vided 51 mg of pale amorphous material (2), completely homogeneous on tlc.

Anal. Calcd exact mass for $C_{19}H_{26}N_2$: 282.2096. Found: 282.2093.

Pertinent spectral data for 2 are as follows: ir ($CHCl_3$) 3484 (N–H), 3012, 2940, 2846 (C–H) cm^{-1}; uv max (EtOH) 229 mμ (log ε 4.21), 283 (3.77), 291 (3.72); mass spectrum (70 eV) *m/e* (rel intensity) 282 (100), 281 (94), 225 (89), 144 (63); nmr ($CDCl_3$) δ 8.06 (s, 1 H), 7.0–7.6 (m, 4 H), 4.44 (t, 1 H), 1.0–3.4 (m, 11 H) 0.9 (s, 9 H).

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Photochemical Conversion of 4-(*o*-Nitrobenzylidene)-4*H*-pyrans to 1-Hydroxy-3-oxospiro[indoline-2,4′-[4′*H*]pyran] Derivatives

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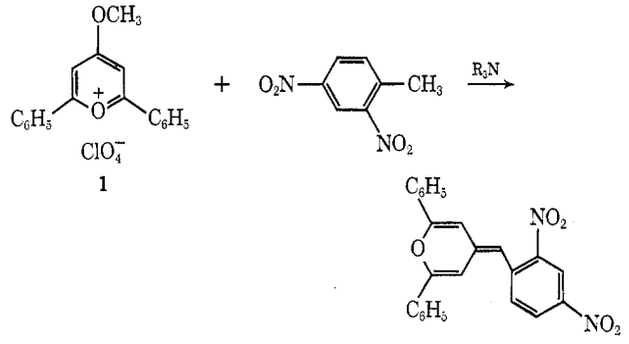
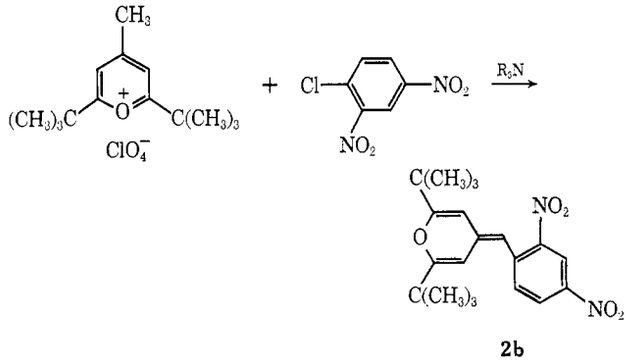
The conversion referred to in the title was investigated for three examples. The structures of the photoproducts were deduced from spectroscopic data and confirmed by chemical transformations.

A variety of compounds have been prepared by the reaction of pyrylium salts with nucleophiles,[1] and we have extended these to include the benzylidenepyran derivative **2a**, which was formed by the reaction of 4-methoxy-2,6-diphenylpyrylium perchlorate (**1**) with 2,4-dinitrotoluene in the presence of a tertiary amine.



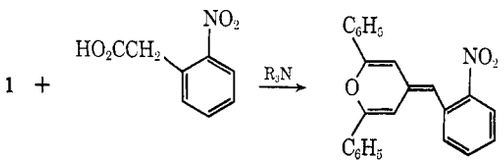
1 **2a**

In the course of handling **2a**, it was noticed that both the solid (KBr pressing) and a dilute solution rapidly faded when exposed to room light leading us to investigate this photoreaction. In order to facilitate the interpretation of nmr spectra of the photoproducts, we synthesized the di-*tert*-butyl analog (**2b**),



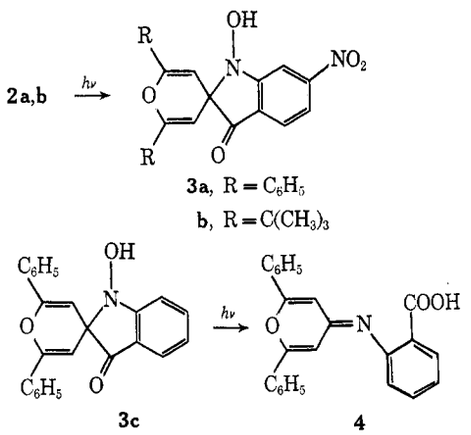
2b

and to simplify the mass spectra and chemical degradation as well as to test the scope of the reaction, we prepared the mononitro derivative **2c** and investigated the photolysis of these three compounds.



2c

The photolysis of **2a** and **2b** gave products that were isomeric with **2a** and **2b** in nearly quantitative yields. As shown below, structures **3a** and **3b** were assigned to these products. On the other hand, the photolysis of the mononitro compound **2c** yielded, besides the corresponding product (**3c**), another isomeric substance (**4**), which was found to be a photochemical rearrangement product of **3c**.



3a, R = C_6H_5
b, R = $C(CH_3)_3$

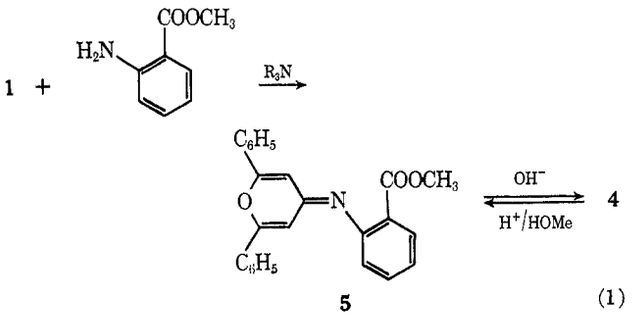
3c **4**

The structure of **4** was established through an independent synthesis shown in eq 1.

A number of chemical transformations were carried out on the photoproducts **3a–c** and are summarized in Scheme I. These and the spectroscopic data, discussed below, were used to elucidate the structure of the photoproducts **3a–c**.

Treatment of compounds **3a–c** with perchloric acid gave the benzisoxazole derivatives **6a–c**, which, in

(1) K. Dimroth, *Angew. Chem.*, **72**, 331 (1960).



5 (1)

turn, were hydrolyzed with aqueous pyridine to give **7a–c**. Compound **7a** with ammonia gave the pyridine derivative **8**.

The photoproducts **3a–c** were readily methylated with methyl iodide and potassium carbonate giving **9a–c**, which, in contrast to **3a–c**, did not undergo the facile rearrangement with acid to benzisoxazoles. Treatment of these methylated derivatives with 60% perchloric acid or trifluoroacetic acid led merely to ring opening to give **10a–c** as was shown by nmr. This reaction is reversible as **9a–c** were recovered on dilution with water. On the other hand, heating **9a–b** with 20% perchloric acid gave **11a–b**.

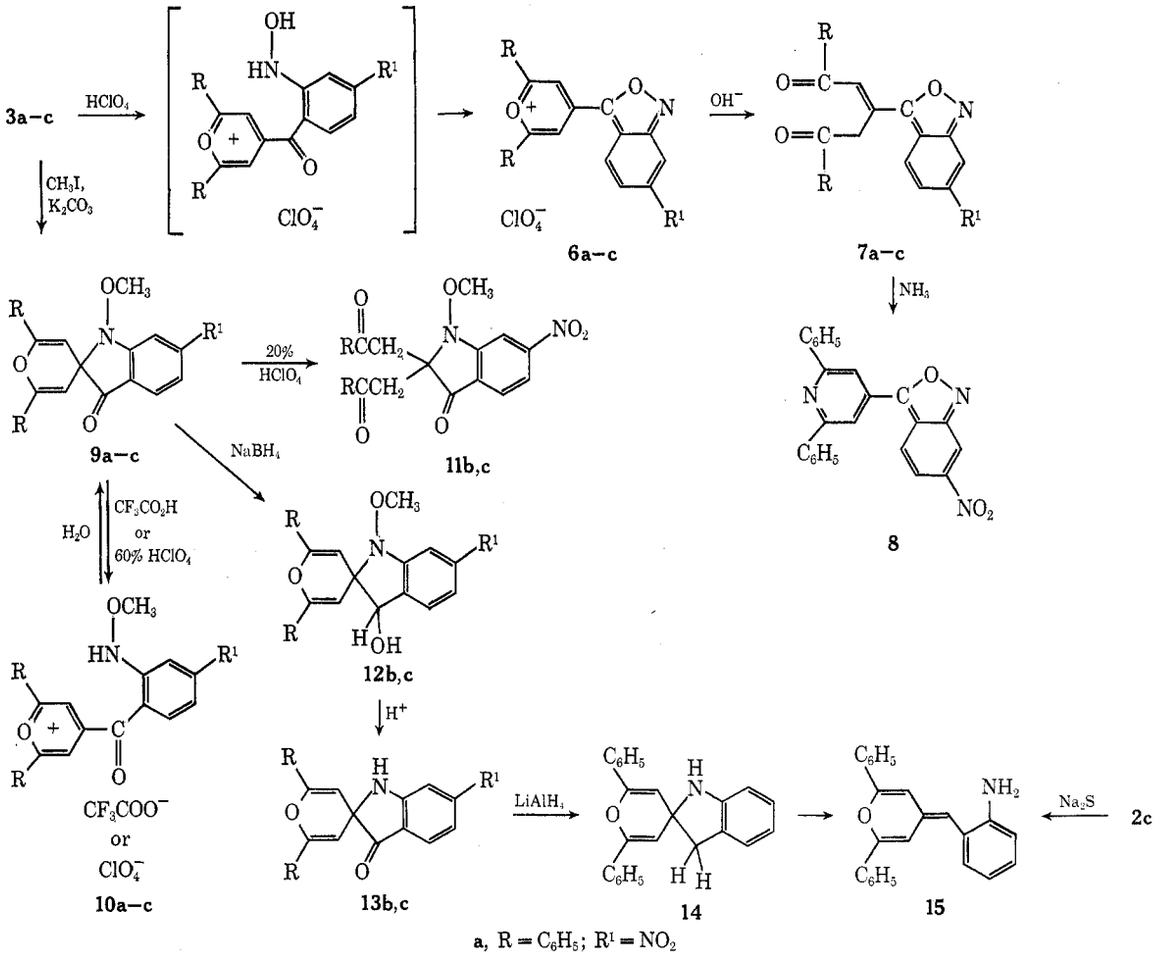
Compounds **9b** and **9c** were reduced with sodium borohydride to the carbinols **12b** and **12c**, which, on treatment with a trace of acid, eliminate methanol to give **13b** and **13c**. Interestingly, solutions of **12b** were very sensitive to aerial oxidation giving the starting ketone **9b**, and, in order to obtain pure **13b**, the reaction had to be carried out under oxygen-free conditions.

Compound **13c** was reduced with lithium aluminum hydride to give an unstable product **14** (identified by nmr), which quantitatively rearranged to the primary amine **15**. This last compound was prepared by an alternative method.

The ir spectrum of **3b** showed a broad hydroxyl band at *ca.* 3400 cm^{-1} and absorptions at 1718 and 1695 cm^{-1}, which we assign to the ketone and the pyran C=C double bond, respectively.

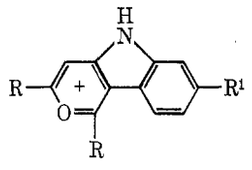
The photoproduct **3b** shows in the visible region a complex spectrum of overlapping bands [in benzene; broad maximum at 395–410 nm (ϵ 1950)]. Ethanol causes a shift to longer wavelength [λ_{max} 440 nm (ϵ 1850)]. Addition of a small amount of pyridine to the benzene solution led to a spectrum similar to that in ethanol. The spectrum of the methylated derivative **9b**, on the other hand, does not display such solvent dependency. Compound **9b** showed two poorly resolved maxima at 385 (ϵ 1890) and 415 nm (ϵ 1850) in either benzene or ethanol. The difference between the two compounds could be attributed to solvation of the hydroxyl compound *via* hydrogen bonding.

SCHEME I



a, R = C_6H_5; R^1 = NO_2
b, R = *t*-Bu; R^1 = NO_2
c, R = C_6H_5; R^1 = H

The photoproducts **3a–c**[2] and their methylated derivatives **9a-c**, as well as the acetylation product of **3a**, show in the mass spectrum an efficient cleavage of OH, OCH_3, or $OCOCH_3$, respectively, which is followed by decarbonylation to give an ion of the probable structure A. In a similar pattern the carbinols **12b**



A

R = C_6H_5 or *t*-Bu
R^1 = H or NO_2

and **12c** cleave OCH_3 and formaldehyde successively to give ion A. This ion is the base peak in the mass spectrum of **13b** and **13c**, which is formed by loss of HCO. The fact that the predominant cleavage of the carboxylic acid **4** is the loss of COOH gives support for the structure of the common ion A.

The two protons of the pyran moiety in the photoproducts **3a–c**, in their methylated derivatives **9a–c**, and in **13b**, **13c**, and **14** are equivalent.[3] The two *tert*-butyl groups in **3b**, **9b**, and **13b** are also equivalent. This equivalence is due to the rapid inversion at the ring nitrogen. The pyran protons in **12b** and **12c** and the *tert*-butyl groups in **12c** are not equivalent. This is due to the asymmetric >CH–OH group, which gives different environments to the substituents on the pyran ring. The measured long-range coupling constants of 2.4 and 2.3 Hz between the pyran protons in **12b** and **12c** are in the expected range.

Owing to internal asymmetry in **11b**, the geminal protons of each CH_2 group are not equivalent (δ 3.02 and 3.52, $|J|$ = 17.7 Hz), whereas both CH_2 groups and all methyl groups of the *tert*-butyl groups are identical. This nonequivalence of the methylene protons is intrinsic to the structure regardless of hindered rotation or preference of conformers. The two methylene protons, however, undergo different $Eu(dpm)_3$-induced shifts in the ratio of 1.2:1. This could be explained in terms of preference to one or more of the different rotamers which would result in uneven statistical distribution of these protons along the orbit they describe by rotation along the ring-carbon–CH_2 bond.

The $LiAlH_4$ reduction product of **13c** shows signals indicative of the spiro compound **14**: equivalent pyran protons (δ 5.82) and benzylic protons at 3.10. This compound, however, is not stable in $CDCl_3$ solution, even when the $CDCl_3$ was treated with $NaHCO_3$ and diluted with a few drops of pyridine-d_5. This spiro derivative underwent conversion into **15** within 1 hr at ~35°.

The photochemical cycloaddition of nitro compounds to olefinic bonds is well known, and reaction mechanisms for this type of reaction have been discussed.[4] From the reaction of nitrobenzene with cyclohexene, a thermally unstable five-membered cycloadduct was isolated.[4] Irradiation ($\lambda \geq 546$ nm) of **2a** or **2c** at −60° in dimethoxyethane or in toluene resulted in decoloration of the deep red solution to a pale yellow. Under these conditions the primary photoproduct appeared to be stable. After the solution had warmed to room temperature, the color changed to green and then rapidly to orange and **3a** or **3c** precipitated.[5] In chloroform or in methylene chloride the primary photoproduct had a much shorter lifetime, and the thermal reactions took place at −60°. This solvent dependency gives support to the nonpolar nature of this intermediate. In order to obtain evidence for an intermediate analogous to that reported for simple nitro compounds,[4] **3a** and **3c** were irradiated at −60° in the cavity of an nmr spectrometer in deuteriotoluene. The signals from the starting materials rapidly disappeared, and a completely washed out spectrum was obtained. This result must be due to the formation of some free radicals during the photolysis.

Experimental Section

Melting points are uncorrected. Infrared spectra were determined with a Perkin-Elmer 467 spectrophotometer, ultraviolet spectra with a Cary Model 15 spectrophotometer, nmr spectra with a Bruker 90-MHz spectrometer, and mass spectra with a Consolidated Electrodynamics Model 21-110B instrument. The nmr chemical shifts are reported on the δ scale downfield from internally added tetramethylsilane. The electronic spectra were determined in acetonitrile. The *m/e* with a relative intensity greater than 5% are listed.

2,6-Diphenyl-4-(2,4-dinitrobenzylidene)-4*H*-pyran (2a).—A mixture of 3.5 g of 1,[6] 2 g of 2,4-dinitrotoluene, 3 ml of diisopropylethylamine, and 20 ml of acetic anhydride was refluxed for 15 min, and chilled. The solid crystallized from acetonitrile yielding 4 g of **2a**: mp 209–210°; λ_{max} ($\epsilon \times 10^{-3}$) 250 (20.2), 315 (10.0), and 490 nm (11.6); mass spectrum *m/e* (rel %), 412 (33), 395 (36), 367 (12), 261 (100), and 105 (95).

Anal. Calcd for $C_{24}H_{16}N_2O_5$: C, 70.0; H, 3.9; N, 6.8. Found: C, 70.3; H, 4.1; N, 6.7.

2,6-Di-*tert*-butyl-4-(2,4-dinitrobenzylidene)-4*H*-pyran (2b).—A mixture of 9 g of 2,6-di-*tert*-butyl-4-methylpyrylium perchlorate,[7] 7 g of 2,4-dinitrochlorobenzene, 8.6 g of diisopropylethylamine, and 100 ml of ethyl alcohol was refluxed for 30 min and chilled; the solid crystallized from alcohol giving 7 g of **2b**: mp 125–126°; mass spectrum *m/e* 372 (41), 355 (63), 327 (13), 221 (100), and 209 (10).

Anal. Calcd for $C_{20}H_{24}N_2O_5$: C, 64.5; H, 6.5; N, 7.5. Found: C, 64.6; H, 6.4; N, 7.3.

2,6-Diphenyl-4-(2-nitrobenzylidene)-4*H*-pyran (2c).—A mixture of 7.4 g of *o*-nitrophenylacetic acid, 14 g of **1**, 12 ml of diisopropylethylamine, and 60 ml of alcohol was refluxed for 30 min and cooled, and 15 ml of 70% perchloric acid was added. After the mixture was chilled, the solid was collected and crystallized from a mixture of pyridine and methanol giving 3 g of **2c**: mp 102–103°; λ_{max} ($\epsilon \times 10^{-3}$) 248 (35.3), ~272 (21.7), 340 (24.5), 400 (12.2) with tail to 500 nm; mass spectrum *m/e* 367 (30), 350 (36), 322 (36), 261 (95), 220 (11), 215 (19), and 105 (100).

Anal. Calcd for $C_{24}H_{17}NO_3$: C, 78.7; H, 4.4; N, 3.8. Found: C, 79.0; H, 4.6; N, 3.5.

(2) The starting materials **2a–c** show in the mass spectrum, besides other ions, a pattern cleavage similar to that of their photolysis products (*i.e.*, successive loss of OH and CO). This could indicate that the electron impact leads to the same photolysis products.

(3) The signals of the pyran protons in the di-*tert*-butyl derivatives appear at δ 4.5 and those in the diphenyl derivatives at δ 5.3–5.8. The signals of the *tert*-butyl groups in the above compounds appear at δ 1.1–1.2.

(4) J. L. Charlton, C. C. Liao, and P. de Mayo, *J. Amer. Chem. Soc.*, **93**, 2463 (1971).

(5) We made use of the stability of this primary photoproduct to prepare **3c** in high purity without its partial photochemical conversion into **4**, which takes place if the irradiation is carried out at room temperature.

(6) J. A. Van Allan, G. A. Reynolds, and D. P. Maier, *J. Org. Chem.*, **33**, 4418 (1968).

(7) A. T. Balaban and C. D. Nenitzescu, *Justus Liebigs Ann. Chem.*, **625**, 74 (1959).

2′,6′-Diphenyl-1-hydroxy-6-nitro-3-oxospiro[indoline-2,4′-[4′*H*]pyran] (3a).—A solution of 1 g of **2a** in 800 ml of methylene chloride in a Pyrex flask was irradiated with a 75-W flood lamp for 1 hr. After the solvent had evaporated, the residue was crystallized from chlorobenzene yielding 0.9 g of **3a**: mp 211–212°; ir (KBr) 3343, (OH) 1714 (CO), 1680 (pyran), 1530, 1365 cm^{-1} (NO_2); λ_{max} ($\epsilon \times 10^{-3}$) 250 (49.0) and 380–450 nm (2.0); mass spectrum *m/e* 412 (27), 395 (100), 367 (32), 351 (14), 321 (41), and 320 (40).

Anal. Calcd for $C_{24}H_{16}N_2O_5$: C, 70.0; H, 3.9; N, 6.8. Found: C, 70.1; H, 4.2; N, 7.1.

2′,6′-Di-*tert*-butyl-1-hydroxy-6-nitro-3-oxospiro[indoline-2,4′-[4′*H*]pyran] (3b).—This compound was prepared by the method described for **3a**: yield 98%; mp 195–196° (from toluene); λ_{max} ($\epsilon \times 10^{-3}$) 249 (30.0) and 425 nm (2.0) very broad; mass spectrum *m/e* 372 (30), 355 (100), 327 (32), 313 (13), 289 (7), 287 (10), 271 (15), 225 (11), 209 (10), and 57 (77).

Anal. Calcd for $C_{20}H_{24}N_2O_5$: C, 64.5; H, 6.5; N, 7.5. Found: C, 64.3; H, 6.8; N, 7.2.

2′,6′-Diphenyl-1-hydroxy-3-oxospiro[indoline-2,4′-[4′*H*]pyran] (3c).—A solution of **2c** (1.0 g) in toluene (50 ml) was divided into five portions and each was irradiated for 40 min at −60° with a 200-W PEK super high pressure Hg arc through a Corning C.S. 3-70 filter (λ >490 nm). The deep red solution turned to pale yellow at the end of the irradiation. When the solution had warmed up to room temperature, its color changed to red and **3c** crystallized out: yield 0.72 g. Another 0.15 g of **3c** was obtained from the concentrated mother liquor: total yield 87%; mp 189–190°; ir (KBr) 3390 (OH), 1724 (CO), and 1695 (pyran); λ_{max} ($\epsilon \times 10^{-3}$) 238 (43.0) and 330–380 (2.0) very broad; mass spectrum *m/e* 367 (17), 350 (57), 322 (93), 246 (11), 218 (13), 217 (16), 105 (100), and 77 (57).

Anal. Calcd for $C_{24}H_{17}NO_3$: C, 78.7; H, 4.4; N, 3.8. Found: C, 78.3; H, 4.8; N, 3.7.

4-(2-Carboxyphenylimino)-2,6-diphenyl-4*H*-pyran (4). Method A.—This compound was prepared from **2c** as described under **3c** by using 1,2-dimethoxyethane as a solvent and irradiating at room temperature. During the irradiation compound **4** crystallized out: yield 75%, mp 203–205° (from dimethoxyethane). The same compound was obtained on starting with **3c** instead of **2c**.

Method B.—A mixture of 0.5 g of 4-(2-carbomethoxyphenylimino)-2,6-diphenyl-4*H*-pyran (**5**) and 0.5 g of potassium hydroxide in 10 ml of methanol was refluxed for 30 min, and the solid was collected and crystallized from aqueous acetic acid giving 0.3 g of **4**, mp 260–262°, which showed spectral properties that were identical with those of **4** prepared by method A. The mass spectrum showed 367 (23), 322 (100), 246 (14), 218 (14), 217 (14), 105 (33), and 77 (42).

Anal. Calcd for $C_{24}H_{17}NO_3$: C, 78.7; H, 4.4; N, 3.8. Found: C, 78.4; H, 4.7; N, 3.8.

4-(2-Carbomethoxyphenylimino)-2,6-diphenyl-4*H*-pyran (5). Method A.—A mixture of 0.6 g of **4** (prepared by method A), 3 ml of concentrated sulfuric acid, and 30 ml of methanol was refluxed for 2 hr and concentrated. The residue was dissolved in water; 3 ml of 60% perchloric acid was added to the solution. The solid was collected and crystallized from ligroin (bp 63–75°) yielding 0.4 g of **5**, mp 149–150°.

Method B.—A mixture of 3 g of **1** and 10 ml of methyl anthranilate was refluxed for 10 min, cooled, diluted with methanol and ether until turbid, and then chilled giving 2.1 g of **5**: mp 150–151°; mass spectrum *m/e* 381 (78), 380 (8), 350 (6), 322 (100), 246 (16), 245 (8), 218 (15), 217 (16), 216 (11), 105 (73), 102 (6), and 77 (60).

Anal. Calcd for $C_{25}H_{19}NO_3$: C, 78.7; H, 5.0; N, 3.7. Found: C, 78.5; H, 5.1; N, 3.6.

4-(6-Nitro-2,1-benzisoxazol-3-yl)-2,6-diphenylpyrylium Perchlorate (6a).—To a solution of 0.5 g of **3a** in 10 ml of formic acid was added 0.5 ml of 70% perchloric acid, and the solid was collected and washed with ether: yield 0.5 g, mp 304° (explodes).

Anal. Calcd for $C_{24}H_{15}ClN_2O_8$: C, 58.1; H, 3.4; N, 5.7. Found: C, 58.0; H, 3.4; N, 5.6.

2,6-Di-*tert*-butyl-4-(6-nitro-2,1-benzisoxazol-3-yl)pyrylium Perchlorate (6b).—Compound **6b** was prepared from **3b** and perchloric acid in acetic acid: mp 244–245°; λ_{max} ($\epsilon \times 10^{-3}$) 244 nm (31.9).

Anal. Calcd for $C_{20}H_{23}ClN_2O_8$: C, 52.8; H, 5.1; N, 6.1. Found: C, 52.8; H, 5.1; N, 6.1.

4-(2,1-Benzisoxazol-3-yl)-2,6-diphenylpyrylium Perchlorate (6c).—Perchloric acid was added to a solution of **3c** in acetic acid giving **6c** in quantitative yield, mp 263–264°.

Anal. Calcd for $C_{24}H_{16}ClNO_6$: C, 64.2; H, 3.6; N, 3.1. Found: C, 63.9; H, 3.6; N, 3.1.

3-(2-Benzoyl-1-phenacylidenethyl)-6-nitro-2,1-benzisoxazole (7a).—A solution of 1 g of **6a** in 8 ml of boiling pyridine was diluted with 20 ml of methanol and chilled giving 0.6 g of **7a**: mp 164–165°; λ_{max} ($\epsilon \times 10^{-3}$) 278 (21.5) and 360 nm (13.0); mass spectrum *m/e* 412 (13), 383 (8), 307 (100), 291 (7), 290 (8), and 105 (off scale).

Anal. Calcd for $C_{24}H_{16}N_2O_5$: C, 69.7; H, 3.9; N, 6.8. Found: C, 70.0; H, 4.0; N, 7.0.

6-Nitro-3-(1,3-dipivaloylpropen-2-yl)-2,1-benzisoxazole (7b).—Compound **7b** was prepared from **6b** by the method described for **7a**: mp 94–95° (from methanol); λ_{max} ($\epsilon \times 10^{-3}$) 276 (16.7), 332 (9.55), and ~360 nm (8.7); mass spectrum *m/e* 372 (75), 352 (10), 315 (100), 288 (25), 287 (32), 273 (20), 271 (25), 260 (10), 259 (20), 245 (30), 231 (65), 204 (25), 203 (18), 85 (100), 57 (off scale), and 41 (100).

Anal. Calcd for $C_{20}H_{24}N_2O_5$: C, 64.5; H, 6.5; N, 7.5. Found: C, 64.7; H, 6.4; N, 7.2.

3-(2-Benzoyl-1-phenacylidenethyl)-2,1-benzisoxazole (7c).—The procedure described for the preparation of **7a** was used and water was added to precipitate the **7c**: yield 68%; mp 109–110° (from aqueous alcohol); mass spectrum *m/e* 367 (8), 339 (6), 338 (8), 262 (50), 246 (6), 245 (6), 234 (5), 105 (100), and 77 (67).

Anal. Calcd for $C_{24}H_{17}NO_3$: C, 78.5; H, 4.6; N, 3.8. Found: C, 78.2; H, 4.9; N, 4.0.

3-(2,6-Diphenyl-4-pyridyl)-6-nitro-2,1-benzisoxazole (8).—A solution of 0.5 g of **7a** and 0.5 g of ammonium carbonate in 20 ml of acetic acid was refluxed for 10 min and cooled. The solid was collected and crystallized from pyridine giving 0.3 g of **8**: mp 221–222°; mass spectrum *m/e* 393 (100), 347 (13), 346 (13), 319 (7), 318 (9), 290 (9), 244 (20), 230 (5), 216 (6), 127 (22), 77 (12).

Anal. Calcd for $C_{24}H_{15}N_3O_3$: C, 73.4; H, 3.8; N, 10.7. Found: C, 73.3; H, 3.6; N, 10.6.

2′,6′-Diphenyl-1-methoxy-6-nitro-3-oxospiro[indoline-2,4′-[4′*H*]pyran] (9a).—A mixture of 1 g of **3a**, 3 ml of methyl iodide, 1 g of potassium carbonate, and 10 ml of acetone was stirred in a stoppered flask for 3 hr and filtered; the filtrate was evaporated to dryness. The residue was crystallized from methyl alcohol giving 0.8 g of **9a**: mp 219–220°; λ_{max} ($\epsilon \times 10^{-3}$) 252 (47.0) and 370–420 nm (2.0); mass spectrum *m/e* 426 (27), 395 (100), 368 (10), 367 (15), 321 (28), 320 (15), 105 (75), 77 (30).

Anal. Calcd for $C_{25}H_{18}N_2O_5$: C, 70.5; H, 4.2; N, 6.4. Found: C, 70.4; H, 4.3; N, 6.5.

2′,6′-Di-*tert*-butyl-1-methoxy-6-nitro-3-oxospiro[indoline-2,4′-[4′*H*]pyran] (9b).—This compound was prepared from **3b** using the procedure described for the preparation of **9a**: yield 98%; mp 156–157° from methanol; ir no hydroxyl absorption, 1726 (CO), 1691 cm^{-1} (pyran); λ_{max} ($\epsilon \times 10^{-3}$) 249 (19.8) and 350–450 nm (1.1); mass spectrum *m/e* 386 (16), 355 (100), 328 (10), 327 (12), 313 (7), 289 (8), 271 (11), 255 (7), 225 (9), and 57 (65).

Anal. Calcd for $C_{21}H_{26}N_2O_5$: C, 65.0; H, 6.8; N, 7.3. Found: C, 65.3; H, 7.0; N, 7.4.

2′,6′-Diphenyl-1-methoxy-3-oxospiro[indoline-2,4′-[4′*H*]pyran] (9c).—Compound **9c** was prepared from **3c** by the method described for **9a**: yield 82%; mp 119–120° from methanol; λ_{max} ($\epsilon \times 10^{-3}$) 238 (41.6) and 330–380 nm (1.8); mass spectrum *m/e* 381 (27), 350 (100), 322 (40), 217 (7), 216 (7), 105 (90), and 77 (37).

1-Methoxy-6-nitro-2,2-diphenacyl-3-indolinone (11a).—A mixture of 1 g of **9a**, 5 ml of 20% perchloric acid, and 25 ml of acetic acid was heated until a solution was obtained. The solution was cooled and diluted with water; the solid recrystallized from a mixture of methanol and pyridine giving 0.6 g of **11a**: mp 174–175°; λ_{max} ($\epsilon \times 10^{-3}$) 250 (48.0) and 300–420 nm (2.1); mass spectrum *m/e* 444 (12), 105 (100), and 77 (28).

Anal. Calcd for $C_{25}H_{20}N_2O_6$: C, 67.6; H, 4.5; N, 6.3. Found: C, 67.7; H, 4.7; N, 6.6.

1-Methoxy-6-nitro-2,2-bispivaloylmethyl-3-indolinone (11b).—The method described for **11a** was used with **9a** giving **11b**, yield 74%, mp 168–169° from methanol.

Anal. Calcd for $C_{21}H_{18}N_2O_6$: C, 62.4; H, 7.0; N, 6.9. Found: C, 62.1; H, 7.1; N, 6.8.

2′,6′-Di-*tert*-butyl-3-hydroxy-1-methoxy-6-nitrospiro[indoline-2,4′-[4′*H*]pyran] (12b).—To a stirred solution of 1 g of **9b** in 75

ml of isopropyl alcohol was added 0.5 g of sodium borohydride, and the solution was stirred for 0.5 hr and diluted with water, and the solid crystallized from alcohol: mp 124–125° dec; λ_{max} ($\epsilon \times 10^{-3}$) 250 (22.8) and 360 nm (1.8); mass spectrum *m/e* 388 (15), 357 (100), 327 (23), 313 (13), 311 (14), 271 (10), 165 (8), and 57 (30).

Anal. Calcd for $C_{21}H_{28}N_2O_5$: C, 64.9; H, 7.3; N, 7.2. Found: C, 64.9; H, 7.0; N, 7.0.

2′,6′-Diphenyl-3-hydroxy-1-methoxyspiro[indoline-2,4′-[4′*H*]-pyran] (**12c**).—Compound **9c** was reduced with sodium borohydride as described for **12b** giving **12c**: mp 127–130°; mass spectrum *m/e* 383 (20), 252 (100), 322 (47), 246 (12), 233 (13), 218 (8), 217 (9), and 105 (36).

Anal. Calcd for $C_{25}H_{21}NO_3$: C, 78.3; H, 5.5; N, 3.7. Found: C, 77.9; H, 5.2; N, 3.5.

2′,6′-Di-*tert*-butyl-6-nitro-3-oxospiro[indoline-2,4′-[4′*H*]pyran] (**13b**).—A solution of 0.5 g of **12b** in 25 ml of degassed chloroform was acidified with 0.5 ml of acetic acid and concentrated under vacuum. The residue was recrystallized from alcohol giving 0.4 g of **13b**: mp 238–239°; λ_{max} ($\epsilon \times 10^{-3}$) 247 (21.6), 273 (15.2), and ~305 nm (11.1); mass spectrum *m/e* 356 (12), 327 (100), 315 (62), 313 (29), 282 (10), 281 (9), 271 (42), 267 (9), 266 (9), 225 (5), and 57 (13).

Anal. Calcd for $C_{20}H_{24}N_2O_4$: C, 67.4; H, 6.8; N, 7.9. Found: C, 67.1; H, 6.7; N, 7.9.

2′,6′-Diphenyl-3-oxospiro[indoline-2,4′-[4′*H*]pyran] (**13c**).—Compound **12c** was allowed to react as described for the preparation of **13b** giving **13c**: yield 65%; mp 208–209° from alcohol; mass spectrum *m/e* 351 (14.3), 324 (6), 323 (35), 322 (100), 246 (11), 218 (13), 217 (17), 216 (8), and 105 (20).

Anal. Calcd for $C_{24}H_{17}NO_2$: C, 82.0; H, 4.9; N, 4.0. Found: C, 81.8; H, 5.0; N, 4.0.

2,′6′-Diphenylspiro[indoline-2,4′-[4′*H*]pyran] (**14**).—A solution of 0.2 g of **13c** in 10 ml of ether was treated with 0.1 g of lithium aluminum hydride. After the mixture had been stirred for 15 min, an nmr spectrum was determined on a sample (for results see discussion of nmr spectrum).

4-(2-Aminobenzylidene)-2,6-diphenyl-4*H*-pyran (**15**). **Method A.**—A solution of 0.5 g of **2c** in 50 ml of hot alcohol was treated with 2 g of sodium sulfide, refluxed overnight, and filtered; the hot filtrate was diluted with water and chilled. The solid was collected and crystallized from aqueous alcohol giving 0.3 g of **15**: mp 107–108°; mass spectrum *m/e* 337 (100), 336 (52), 232 (19), 230 (14), 168.5, 115 (7), 105 (26), and 77 (24).

Anal. Calcd for $C_{24}H_{19}NO$: C, 85.4; H, 5.6; N, 4.1. Found: C, 85.3; H, 5.5; N, 4.2.

Method B.—The ether solution of **14** was allowed to stand for 1 hr, and the nmr spectrum was identical with that of **15** prepared by method A.

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Registry No.—**1**, 17539-77-4; **2a**, 40576-44-1; **2b**, 40576-45-2; **2c**, 40576-46-3; **3a**, 40576-47-4; **3b**, 40576-48-5; **3c**, 40576-49-6; **4**, 40576-50-9; **5**, 40576-51-0; **6a**, 40576-52-1; **6b**, 40576-53-2; **6c**, 40576-54-3; **7a**, 40576-55-4; **7b**, 40576-56-5; **7c**, 40576-57-6; **8**, 40576-58-7; **9a**, 40576-59-8; **9b**, 40576-60-1; **9c**, 40576-61-2; **11a**, 40576-62-3; **11b**, 40576-63-4; **12b**, 40576-64-5; **12c**, 40576-65-6; **13b**, 40576-66-7; **13c**, 40576-67-8; **14**, 40576-68-9; **15**, 40576-69-0; 2,6-di-*tert*-butyl-4-methylpyrylium perchlorate, 14604-52-5; *o*-nitrophenylacetic acid, 3740-52-1; 2,4-dinitrotoluene, 121-14-2; 2,4-dinitrochlorobenzene, 97-00-7.

Intermediates in Nucleophilic Aromatic Substitution. X.[1] Synthesis of *N*-Methyl-β-aminoethyl Nitroaryl Ethers *via* an Unusual Smiles Rearrangement

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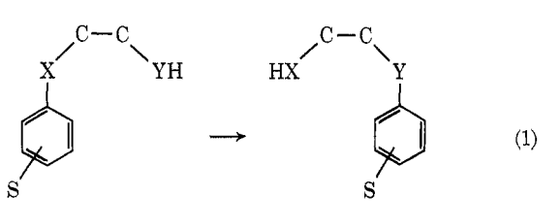
N-Methyl-β-aminoethyl nitroaryl ethers undergo a Smiles rearrangement into *N*-methyl-*N*-β-hydroxyethylnitroarylamines so readily that the aryl ethers cannot be prepared by obvious methods. However, when the aromatic system is sufficiently activated so that in the presence of base the aryl amine can be converted into a cyclic Meisenheimer complex, the Smiles rearrangement can be reversed and the ether obtained by rapidly acidifying the Meisenheimer complex. The aryl ether is the kinetically controlled product of the ring opening of the complex and can be trapped and isolated in the form of its ammonium salt.

Intramolecular rearrangements of the type shown in eq 1 are known as Smiles[3] rearrangements. The reaction is in fact an intramolecular activated (S = activating substituent) nucleophilic aromatic substitution. In most cases the displacement is by Y^- rather than by YH and thus the presence of a strong base is usually required. When YH is NH_2 or NHR a base may or may not be necessary for the reaction to proceed. The carbon chain joining X and Y may be saturated or be part of an aromatic system. The field has been reviewed recently.[4]



(1)

In this paper we are concerned with X = O, YH = NH_2 or NHR, and in particular with the inverse combination X = NH or NR, YH = OH. Most examples from the early literature[5] involve compounds where the C–C chain is part of an aromatic ring.[6]

More recently examples where the C–C chain is saturated have been reported by Kleb;[7] reaction 2 is representative. The rearrangement of **1** to **2** occurs so rapidly that **1** and a variety of similar β-aminoalkyl 4-nitrophenyl ethers could not be prepared from obvious starting materials. In fact the occurrence of reaction 2

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