21, 16617-46-2; 2-oxocyclohexanecarbonitrile, 4513-77-3; imidazole-4-carboxaldehyde oxime, 57090-90-1; 6-amino-1,4-dioxaspiro[4.4]nonane, 57090-91-2; 6-phthalimido-1,4-dioxaspiro[4.4]nonane, 10442-96-3; cyclopentanone oxime *p*-toluenesulfonate, 10442-97-4; 1,4-dioxaspiro[4.5]decane-6-carboxamide, 57090-92-3; ethyl 1,4-dioxaspiro[4.5]decane-6-carboxylate, 13747-72-3; 2-oxocyclohexanecarboxamide, 22945-27-3; 3-methylpyrazole, 1453-58-3.

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Thallium in Organic Synthesis. XLI. Synthesis of 1-Substituted 2(1*H*)-Pyridones. A New Synthesis of Unsymmetrical Biphenyls via Photochemical N–O Bond Cleavage of 1-Aroyloxy-2(1*H*)-pyridones[1,2]

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Reaction of the thallium(I) salt of 1-hydroxy-2(1*H*)-pyridone with alkyl iodides, arylsulfonyl chlorides, and aroyl chlorides gave a series of 1-alkoxy-, 1-arylsulfonyloxy-, and 1-aroyloxy-2(1*H*)-pyridones. A similar series was prepared from the thallium(I) salt of 1-hydroxy-3,5-dinitro-2(1*H*)-pyridone. Irradiation of the 1-aroyloxy-3,5-dinitro-2(1*H*)-pyridones in benzene gave unsymmetrical biphenyls in moderate yield. It is suggested that these stable, crystalline pyridone derivatives may be generally useful as sources of aryl radicals.

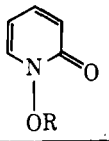
We have recently described a convenient, high-yield synthesis of 1-acyloxy-2(1*H*)-pyridones by reaction of the thallium(I) salt of 1-hydroxy-2(1*H*)-pyridone (1) with acyl halides in ether suspension.[4] Intrigued by the utility of these active esters for peptide synthesis,[4-6] we have examined the preparation and reactivity of a number of other 1-substituted 2(1*H*)-pyridones which were similarly prepared.

Although 1 was unreactive toward alkyl halides at room temperature in ether suspension, reaction was quantitative when 1 was heated under reflux with an excess of the alkyl halide.[7] Lower boiling halides and secondary halides needed longer reaction times, and not surprisingly, iodobenzene proved unreactive. 1-Phenoxy-2(1*H*)-pyridone was, however, readily prepared in 90% yield by stirring 1 with 1 equiv of diphenyliodonium chloride in *tert*-butyl alcohol for 16 hr at 30°.

1-Aroyloxy-2(1*H*)-pyridones were similarly prepared from 1 and the appropriate aroyl halide at room temperature in ethyl acetate suspension. The various 1-alkoxy- and 1-aroyloxy-2(1*H*)-pyridones prepared in this study, along with pertinent physical data and yields, are summarized in Table I.

An analogous series of 1-alkoxy and 1-aroyloxy derivatives was prepared from the thallium(I) salt of 1-hydroxy-3,5-dinitro-2(1*H*)-pyridone (2). As expected, 2 was weakly nucleophilic and proved to be relatively sluggish in its reac-

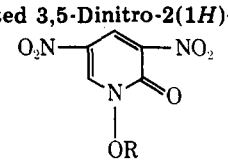
Table I
1-Substituted 2(1*H*)-Pyridones[a]

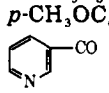
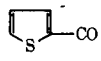


Registry no.	R	Reaction time, hr	Temp, °C	Ir carbonyl, cm^{-1} Pyridone	Ester	% yield	Mp or bp, °C (mm)
40775-55-1	CH_3	18	42	1665		98.5	87–90 (0.04)
56960-56-6	$CH_3CH_2CH_2$	3	101	1665		99.5	105–108 (0.08)
32846-47-2	$(CH_3)_2CH$	18	89	1665		97	90–94 (0.1)
4377-30-4	$CH_2{=}CHCH_2$	1	102	1670		99	*d*
5279-98-1	$CH_3CH_2CH_2CH_2$	1	130	1665		98	*d*
56960-57-7	CH_2CH_2Br	4	131	1670		93[b,e]	
56960-58-8	C_6H_5[c]			1660			
886-27-1	C_6H_5CO	1	20	1670	1780	86	139–141 (ref 6)
56960-59-9	*o*-ClC_6H_4CO	3	20	1660	1785	86	100–101
5037-55-8	*m*-BrC_6H_4CO	1	20	1670	1790	88	138–140 (ref 6)
5037-58-1	*m*-$NO_2C_6H_4CO$	1	20	1680	1790	93	136–138 (ref 6)
5037-59-2	*p*-$NO_2C_6H_4CO$	1	20	1670	1785	90	156–157 (ref 6)
56960-60-2	*m*-$CH_3C_6H_4CO$	1	20	1660	1770	78	94–95
5033-24-9	*p*-$CH_3OC_6H_4CO$	2	20	1660	1770	82	116–118 (ref 6)
56960-61-3		1	20	1660	1785	91	110–112

[a] Satisfactory microanalytical data for all new compounds listed in the table (except as noted) were submitted for review. [b] This compound decomposed upon distillation. [c] See Experimental Section. [d] L. A. Paquette, *Tetrahedron*, 22, 25 (1966). [e] Anal. Calcd for $C_7H_6BrNO_2$: C, 38.60; H, 3.67; N, 6.43. Found: C, 41.40; H, 4.31; N, 6.99.

Table II
1-Substituted 3,5-Dinitro-2(1*H*)-pyridones[a]



Registry no.	R	Reaction time, hr	Temp, °C	Ir carbonyl, cm^{-1} Pyridone	Ester	% yield	Mp, °C
56960-62-4	CH_3			1720		57	146–147
56960-63-5	CH_3CH_2	7 days	72	1720		96	123–124
56960-64-6	$CH_3CH_2CH_2$	3 days	101	1720		90	85–86
56960-65-7	$CH_3CH_2CH_2CH_2$	2 days	130	1715		82	92–93
56960-66-8	CH_3CO	3	20	1740	1820	95	148–150
56960-67-9	C_6H_5CO	1	20	1725	1775	89	148–149
56960-68-0	*o*-ClC_6H_4CO	3	20	1735	1810	85	170–171
56960-69-1	*m*-BrC_6H_4CO	3	20	1730	1785	89	167–168
56960-70-4	*m*-$NO_2C_6H_4CO$	2.5	20	1730	1795	64	171–172
56960-71-5	*p*-$NO_2C_6H_4CO$	1	20	1730	1800	51	190–191
56950-72-6	*m*-$CH_3C_6H_4CO$	3	20	1725	1795	86	173–174
56960-73-7	*p*-$CH_3OC_6H_4CO$	3	20	1725	1780	84	192–193
56960-74-8		3	20	1725	1790	76	171–172
56960-75-9		3	20	1725	1785	69	146–147

[a] Satisfactory microanalytical data for all new compounds reported in the table were submitted for review.

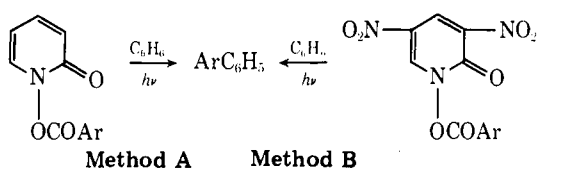
tions. For example, 1 reacted with benzenesulfonyl chloride within 1 hr to give 1-benzenesulfonyloxy-2(1*H*)-pyridone, but reaction with 2 was only partially complete after 12 days. Similarly, unreacted 2 was quantitatively recovered when 2 was heated under reflux in methyl iodide for 1 week. On the other hand, reaction of 1 with refluxing methyl iodide was complete in less than 1 day. 1-Methoxy-3,5-dinitro-2(1*H*)-pyridone could be obtained, however, by reaction of 1-hydroxy-3,5-dinitro-2(1*H*)-pyridone with diazomethane.[8] The various 1-alkoxy- and 1-aroyloxy-3,5-dinitro-2(1*H*)-pyridones prepared in this study, along with appropriate yield data and physical properties, are summarized in Table II.

It appears to be well documented that increased reactivity in nucleophilic reactions involving carbonyl groups is paralleled by a marked shift of the ir absorption of the carbonyl band toward shorter wavelengths.[9,10] In accordance with these observations, the reactive 1-acyloxy-2(1*H*)-pyridones exhibit a carbonyl band in the region between 1700 and 1800 cm^{-1}. Since the corresponding 3,5-dinitro derivatives show carbonyl absorptions at even shorter wavelengths (1790–1820 cm^{-1}), it was anticipated that these latter derivatives would be even more useful as active esters for peptide synthesis. We were thus surprised to discover that their reaction with nucleophiles, contrary to prediction, was much slower. For example, although 1-acetoxy-

2(1*H*)-pyridone was completely hydrolyzed within 1 hr at room temperature in aqueous solution, 1-acetoxy-3,5-dinitro-2(1*H*)-pyridone required 30 min of reflux for complete hydrolysis. 1-Aroyloxy-3-nitro- or 5-nitro-2(1*H*)-pyridones appear to be of intermediate activity, since they are reactive enough to form amides and esters upon reaction with amines and alcohols, respectively.[11] It would appear that, contrary to the generalization made in the past, the position of the ir active ester carbonyl band is not a reliable criterion of reactivity.

There are many precedents for both thermal and photolytic homolysis of the N–O bond in various hydroxylamine derivatives,[12–15] including 1-alkoxy-2(1*H*)-pyridones.[16] We have now found that photolysis of either the 1-acyloxy-2(1*H*)-pyridones or the 1-acyloxy-3,5-dinitro-2(1*H*)-pyridones in benzene results in the formation of unsymmetrical biphenyls in low to moderate yield. This reaction presumably involves homolysis of the N–O bond to give a carboxylate radical which then loses carbon dioxide to give an aryl radical.[17–20] This then reacts with the solvent benzene to give the observed biphenyl (see Table III).[21] Consistent

Table III
Unsymmetrical Biphenyls from Photolysis in Benzene of 1-Aroyloxy-2(1*H*)-pyridones



Method A Method B

Ar	Product	% yield[a] from A	% yield[a] from B	Registry no.
C_6H_5	Biphenyl	40[b]	57	92-52-4
o-ClC_6H_4	*o*-Chlorobiphenyl	27[c]	48[d]	2051-60-7
m-BrC_6H_4	*m*-Bromobiphenyl	30[e]	56[f]	2113-57-7
m-$NO_2C_6H_4$	*m*-Nitrobiphenyl	15[g]	40[h]	2113-58-8
p-$NO_2C_6H_4$	*p*-Nitrobiphenyl	17[i]	36[j]	92-93-3
m-$CH_3C_6H_4$	*m*-Methylbiphenyl	44[k]	57[l]	643-93-6
p-$CH_3OC_6H_4$	*p*-Methoxybiphenyl	9[m]	20[n]	613-37-6
3-Pyridyl	3-Phenylpyridine	26[o]	42[p]	1008-88-4

[a] Yield determined by GLC. [b] + 20% benzoic acid. [c] + 3% biphenyl, 2% chlorobenzene, 35% *o*-chlorobenzoic acid. [d] + 3% biphenyl. [e] + 3% biphenyl, 2% bromobenzene, 28% *m*-bromobenzoic acid. [f] + 1% biphenyl, 22% *m*-bromobenzoic acid. [g] + <1% biphenyl, <1% nitrobenzene, 35% *m*-nitrobenzoic acid. [h] + 6% biphenyl, <1% nitrobenzene, 43% *m*-nitrobenzoic acid. [i] + <1% biphenyl, <1% nitrobenzene, 12% *p*-nitrobenzoic acid. [j] + 5% biphenyl, 1% nitrobenzene, 48% *p*-nitrobenzoic acid. [k] + 2% biphenyl, 2% toluene, 19% *m*-toluic acid. [l] + 2% biphenyl. [m] + 25% biphenyl. [n] + 7% biphenyl, 4% anisole. [o] + 2% biphenyl, 2% pyridine, 28% nicotinic acid. [p] + 2% biphenyl.

with this interpretation is the observation that the photolysis of 1-(thiophene-2-carbonyloxy)-3,5-dinitro-2(1*H*)-pyridone gave a mixture of biphenyl and phenyl thiophene-2-carboxylate. Unlike most aroyloxy radicals, the thiophene-2-carbonyloxy radical is known to be relatively stable, presumably because of stabilization of the odd electron by sulfur.[22] Also consistent with the above mechanistic interpretation is the observation that substantially improved yields of unsymmetrical biphenyls are obtained utilizing the 3,5-dinitro-2(1*H*)-pyridone intermediates, in line with the known ability of electron-withdrawing groups to promote homolytic N–O bond scission by stabilizing the odd electron fragments.[12,23]

It is interesting to compare this procedure for the phenylation of arenes with the classical one involving thermolysis of a diaroyl peroxide.[20,24,25] Both methods start with the corresponding aroyl chloride, but our new procedure possesses the distinct advantage of utilizing the intermediate 1-acyloxy-2(1*H*)-pyridones which, in contrast to the thermally unstable diaroyl peroxides, are indefinitely stable (even to heat), crystalline compounds. Furthermore, it is significant that, in contrast to the peroxide route to aryl radicals,[26] phenyl aroates were not generally observed as by-products in the photolytic decomposition of 1-aroyloxy-2(1*H*)-pyridones in benzene. We suggest, therefore, that the reaction pathway involving the conversion of an acid chloride to a 1-aroyloxy-3,5-dinitro-2(1*H*)-pyridone, followed by photolysis in benzene, provides a useful synthetic complement to the classical procedure involving the intermediacy of diaroyl peroxides. We are currently investigating other synthetic applications of this new procedure for the generation of aryl radicals.

Experimental Section[27]

Thallium(I) Salt of 1-Hydroxy-3,5-dinitro-2(1*H*)-pyridone (2). Thallium(I) ethoxide (10 g, 0.04 mol) was added to a vigorously stirred solution of 1-hydroxy-3,5-dinitro-2(1*H*)-pyridone[28] (8.04 g, 0.04 mol) in 350 ml of absolute ethanol. The orange salt which immediately precipitated was collected by filtration, washed with ethanol, and dried to give 16.0 g (99.5%) of analytically pure **2**, mp >195° dec.

Anal. Calcd for $C_5H_2N_3O_6Tl$: C, 14.85; H, 0.50; N, 10.15. Found: C, 14.92; H, 0.46; N, 9.92.

1-Alkoxy-2(1*H*)-pyridones. The thallium(I) salt of 1-hydroxy-2(1*H*)-pyridone (9.42 g) was suspended in 20 ml of the appropriate alkyl halide and then heated gently under reflux for the period of time specified in Table I. The insoluble thallium(I) halide was removed by filtration and washed thoroughly with ethyl acetate. The combined filtrates were then evaporated, the last traces of alkyl halide removed under high vacuum, and the crude product distilled. Yields and properties of the various compounds prepared by this procedure are listed in Table I.

1-Alkoxy-3,5-dinitro-2(1*H*)-pyridones. The same procedure was employed as described above except that the thallium(I) salt of 1-hydroxy-3,5-dinitro-2(1*H*)-pyridone was employed. However, the products in this series are solids and could be separated directly from the distillation residue by suspension in petroleum ether (bp 30–60°)–ethyl acetate followed by filtration. Recrystallization from the same solvent mixture then gave the products listed in Table II.

1-Methoxy-3,5-dinitro-2(1*H*)-pyridone. To a solution of 1.0 g of 1-hydroxy-3,5-dinitro-2(1*H*)-pyridone in 150 ml of anhydrous ether and 50 ml of anhydrous ethyl acetate was added an excess of ethereal diazomethane. Evaporation of the solvents then gave 0.61 g (57%) of 1-methoxy-3,5-dinitro-2(1*H*)-pyridone, mp 140–143°. The product was obtained as colorless needles, mp 146–147°, upon recrystallization from petroleum ether–ethyl acetate.

1-Aroyl-2(1*H*)-pyridones and 1-Aroyl-3,5-dinitro-2(1*H*)-pyridones. General Procedure. A suspension of the thallium(I) salt of 1-hydroxy-2(1*H*)-pyridone or 1-hydroxy-3,5-dinitro-2(1*H*)-pyridone in anhydrous ether or anhydrous ethyl acetate was treated with 1 equiv of the appropriate aroyl chloride, and the mixture was stirred at room temperature (see Tables I and II). The precipitated thallium(I) chloride was then removed by filtration through Celite, the filtrate evaporated to about half its volume, and petroleum ether added to cloudiness. Refrigeration then resulted in separation of the product which was collected by filtration and recrystallized from the appropriate solvent (see Tables I and II).

1-Phenoxy-2(1*H*)-pyridone. A suspension of 3.14 g (0.01 mol) of the thallium(I) salt of 1-hydroxy-2(1*H*)-pyridone and 3.17 g (0.01 mol) of diphenyliodonium chloride in 30 ml of *tert*-butyl alcohol was stirred for 16 hr at 30°, and the white precipitate of thallium(I) chloride which had separated was collected by filtration and washed with ethyl acetate. The combined filtrates were then evaporated under reduced pressure and the residual tan solid washed with *n*-hexane (to remove iodobenzene). The residual solid weighed 1.68 g (90%), mp 99–101°. Recrystallization from ethyl acetate–*n*-hexane raised the melting point to 102–103°.

Anal. Calcd for $C_{11}H_9NO_2$: C, 70.57; H, 4.85; N, 7.48. Found: C, 70.37; H, 4.80; N, 7.37.

***m*-Bromobiphenyl.** A solution of 1.92 g (0.005 mol) of 1-*m*-bromobenzoyloxy-3,5-dinitro-2(1*H*)-pyridone in 300 ml of benzene

was placed in a 500-ml quartz photolysis vessel and the stirred solution purged with nitrogen for approximately 15 min. The vessel was then fitted with a reflux condenser, and the solution was photolyzed in a Rayonet photochemical reactor with 300-nm light for 18 hr. The dark orange solution was evaporated under reduced pressure and the residue dissolved in 50 ml of chloroform and washed with 25 ml of saturated aqueous sodium bicarbonate. The bicarbonate layer was then separated and extracted with another 25-ml portion of chloroform. The combined chloroform extracts were then washed with distilled water, dried (anhydrous $MgSO_4$), and evaporated to dryness. The residual red oil was chromatographed on a 10-g column of silica gel using *n*-hexane–ether (3:1 v:v) as the eluent. Evaporation of the solvent then gave 0.65 g (56%) of *m*-bromobiphenyl and 1% of biphenyl. Acidification of the aqueous sodium bicarbonate layer above, extraction with two 25-ml portions of ether, and evaporation of the ether extracts gave 0.22 g (22%) of *m*-bromobenzoic acid.

The other unsymmetrical biphenyls listed in Table III were similarly prepared by photolysis of the appropriate 1-aroyloxy-2(1*H*)-pyridone or 1-aroyloxy-3,5-dinitro-2(1*H*)-pyridone in benzene.

Registry No.—**1**, 23595-81-5; **2**, 56960-55-5; thallium(I) ethoxide, 20398-06-5; 1-hydroxy-3,5-dinitro-2(1*H*)-pyridone, 822-89-9; diazomethane, 334-88-3; benzoyl chloride, 98-88-4; *o*-chlorobenzoyl chloride, 609-65-4; *m*-bromobenzoyl chloride, 1711-09-7; *m*-nitrobenzoyl chloride, 121-90-4; *p*-nitrobenzoyl chloride, 122-04-3; *m*-methylbenzoyl chloride, 1711-06-4; *p*-methoxybenzoyl chloride, 100-07-2; 3-pyridinecarbonyl chloride, 10400-19-8; diphenyliodonium chloride, 1483-72-3.

References and Notes

(1) For the previous paper in this series, see E. C. Taylor, H. W. Altland, and A. McKillop, *J. Org. Chem.*, **40**, 2351 (1975).
(2) This work was supported by grants to Princeton University from the National Science Foundation (MPS72-00327) and Eli Lilly and Co.
(3) NRCC Postdoctoral Fellow, 1968–1970.
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(5) L. A. Paquette, *Tetrahedron*, **22**, 25 (1966).
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(8) Reaction of 1-hydroxy-2(1*H*)-pyridone with diazoethane has been reported to give a mixture of 1-ethoxy-2(1*H*)-pyridone and 2-ethoxypyridine 1-oxide.[7] In our case, we could find no trace of 2-methoxypyridine 1-oxide.
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(27) Melting points were determined on a Thomas-Hoover apparatus and are uncorrected. NMR spectra were measured on a Varian A-60A instrument, and ir spectra were recorded on a Perkin-Elmer Model 237-B grating infrared spectrophotometer. The irradiation experiments were performed with a Rayonet photochemical reactor (the Southern New England Ultraviolet Co., Middletown, Conn.), fitted with 300-nm phototubes. GLC studies were conducted with an Aerograph Model 90-P instrument utilizing a 30 ft × 0.375 in. column with 30% QF-1 on 45/60 Chromosorb W. We are indebted for the microanalyses to Dr. Franz Scheidl, Hoffmann-La Roche Inc., Nutley, N.J.
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