(2 × 10 mL). The acidic phase was rendered basic with 2 N NaOH and extracted with Et_2O (4 × 12 mL). After drying over Na_2SO_4, the Et_2O was carefully removed, and the residue was distilled)65 °C (24 torr)] to yield 68 mg (65%) of 17: IR (CCl_4) 2870 (m), 2830 (w), 1471 (m), 1462 (m), 1451 (w), 1382 (w), 1344 (w), 1292 (w), 1187 (w), 1161 (sh, w), 1142 (w), 1111 (w), 1078 (nw), 902 (w) cm^{-1}; ^1H NMR (220 MHz, $CDCl_3$) δ 0.92 (t, 3 H, J = 6.5 Hz CH_3C), 1.15–1.90 (m, 10 H), 2.08 (m, 1 H), 2.20–2.55 (m, 2 H), 2.65 (m, 1 H), 2.87 (m, 1 H), 3.38 (m, 1 H, H_8); CI mass spectrum, 154 (M^+ + 1).

Acknowledgment. We thank Dr. P. Wehrli, Chemical Research Department, Hoffmann-La Roche Inc., for having supported this project with the preparation of substantial amounts of intermediates.

Registry No. 1, 18356-28-0; 2, 80262-59-5; 3, 80243-72-7; 4, 80243-73-8; 5, 80243-74-9; 6, 80243-75-0; 7, 80243-76-1; 8, 80243-77-2; 9, 80243-78-3; 10, 80243-79-4; 11, 80243-80-7; 12, 80243-81-8; 13, 80243-82-9; 14, 80243-83-0; 15, 80243-84-1; 16, 80243-85-2; 17, 80243-86-3.

Novel Synthesis of the Mesoionic System 1,3-Oxazolium-4-olate

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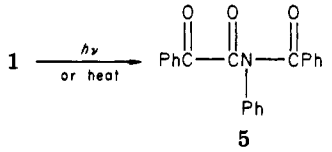
Thermolysis or photolysis of *N*-phenyldibenzoylnitrone (1) produces *N*-benzoylphenylglyoxanilide (5) and not the previously reported oxaziridine 2. Treatment of imide 5 with triethyl phosphite produced 2,3,5-triphenyl-1,3-oxazolium-4-olate (8), a new member of this little-known mesoionic system. Hydrolysis of 8 produced *O*-benzoylmandelanilide (9) and reaction of 8 with *N*-phenylmaleimide yielded a mixture of exo and endo cycloaddition products, **10a** and **10b**.

During the process of writing a review on oxaziridines,[1] we observed a report of a remarkable exception to the general photolytic rearrangement of *N*-arylnitrones and aromatic *N*-oxides to amides and lactams, respectively. It was claimed that *N*-phenyldibenzoylnitrone (1) rearranged photochemically to give "*N*-phenyldibenzoyloxazirine" (2) in essentially quantitative yield.[2] Later, others reported[3] the same compound was obtained thermally from 1 at the reflux temperature of *p*-xylene.

Moreover, it was claimed that oxaziridine 2 "can be recovered unchanged after heating to 250 °C in an inert atmosphere". Further chemical transformations were carried out and the products were assigned the structures shown in Scheme I.

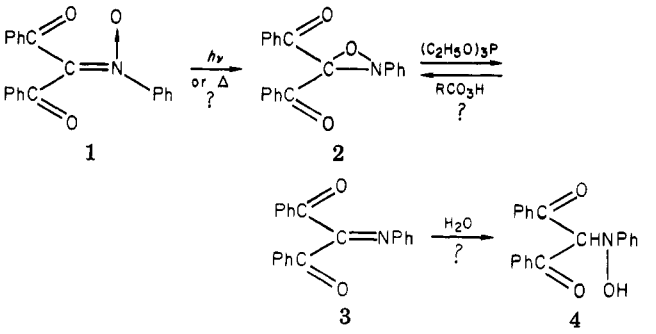
We have found that both the photolysis and thermolysis of nitrone 1 lead to *N*-benzoylphenylglyoxanilide (5), not



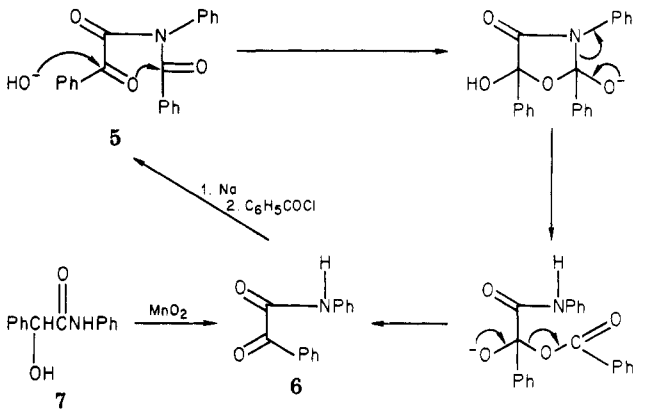
oxaziridine 2. The ^{13}C NMR spectrum of 5 showed, in addition to the aromatic carbons, three peaks at δ 170.08, 171.74, and 187.11, indicating the presence of three carbonyl groups.

Imide 5 did not oxidize potassium iodide as would be expected of an oxaziridine. On the other hand, basic hydrolysis of 5 under rather mild conditions gave phenylglyoxanilide 6 (Scheme II). The unexpectedly fast rate of hydrolysis of imide 5 and the selective removal of the benzoyl rather than the more electrophilic phenylglyoxalyl group is most likely due to neighboring participation as shown below. The identity of 6 was confirmed by manganese dioxide oxidation of mandelanilide 7 into 6. Finally, treatment of the sodium salt of 6 with benzoyl chloride gave a compound identical with imide 5 (mixture melting

Scheme I



Scheme II



point, IR, and chemical transformations).

Heating imide 5 with triethyl phosphite gave an orange-red solid[2] to which we assign the mesoionic structure 8 rather than that of anil 3 proposed earlier.[2] The reaction

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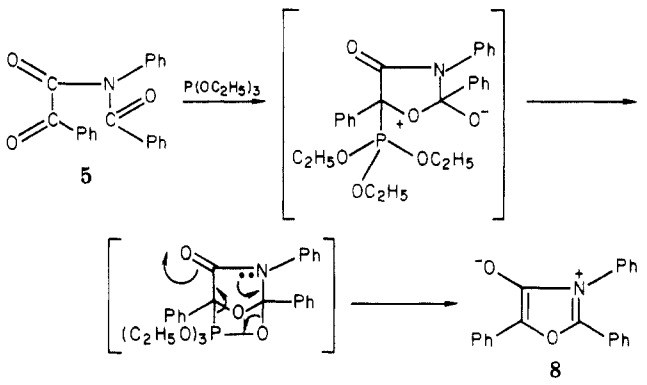
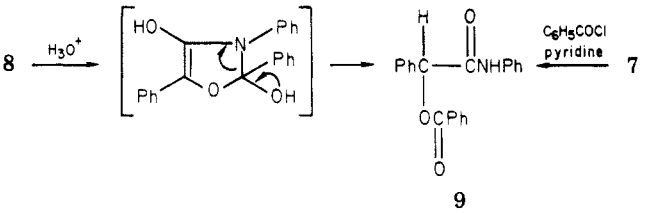
Scheme III



Scheme IV

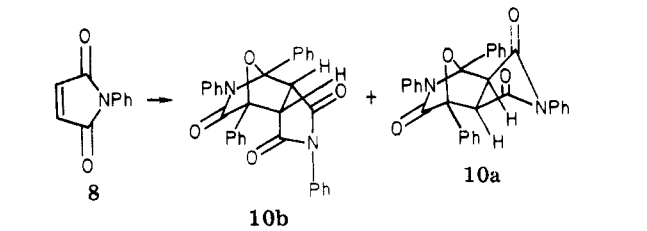


is so fast that a red coloration develops immediately on contact of the phosphite with imide **5** (Scheme III).

The formation of 2,3,5-triphenyl-1,3-oxazolium-4-olate (**8**) is analogous to the conversion of 2-ene-1,4-diones into furans by the action of triethyl phosphite.[4] The earlier method for preparing this class of mesoionic compound from diazoimides is due to Hamaguchi and Ibata.[5]

Compound **8** hydrolyzed in aqueous acid to give *O*-benzoylmandelanilide (**9**, Scheme IV) which was identical with an authentic sample prepared by the reaction of **7** with benzoyl chloride. A similar hydrolysis of a mesoionic compound of this type was reported recently.[6] Compound **9** corresponds to that previously reported[2] as **4**[7] and fits the NMR data reported in that it has only one exchangeable proton and a low-field nonexchangeable proton.

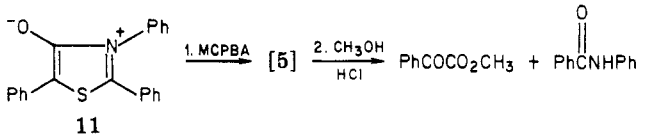
Mesoionic compound **8**, as expected of such a structure, reacted immediately with *N*-phenylmaleimide to give a mixture of exo and endo adducts **10a,b** in a ratio of 1:2.



The stereochemical assignment of **10a** and **10b** is based only on NMR evidence. The endo adduct shows a multiplet for the ortho protons of the *N*-phenylimide group at relatively higher field (δ 6.8) than the corresponding protons in the exo adduct. This argument has been used by Cava and co-workers in the establishment of the structures of analogous *N*-phenylmaleimide cycloadducts.[8]

A similar adduct of a mesoionic compound of this type, suggested to be the endo isomer, has been reported.[9]

Finally, the reported[2] oxidation of the compound we have now assigned the mesoionic structure **8** back to imide **5** has recently found precedent in a study of the peracid oxidation of a closely related group of mesoionic compounds.[10] For example, oxidation of **11** with *m*-chloroperbenzoic acid, followed by acidic methanolysis, yielded methyl phenylglyoxalate; imide **5** was proposed to be an intermediate.



When **8** was treated with 10% peracetic acid, imide **5** was indeed obtained but in low yield in a mixture of other unidentified materials.

Experimental Section

All melting points were taken on a Fisher-Johns melting point apparatus and are uncorrected. Infrared spectra were recorded on Perkin-Elmer 257 and 398 spectrophotometers using potassium bromide disks or Nujol mulls. H^1 NMR spectra were taken on a Varian EM 360E instrument in $CDCl_3$ with Me_4Si as an internal standard. ^{13}C NMR spectra were determined on a Varian XL-100 spectrometer. TLC was carried out on freshly prepared Merck GF_{254} Type 60 silica gel plates.

N-Phenyldibenzoylnitrone[11] (**1**) and mandelanilide[12] (**7**) were prepared according to literature methods.

***N*-Benzoylphenylglyoxanilide (5).** Photolysis[2] or heating[3] of **1** gave **5** in yields comparable to those reported in the literature:[2,3] mp 131 °C (lit.[2] 121 °C; corrected[3] to 131 C); IR (KBr) 1685, 1600, 1450, 1260, 1170, 985, 840, 800, 760, 720, 705, 675, 650 cm^{-1}; C^{13} NMR δ 187.11, 171.74, 170.08, 136.71, 133.99, 132.67, 132.52, 131.96, 129.75, 129.64, 129.34, 128.57, 128.38, 128.07, 127.85.

2,3,5-Triphenyl-1,3-oxazolium-4-olate (8). Imide **5** (0.8 g) was placed in a 50-mL Erlenmeyer flask. Triethyl phosphite (2.5 mL) was added. An immediate reddish coloration ensued. The mixture was heated at the boiling point of triethyl phosphite for 7 min during which an orange-red solid precipitated. Cold toluene (10 mL) was added to the cold mixture, and the orange-red **8** was collected by suction filtration, washed with more toluene, and dried: 0.45 g (50%); mp 175–177 °C (the melting point is not sharp and depends on the rate of heating); IR (Nujol) 1665, 1600, 1532, 1500, 1175, 750, 690 cm^{-1}. Anal. Calcd for $C_{21}H_{15}NO_2$: C, 80.39; H, 4.82; N, 4.47. Found: C, 79.41; H, 4.93; N, 4.31.

Hydrolysis of *N*-Benzoylphenylglyoxanilide. Imide **5** (0.20 g) was dissolved in 10 mL of hot methanol, and 1 mL of water was added, followed by 2 mL of 5% methanolic potassium hydroxide. The solution, which turned yellow immediately, was heated to boiling, cooled, diluted with water, and extracted with ether. The dried extracts were concentrated to give 0.115 g of a yellow oil which solidifed on cooling. The product was purified by TLC, and 85 mg of phenylglyoxanilide **6** was obtained: mp 62–63 °C (lit.[13] mp 63–64 °C); IR (Nujol) 3310, 1690, 1660, 1600, 1590, 1530, 1275, 1165, 990, 880, 750, 740, 680 cm^{-1}; mass spectrum, *m/e* 225 (M^+, 55), 105 ($C_6H_5CO^+$, 100). The IR and melting and mixture melting points were identical with those of **6** prepared by the oxidation of **7** with MnO_2 (below).

Oxidation of Mandelanilide. Mandelanilide (**7**, 1.0 g) was dissolved in 100 mL of ether, 7 g of freshly prepared[14] MnO_2 was added, and the mixture was stirred for 10 h at room temperature.

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(8) (a) Cava, M. P.; Pollack, N. M.; Manner, O. A.; Mitchell, J. M. *J. Org. Chem.* **1971**, *36*, 3932–3937. (b) Haddadin, M. J.; Chelhot, N. C.; Pieridou, M. *Ibid.* **1974**, *39*, 3278–3281.
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Solids were removed by filtration, and evaporation of the MnO_2-free ether gave a dark oil which solidified on cooling. Recrystallization from ether/*n*-hexane gave long yellow needles of **6**: 0.6 g; mp 62–63 °C. **6** was identical (IR, mixture melting point) with that prepared from the hydrolysis of **5**. Other methods of oxidation (CrO_3–CH_3COOH, $KMnO_4$–acetone) were inferior to the above method.

Hydrolysis of Mesoionic Compound 8 to *O*-Benzoylmandelanilide (9). Mesoionic **8** (100 mg) was suspended in 20 mL of ether. Dilute HCl (10 mL) was added, and the mixture was stirred at room temperature until the orange color of **8** disappeared (20 min). The dried ether layer was evaporated and the residue was recrystallized from methanol to give 40 mg of **9**: mp 181–182 °C (lit.[15] mp 177 °C); IR 3225, 1725, 1665, 1600, 1550, 1500, 1280, 1260, 1250, 1115, 750, 710 cm^{-1}; NMR δ 6.4 (s, 1 H), 7.3 (m, 13 H), 8.1 (m, 3 H). Compound **9** was also prepared by the heating of mandelanilide (**7**, 0.5 g) and benzoyl chloride (0.5 g) in pyridine (5 mL) for 5 h on a steam bath. Dilution with water gave a white solid which was recrystallized from methanol: 0.65 g; mp 182–183 °C. The IR, NMR, and mixture melting point were identical with those of **9** isolated from the hydrolysis of **8**.

Preparation of 5 from 6. Phenylglyoxanilide (**6**, 0.6 g) was dissolved in 970 mL of dry ether. Sodium wire (0.5 g) was added, and the mixture was stirred at room temperature for 10 min after which a solution of 0.4 g of benzoyl chloride in 30 mL of dry ether was added dropwise. The mixture was stirred for an additional 20 min. The mixture was filtered and evaporated to leave a dark yellow residue which was treated with methanol (5 mL). The resulting white solid was collected by suction filtration, washed with methanol, and dried to give 0.26 g of **5**, mp 131 °C. The product was identical (IR and mixture melting point) mmp) with **5** prepared by the photolytic or thermal rearrangement of **1**.

Exo and Endo Adducts 10a and 10b. Mesoionic **8** (0.3 g) was mixed with toluene (100 mL) at room temperature. *N*-Phenylmaleimide (0.18 g) was added to the mixture. The orange-red color of **8** disappeared immediately. Evaporation of toluene followed by separation of the major two products by thick-layer chromatography ($CHCl_3$/$PhCH_3$, 1:1) gave 60 mg of *exo*-**10a** [mp 240–242 °C; IR 1735, 1712, 1600, 1500, 1375, 1330, 1195, 1180, 1025, 1010, 760, 750, 695, 640 cm^{-1}; NMR δ 4.05 (d, 1, J = 4 Hz), 4.46 (d, 1, J = 4 Hz), 7.1, 7.4, 8.1 (m, 20)] and 130 mg of *endo*-**10b**: mp 253–254 °C; IR 1735 (sh), 1716, 1600, 1500, 1375, 1335, 1195, 1090, 1010, 930, 870, 815, 750, 718, 690 cm^{-1}; NMR δ 3.91 (1 H, J = 4 Hz), 4.30 (1 H, J = 4 Hz), 6.8, 7.2, 7.4, 7.6, 7.8 (m, 20 H). Anal. Calcd for $C_{31}H_{22}N_2O_4$: C, 76.52; H, 4.55; N, 5.76. Found for **10a**: C, 76.07; H, 4.57; N, 5.53. Found for **10b**: C, 76.19; H, 4.71; N, 5.72. Heating of either **10a** or **10b** above their melting points resulted in the formation of a red product which is presumed to be **8**.

Registry No. **1**, 30121-36-9; **5**, 80263-47-4; **6**, 4732-66-5; **7**, 4410-33-7; **8**, 80263-48-5; **9**, 24334-54-1; *exo*-**10a**, 80263-49-6; *endo*-**10b**, 80300-25-0; *N*-phenylmaleimide, 941-69-5.

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Synthesis and Intramolecular Cycloaddition Reactions of Some 3-Substituted 6-Azidohexa-2,4-dienoate Esters

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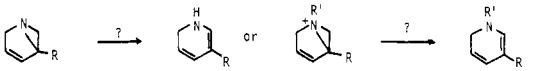
Several 3-substituted (methyl, *n*-butyl, phenyl) 6-azidohexa-2,4-dienoate esters were synthesized by conjugate addition of [(*Z*)-3-[(tetrahydropyranyl)oxy]-1-propenyl]copper to the appropriate acetylenic ester, followed by conversion to the azide by depyranylation, mesylation, and azide substitution. In the methyl and butyl cases, the addition was nonstereoselective under the conditions used, while the phenyl case gave nearly completely the product of anti addition. The azides all undergo intramolecular cycloaddition to form 3a,6-dihydro-3*H*-pyrrolo[1,2-*c*][1,2,3]triazoles at rates which depend upon the stereochemistry and substitution of the 6-azidohexa-2,4-dienoate. All of these adducts are unstable with respect to decomposition to a 2-substituted pyrrole, again at rates which are both substituent and solvent dependent. Under certain circumstances, the 3a,6-dihydro-3*H*-pyrrolo[1,2-*c*][1,2,3]triazoles are converted to the open chain valence tautomers which are α-diazo-2,5-dihydropyrrole-2-acetate esters. Possible factors contributing to the observed substituent and stereochemical effects are considered.

1,2-Dihydropyridines are useful synthetic intermediates, but there exist limitations on the types of substitution patterns which are routinely available.[1] One significant but elusive structure is the 5-substituted-1,2-dihydro system.[2] We wished to explore the possibility that 1-azabicyclo[3.1.0]hex-3-enes or the corresponding salts might be thermally converted to 1,2-dihydropyridines. We



decided to approach the desired bicyclic system via an intramolecular cycloaddition, following a pattern observed for substituted 5-azido-1-pentenes by Logothetis.[3] This paper describes the synthesis of the required azides and the observation that the intramolecular cycloadducts are unstable with respect to decomposition to 2-substituted pyrroles and/or α-diazo-2,5-dihydropyrrole-2-acetate esters. Both the rates of formation and subsequent decomposition of the intramolecular cycloadducts are sensitive

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(2) A recent approach by C. Marazano, M.-T. LeGoff, J.-L. Fourey, and B. P. Das, *Chem. Commun.*, 389 (1981), appears promising. Nucleophilic adducts capable of serving as synthetic equivalents have also been studied: D. S. Grierson, M. Harris, and M.-P. Husson, *J. Am. Chem. Soc.*, *102*, 1064 (1980).

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