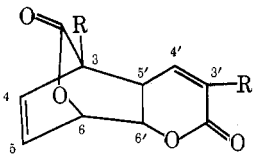
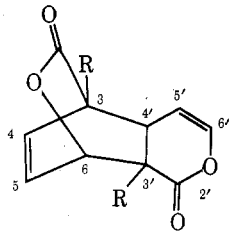


1 (endo), R = H
2 (exo), R = H
4 (endo), R = O-acetyl
6 (exo), R = O-acetyl
7 (exo), R = OH



3 (exo), R = H
5 (exo), R = O-acetyl

that of either of the photodimers, its similarity to that of **2** is such that it is clear that the difference between the two is in the stereochemistry of the ring junctures, the former being endo and the latter exo. The stereochemical assignments of these and subsequently described dimers stem from comparison of their coupling constants with those of several model compounds.[6a-c]

Pressurization of 50% solutions of 3-acetoxy-2-pyrone in either toluene or 2-butanone at up to 7 kbar at ca. 70 °C for ca. 45 h affords a crystalline material identified as endo dimer **4** through comparison of its ^{1}H NMR spectral properties with those of the 2-pyrone [2 + 4] dimers. This dimer can also be obtained by heating neat 3-acetoxy-2-pyrone at 110–120 °C for 70 h.

Irradiation of acetophenone in the presence of 3-acetoxy-2-pyrone affords two dimers which appear to be analogous to those similarly prepared from 2-pyrone. Again, the ^{1}H NMR spectral properties of one photodimer, **5** are very unlike those of the thermal dimer while those of the second, **6**, are quite similar with the exception of certain key coupling constants about the ring juncture. Endo and exo structures have been assigned to the thermal dimer **4** and photodimers **5** and **6**, respectively.

No dimer could be prepared by pressurization of 3-hydroxy-2-pyrone, methyl coumalate, or 4,6-dimethyl-5-carbethoxy-2-pyrone, although the first yielded an insoluble, high-melting, and presumably polymeric material. However, photosensitization of 3-hydroxy-2-pyrone affords a single dimer, the protons of which differ in chemical shifts, but not in coupling constants, from those of the 3-acetoxy-2-pyrone photodimer **6**. This dimer has accordingly been assigned the exo structure **7**.

The 2-pyrone photodimer **3**, in which the 3,4 double bond of 2-pyrone is the dienophile, has for $J_{3',6}$ a value very near those of $J_{6,6'}$ in photodimers **2** and **6** to which exo geometry has been assigned. It may thus be concluded that photodimer **3** also has the exo configuration. No such comparison can be made for photodimer **5**, which lacks the analogous coupling constant. The assignment of exo configuration to **5** follows from the stereochemistry of the other photodimers.

Thermolysis of the Dimers. On being heated at 200 °C both 2-pyrone dimers **1** and **2** yield 2-pyrone and second GLC identical components. In the case of **2**, this second component was identified as *cis*-cinnamic acid. Since *cis*-cinnamic acid is known to rearrange to the more stable trans isomer, such rearrangement could plausably occur under Seyferth's original reaction conditions.[2] The other photodimer, **3**, slowly decarboxylates in boiling acetonitrile to afford 9,10-dihydroisocoumarin which can be dehydrogenated over palladium to afford isocoumarin. Heated at its melting point, the thermal dimer of 3-acetoxy-2-pyrone reverts completely to monomer; no 3-acetoxycoumarin could be detected by ^{1}H NMR. If this dimer is indeed the 3-acetoxycoumarin precursor in Chavanne's reaction, then, at 200 °C where that reaction is carried out, the equilibrium concentration of the dimer must be quite small. However, the irreversible decarboxylation of even a minute portion of this dimer could ultimately afford 3-acetoxycoumarin as a major product.

Registry No.—**1**, 59041-90-6; **2**, 21044-75-7; **3**, 21044-74-6; **4**, 58983-22-5; **5**, 58983-23-6; **6**, 59091-52-0; **7**, 58983-24-7; 2-pyrone, 504-31-4; 3-acetoxy-2-pyrone, 51270-29-2; 3-hydroxy-2-pyrone, 496-64-0; acetophenone, 98-86-2; 3-acetoxycoumarin, 58983-26-9; coumarilic acid, 496-41-3; maleic anhydride, 108-31-6; *cis*-cinnamic acid, 102-94-3; 9,10-dihydroisocoumarin, 58983-27-0; isocoumarin, 491-31-6; **10**, 58983-25-8; acetonitrile, 75-05-8.

Supplementary Material Available. Tables of ^{1}H and ^{13}C NMR spectra of the dimers, a discussion of the assignment of endo and exo structures from ^{1}H NMR spectra of model compounds, and experimental procedures (17 pages). Ordering information is given on any current masthead page.

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A Reaction of α-Pyrone and Nitrosobenzene

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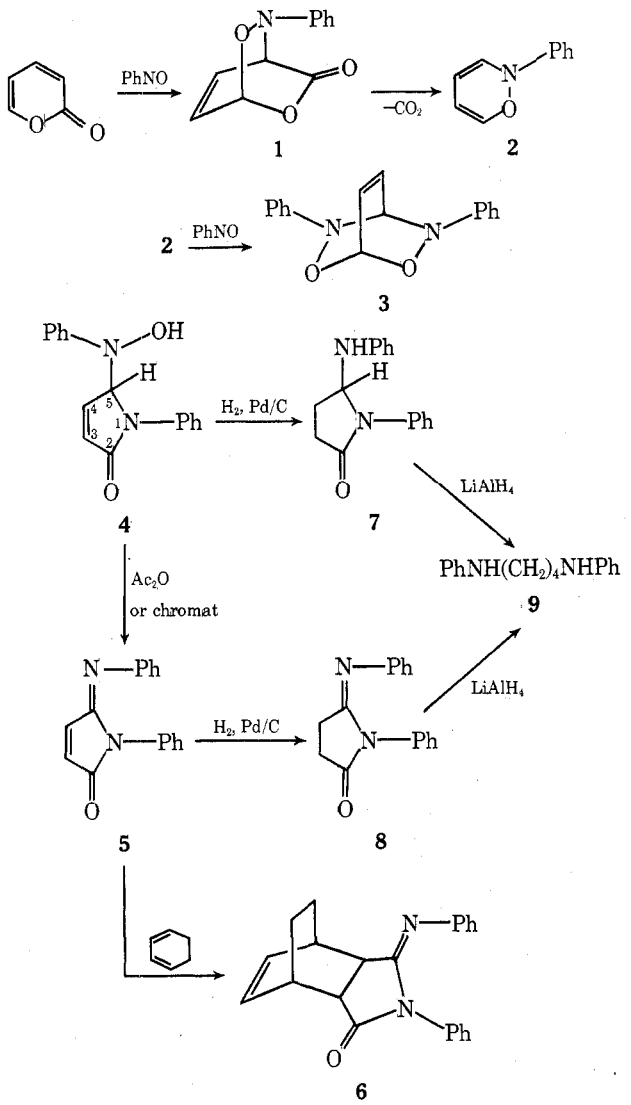
1,2-oxazine[1,2] and its N-substituted derivatives, such as **2**, is an elusive molecular system. Its thermal instability can be understood when bond energies and the antiaromatic character are considered.[3,4] Its chemical reactivity can be rationalized in terms of the available electrocyclic ring opening reaction which may yield an unsaturated imino aldehyde. A controversy has arisen around the structure of several substituted 1,2-oxazines;[5-7] however, the parent system **2** (with *N*-alkyl or aryl substituents) has neither been prepared nor detected as a transitory species. A very recent attempt to obtain 1-cyclohexyl-1,2-oxazine has failed.[1]

We expected the formation of **2** by a simple 1,4-cycloaddition reaction of nitrosobenzene and α-pyrone with subsequent loss of CO_2 from the intermediate (**1**) or from its isomeric adduct.

Indeed our experiments show that when α-pyrone and nitrosobenzene are brought into contact (in ether, methylene chloride, or benzene solutions) at 0 °C, the starting materials disappear and CO_2 is evolved. However, the products isolated after chromatography are azoxybenzene (18.8%) and a colorless solid (24%), which was not the anticipated 1-phenyl-1,2-oxazine. Its mass spectrum (M^+ *m/e* 266) and elemental analysis ($C_{16}H_{14}N_2O_2$) indicate a formal 2:1 adduct of nitrosobenzene/α-pyrone with the loss of CO_2.

A logical structural candidate (**3**), or its isomeric adduct, which could have originated from a second 1,4 polar addition of nitrosobenzene and **2**, was ruled out on the basis of spectral and chemical properties, which suggest the alternative structure **4**.

The ir spectrum ($CHCl_3$) exhibits intense bands at 3550, 3300 (OH stretching), and 1705 cm^{-1} (conjugated carbonyl). The NMR spectrum was not very informative inasmuch as the only signals recorded were several sets of multiplets in the



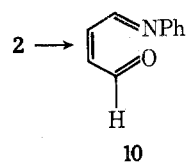
region δ 6.20–7.80. A singlet (1 H) of an exchangeable proton was recorded at δ 8.0, in agreement with the ir findings. In order to clarify the NMR spectrum we have repeated the reaction using nitrosobenzene-d_5. An AB quartet (J = 6.0 Hz) with further unequal doubling of each branch (J = 1.2 and 1.8 Hz) was clearly evident in the olefin region of the NMR spectrum. This quartet was assigned to the C-3 and C-4 protons of **4**. An additional apparent triplet signal (1 H) (allylic spin coupling) was assigned to the C-5 proton. Although an alternative assignment of the signals is possible, the spectral pattern is in accord with structure **4**.

Compound **4** readily loses a molecule of water either by chromatography on basic alumina or by treatment with Ac_2O to yield the yellow maleimide derivative **5**. Besides the correct analysis and the mass spectral data, the phenyl-d_{10} derivative of **5** exhibits a single uncoupled AB quarter (J = 6.0 Hz) in the NMR spectrum, confirming the spectral assignments of **4**. Compound **5** proved to be a dienophile inasmuch as it gave a cycloaddition product (**6**) with cyclohexadiene.

Finally, the structure of **4** has been rigorously established by chemical transformations. Catalytic hydrogenation of **4** (uptake of 2 molar equiv of H_2) led to a crystalline product (**7**). Its mass spectrum (M^+ m/e 250) and NMR analysis have indicated that both hydrogenation of the double bond and hydrogenolysis of the N–OH bond took place. Similarly, catalytic hydrogenation of **5** (uptake of 1 molar equiv of H_2) led to a colorless solid, for which structure **8** has been assigned on the basis of spectral and analytical data. Chemical reduction ($LiAlH_4$) of both **7** and **8** led to a single known compound, 1,4-dianilinobutane (**9**).

The structural data and analysis presented in this work leave little doubt regarding the suggested structure for the primary compound isolated from the reaction of α-pyrone and nitrosobenzene (**4**). Unfortunately our idea of the simple reaction scheme had not materialized inasmuch as the desired oxazine could not be isolated nor detected. We cannot at this stage state whether 1-phenyl-1,2-oxazine is an intermediate in the observed reaction. Three possible general routes for the formation of **4** were considered.

1. Skeletal rearrangement of **3**, accompanied by H or hydride shift.
2. Electrophilic substitution of α-pyrone by nitrosobenzene followed by 1,4 addition of nitrosobenzene, elimination of CO_2, and skeletal rearrangement.
3. The imino aldehyde (**10**) can be considered to arise from the electrocyclic ring opening reaction of the oxazine (**2**).



Simple bond energies calculations indicate its thermal stability over **2**. Hydride or H removal of the aldehyde hydrogen of **10** followed by addition of PhNOH (radical or anion) and subsequent cyclization may give rise to **4**.

Experimental Section

Reaction of α-Pyrone and Nitrosobenzene. A solution of 0.90 g (0.00935 mol) of α-pyrone and 2.0 g (0.0187 mol) of nitrosobenzene in chloroform (10 ml) was kept at 0 °C for 5 h under nitrogen; the evolution of CO_2 was noticed and confirmed by sweeping the evolved gas into a saturated $Ba(OH)_2$ solution. The solvent was evaporated and the residual dark oil was chromatographed on Silicar (80 g). Azoxybenzene (0.376 g) was eluted with 1:4 CH_2Cl_2–petroleum ether mixture. Gradual increase of CH_2Cl_2 concentration eluted 0.594 g (24%) of **4** homogenous by TLC, crystallized from benzene–petroleum ether: mp 129.5–130 °C; NMR (acetone-d_6) δ 8.9 (1 H, s, exchangeable with D_2O), 6–7.7 (13 H, m); uv λ_{max} (EtOH) 280 nm (ε 4720), 230 (11 900); ir ($CHCl_3$) 3550 and 3300 (OH free and bonded), 1705 (C=O), 1600 and 1500 cm^{-1} (phenyl); ir (KBr) 3220, 1680 cm^{-1}; mass spectrum m/e 266 (M^+), 248 ($M^+ - H_2O$).

Anal. Calcd for $C_{16}H_{14}N_2O_2$: C, 72.2; H, 5.26; N, 10.5. Found: C, 72.4; H, 5.02; N, 10.5.

Lower yields of **4** resulted when equimolar quantities of α-pyrone and nitrosobenzene were used.

Nitrosobenzene-d_5. Benzene-d_6 was nitrated[8] (76%) and then reduced[9] to give nitrosobenzene-d_5 (37%), mp 65–67 °C, ^1H NMR ($CHCl_3$) no detectable signals at 10% concentration.

Reaction of α-Pyrone and Nitrosobenzene-d_5. The reaction and isolation of product were carried out as described above: mp 129.5–130 °C; NMR (acetone-d_6) δ 8.85 (1 H, s, exchangeable), 7.17 (1 H, pair of doublets, J = 6.0 and 1.8 Hz), 6.35 (1 H, pair of doublets, J = 6.0 and 1.2 Hz), 6.50 (1 H, t, $J \simeq$ 1.3 Hz).

1-Phenyl-2-phenyliminomaleimide (5). The crude reaction product of **4** was chromatographed on basic alumina (III) instead of Silicar. With 2:3 CH_2Cl_2–petroleum ether mixture there was eluted 0.522 g (23%) of **5**, yellow needles: mp 136–137 °C after crystallization from CH_2Cl_2–petroleum ether; NMR (acetone-d_6) δ 6.7–7.4 (m); uv λ_{max} (EtOH) 377 nm (ε 3460), 250 (21 200); ir ($CHCl_3$) 1730 (C=O), 1658 (C=N), 1594, 1500 cm^{-1} (phenyl); mass spectrum m/e 248 (M^+).

Anal. Calcd for $C_{16}H_{12}N_2O$: C, 77.5; H, 4.84; N, 11.3. Found: C, 77.6; H, 4.96; N, 11.1.

An identical substance was obtained by treating **4** with Ac_2O.

A mixture of **4** (0.2 g) and 1,3-cyclohexadiene (1 ml) was kept at room temperature for 48 h. The solid which crystallized was chromatographed on basic alumina: 0.16 g (60%) of **6**; mp 185–187 °C; NMR ($CDCl_3$) δ 6.8–7.5 (10 H, m), 6.22 (2 H, m), 3.4 (1 H, dd, J = 10 and 3 Hz), 3.22 (1 H, m), 2.94 (1 H, dd, J = 10 and 2 Hz), 2.5 (1 H, m), 1.1–1.8 (4 H, broad); ir ($CHCl_3$) 1740 (C=O), 1665 (C=N), 1595 and 1500 cm^{-1} (phenyl); mass spectrum m/e 328 (M^+).

1-d_5-Phenyl-2-d_5-phenyliminomaleimide. This compound was prepared from the d_{10}-phenyl derivative of **4**, as described in the above procedure: mp 136–137 °C; NMR (acetone-d_6) δ 7.05 (1 H, d, J = 6.0 Hz), 6.65 (1 H, d, J = 6.0 Hz); mass spectrum m/e 258 (M^+).

5-Anilino-1-phenylpyrrolid-2-one (7). A 50-mg sample of **4** was hydrogenated at room temperature and atmospheric pressure using Pd/C. After 12 h 2 molar equiv of H_2 was absorbed. The residue after evaporation of the solvent was crystallized (EtAc/petroleum ether): 38 mg of colorless crystals; mp 137–139 °C; NMR ($CDCl_3$) δ 6.4–7.6 (10 H, complex, multiplet), 5.65 (1 H, m), 4.10 (1 H, broad singlet, exchangeable), 1.7–2.8 (4 H, complex multiplet); ir ($CHCl_3$) 3410 (NH) and 1695 cm^{-1} (CO); uv λ_{max} (EtOH) 287 nm (ϵ 1700), 245 (12 500); mass spectrum m/e 252 (M^+, $C_{16}H_{16}N_2O$), 160 ($M^+ - C_6H_5NH$).

Phenylimino-*N*-phenylsuccinimide (8). **5** (250 mg, 1 mmol) and 50 mg of 10% Pd/C in ethyl acetate (15 ml) was hydrogenated at atmospheric pressure and room temperature. One molar equivalent of H_2 was absorbed after 5 h. The mixture was filtered through Celite, the solvent was evaporated, and the residue was twice crystallized from EtAc/petroleum ether: colorless, prismatic crystals; mp 139–140.5 °C; NMR ($CDCl_3$) δ 6.70–7.60 (10 H, complex multiplet), 2.70 (4 H, s); ir ($CHCl_3$) 1780 and 1665 cm^{-1}; mass spectrum m/e 250 (M^+, $C_{16}H_{14}N_2O$).

1,4-Dianilinobutane (9). To a solution of 200 mg of **8** in THF (20 ml) there was added portionwise $LiAlH_4$ (400 mg). The mixture was refluxed for 4 h, the solvent was evaporated, ether was added, and to the cooled mixture a 20% aqueous NaOH solution was added. The ether was decanted off, and the solid was triturated with portions of chloroform which were combined with the ether phase, dried (K_2CO_3), and evaporated. The residue was distilled with Kugelrohr (0.005 mm). The distillate (148 mg) was crystallized from ether–petroleum ether at 0 °C, crystals, mp 36–37 °C (lit.[10] mp 37 °C).

A 300-mg sample of **7** was reduced as described above, also yielding 1,4-dianilinobutane (65%).

Registry No.—**4**, 58966-81-7; **4** d_{10}-phenyl derivative, 58966-82-8; **5**, 58966-83-9; **5** d_{10} phenyl derivative, 58966-84-0; **6**, 58966-85-1; **7**, 58966-86-2; **8**, 58966-87-3; **9**, 13170-61-1; nitrosobenzene, 586-96-9; α-pyrone, 504-31-4; nitrosobenzene-d_5, 18628-43-8; benzene-d_6, 1076-43-3; 1,3-cyclohexadiene, 592-57-4.

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Reaction of Amines with Thiophthalimides. Anomalous Formation of a Thiooxamide[1]

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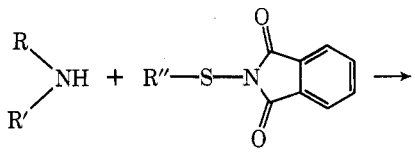
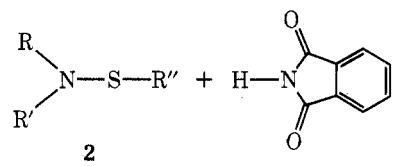
The reaction of various amines with thiophthalimides (**1**) has been shown to be a useful, general method for the preparation of sulfenamides **2**.[2a,b] The only observed exception to this behavior appears to be in the reaction of primary amines with thiophthalimides which have bulky groups. In these cases the nitrogen nucleophile reacts at the carbonyl carbon to give a ring-opened product (**3**).[2a,c] We have discovered an instance where the reaction of a primary amine with an unhindered thiophthalimide proceeds by an alternate route giving two



1



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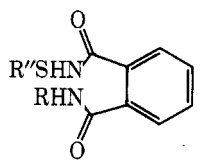

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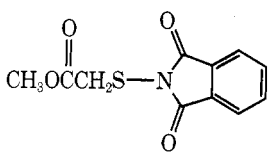
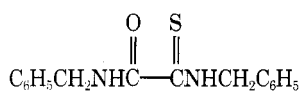


4

products which can be rationalized by an α-elimination process (vide infra).

Thiophthalimide **4**[3] was treated with 2 equiv of benzylamine (**5**), the by-product phthalimide collected (69%), and the remaining material chromatographed to provide a mixture of unidentified components as well as two pure compounds.

One of the latter products (**6**) was identified as *N*-benzylphthalamide (16% yield) (see Experimental Section). The other substance is a solid, mp 120–122 °C. It shows NMR ($CDCl_3$) δ 4.40 (d, 2 H), 4.75 (d, 2 H) (J = 6 Hz), 7.2 (s, 10 H), 8.38 (broad, 1 H), 9.71 (broad, 1 H). After treatment with $NaOD/D_2O$, the two high-field doublets collapsed to singlets and the low-field signals disappeared. Infrared, combustion, and MS analyses are consistent with thiooxamide **7** as the structure.



7

The formation of both **6** and **7** may be envisioned to arise via abstraction of an acidic methylene proton in **4** by benzylamine (**5**), thus eliminating phthalimide and generating the intermediate thioaldehyde **8**.[4a] The latter species probably suffers further attack by the amine, resulting in both amida-