Intramolecular Cycloaddition Reactions of *N*-Sulfonyl Nitrile Imides Bearing Alkenyl Groups

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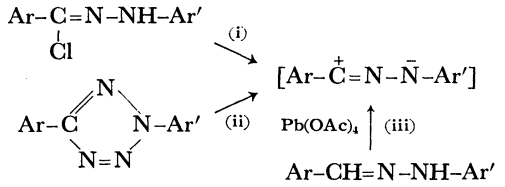
The reaction of the *p*-tolyl(or phenyl)sulfonylhydrazones of some 2-(alkenyloxy)benzaldehydes with lead tetraacetate leads, *via* the nitrile imide intermediates, Ar–C(+)=N–N(−)–SO_2–C_6H_4–X-*p*, to intramolecular 1,3-dipolar cycloadducts and 1-acetyl-2-aroyl-1-[*p*-tolyl(or phenyl)sulfonyl]hydrazines in 20—65% and 7—70% yields respectively, while the intermolecular reactions of the benzaldehyde *p*-tolylsulfonylhydrazone with a dipolarophile such as acrylonitrile or styrene in the presence of lead tetraacetate gives only 1-acetyl-2-benzoyl-1-(*p*-tolylsulfonyl)-hydrazine. The treatment of the *N*-(*p*-tolylsulfonyl)-*o*-(allyloxy)benzohydrazonoyl chloride (**10**) with triethylamine or by refluxing a benzene solution of **10** also gives an intramolecular 1,3-dipolar cycloadduct in a good yield.

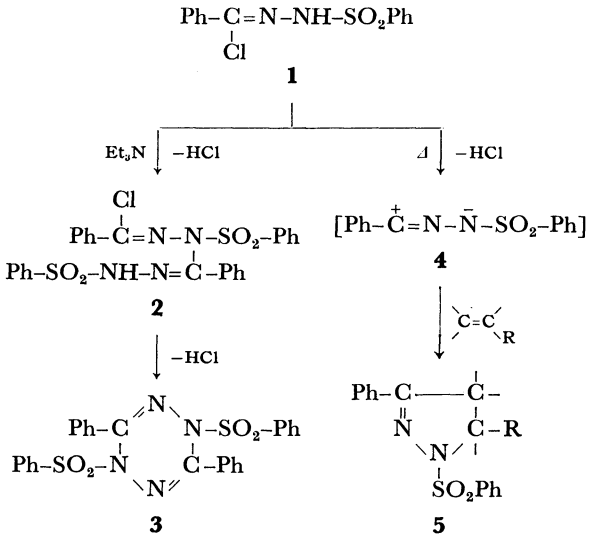
1,3-Dipolar cycloaddition reactions are one of the most useful methods for the preparation of five-membered heterocyclic rings.[1] These reactions are usually regarded as concerted reactions,[2] but sometimes a diradical intermediate has been postulated.[3] The stereochemistry of the dipolarophiles is usually maintained, and the orientation phenomena can be ascribed to frontier orbital interactions.[4]

In this decade, many studies of intramolecular 1,3-dipolar cycloaddition reactions have been reported.[5–10] The most interesting aspects of these reactions are as follows: first, the reaction products are complex polycyclic, annelated, and fused ring molecules which are difficult to prepare by any other methods. Second, a comparison of the results of an intermolecular reaction with that of an intramolecular reaction suggests several things. For example, much information has been obtained from the various intramolecular cycloadditions of nitrile oxides,[5] nitrile imines,[6] nitrones,[7] nitrile ylides,[8] azides,[9] diazoalkanes,[10] and azomethine imines[6b,7b] as dipoles.

Except for a few instances, most dipoles are prepared by multistep reactions and, consequently, in low yields. For example, nitrile imines are generally generated (i) from hydrazonyl halides by treatment with a base[11] or (ii) from the thermal decomposition of 2,5-disubstituted tetrazoles.[12] These methods, while moderately satisfactory, are rather combersome. However, a new method (iii) reported by Gladstone[13] has been shown to be a simpler preparative method for nitrile imines.



Several attempts to prepare the *N*-sulfonyl nitrile imide (**4**) have been made.[14,15] It has been reported that the reaction of *N*-sulfonyl hydrazonoyl chloride (**1**) with triethylamine gave only a dimer (**3**) *via* the intermediate (**2**).[14] On the other hand, when a toluene solution of **1** and a dipolarophile was refluxed, the 1,3-dipolar cycloadduct (**5**) was obtained.[15] We found



that the new method reported by Gladstone was equally useful for the preparation of *N*-sulfonyl nitrile imide from *p*-tolylsulfonylhydrazone of aromatic aldehyde.

$$\text{Ar–CH=N–NH–SO}_2\text{–Tol-}p \xrightarrow{\text{Pb(OAc)}_4} \mathbf{4'}$$

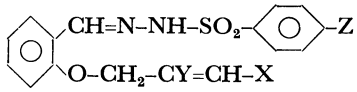
This paper will describe some smooth intramolecular cycloaddition reactions using these sulfonylhydrazones.

Results and Discussion

An expected intramolecular cycloadduct, 2,3,3a,4-tetrahydro-2-*p*-tolylsulfonyl[1]benzopyrano[4,3-*c*]-pyrazole (**7a**), and the unexpected 1-acetyl-2-(*o*-allyloxy)benzoyl-1-*p*-tolylsulfonylhydrazine (**8a**) were isolated from a reaction mixture of *p*-tolylsulfonylhydrazone of 2-(*o*-allyloxy)benzaldehyde (**6a**) and lead tetraacetate by fractional recrystallization and/or column chromatography. Some of the hydrazones (**6**), shown in Table 1, also gave the intramolecular cycloadducts (**7**) and *N*-acetylated hydrazines (**8**). These results are shown in Tables 2 and 3 respectively.

The structure of **7a** was established on the basis of elemental analysis and the spectral data, IR (cm^{-1}): 1180 (N–SO_2); NMR ($CDCl_3$) δ: 2.40 (3H, s, CH_3), 2.60—4.70 (4H, m), 6.7—7.5 (5H, m), and 7.7—7.95 (3H, m). The assignment of the structure **7a** was further

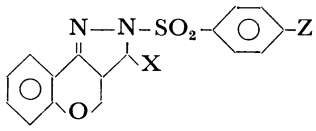
TABLE 1. YIELDS AND MELTING POINTS OF THE HYDRAZONES (**6**)[a]



6	X	Y	Z	Mp/°C	Yield/%
a	H	H	CH_3	116—117[b]	quanti.
b	H	H	H	141—142	95
c	Ph	H	CH_3	128—130	quanti.
d	Ph	H	H	113—114	83
e	H	Br	CH_3	114—115	52
f	H	Br	H	144—145	50
g	CN	H	CH_3	144—146	quanti.
h	CN	H	H	165—167	81
i	CH_3	H	CH_3	127—128	66
j	CH_3	H	H	136—137	88

a) Satisfactory analytical data were obtained for new compounds. b) Lit,[10c] mp 119 °C.

TABLE 2. YIELDS, MELTING POINTS, AND ANALYTICAL DATA OF THE PYRAZOLINES (**7**)

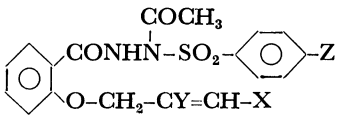


7	X	Z	Mp/°C	Yield/%	Found(%) (Calcd(%)) H	C	N
a	H	CH_3	205—207	40	4.93 (4.91	62.56 62.19	8.35 8.53)
b	H	H	252—254	30	4.42 (4.49	61.17 61.14	8.83 8.91)
c	Ph	CH_3	243—246	20	5.00 (4.99	67.45 68.30	6.68 6.93)
d	Ph	H	206—210	65	4.60 (4.65	67.23 67.67	7.02 7.17)
g	CN	CH_3	204—206	20	4.17 (4.28	61.20 61.18	11.67 11.89)
h	CN	H	212—215	25	3.68 (3.83	60.32 60.17	12.46 12.38)
i	CH_3	CH_3	183—188	24	5.16 (5.30	62.87 63.14	8.10 8.18)
j	CH_3	H	191—194	20	4.94 (4.91	62.53 62.18	8.44 8.53)

supported by the following experiment: the hydrolysis and then the dehydrogenation of **7a** by treatment with potassium hydroxide gave 2,4-dihydro[1]benzopyrano-[4,3-*c*]pyrazole (**9a**), IR (cm^{-1}): 3210 (NH); NMR ($CDCl_3$) δ: 5.24 (2H, s), 6.7—7.35 (4H, m), and 7.5—7.7 (1H, m) (see Table 4). The NMR spectra of pyrazolines (**7**) and pyrazoles (**9**) are consistent with those of analogous polycyclic pyrazolines and pyrazoles reported in the literature.[6b-d] These results show that the new method is satisfactory for the preparation of benzopyranopyrazoles (**7** and **9**).

Although no appreciable difference in reactivity was observed when the substituent of X and Z on **6** was varied, the introduction of bromine at the Y position

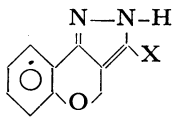
TABLE 3. YIELD AND MELTING POINTS OF THE *N*-ACETYLATED COMPOUNDS (**8**)[a]



8	X	Y	Z	Mp/°C	Yield/%
a	H	H	CH_3	—	—
b	H	H	H	108—109	7
c	Ph	H	CH_3	—	—
d	Ph	H	H	≃100	trace
e	H	Br	CH_3	136—138	17
f	H	Br	H	139—141	70
g	CN	H	CH_3	180—181	27
h	CN	H	H	145—148	37
i	CH_3	H	CH_3	110—111	21
j	CH_3	H	H	126—128	20

a) Satisfactory analytical data were obtained for these compounds.

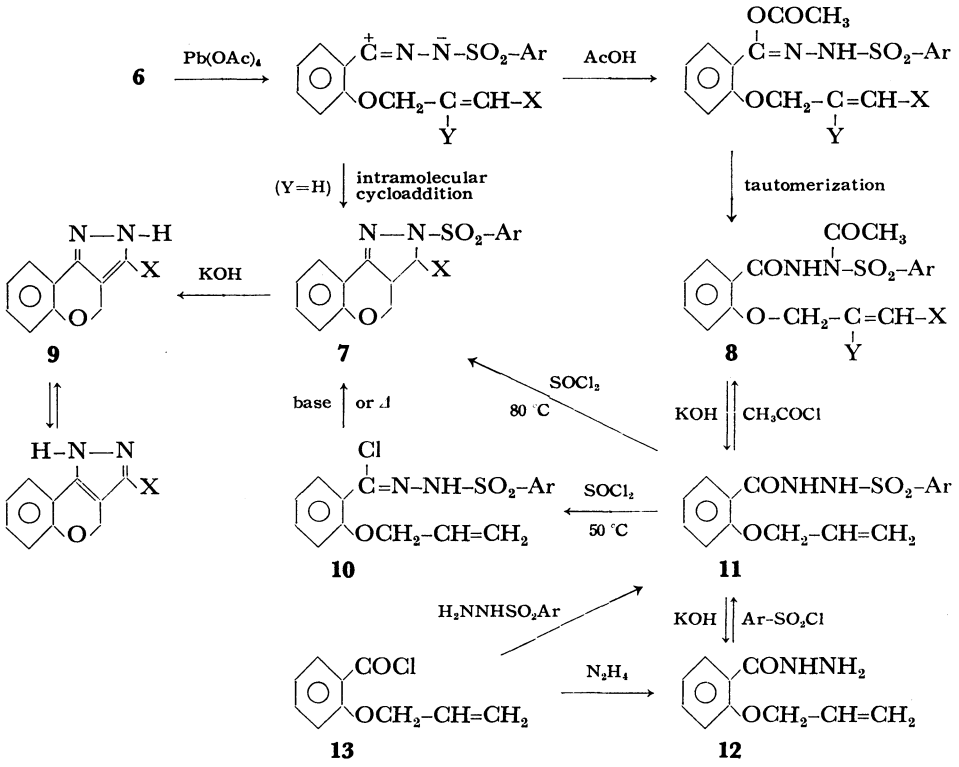
TABLE 4. MELTING POINTS AND ANALYTICAL DATA OF THE PYRAZOLES (**9**)



9	X	Mp/°C	Found(%) (Calcd(%)) H	C	N
a,b	H	171—173	4.69 (4.68	71.23 69.75	16.11 16.27)
c,d	Ph	230—233	5.00 (4.87	76.10 77.40	10.99 11.28)
g,h	$CONH_2$	≃305	4.17 (4.22	58.69 61.39	18.07 19.53)
i,j	CH_3	197—202	5.30 (5.41	71.24 70.95	14.31 15.04)

gave only *N*-acetylated compounds (**8e** and **8f**); no 1,3-dipolar cycloadducts could be detected. Our method described above gave **7a** in 40% total yield *via* only two reaction steps from salicylaldehyde. Though Compound **7a** was also prepared in a 26% overall yield *via* hydrazonoyl chloride (**10**) from methyl salicylate (see Scheme 1), this method is rather combersome because it involves six reaction steps. It is interesting that *N*-sulfonyl hydrazonoyl chloride (**10**), another precursor of the nitrile imide for the cycloadduct, also gave the cycloadduct (**7a**) when treated with triethylamine. Even in the absence of triethylamine, the precursor (**10**) yielded **7a** with liberating hydrogen chloride when subjected to reflux in a benzene solution. In these reactions, no dimer like **3** was detected; this indicates a favorable intramolecular cycloaddition reaction.

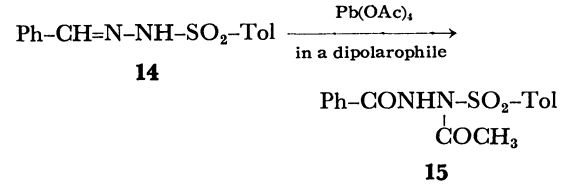
The structure of the *N*-acetylated compound (**8a**) was assigned on the basis of a comparison of the spectra with those of analogous compounds reported by Scott *et al.*[16] The following results also support the structure



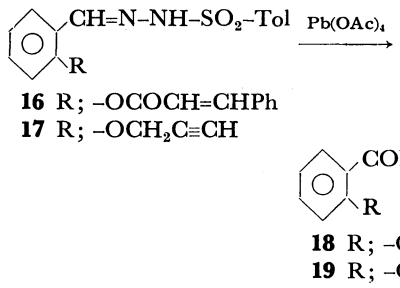
Scheme 1.

(**8a**): the deacetylation of **8a** with aqueous potassium hydroxide under mild conditions gave 2-[*o*-(allyloxy)-benzoyl]-1-(*p*-tolylsulfonyl)hydrazine (**11a**), which was then further hydrolyzed to [*o*-(allyloxy)benzoyl]-hydrazine (**12a**) under more severe conditions. These compounds, **11a** and **12a**, have properties identical with those of authentic specimens prepared by the reaction of *o*-(allyloxy)benzoyl chloride (**13**) with *p*-tolylsulfonylhydrazine or hydrazine hydrate respectively. **8a** can be prepared by the reaction of **11a** with acetyl chloride.

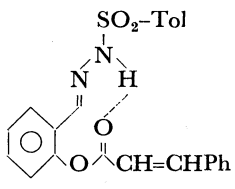
Since the intramolecular 1,3-dipolar cycloadducts (**7**) were obtained from the reaction of sulfonylhydrazones (**6**) with lead tetraacetate, the possibility of the intermolecular cycloaddition reactions was examined under the same conditions. When benzaldehyde *p*-tolylsulfonylhydrazone (**14**) was treated with lead tetraacetate in a dipolarophile such as styrene, acrylonitrile, diethyl maleate, diethyl fumarate or allyl phenyl ether, no cycloadducts were obtained; the only isolated compound was the *N*-acetylated compound (**15**) in any case. These results suggest that *N*-sulfonyl nitrile



imide is less reactive for 1,3-dipolar cycloaddition reactions and, consequently, undergoes an entropically favored reaction as intramolecular cycloaddition[7b] or the reaction with the acetic acid which exists near the nitrile imide when it is generated. A similar reaction was carried out using the compound bearing a cinnamoyl (**16**) or propargyl group (**17**), which groups are usually more reactive dipolarophiles toward nitrile imine, but *N*-acetylated compounds (**18** and **19**) were the only products isolated from the reaction mixture in each case. There may be many explanations for this result, but



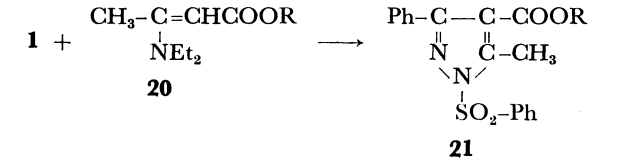
we have no definitive information in this connection. While the carbonyl absorption of phenyl cinnamate appears at 1730 cm^{-1}, that of **16** does so at 1695 cm^{-1}. The broad NH absorption of the hydrazone (**16**) at 3130 cm^{-1} is in sharp contrast with that of the compounds (**6**) which show a sharp absorption at 3200 cm^{-1}. This is presumably a result of an intramolecular hydrogen bonding such as **16'**, in which case the double bond of **16** is relatively remote from the hydrazone group.



It is thought that compound (**17**) can not attain the optimum overlap needed for cycloaddition reaction because the propargyl group has a linear configuration. While the diaryl nitrile imine, which has a propargyl group, really gave the intramolecular cycloadduct,[6c] no cycloadducts were isolated from the reaction of *N*-sulfonyl hydrazonoyl chloride (**1**) with phenylacetylene or ethyl propiolate.[15]

These results may be explained on the basis of the strong electron-withdrawing property of the sulfonyl group. Thus, the *N*-sulfonyl nitrile imide should function as an electron-accepting one and should react with electron-rich olefins in the dipole-LUMO controlled manner,[20] not with an electron-poor one such as cinnamate.

Though the successful intramolecular cycloadditions may be interpreted in terms of a dipole-LUMO controlled 1,3-dipolar cycloaddition reaction with an allyloxy group which is moderately electron-rich, a step-by-step mechanism can also be considered. An interesting reaction of **1** with enamines (**20**) has been reported.[14] Though the cycloadducts **21** are obtained from the reaction mixture in good yields, this pyrazole



20 **21**

formation is interpreted in terms of a step-by-step process involving the nucleophilic attack of the enamines on the hydrazonoyl chloride.

Finally, we may resonably suppose that the intermediate in the reaction of **6** to **7** and **8** is the 1,3-dipole shown in Scheme 1 and that the *N*-sulfonyl nitrile imides which are prepared by the reaction of **6** with lead tetraacetate usually do not undergo 1,3-dipolar cycloadditions except for the case of an intramolecular reaction which is entropically favored.

Experimental

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

Materials. The lead tetraacetate (90.6%) was commercially obtained (Nakarai Chem. Co.) and was used without further purification. The (*o*-alkenyloxy)benzaldehydes were prepared from salicylaldehyde and 1-substituted 3-bromopropenes according to the method in the literature.[5,18] The *N*-(phenylsulfonyl)benzohydrazonoyl chloride (**1**) was prepared by the method of Ito *et al.*[14]

Preparation of the Sulfonylhydrazone. The sulfonylhydrazones (**6**) were prepared by the method of Kirmse *et al.*[10c] The structure of **8b—j** was confirmed on the basis of IR and NMR; IR (Nujol): 3175—3200 (NH), 1160—1172 (N-SO_2) and 2240 cm^{-1} (CN); NMR ($CDCl_3$) δ: 8.2—8.3 (s, NH), 4.4—4.8 (O-CH_2-), 2.3—2.4 [s, -CH_3(Z)] and 1.70 [d, J=4 Hz, -CH_3(X)].

Reaction of Sulfonylhydrazones (6) with Lead Tetraacetate. General Procedure: To a stirred solution of lead tetraacetate (15 mmol) in chloroform (300 ml), we added, drop by drop, a solution of sulfonylhydrazone (**6**) (10 mmol) in chloroform (100 ml) at 0 °C over a period of 30 min. The mixture was stirred at the same temperature for 1 h and then at room temperature overnight. The insoluble material thus precipitated was filtered off using a Celite bed. The filtrate was washed with water (500 ml), and the mixture was filtered using the Celite bed. The organic layer was washed with additional water several times and dried over magnesium sulfate. The subsequent evaporation of the organic layer yielded a viscous oil which solidified upon scraching with a glass rod. Recrystallization from ethanol gave colorless needles of the cycloadduct (**7**) and then an *N*-acetylated compound (**8**). The residue of the concentration of the filtrate from the recrystallization was chromatographed (silica gel) with chloroform to give additional needles, **7** and **8**. For **7a**, the spectral data are shown in the text; the other compounds (**7b—j**) show similar spectral data with an absence of NH absorption in the IR spectrum and an absence of olefinic protons in the NMR spectrum. The spectral data for **8** were as follows: IR (Nujol): 3350—3395 (NH), 1720—1725 (-CONH-), 1675—1690 (CON), 1165—1170 (N-SO_2) and 2240 cm^{-1} (CN), and NMR (DMSO-d_6) δ: 10.2 (s, NH), 2.10 (s, -$COCH_3$), 2.40 [s, -CH_3(Z)] and 1.80 [d, J=4 Hz, -CH_3(X)].

Reaction of 16 with Lead Tetraacetate. The reaction was carried out by the General Procedure. 4.4 g (10 mmol) of **16** were treated with lead tetraacetate (10 g, 20 mmol) to give white crystals (**18**) in a 62% yield; mp 185 °C (from ethanol). IR (Nujol): 3375 (NH), 1730 and 1685 (three carbonyl groups), and 1160 cm^{-1} (N-SO_2); NMR ($CDCl_3$) δ: 2.10 (s, 3H, -$COCH_3$), 2.37 (s, 3H, -CH_3), 6.68 (d, 1H, J=16 Hz, =C<u>H</u>-Ph), 7.1—8.1 (m, 14H, aromatic protons and -CO-C<u>H</u>=) and 9.06 (s, 1H, NH). Found: C, 63.24; H, 4.75; N, 5.78%. Calcd for $C_{25}H_{22}O_6N_2S$; C, 62.75; H, 4.63; N, 5.85%.

Reaction of 17 with Lead Tetraacetate. The reaction was carried out by the General Procedure. 3.3 g (10 mmol) of **17** were treated with lead tetraacetate (9 g, 18 mmol) to give white crystals (**19**) in a 30% yield; mp 166—168 °C (from ethanol). IR (Nujol): 3400 (NH), 3300 (≡CH), 2130 (C≡C), 1730 and 1690(two carbonyl groups) and 1170 cm^{-1}(N-SO_2); NMR ($CDCl_3$) δ: 2.13 (s, 3H, -$COCH_3$), 2.43 (s, 3H, CH_3), 2.63 (t, J=2.6 Hz, 1H, ≡CH), 4.93 (d, J=2.6 Hz, 2H, -CH_2-), 7.0—7.73 (m, 5H, aromatic protons), 7.90—8.27 (m, 3H, aromatic protons) and 9.97 (s, 1H, NH). Found: C, 59.61; H, 4.92%. Calcd for $C_{19}H_{18}O_5N_2S$; C, 59.06; H, 4.70%.

Treatment of 14 with Lead Tetraacetate in Dipolarophiles. To a stirred solution of lead tetraacetate in 100 ml of dipolarophile and benzene (1: 1) we added, drop by drop, a solution of hydrazone (**14**) (10 mmol) in benzene (50 ml) at room temperature. The mixture was then stirred at room temperature overnight. After the usual work-up, shown in the General Procedure, a 70% yield of 1-acetyl-2-benzoyl-1-(*p*-tolylsulfonyl)hydrazine (**15**) was obtained; mp 204—205 °C (from ethanol) [lit,[16] mp 197—198 °C]; IR (Nujol): 3310 (NH), 1723 and 1675 (two carbonyl groups) and 1160 cm^{-1} (N-SO_2); NMR (DMSO-d_6) δ: 2.10 (s, 3H, -$COCH_3$), 2.40 (s, 3H, -CH_3), 7.26—8.21 (m, 9H, aromatic protons) and 11.6 (s, 1H, NH).

Hydrolysis of the Cycloadducts (7) with Potassium Hydroxide. To a solution of potassium hydroxide (2 g, 36 mmol) in 95% aqueous ethanol (60 ml) we added 300 mg of **7**, after which the mixture was stirred for 1 h under refluxing. After the evaporation of the solvent of the reaction mixture, the residue was treated with water (60 ml) and extracted with benzene (50 ml). The organic layer was dried over anhydrous sodium sulfate. The subsequent evaporation of the solvent yielded the pyrazoles (**9**) in 90—95% yields; they were recrystallized from ethanol to give colorless substances. The spectral data for these pyrazoles were as follows: IR (Nujol): 3100—3120

(NH), 3230 [NH_2(**9g, h**)] and 1705 cm^{-1} [CON(**9g, h**)], and NMR ($CDCl_3$) δ: 5.24—5.5 (s, 2H, $-CH_2O-$) and 9.33—11.4 (br NH).

Hydrolysis of the N-*Acetylated Compound (8a) with Potassium Hydroxide.* To a solution of potassium hydroxide (600 mg, 11 mmol) in 95% aqueous ethanol (50 ml) we added **8a** (300 mg, 0.77 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 150 mg (56%) of **11a**; mp 127—128 °C (from ethanol). IR (Nujol): 3370, 3140 (NH) and 1160 cm^{-1} ($N-SO_2$); NMR ($CDCl_3$) δ: 2.34 (s, 3H, $-CH_3$), 4.72 (d, J=6 Hz, $-OCH_2-$), 5.13—5.66 (m, 2H, $=CH_2$), 5.8—6.5 (m, 1H, $-CH=$), 5.8—6.5 (m, 1H, $-CH=$), 6.80—8.00 (m, 9H, aromatic protons and NH) and 9.66 (d, J=6 Hz, NH).

Hydrolysis of 11a with Potassium Hydroxide. To a solution of potassium hydroxide (2 g, 36 mmol) in 95% aqueous ethanol (50 ml) we added **11a** (150 mg, 0.43 mmol), after which the mixture was refluxed for 1 h with stirring. After the subsequent removal of the solvent from the mixture, the residue was treated with water (50 ml) and extracted with ether (50 ml). The evaporation of the solvent yielded 50 mg (60%) of **12a**; mp 51—54 °C. IR (Nujol): 3250 (NH) and 1615 cm^{-1} (C=O); NMR ($CDCl_3$) δ: 4.17 (s, 2H, NH_2), 4.57 (d, J=5 Hz, 2H, $-CH_2-$), 5.07—5.55 (m, 2H, $=CH_2$), 5.67—6.33 (m, 1H, $-CH=$), 6.67—7.50 (m, 3H, aromatic protons), 7.90—8.23 (m, 1H, aromatic proton) and 8.87 (s, 1H, NH).

Methyl o-*(Allyloxy)benzoate.* To a mixture of methyl salicylate (76 g, 0.5 mol), allyl bromide (70 g, 0.58 mol) and acetone (250 ml) we added potassium carbonate (100 g, 0.72 mol), after which the mixture was refluxed overnight with stirring. After the filtration of the inorganic salts and the evaporation of the acetone, the residue was distilled *in vacuo* to give the ester; bp 147—151 °C/19 mmHg; 96 g (quantitative).

o-*(Allyloxy)benzoic Acid.* To a solution of sodium hydroxide (50 g, 1.25 mol) in 90% aqueous ethanol (300 ml) we added methyl *o*-(allyloxy)benzoate (80 g, 0.42 mol), after which the mixture was refluxed overnight with stirring. The reaction mixture was acidified with hydrochloric acid and extracted with benzene (200 ml). The subsequent evaporation of the solvent yielded 69 g (95%) of *o*-(allyloxy)benzoic acid; mp 85 °C (lit,[8a] 64—65 °C). The NMR spectra of this compound agreed with the previously reported one.[8a]

o-*(Allyloxy)benzoyl Chloride (13).* This compound was prepared by the reaction of the corresponding carboxylic acid and thionyl chloride by the method of Padwa *et al.*[8a]

Reaction of 13 with p-*Tolylsulfonylhydrazine.* To a mixture of *p*-tolylsulfonylhydrazine (19 g, 0.1 mol) and triethylamine (20 g, 0.2 mol) in benzene (150 ml) we added, drop by drop, a solution of **13** (15 g, 76 mmol) in benzene over a period of 30 min at room temperature. The mixture was then refluxed for 3 h with stirring. After the filtration of the triethylamine hydrochloride, the filtrate was washed with water and dried over anhydrous sodium sulfate. The subsequent evaporation of the solvent gave **11a** in a 57% (15 g) yield; it was recrystallized from ethanol to give a colorless substance; mp 127—128 °C. IR (Nujol): 3380, 3150 (NH), 1650 (C=O) and 1163 cm^{-1} ($N-SO_2$); NMR ($CDCl_3$) δ: 2.34 (s, 3H, $-CH_3$), 4.72 (d, J=6 Hz, 2H, $-CH_2-$), 5.23—5.66 (m, 2H, $=CH_2$), 5.83—6.53 (m, 1H, $-CH=$), 6.83—7.63 (m, 5H, aromatic protons), 7.63—8.00 (m, 4H, aromatic protons and NH) and 9.71 (d, J=6 Hz, 1H, NH).

Reaction of 11a with Acetyl Chloride. A solution of **11a** (2 g, 5.78 mmol) in acetic acid–acetyl chloride (1: 1) (100 ml) was refluxed for 1 h. The reaction mixture was poured into the water (200 ml) and extracted with ether (150 ml). The ethereal layer was dried over anhydrous sodium sulfate and evaporated to give **8a** in a 54% (1.2 g) yield; mp 122—123 °C (from ethanol).

Reaction of 11a with Thionyl Chloride. (A) A mixture of **11a** (3 g, 8.67 mmol) and thionyl chloride (5 g, 42 mmol) was refluxed for 4 h. After cooling, ethanol (20 ml) and then water (100 ml) were added to the reaction mixture, and it was extracted with ether (70 ml). The subsequent evaporation of the solvent gave **7a** in a 21% (0.7 g) yield; mp 199—200 °C (from ethanol). (B) A mixture of **11a** (2.3 g, 6.65 mmol) and thionyl chloride (5 g, 42 mmol) was stirred at 50—60 °C for 3 h. After cooling, the reaction mixture was added, drop by drop, to ice water and then extracted with chloroform (50 ml). The subsequent evaporation of the solvent gave **10** in a 78% (1.9 g) yield; mp 199—201 °C.

Reaction of Methyl o-*(Allyloxy)benzoate with Hydrazine Hydrate.* A mixture of methyl *o*-(allyloxy)benzoate (15.2 g, 0.1 mol), hydrazine hydrate (50 g, 1 mol), and methanol (50 ml) was refluxed for 6 h. After the distillation of the methanol and the hydrazine hydrate, the residue was solidified to give [*o*-(allyloxy)benzoyl]hydrazine (**12**) in a 75% (11.4 g) yield.

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