Syntheses of [1]Benzopyrano[4,3-*c*]pyrazoles and -[3,4-*d*]isoxazoles

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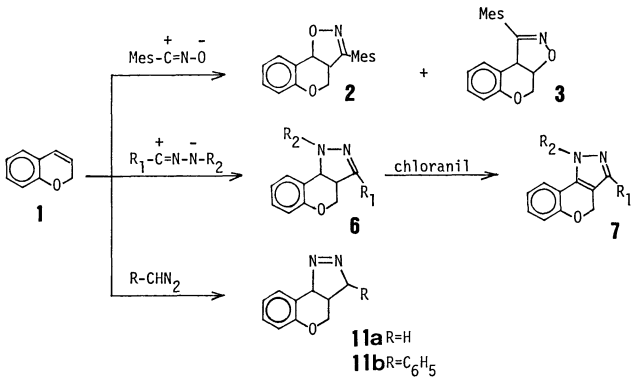
The reaction of 2*H*-1-benzopyran with several 1,3-dipoles gives cycloadducts in good yields. The orientation of the cycloaddition is qualitatively interpreted in terms of FMO theory. These heteropolycyclic compounds were also obtained from hydrazones of 3-aroyl-2*H*-1-benzopyrans, prepared from 3-cyano-2*H*-1-benzopyran.

Interest in the pharmacological activity[1a] and industrially useful chemical properties[2b] of a wide variety of heteropolycyclic compounds, for example, benzopyranopyrazoles,[2] -isoxazoles,[3] and -pyrroles,[4] has considerably increased in the past several years. These compounds have thus far prepared conveniently by intramolecular 1,3-dipolar cycloaddition reactions.[5]

Although the intermolecular reactions of various 1,3-dipoles with polycyclic compounds, such as benzofuran,[6,7] 1-benzothiophene,[6] indene,[7] and 2*H*-1-thiobenzopyran,[8] have been investigated, the reaction with 2*H*-1-benzopyran(**1**) has not been reported. The present paper describes a new, direct synthesis of [1]benzopyrano[4,3-*c*]pyrazoles by the reaction of 2*H*-1-benzopyran with several 1,3-dipoles and the structural determination of the cycloadducts.



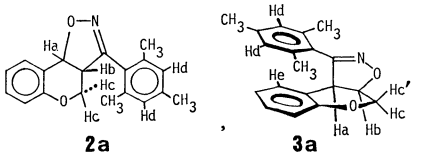
Scheme 1.

Results and Discussion

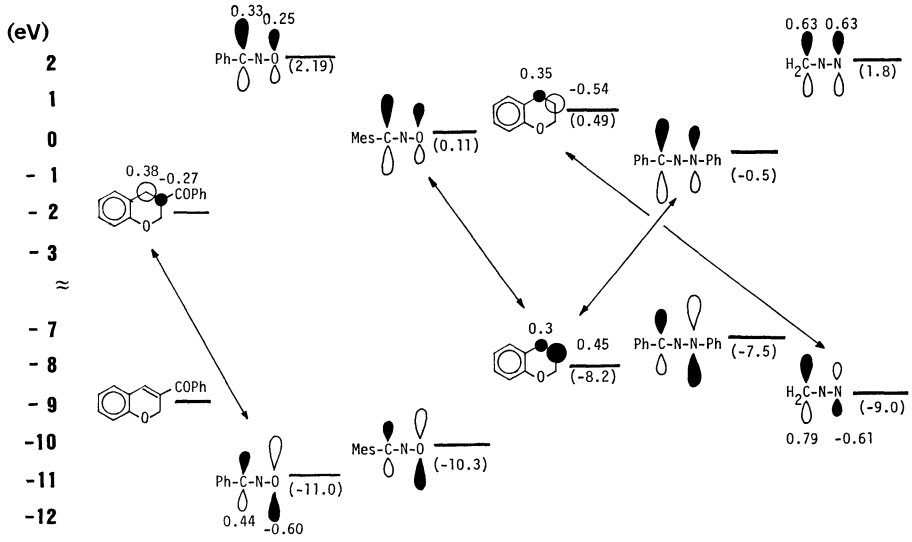
2*H*-1-Benzopyran(**1**) reacts readily with mesitonitrile oxide (MNO) in refluxing ether for over 4 h. The products are a mixture of the two regioisomers of a simple 1:1 cycloadduct (**2a** and **3a** in 35 and 4% yields respectively). Each regioisomer was isolated and characterized on a crystalline basis (see Table 1). In **3a**, the two benzene rings may lie on planes parallel to each other for steric reasons. Thus, the He proton in the benzopyran benzene ring is shielded and shifts upfield[9] (δ 6.4). While the chemical shift of normal *o*-methyl in the mesityl group usually appears about δ 2.2 (in **2a**, they appear at δ 2.33), one of the *o*-methyl group of **3a** does appear at δ 1.47. This upfield shift can also be ascribed to the shielding effect of the benzopyran benzene ring. One proton doublet at δ 5.6 is only compatible with the methine of benzyl ether (Ha in **2a**) (Table 1).

Benzonitrile oxide(BNO) failed to yield an isolable adduct with **1** under a variety of conditions, and 1,2,5-oxadiazole *N*-oxide (furoxan; a dimer of BNO) was the only isolable compound from the reaction mixture. The difference in the chemical reactivity between BNO and MNO and the regioselectivity of the cycloaddition may be explained in terms of the frontier molecular orbital (FMO) interactions[10] (Scheme 2). BNO has a much higher LUMO (2.19 eV) energy and a lower HOMO (−11.03 eV) energy[10a] than

TABLE 1. YIELDS, MELTING POINTS, AND ANALYTICAL DATA OF **2a** AND **3a**

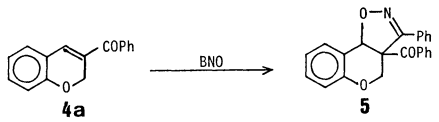


	Yield %	Mp °C	Found(Calcd)(%) C	H	N	NMR (δ) $CDCl_3$
2a	35	140—142	77.6 (77.8)	6.39 (6.48)	4.68 (4.78)	2.23(s, 6H, *o*-CH_3), 2.27(s, 3H, *p*-CH_3), 3.7—4.2(m, 3H, Hb and Hc), 5.6(d, 1H, Ha, J_{ab}=8 Hz), 6.9(s, 2H, Hd), 6.7—7.6(m, 4H)
3a	4	127—130	77.5	6.46	4.76	1.5(s, 3H, *o*-CH_3), 2.27(s, 3H, *o*-CH_3), 2.37(s, 3H, *p*-CH_3), 4.03(dd, 1H, Hc), 4.40(dd, 1H, Hc'), 4.67(d, 1H, Ha, J_{ab}=11 Hz), 5.27(dt, 1H, Hb, J_{bc}=4 Hz), 6.4(d, 1H, He, J=8 Hz), 6.73(s, 2H, Hd), 6.6—7.35(m, 3H)



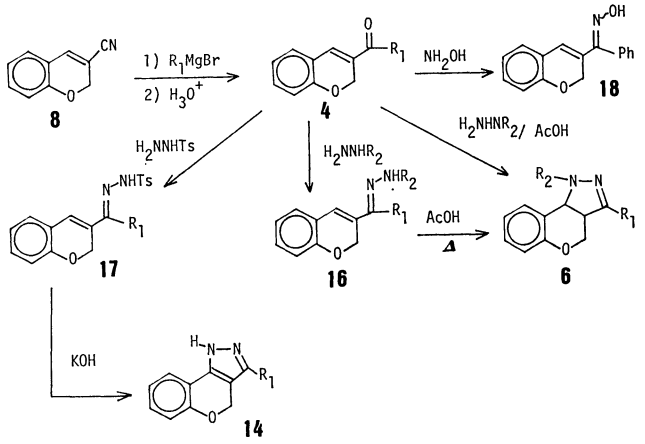
Scheme 2. Interaction scheme[a] of some 1,3-dipoles with 2*H*-1-benzopyrans.
a) The radii of the circles or lobes represent the magnitudes of FMO coefficients at each center. The coefficients and energies of the 1,3-dipoles are shown in the literature and those of 2*H*-1-benzopyrans were estimated from the data of analogous structure (see text).

MNO (0.11 and −10.3 eV[7]) respectively). Both nitrile oxides have a larger LUMO coefficient at the carbon atom than at the oxygen atom.[10a] The coefficients and energies of FMO of **1** are qualitatively estimated by considering the data[7] reported for analogous compounds, such as styrene or indene (all of these compounds have comparable values) and the conception given by Houk *et al.*[10] Thus, the 3-C atom has much larger coefficients than the 4-C atom in both the HOMO and LUMO. Consequently, an energetically favorable LUMO(MNO)-HOMO(**1**) interaction gives **2a** as the main product. On the other hand, the dimerization of BNO is faster than the cycloaddition with **1** because of the large HOMO-LUMO separation in both of the combinations (Scheme 2). This disadvantage might be largely overcome by introducing an electron donor or attracting groups into **1**. Thus, BNO reacts with 3-benzoyl-2*H*-1-benzopyran (**4a**) to give a cycloadducts (**5**) in a good yield. The regiochemistry of **5** was assigned mainly



on the basis of the NMR spectrum. The regioselectivity of this reaction may be explained as below. The FMO coefficients and energies of **4a** are qualitatively estimated to be as shown in Scheme 2 by considering the data[11] reported for 1,3-diphenyl-2-propen-1-one (chalcone). As the coefficient at the 4-C atom of **4a** in the LUMO is larger than that of the 3-C atom, a favorable HOMO(BNO)-LUMO(**4a**) interaction gives **5** as the product.

The reaction of **1** with nitrilimines gave cycloadducts (**6**) in good yields, and in these cases no regioisomers were obtained. The cycloadducts (**6**) can be converted to pyrazoles (**7**) in high yields by treatment with chloranil. These results are summarized in Table



Scheme 3.

2. The regiochemistry of these adducts (**6**) was confirmed by comparison with the authentic specimens which had been prepared from 3-cyano-2*H*-1-benzopyran (**8**) (see Scheme 3). The regioselectivity of this cycloaddition may also be explained in terms of FMO interaction. The frontier orbital energies[10a] and coefficients[12] of diphenylnitrilimine are given in the literatures. It seems reasonable from Scheme 2 that a slightly favorable LUMO (nitrilimine)-HOMO (**1**) interaction gave **6**. The introduction of substituents into phenyl groups of diphenylnitrilimine lowers its LUMO energy, and so the dipole-LUMO controlled reaction may be the more favorable one.

The reaction of **1** with diazomethane was carried out for several weeks in the dark. The removal of the starting materials from the reaction mixture gave an oily material, the spectrum of which was similar in gross features to that of the known material[2c] pre-

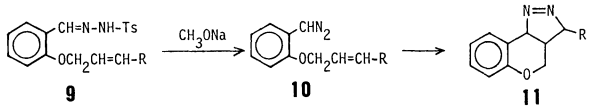
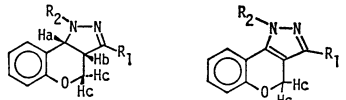


TABLE 2. YIELDS, MELTING POINTS, AND ANALYTICAL DATA OF **6**, **7**, AND **14**

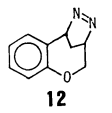


6 , **7** and **14**

	R_1	R_2	Method[a]	Yield %	Mp[b] °C	Found(Calcd) (%) C	H	N	NMR (δ)[c]
6a	C_6H_5	C_6H_5	A	41	129—130	81.0	5.32	8.67	3.6—4.6(m, 3H, Hb and Hc), 4.7(d, 1H, Ha, J_{ab}=7
			B	75		(80.9)	(5.56)	(8.58)	Hz), 6.8—8.0(m, 14H)
6b	C_6H_5	$C_6H_4NO_2$-*p*	A	40	230—233	69.4	4.38	10.5	4.0—4.9(m, 3H, Hb and Hc), 6.17(d, 1H, Ha, J_{ab}=
			B	50		(71.2)	(4.61)	(11.3)	10 Hz), 6.8—8.0(m, 11H), 8.15(d, 2H, J=9 Hz)
6c	$C_6H_4NO_2$-*p*	C_6H_5	A	51	187—189	71.0	4.48	11.2	3.6—4.9(m, 3H, Hb and Hc), 4.94(d, 1H, Ha, J_{ab}=
						(71.2)	(4.61)	(11.3)	8 Hz), 6.7—7.6(m, 9H), 7.7—8.4(m, 4H)
6d	$C_6H_4CH_3$-*p*	C_6H_5	A	48	179—180	80.7	5.89	8.22	2.33(s, 3H, CH_3), 3.5—4.5(m, 3H, Hb and Hc), 4.58
			B	58		(81.2)	(5.92)	(8.23)	(d, 1H, Ha, J_{ab}=7 Hz), 6.67—7.37(m, 11H), 7.57(d,
									2H, J=8 Hz)
6e	$C_6H_4CH_3$-*p*	$C_6H_4NO_2$-*p*	A	47	242—244	70.9	4.86	10.8	2.37(s, 3H, CH_3), 3.9—4.85(m, 3H, Hb and Hc), 6.15
						(71.7)	(4.97)	(10.9)	(d, 1H, Ha, J_{ab}=10 Hz), 6,66—7,83(m, 10H), 8.13(d,
									2H, J=9 Hz)
6f	CH_3	$C_6H_4NO_2$-*p*	B	40	209—210	65.5	4.80	13.5	2.15(s, 3H, CH_3), 3.75—4.8(m, 3H, Hb and Hc), 5.97
						(66.0)	(4.89)	(13.6)	(d, 1H, Ha, J_{ab}=9 Hz), 6.7—7.7(m, 6H), 8.13(d, 2H,
									J=9 Hz)
7a	C_6H_5	C_6H_5	—	45	140—142	80.1	5.03	8.50	5.5(s, 2H, Hc), 6.6—7.8(m, 14H)
						(81.5)	(4.97)	(8.46)	
7b	C_6H_5	$C_6H_4NO_2$	—	52	236—241	71.2	4.05	10.9	5.5(s, 2H, Hc), 6.6—7.7(m, 11H), 8.16(d, 2H, J=9 Hz)
						(71.5)	(4.09)	(11.4)	
7c	$C_6H_4NO_2$	C_6H_5	—	50	220—224	70.8	4.01	11.2	5.5(s, 2H, Hc), 6.6—7.5(m, 9H), 7.6—8.4(m, 4H)
						(71.5)	(4.09)	(11.4)	
7d	CH_3	C_6H_5	—	38	148—149	77.6	5.45	10.1	2.2(s, 3H, CH_3), 4.58(d, 1H, Hc, J_{cc}=10 Hz), 4.82(d,
						(77.8)	(5.38)	(10.7)	1H, Hc), 6.6—7.4(m, 9H)
14a	C_6H_5	H	B	72	230[d]				——————————[f]
14b	CH_3	H	B	63	190[e]				——————————[f]

a) A; Prepared by the cycloaddition reaction, B; Prepared by the reaction of **4** with aryl(or tosyl)hydrazines. b) Recrystallized from ethanol. c) **6b**, **6e**, **6f**, **14a**, and **14b** were dissolved in DMSO-d_6, the others were dissolved in $CDCl_3$. d) Lit,[2d] mp 230—233 °C. e) Lit,[2d] mp 197—202 °C. f) The IR and NMR spectra of these compounds were completely identical with authentic specimens.[2d]

pared by the intramolecular 1,3-dipolar cycloaddition reaction of *o*-allyloxyphenyldiazomethane (**10**). This result suggests that the structure of the intramolecular cycloadduct of **10** and the intermolecular cycloadduct of **1** with diazomethane is the same one (**11**), inconsistent with the regioisomers (**12** and **13** respectively).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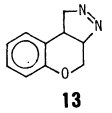
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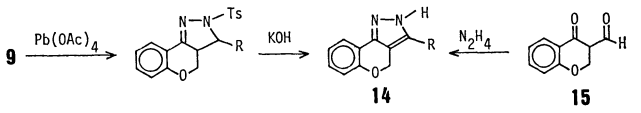
The regioselectivity of this reaction may be explained in terms of a dipole-HOMO controlled 1,3-dipolar cycloaddition (see Scheme 2). The treatment of phenyldiazomethane with **1** under similar conditions also gave an oily product, which was found to be compatible with the assigned structure (**11b**, R=C_6H_5). Several attempts to isolate the cycloadducts in the crystalline state were unsuccessful, and it is known that the pyrazolines(**11**) generally exhibit low melting points and are moderately sensitive to heating.[2c]

1 failed to undergo cycloadditions with other 1,3-dipoles, such as phenylazide or diphenylnitrone, under a variety of conditions.

While the 1,3-dipolar cycloadditions reported here gave reasonable yields of polycyclic heterocycles, it is hoped to develop methods of preparing authentic specimens with an unequivocal regiochemistry. In our previous paper,[2d] [1]benzopyrano[4,3-*c*]pyrazoles (**14**) were prepared from the reaction of **9** with Pb(OAc)$_4$ and subsequent treatment with potassium hydroxide. The structures of these pyrazoles were determined by comparison with an authentic specimen, prepared by the reaction of 3-formyl-4-chromanone (**15**) with hydrazine hydrochloride.[9] This latter method is rather cumbersome, however, because the synthesis of **15** involves multistep reactions. We found that the synthesis of **14** from 3-cyano-2*H*-1-benzopyran (**8**) shown in Scheme 3 gave more satisfactory results.


14 **15**

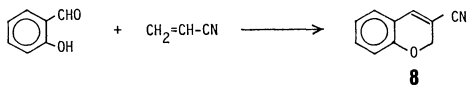

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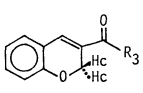
Table 3. Yields, melting and boiling points, and analytical data of **4**, **16**, and **17**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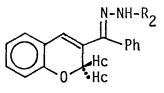
16 and **17**

	R_1	R_2	Yield %	Mp(Bp) °C	Found(Calcd) (%) C	H	N	IR (cm^{-1})	NMR(δ) DMSO-d_6(**16d** and **17b**) $CDCl_3$(Others)
4a	C_6H_5	—	33	(171/4 mmHg)	81.2 (81.3)	5.17 (5.12)	0 (0)	1640(C=O)	5.13(d, 2H, Hc, J=2 Hz), 6.67—7.83(m, 10H)
4b	$C_6H_4CH_3$-*p*	—	22	104 (182/4 mmHg)	81.4 (81.6)	5.60 (5.64)	0 (0)	1640(C=O)	2.5(s, 3H, *p*-CH_3), 5.2(s, 2H, Hc), 6.8—7.9(m, 9H)
4c	CH_3	—	41	(124/2 mmHg)	75.7 (75.8)	5.77 (5.79)	0 (0)	1660(C=O)	2.25(s, 3H, CH_3), 4.87(d, 2H, Hc, J=2 Hz), 6.6—7.3(m, 5H)
16a	C_6H_5	C_6H_5	70	155—158	80.9 (81.0)	5.79 (5.56)	8.66 (8.58)	3320(NH)	5.33(s, 2H, Hc), 5.95(s, 1H), 6.6—7.7(m, 15H)
16b	C_6H_5	$C_6H_4NO_2$-*p*	65	189—192	70.9 (71.2)	4.67 (4.61)	11.0 (11.3)	3300(NH)	5.30(d, 2H, Hc, J=2 Hz), 6.10(s, 1H), 6.7—7.9(m, 12H), 8.07(d, 2H, J=9 Hz)
16c	CH_3	C_6H_5	77	150—151	77.5 (77.3)	6.01 (6.10)	10.6 (10.6)	3350(NH)	1.97(s, 3H, CH_3), 5.2(d, 2H, J=1 Hz), 6.5(s, 1H), 6.6—7.4(m, 10H)
16d	CH_3	$C_6H_4NO_2$-*p*	88	202—204	66.3 (66.0)	4.77 (4.89)	13.8 (13.6)	3320(NH)	2.1(s, 3H, CH_3), 5.1(s, 2H, Hc), 6.67—7.4(m, 7H), 8.05(d, 2H, J=9 Hz), 10.1(s, 1H, NH)
17a	C_6H_5	SO_2-Tol-*p*	55	162—164	68.6 (68.3)	5.09 (4.99)	6.71 (6.93)	3220(NH) 1164(SO_2)	2.4(s, 3H, *p*-CH_3), 5.1(d, 2H, Hc, J=2 Hz), 6.05(s, 1H), 6.65—8.0(m, 14H)
17b	CH_3	SO_2-Tol-*p*	79	184—186	63.4 (63.2)	5.28 (5.30)	8.13 (8.18)	3220(NH) 1150(SO_2)	2.0(s, 3H, CH_3), 2.37(s, 3H, *p*-CH_3), 4.85(s, 2H, Hc), 6.67—8.0(m, 9H), 10.57(s, 1H, NH)

While the synthesis of benzopyrano derivatives using the Wittig reaction is very useful,[13] it is generally difficult to prepare 3-substituted-2*H*-1-benzopyran by this method.[14] A convenient one-step synthesis[16] of **8** (20% yield) is known, it is shown below. A modification of this preparative method was used, since, in our hands, it gave more satisfactory results (40—50% yield) when the reaction mixture was distilled. The **8** was treated with Grignard reagents, and the subsequent hydrolysis of the adducts gave 3-aroyl (or acetyl)-2*H*-1-benzopyrans (**4**). The treatment of **4** with arylhydrazines, *p*-tolylsulfonylhydrazine, or hydroxylamine gave the corresponding arylhydrazones (**16**), *p*-tolylsulfonylhydrazone (**17**), and oxime (**18**) respectively. The yields, melting points, and analytical data for these compounds (**4**, **16**—**18**) are given in Table 3. The treatment of **16** with acetic acid at 110 °C, or the treatment of the mixture of **4** and arylhydrazines with acetic acid at the same temperature, gave cyclized compounds which showed the same physical properties as the **6** prepared by the reaction of **1** with nitrilimines. The treatment of **17** with potassium hydroxide gave cyclized compounds which have the same physical properties as the specimens previously reported.[2d] All attempts to cyclize **18** to **2** failed.

Experimental

Measurements. All the melting and boiling points are uncorrected. The IR spectra were recorded with a Hitachi 215 Infrared Spectrophotometer. The NMR spectra were measured on a Varian T-60A instrument, with TMS as an internal standard.

Materials. 2*H*-1-Benzopyran was prepared by the method of Ide *et al.*[17]

*Preparation of 3-Cyano-2*H*-1-benzopyran(8).* The reaction of salicylaldehyde with acrylonitrile was carried out according to the literature.[16] The reaction mixture was poured into water and extracted with ether several times. A modification of a work-up by distillation *in vacuo* gave **8** (40—50% yield), which solidified in the condenser; bp 105—110 °C/2 mmHg, mp 48—49 °C (from ethanol) (lit,[16] 48—49 °C).

*Preparation of 3-Aroyl(or Acetyl)-2*H*-1-benzopyrans(4).* To an anhydrous ether solution of phenylmagnesium bromide (0.12 mol), we added, drop by drop, an anhydrous ether solution of **8** (0.1 mol) at 10—20 °C. After insoluble materials had thus been precipitated, the mixture was refluxed for 6 h. After cooling, 30% sulfuric acid (100 ml) was added, drop by drop, at 5—10 °C, and then the mixture was refluxed for 2 h. The insoluble material was filtered off using a Celite bed, and the ethereal layer was washed with a 5% sodium carbonate solution and dried over anhydrous sodium sulfate. The subsequent evaporation of the solvent yielded an oily material, which was subsequently distilled *in vacuo* to give **4a** in a 40% yield; bp 171—173 °C/4 mmHg. The spectral data are shown in Table 3.

Reaction of 1 with Mesitonitrile Oxide. A mixture of **1** (8 g, 60 mmol), mesitonitrile oxide (5 g, 31 mmol), and ether (70 ml) was refluxed for 4 d. The subsequent evaporation of the solvent yielded white crystals. Recrystallization from ethanol gave colorless needles of the cycloadduct (**2a**) (mp 140—142 °C, 3.2 g) and then **3a** (mp 127—130 °C, 350 mg). The spectral data are shown in Table 1.

Reaction of 1 with Nitrilimines. To a mixture of **1** (4 g, 30 mmol), triethylamine (4 g, 40 mmol), and benzene (50 ml), we added a benzene solution of hydrazonoyl chlorides (30 mmol), after which the mixture was refluxed for 20 h. The mixture was washed with water, and the subsequent evaporation of the solvent yielded pale yellow crystals. Recrystallization from ethanol gave the cycloadducts (**6**). The spectral data are shown in Table 2.

Dehydration of 6. The dehydration of **6** to **7** was carried out according to the literature.[18]

Reaction of 1 with Diazomethane. To an ether solution of **1** (5 g, 38 mmol), we introduced diazomethane gas (about 0.1 mol) at −15 °C in the dark, after which the mixture was stirred for 4 h at that temperature. Then the mixture was further stirred for 4 d at room temperature. After the evaporation of the solvent, the unreacted 2*H*-1-benzopyran was distilled *in vacuo* (2 mmHg). The NMR spectrum of the residue is completely identical with a previously reported one.[2c]

The Reaction of 4 with Aryl(or p-*Tolylsulfonyl)hydrazines.* An ethanol solution of **4** (20 mmol) and aryl (or *p*-tolylsulfonyl)hydrazines (20 mmol) was refluxed for 6 h. The subsequent evaporation of the solvent yielded a viscous oily material which solidified upon scratching with a glass rod. Recrystallization from ethanol gave colorless needles (**16** or **17**). The spectral data are shown in Table 3. We may also carry out this reaction at room temperature in acetic acid.

The Reaction of 4 with Hydroxylamine. This reaction was carried out in the manner described above.

The Treatment of 4 with Aryl (or p-*Tolylsulfonyl)hydrazines in Acetic Acid.* A mixture of **4** (20 mmol) and aryl (or *p*-tolylsulfonyl)hydrazines in acetic acid (100 ml) was refluxed for 4 h, poured into water, and extracted with benzene. The organic layer was dried over anhydrous sodium sulfate. The subsequent evaporation of the solvent yielded pyrazolines (**6**) in good yields.

The Treatment of 16 with Acetic Acid. A solution of **16** in acetic acid was refluxed for 3 h. The treatment of the reaction mixture in the manner described above yielded pyrazolines (**6**) in good yields.

The Treatment of 17 with Potassium Hydroxide. To a solution of potassium hydroxide (0.4 g, 3 mmol) in 95% aqueous ethanol (50 ml), we added **17** (2 mmol), after which the mixture was stirred for 1 h under refluxing. After the subsequent removal of the solvent from the reaction mixture, the residue was treated with water (50 ml) and extracted with ether (50 ml). The ethereal layer was then dried over anhydrous sodium sulfate. The evaporation of the solvent yielded **14** (about 70% yields).

*Reaction of 3-Benzoyl-2*H*-1-benzopyran with Benzonitrile Oxide (BNO).* To a benzene solution of **4a** (4.7 g, 20 mmol) and α-chlorobenzaldoxime (4 g, 26 mmol), we added a dilute solution of triethylamine (3 ml) in benzene (20 ml) at 5 °C and the mixture was further stirred at room temperature overnight. The mixture was washed with water and the organic layer was dried over sodium sulfate. The evaporation of the solvent yielded **5** in a 30% yield (2.1 g); mp 178—179 °C (from ethanol). NMR ($CDCl_3$) δ: 4.2 (d, 1H, J=11 Hz), 4.95 (d, 1H, J=11 Hz), 6.0 (s, 1H), 6.8—7.8 (m, 12H), and 7.8—8.1 (m, 2H). IR (Nujol): 1680 cm^{-1} (C=O). Found: C, 77.0; H, 4.85; N, 3.88%. Calcd for $C_{23}H_{17}O_3N$; C, 77.7; H, 4.82; N, 3.94%.

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