09; N, 11.38%.

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References

1) R. Huisgen, *Angew. Chem. Int. Ed. Engl.*, **2**, 565 (1963).
2) R. Huisgen, *Angew. Chem. Int. Ed. Engl.*, **2**, 633 (1963).
3) R. Huisgen, *J. Org. Chem.*, **41**, 403 (1976).
4) R. Huisgen, M. Seidel, G. Wallbillich, and H. Knupfer, *Tetrahedron*, **17**, 3 (1962).
5) R. Huisgen, J. Sauer, and M. Seidel, *Chem. Ber.*, **94**, 2503 (1961).
6) W. A. F. Gladstone, J. B. Aylward, and R. O. C, Norman, *J. Chem. Soc., C*, **1969**, 2583.
7) R. E. Lutz and J. C. Gillespie, Jr., *J. Am. Chem. Soc.*, **72**, 344, 2002, 5058 (1950).
8) a) K. Tada, T. Yamada, and F. Toda, *Bull. Chem. Soc. Jpn.*, **51**, 1839 (1978). b) L. I. Smith and K. L. Howard, *J. Am. Chem. Soc.*, **65**, 159 (1943).
9) R. Huisgen, H. Knupfer, R. Sustmann, G. Wallbillich, and V. Weberndorfer, *Chem. Ber.*, **100**, 1580 (1967).
10) R. Sustmann, R. Huisgen, and H. Huber, *Chem. Ber.*, **100**, 1802 (1967).
11) R. G. Micetich, *Can. J. Chem.*, **40**, 3753 (1970).
12) R. Fusco and P. D. Croce, *Tetrahedron Lett.*, **1970**, 3061.
13) M. E. Munk and Y. K. Kim, *J. Am. Chem. Soc.*, **86**, 2213 (1964).
14) D. Pocar, L. M. Ross, and R. Stradi, *Synthesis*, **10**, 684 (1976).
15) H. Bredereck and G. Simchen, *Chem. Ber.*, **97**, 3397 (1964).
16) a) P. Rutan and C. E. May, *J. Am. Chem. Soc.*, **69**, 2018 (1947). b) I. Iwai, Y. Okajima, and T. Konotsune, *Yakugaku Zasshi*, **78**, 505 (1958).
17) K. N. Houk, J. Sims, C. R. Watts, and C. J. Luskus, *J. Am. Chem. Soc.*, **95**, 7301 (1973).
18) a) E. Buchner and L. Perkel, *Ber.*, **36**, 3774 (1903). b) R. C. Elderfield, *Heterocyclic Compounds*, **5**, 108 (1957).