171 mg (76%) of off-white solid, mp 100–105°. Recrystallization from 95% ethanol gave 160 mg of pyrazole **5**, mp 103.5–104.5°. Some other apparently identical preparations melted at 112–114°. The lower melting form could be converted to the higher melting form by finely pulverizing it. Its nmr spectrum ($CDCl_3$) showed absorption at τ 2.41 and 2.79 (ten aromatic protons in unresolved multiplets), 4.09 and 4.72 (one olefinic proton in each doublet, J = 1.35 cps), 5.96 and 6.05 (total of five protons—one methoxyl group and the methylene group), and 6.35 (three protons in methoxyl group). Significant peaks in the infrared region (KBr) were at 5.71 (with slight shouldering) (C=O), 10.97μ. However, in the Nujol mull the carbonyl peak was distinctly shouldered absorbing at 5.71 and 5.74 μ (shoulder). In methylene chloride it was sharp at 5.71 μ. The ultraviolet spectrum showed one rather broad peak: $\lambda_{\max}^{\mathrm{MeCN}}$ 257 mμ (log ϵ 4.40), $\lambda_{\max}^{\mathrm{MeOH}}$ 258 mμ (log ϵ 4.37).

Anal. Calcd for $C_{22}H_{20}N_2O_4$: C, 70.20; H, 5.36; N, 7.44. Found: C, 69.92; H, 5.57; N, 7.29.

Hydrolysis of Pyrazole 5.—A solution of 89 mg (0.23 mmole) of pyrazole **5** and 0.58 mmole of KOH in 2.6 ml of methanol was heated at reflux for 4.5 hr. After the solvent was removed under vacuum, the residue was dissolved in 6 ml of water and extracted two times with ether. The aqueous solution was acidified with 2 N hydrochloric acid and extracted with methylene chloride. After drying the solution, evaporation of the solvent and washing the residue with pentane–ether gave 62 mg (86% yield) of 3- (or 5-) carboxymethyl-4-(β-styryl)-5- (or 3-) phenylpyrazole (**6**). The melting point was 166–168° and two recrystallizations gave an analytically pure sample, mp 167–168.5°. Significant infrared absorptions (KBr) were at 2.99 (N–H), 3.27 (aromatic C–H), 3.41 (aliphatic C–H), 4.05 (broad) (acid O–H), 5.31 (broad), 5.85 (acid C=O), and 11.09 μ. The ultraviolet spectrum (MeOH) shows absorption at 248 mμ (log ϵ 4.29).

Anal. Calcd for $C_{19}H_{16}N_2O_2$: C, 74.98; H, 5.30; N, 9.20. Found: C, 75.10; H, 5.44; N, 8.97.

Base-Catalyzed Reaction of Pyrazole 5 in Methanol.—The progress of the hydrolysis of **5** with equivalent amounts of KOH in methanol was followed by tlc with visualization by quenching of the fluorescent indicator in the adsorbent. Development of the spots with ether–acetone (1:1) on silica gel showed compound **6** having an R_f value of 0.80 and the hydrolysis product having an R_f value 0.05. However, when the basic solution was spotted immediately after dissolution of **5**, a spot was present at 0.75 which disappeared during the course of the hydrolysis with concurrent increase in the area of the low R_f value spot. A solution of **5** and KOH in methanol in an equivalent ratio of 20:1 gave similar results when analyzed by tlc, *i.e.*, only one spot was visible under ultraviolet light and that was of lower R_f value than that of **5**.

A suspension of pyrazole **5** (75 mg, 0.189 mmole) in 1.5 ml of dry methanol was treated with a solution of 1 mg of sodium methoxide in 1 ml of methanol at room temperature. The solid dissolved rapidly and tlc of a sample of the solution showed one spot of R_f value 0.62 (pyrazole **5**; R_f value 0.70). The solution was concentrated and diluted with carbon tetrachloride prior to preparative tlc on silica gel (*ca.* 1.0-mm layer) with acetone–ether (1:1). Extraction of the front band with acetone gave 55 mg of a viscous oil (**6**) which could not be induced to crystallize. It had significant peaks in the infrared region (CCl_4) at 3.14 (N–H), 5.71 (C=O), and 11.05 μ. The nuclear magnetic resonances (CCl_4) were at τ 1.14 (N–H singlet), 2.61 and 2.90 (unresolved aromatic multiplets), 4.29 and 4.85 (slightly split olefinic resonances), 6.57 (methoxyl and methylenic protons), and 8.78 (complex resonances). The relative areas were 1.2, 10 (total aromatic), 0.8, 0.8, 4.3, and 0.6. The ultraviolet spectrum was obtained by dissolving a known amount of pyrazole **5** in methanol, measuring the absorbances, and then adding a trace of sodium methoxide to the solution. After shaking the solution for a few seconds, the spectrum of monester was obtained, $\lambda_{\max}^{\mathrm{MeOH}}$ 250 mμ (log ϵ 4.33). This peak was unchanged in position or intensity after several hours. When a small portion of the carboxylic acid described in the previous experiment was treated with diazomethane, tlc showed a single spot. This spot had an R_f value the same as that of the oil described above.

In one case, a small-scale, base-catalyzed reaction was run in a methanol–ether mixture. Tlc of the solution again showed only one spot. However, upon vapor phase chromatography (5 ft × $^1/_8$ in. column of 6% Apiezon L on Chromsorb Z at 30°) of the solution, a peak appeared at a retention time that was the same as that of dimethyl carbonate.

3-Phenyl 4-(β-Styryl)-5-carbomethoxy-5-carbomethyoxymethylpyrazolenine (?) (4).—A carbon tetrachloride solution of the red diazomethane **3** was allowed to remain in a freezer for 38 days. The faintly colored solution was then chromatographed on 20 g of silica gel in an ice-water-jacketed column. Elution with pentane–ether (9:1, followed by 4:1) gave some small oily fractions followed by several cuts which were indicated by tlc to contain only one component in appreciable amounts. Its colorless thin layer spot became deep red when treated with 50% H_2SO_4 and heated. The R_f value of the compound was slightly less than that of **3** when developed with hexane–ether. This product was obtainable only as a moderately stable oil which could be maintained with little loss only at freezer temperatures or below.

The purest chromatography cuts were concentrated and the solvents were replaced with carbon tetrachloride for spectral data. Tlc indicated the presence of two minor impurities in the resulting solution. The nmr spectrum of the solution at −5° showed absorptions at τ 1.99 and 2.83 (aromatic protons) and at 4.26 and 4.80 (terminal olefinic protons) with areas in the ratio of 2:8:1:1. Two resonances of unequal area at τ 6.55 (methoxyl protons) and 6.70 (methoxyl and methylenic protons) had a total area of 7.6 relative to 10 for the aromatic protons. In addition there were small unassigned absorptions at τ 6.35, 7.17, 7.48, 8.02, and 8.83 (total relative area *ca.* 2.7). The infrared spectrum (CCl_4) exhibited significant peaks at 5.71 (sharp) (unconjugated C=O) and 10.95 μ. Absorption in the ultraviolet spectrum (MeCN) appeared at 242 and 303 mμ with relative extinction coefficients *ca.* 1.0:0.2.

Registry No.—**1**, 1669-47-2; **2**, 14565-27-6; **3**, 14638-75-6; **4**, 14638-76-7; **5**, 14565-28-7; **6**, 14565-29-8; diazomethane, 334-88-3.

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Chemistry of Furazan Derivatives. II.[1] The Reaction of Dibenzoylfuroxanes with Diazomethane

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It is known[3] that diazomethane reacts with aldehydes and ketones to give oxides or homologous ketones. The reaction occurs with liberation of nitrogen and is catalyzed by alcohols or water. We have now investigated the reaction of dibenzoylfuroxanes with diazomethane. No reaction occurs in dry carbon tetrachloride or chloroform, but addition of a small amount (0.5%) of methanol results in initiation of the evolution of nitrogen. Larger amounts of methanol cause degradation to the corresponding methyl benzoate derivatives. The main products of the reaction of **1** and **2** with diazomethane were isolated in about

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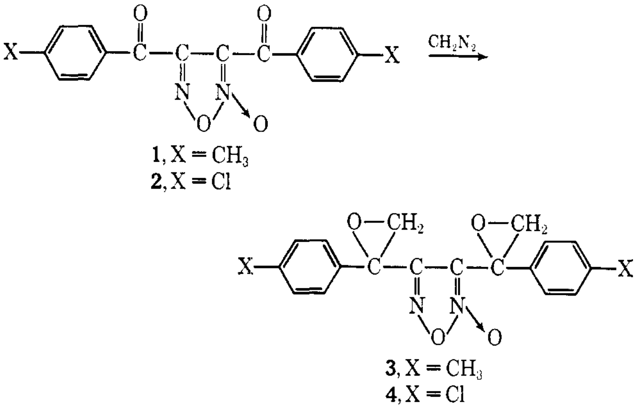
[1] Part I: A. R. Daniewski and T. Urbański, *Roczniki Chem.*, in press.

[2] To whom inquires should be addressed.

[3] C. D. Gutsche, *Org. Reactions*, **8**, 364 (1954).

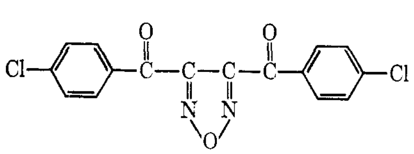
60% yield. The products were solids, melting at temperatures close to those for the starting compounds, but showing large melting point depressions for the corresponding mixtures. The infrared spectra of the products did not show the carbonyl stretching frequencies observed for the original furoxanes at about 1650–1680 cm^{-1}. The very strong absorption at about 1600 cm^{-1}, characteristic of the furoxane ring,[4] remains in the spectra of the products. Since diphenylfuroxane does not react with diazomethane, one may expect that the furoxane ring of **1** and **2** remains intact in the reaction. The spectra of product **4** show aliphatic C–H stretching frequencies at about 2950 cm^{-1} in addition to the aromatic C–H stretching vibrations observed for substance **2**. From these data tentative structures with oxirane rings were assigned to the products.



1, X = CH_3
2, X = Cl

3, X = CH_3
4, X = Cl

Conclusive evidence for structures **3** and **4** was obtained from nmr spectra and the lithium aluminum hydride reduction of **4**. The spectra of benzoylfuroxanes **1** and **2** show two AA'BB' systems in the region of aromatic absorption, corresponding to the two *para*-substituted benzene rings which are nonequivalent because of the asymmetry of the furoxane ring. The signal of the methyl groups in **1** is not split, which indicates that the long-range effect of the ⩾N→O group vanishes at that distance. A comparison of the chemical shifts of the aromatic protons for **2** (1.83, 2.47 ppm, one AA'BB' system; 2.22, 2.49 ppm, another AA'BB' system) with those for the corresponding furazane **5** (1.95, 2.49 ppm) shows that the signals at τ ~2.5 ppm in both the spectra correspond to the protons *ortho* to the chlorine atom while the signals at τ ~1.8–1.9 ppm are due to the protons *ortho* to the carbonyl group in **5** and to those in **2** which are on opposite side of the furoxane ring with respect to the ⩾N→O group. The other pair of aromatic protons, *ortho* to the carbonyl group in **2**, gives rise to a signal at τ 2.22 ppm thus indicating a statistical effect of magnetic shielding by the ⩾N→O group. Since the observed patterns for the aromatic protons belong to the AA'BB' type, the benzene ring must rotate around the carbonyl-phenyl bond at a rate sufficient to average out the differences resulting from different orientations of the protons relative to the C=O group.



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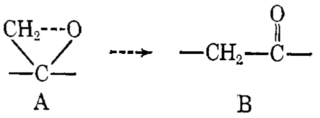
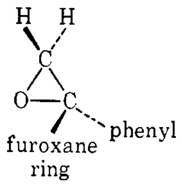
The spectra of the products **3** and **4** contain two AA'BB' patterns from aromatic protons (**3**, 3.00/3.26 and 3.06/3.06 ppm; **4**, 3.00/3.17 and 3.14/3.14 ppm) and two AB patterns in the range of τ 6.3–7.2 ppm (**3**, 6.38/7.10 and 6.88/7.19 ppm; **4**, 6.35/7.10 and 6.77/7.14 ppm) representing the $-CH_2-$ groups introduced into the molecule by action of diazomethane. The coupling constants revealed by the AB systems are $J = 6$ cps. This is quite a low value for geminal coupling constants and is consistent with structure A rather than B or other open-chain structures. A similar value of the geminal

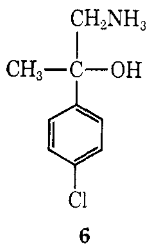


coupling constant, 6 cps, and the chemical shifts have been found for styrene oxide.[5] Magnetic nonequivalence of the two methylene groups is a result of long-range effects of the ⩾N→O group. One should note that the low-field halves of the AB systems show appreciable differences in chemical shifts, while the high-field parts lie at almost the same field. Considering the probable spatial arrangement of the molecule,



one may assign the signals at lower fields to the protons *cis* to the furoxane ring, as they should be much more affected by the long-range ⩾N→O effects than the *trans* protons. The chemical shifts for the aromatic protons of **3** and **4** suggest a diamagnetic shielding effect of the ⩾N→O group on the aromatic protons *ortho* to the epoxy function in the benzene ring that is nearer to the ⩾N→O group.

Reduction of **4** with lithium aluminum hydride, carried out as described in the literature[6–10] gave 1-amino-2-(*p*-chlorophenyl)-2-propanol hydrochloride (**6**).



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The structure was substantiated by the nmr spectrum. It shows four aromatic protons, an isolated methyl group, and an isolated $-CH_2-$ group adjacent

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[4] N. E. Boyer, G. M. Czerniak, H. S. Gutowsky, and H. R. Snyder, *J. Am. Chem. Soc.*, **77**, 4238 (1955).

[5] NMR Spectra Catalog, Vol. I, Varian Associates, Palo Alto, Calif., 1962, spectrum no. 193.

[6] A. Dornow, K. Fust, and H. D. Jordan, *Ber.*, **90**, 2124 (1957).

[7] A. F. Holleman, *ibid.*, **21**, 861 (1888).

[8] H. R. Snyder and N. E. Boyer, *J. Am. Chem. Soc.*, **77**, 4233 (1955).

[9] I. de Paolini, *Gazz. Chim. Ital.*, **57**, 656 (1927).

[10] C. R. Meloy and D. A. Shirley, *J. Org. Chem.*, **32**, 1255 (1967).

to a nitrogen atom. The infrared spectrum shows an OH peak at 3380 cm^{-1} and a broad absorption at 2500–3000 cm^{-1} characteristic of amine hydrochlorides.

Experimental Section

3,4-Di(4′-methylbenzoyl)furoxane[7] (1), mp 124°, 3,4-di(4′-chlorobenzoyl)furoxane[8] (2), mp 124°, and 3,4-di(4′-chlorobenzoyl)furazane[9] (5), mp 115°, were prepared according to procedures given in the literature.

3,4-Di(4′-methylphenyloxiranyl)furoxane (3).—To a solution of 1 g of **1** in 20 ml of dry chloroform was added ethereal diazomethane from 2 g of nitrosomethylurea and 0.5 ml of methanol. The mixture was left for 5 hr at room temperature. The solvents were distilled off under reduced pressure, and methanol (4 ml) was added to the residue. The product **3** crystallized and was purified by recrystallization from methanol. The yield was 0.65 g, 60%, mp 126°.

Anal. Calcd for $C_{20}H_{18}N_2O_4$: C, 68.65; H, 5.1; N, 8.0. Found: C, 68.5; H, 5.1; N, 7.8.

3,4-Di(4′-chlorophenyloxiranyl)furoxane (4).—The same procedure as above was used with 1 g of **2**. The product **4**, 0.7 g, yield 65%, melted at 128°.

Anal. Calcd for $C_{18}H_{12}Cl_2N_2O_4$: C, 55.3; H, 2.9; N, 7.2. Found: C, 55.4; H, 2.9; N, 7.1.

Reduction of 4 to 1-Amino-2-(*p*-chlorophenyl)-2-propanol Hydrochloride (6).—A solution of **4** (0.6 g) in anhydrous ether (20 ml) was added dropwise to lithium aluminum hydride (0.2 g) in anhydrous ether (20 ml) in a flask protected from atmospheric moisture. The reaction mixture boiled spontaneously, after which it was heated under reflux for *ca.* 15 min. Aqueous sodium hydroxide (2 ml of 10%) was added cautiously to the mixture; the precipitate was filtered off and the filtrate was dried over magnesium sulfate. The ether was distilled off and the residue was treated with ether saturated with HCl. A crystalline hydrochloride, **6**, resulted. It was recrystallized from an acetone–ethanol mixture. The yield was 0.4 g (63.5%), mp 190–193°.

Anal. Calcd for $C_9H_{13}Cl_2NO$: C, 48.7; H, 5.9; N, 6.3. Found: C, 49.0; H, 6.0; N, 6.3.

The nmr spectra were measured at 60 Mc/sec with a Varian HR-60 apparatus using 10% solutions in carbon tetrachloride of the substances **1** and **5** and with tetramethylsilane as standard. The product **6** was examined as a 10% solution in deuterium oxide with acetone as the standard.

The infrared spectra were measured with a Unicam SP-200 spectrometer.

Registry No.—**3**, 14002-09-6; **4**, 14002-10-9; **6**, 14002-11-0; diazomethane, 334-88-3.

Synthesis of 4H-3,1-Benzoxazin-4-ones from 2-Isocyanatobenzoyl Chloride and Aliphatic Amines

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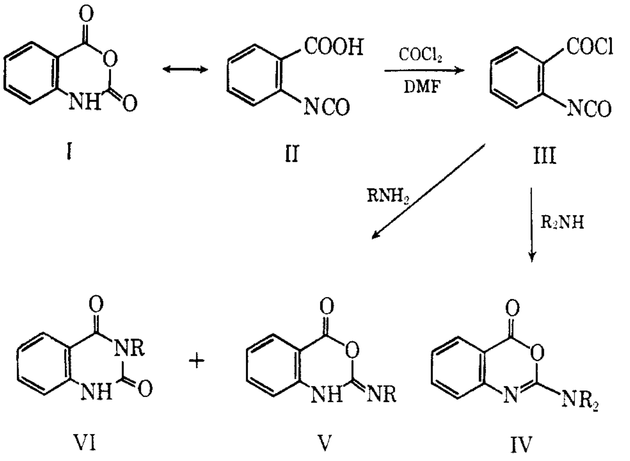
Received June 16, 1967

Whereas the reaction of 2-isocyanatobenzoyl chloride (III) with aromatic amines has been reported to afford ureidoamides,[1] we have found the reaction of III with primary and secondary aliphatic amines to give rise to the cyclic 4H-3,1-benzoxazin-4-ones V and IV, respectively (Scheme I). Compound IV was formed exclusively from the secondary amines, but an isomeric mixture of V and VI was obtained from the primary amines. The rearrangement of 1,2-dihydro-2-alkylimino-4H-3,1-benzoxazin-4-ones (V) to the 3-alkyl-2,4-quinazolinediones (VI) has been reported.[2,3]

Scheme I



The unequivocal synthesis of 4H-3,1-benzoxazin-4-ones (IV), having an endocyclic carbon–nitrogen double bond, verifies the hypothesis of Kurihara and Yoda,[4a] who predicted that the intensity of the C=N absorption band should be weaker than that of the C=O band in endocyclic C=N bond-containing 4H-3,1-benzoxazin-4-ones. Although the position of these absorptions in IV (C=N, 1667 cm^{-1}; C=O, 1761 cm^{-1}) are quite near to those of compound V (C=N, 1640–1690 cm^{-1}; C=O, 1730–1760 cm^{-1}),[3,4] for which the exocyclic structure has been postulated,[4a] the predicted order of intensity was verified in all cases.

The 2-isocyanatobenzoyl chloride (III) was prepared by the phosgenation of isatoic anhydride (I) in the presence of a catalytic[5] amount of N,N-dimethylformamide and the reaction proceeds most likely *via* 2-isocyanatobenzoic acid (II) as the intermediate. In the absence of catalyst no reaction took place.

The reaction of compound III with di-*n*-butylamine can be used as a quantitative analytical method. In the standard di-*n*-butylamine titration method for the determination of isocyanate equivalents,[6] for example, III consumes 2 equiv of the amine, thereby showing that the intermolecular reaction (which would require 3 equiv of amine) occurs at a much slower rate than does the intramolecular reaction.

Experimental Section[7]

2-Isocyanatobenzoyl Chloride (III).—To a suspension of isatoic anhydride (16.3 g, 0.1 mole) in chlorobenzene (165 ml) was added N,N-dimethylformamide (0.33 g, 2% by weight). Phosgene was passed through the mixture until a clear solution

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(1) Y. Iwakura, H. Uno, and S. Kang, *J. Org. Chem.*, **31**, 142 (1966). These authors obtained 3-phenylquinazoline-2,4-dione (VI, R = C_6H_5) by reacting 2-isocyanatobenzoyl chloride with aniline in the presence of tri-*n*-butylamine.

(2) H. Herlinger, *Angew. Chem.*, **76**, 437 (1964).

(3) J. C. Sheehan and G. D. Daves, Jr., *J. Org. Chem.*, **29**, 3599 (1964).

(4) (a) M. Kurihara and N. Yoda, *Tetrahedron Letters*, 2597 (1965); (b) G. Doleschall and K. Lempert, *ibid.*, 1195 (1963); (c) K. Lempert and G. Doleschall, *Monatsh. Chem.*, **95**, 950 (1964).

(5) The catalytic effect of N,N-dimethylformamide on the conversion of carboxylic acids to carboxylic acid chlorides, using phosgene, has been reported by H. H. Bosshard, R. Mory, M. Schmid, and H. Zollinger, *Helv. Chim. Acta*, **42**, 1653 (1959).

(6) S. Siggia and J. G. Hanna, *Anal. Chem.*, **20**, 1084 (1948).

(7) Analyses were by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Infrared spectra were determined on a Perkin-Elmer 21 spectrometer.