Anal. Calcd for $C_{13}H_9O_2N_5$: C, 58.42; H, 3.39; N, 26.21. Found: C, 58.40; H, 3.39; N, 26.15.

Reaction of *N*-Carbomethoxy-6-carbethoxy-2-azabicyclo[3.1.0]hex-3-ene (2b) with Dimethyl Acetylenedicarboxylate. To a Pyrex tube was added 316 mg of **2b** and 228 mg of DMAD. The tube was flushed with argon and sealed. The reaction mixture was heated in an oil bath at 170° for 24 hr. Nmr analysis, by comparing the bridgehead to total methoxyl hydrogens of the crude product, reveals an 87% yield of **9**. The product was purified first by molecular distillation and then by vapor phase chromatography (1 ft × 0.25 in., 212°, 3% SE-30 on Chromosorb Cr 60/70, He 50 cc/min): nmr ($CDCl_3$) τ 3.38–3.73 (m, 1 H), 4.12–4.47 (m, 1 H), 4.42 (s, broad, $W_{1/2}$ = 3 Hz), 5.75 (q, J = 7 Hz, 2 H), 6.18 (s, 6 H), 6.32 (s, 3 H), 6.68–6.83 (m, 1 H), and 8.53 (t, J = 7 Hz, 3 H); ir (neat) 1721 (C=O) and 1645 cm^{-1} (C=C).

Anal. Calcd for $C_{16}H_{19}NO_8$: C, 54.39; H, 5.42. Found: C, 54.12; H, 5.42.

Attempts to purify the above product by preparative thin layer chromatography (20 × 20 × 0.2 cm silica gel, 3:1 ether–benzene) resulted in the production of isomeric compound **11**: nmr ($CDCl_3$) τ 3.17–3.38 (m, 1 H), 4.55 (s, broad, $W_{1/2}$ = 2.5 Hz, 1 H), 4.90 (d, broad, $W_{1/2}$ = 3 Hz, 1 H), 5.77 (q, J = 7 Hz, 2 H), 6.20 (s, 3 H), 6.22 (s, 3 H), 6.30 (s, 3 H), 6.87–7.95 (m, 2 H), and 8.80 (t, J = 7 Hz, 3 H); ir (neat) 1726 cm^{-1} (C=O).

Anal. Calcd for $C_{16}H_{19}NO_8$: C, 54.39; H, 5.42. Found: C, 54.11; H, 5.25.

Kinetics of the Cycloaddition of 2 with Dimethyl Acetylenedicarboxylate. To an nmr tube were added controlled amounts of **2a** or **2b**, DMAD, and C_6D_6. C_6H_6 was used as an internal standard with the total volume being recorded. (The initial concentration of reactants was approximately 1 *M*.) The tube was flushed with nitrogen, sealed under vacuum, and maintained at the appropriate temperature (±0.1°) in an oil bath. Determinations for **2a** were made at 70.5, 80.7, and 91.4° while for **2b** determinations were made at 106.3, 113.6, and 120.9°. The disappearance of **2a** was monitored by periodic integration of the upfield endo cyclopropyl peak in the nmr spectrum of the reaction mixture. The disappearance of **2b** was followed by periodic integration of the cyclopropyl proton at position 5 in **2b**. Second-order rate constants and activation energies were obtained by least-squares fitting.

Acknowledgments. We wish to express our gratitude to the National Science Foundation (Research Grant GP-20099) for support of this work. We would also like to thank Professor R. Huisgen for his helpful comments.

Registry No.—**2a**, 31709-40-7; **2b**, 25088-90-8; **4**, 31709-41-8; **5**, 941-69-5; **6**, 51869-43-3; **7**, 51898-46-5; **8**, 51869-44-4; **9**, 31887-68-0; **11**, 51911-67-2; **12a**, 51869-45-5; **12b**, 51869-46-6; DMAD, 762-42-5; TCNE, 670-54-2.

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Reactions of *N*-Aryl Nitrogen Oxides. 1. Selective Ortho Chlorination in the Reactions of Aryl Nitrones and Amine Oxides with Thionyl Chloride or Phosgene

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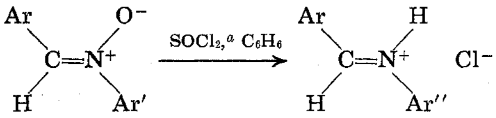
N-Aryl nitrones react rapidly with phosgene or thionyl chloride to produce ring-chlorinated imine hydrochlorides in high yield. Ring chlorination is shown to proceed exclusively on the aryl system adjacent to the nitrogen atom. The generality of this reaction with other *N*-aryl nitrogen oxides is discussed and a mechanism based upon the experimental observations is proposed.

The classes of *N*-aryl nitrogen oxides which are of current interest in this laboratory include, *inter alia*, *N*-aryl nitrones, *N*-aryl tertiary amine *N*-oxides, *N,N'*-diarylazoxy compounds, nitroaromatic compounds, and *N*-aryl-*N*-nitroso dimers. A few of the above have been reported to react with acid chlorides and anhydrides to yield ring-substituted products. For example, in an investigation of the Polonovski reaction, Huisgen, *et al.*,[1] have observed the production of small to moderate amounts of ortho-acetylated *N,N*-dimethylanilines when ring-substituted *N,N*-di-

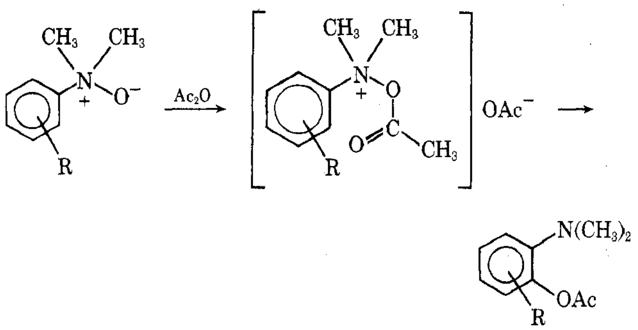
Table I



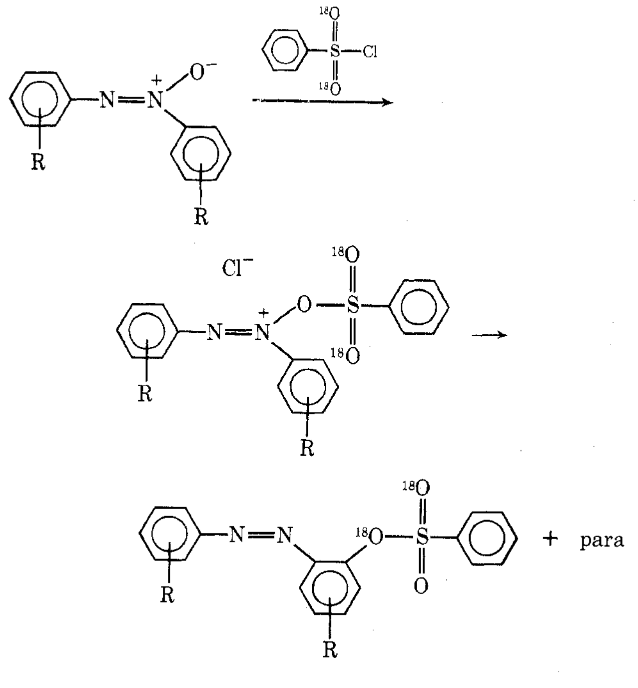
Reactants				Products[b]			
Compd	Ar	Ar′	Registry no.	Compd	Ar″	Isolated yield, %	Registry no.
1	C_6H_5	C_6H_5	1137-76-8	**2**	$2\text{-}ClC_6H_4$	81	884-29-7
				3	$4\text{-}ClC_6H_4$	6	780-21-2
4	C_6H_5CHCH	C_6H_5	37056-75-0	**5**	$2\text{-}ClC_6H_4$	72	42549-55-3
				6	$4\text{-}ClC_6H_4$	3	42549-56-4
7	$4\text{-}NO_2C_6H_4$	C_6H_5	3585-90-8	**8**	$2\text{-}ClC_6H_4$	83[c]	42597-13-7
10	C_6H_5	$4\text{-}CH_3C_6H_4$	19064-77-8	**11**	$2\text{-}Cl\text{-}4\text{-}CH_3C_6H_3$	91	42549-58-6
12	C_6H_5	$4\text{-}ClC_6H_4$	19865-58-8	**13**	$2,4\text{-}Cl_2C_6H_3$	92	42549-59-7
14	$4\text{-}CH_3OC_6H_4$	$4\text{-}ClC_6H_4$	51911-70-7	**15**	$2,4\text{-}Cl_2C_6H_3$	90	51911-72-9
16	C_6H_5	$4\text{-}H_5C_2O_2CC_6H_4$	51911-71-8	**17**	$2\text{-}Cl\text{-}4\text{-}H_5C_2O_2CC_6H_3$[d]	94	51911-73-0

[a] No significant differences in product ratios were observed when phosgene was used in place of thionyl chloride. [b] The structures of the products (except **17**) were determined by comparison of their physical and spectral properties with those of authentic samples which were prepared independently. [c] Slight heating was necessary to initiate this reaction. [d] The structure of **17** was determined by mass spectrometry, elemental analysis, and chemical degradation to known substances.

methylaniline *N*-oxides were allowed to react with acetic anhydride. The reaction was thought to proceed through an *N*-acetoxy-*N*,*N*-dimethylanilinium acetate as shown below.



Similarly, although *N*,*N*′-diarylazoxy compounds undergo deoxygenation when treated with most acid chlorides,[2] they yield ortho and para ring-substituted products when allowed to react with benzenesulfonyl chloride.[3] The ortho-substituted product has been shown by ^{18}O isotope labeling to be formed from an intermediate similar to the one proposed by Huisgen for the amine oxide reaction.



N-Aryl nitrones are reported to isomerize to the corresponding amides when allowed to react with most acid chlorides and anhydrides.[4] However, in a preliminary communication, we recently reported that *N*-aryl nitrones react rapidly with thionyl chloride or phosgene at room temperature to yield the corresponding ortho-chlorinated imine hydrochlorides in high yield.[5] The remarkable positional selectivity of this reaction prompted us to investigate the mechanism by which it occurs and to test its generality with other *N*-aryl nitrogen oxides and analogous systems. We now report the results of our investigation.

Results and Discussion

A. Nitrones. In general, the reactions are performed as follows. The aryl nitrone is dissolved at room temperature in dry benzene and thionyl chloride (or phosgene dissolved in benzene) is added dropwise. The evolution of a gas and simultaneous production of a precipitate occur almost immediately. After the addition is completed the precipitate is collected and washed with pentane. Although this procedure is usually sufficient to obtain a reasonably pure product, further purification can be accomplished by vacuum sublimation. The results are summarized in Table I.

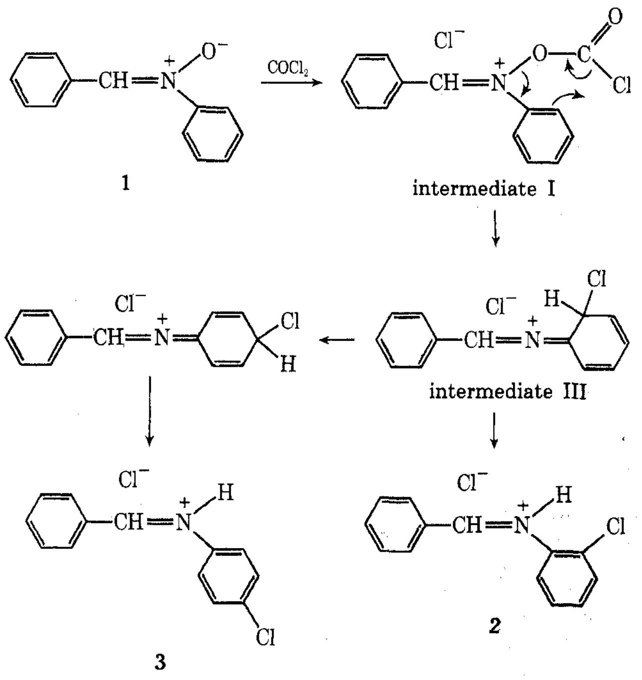
Since aryl nitrones are readily available by several methods,[6,7] the above reaction appears generally useful for the selective, rapid synthesis of ortho-chlorinated imines, and, by hydrolysis, the corresponding amines in high yield.

While several pathways might be proposed for this reaction, only one is reasonable in light of the evidence at hand. This is illustrated in Scheme I for the reaction of α,*N*-diphenylnitrone (**1**) with phosgene.

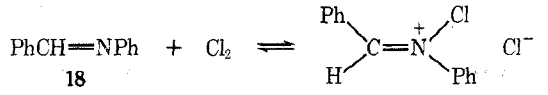
The first step of the reaction undoubtedly involves nucleophilic attack on the phosgene by the negatively charged oxygen atom of the nitrone, yielding intermediate I. An appropriately positioned nitro group would therefore be expected to decrease the rate of reaction by delocalization of the negative charge, and, in fact, α-(4-nitrophenyl)-*N*-phenylnitrone (**7**) is the only nitrone among those investigated which requires heating for the reaction to occur. The intermediate I may be viewed as decomposing to products *via* a concerted decarboxylation with ring chlorination followed by hydrogen transfer with rearomatization.

The positional selectivity of the reaction rules out two other possible mechanisms which might have been worthy of consideration. For the first of these, intermediate I would be considered to rearrange to an *N*-chloroimmonium

Scheme I



species (intermediate II) followed by ring substitution. As intermediate II is an expected constituent of an equilibrium mixture of 18 and chlorine,[8] generation of this species by addition of a dilute solution of chlorine in benzene to the anil 18 is possible. In fact, when this experiment was performed, a precipitate formed immediately, analysis of which indicated it to be an equal mixture of benzylideneaniline hydrochloride and benzylidene-*p*-chloroaniline hydrochloride;[9] *no ortho isomer was detected.* This result precludes the possibility of the reaction proceeding through intermediate II.[10] Another alternative mechanism, that of chloride attack on the *N*-aryl ring of intermediate I, is excluded as well, as that route would be expected to yield a significant proportion of para product.



The extremely high ortho:para ratio observed in all reactions is indeed significant evidence for the reaction to be considered as proceeding through a six-centered transition state. Comparison with other ring-halogenation processes involving *N*-chloro intermediates is illustrative of this point. Whereas, for example, *N*-chloro-*N*-methylaniline is reported to rearrange to ring-chlorinated products with an ortho:para ratio of approximately 2:1,[11] the products of these nitrone reactions had ortho:para ratios ranging from a minimum value of about 13.5:1 to those cases where no para isomer could be detected.[12] Thus, we consider the reaction to proceed *via* the six-centered transition state and therefore to be analogous to the reactions reported by Huisgen, *et al.*,[1] and by Oae, *et al.*[3] (*vide supra*). In view of this it is not surprising that in all the nitrone reactions studied chlorination was observed only on the *N*-aryl ring even when the *C*-aryl ring contained substituents highly activating for electrophilic substitution, *e.g.*, **14**.

B. Amine Oxides. Since thionyl chloride and phosgene react with *N*-aryl nitrones so selectively, it was of interest to determine if other *N*-aryl nitrogen oxides would react in a similar fashion. To this end, *N*,*N*-dimethylaniline *N*-oxide (**19**), prepared from *N*,*N*-dimethylaniline (**20**) and hydrogen peroxide in aqueous methanol,[13] was allowed to react with thionyl chloride. Because of the hygroscopic nature of **19**, the reaction was performed in a glove bag in a nitrogen atmosphere. Various solvents were used (benzene, chloroform, tetrahydrofuran, petroleum ether). The major competing process with ring chlorination proved to be deoxygenation of the amine oxide to **20**. This latter reaction could be minimized by working with dilute solutions of the amine oxide in petroleum ether or tetrahydrofuran, in which case approximately 90% *N*,*N*-dimethyl-2-chloroaniline (**21**) was obtained. This compares with 30% **21** and 70% **20** being obtained when the reaction was performed in more concentrated solutions.

Although reaction conditions can be optimized to give good yields of ring-chlorinated product, the reaction is restricted to tertiary amine systems, and hence is less versatile than the ortho chlorination of nitrones. Nevertheless, as this reaction appears to be basically similar to that of nitrones, it is obvious that a π-bonded nitrogen is not required.

C. Other Systems. Other *N*-aryl oxides which might be expected to react with thionyl chloride or phosgene in a similar fashion to nitrones or amine oxides apparently do not.

Nitroaromatic compounds appear to react very slowly with thionyl chloride. A small amount of reaction appears to occur upon setting to reflux for 1 week a mixture of nitrobenzene (**22**) with thionyl chloride, as the solution becomes distinctly purple in color. Nevertheless, it has not proven possible to identify any organic compounds other than **22** in the reaction mixture.

The reaction of *N*,*N'*-diaryl azoxy compounds with a number of acid chlorides including thionyl chloride has been previously investigated.[2] We confirmed that deoxygenation appears to be the major process, with ring chlorination as a minor competing side reaction.

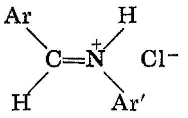
Nitroso compounds exist in the dimeric *N*-oxide form only in the solid state. We have shown in this laboratory that reaction does occur between nitrosobenzene (**23**) and thionyl chloride, but along different lines from the amine oxide and nitrone reactions. The major product is 2,4-dichloroaniline (**24**), presumably arising from rearrangement of *N*,*N*-dichloroaniline.[14] Iodosobenzene (**25**) when treated with thionyl chloride yields iodobenzene dichloride (**26**) quantitatively.[15]

Experimental Section

General. All melting points were measured using a Thomas-Hoover capillary melting point apparatus and are uncorrected. Unless otherwise stated, infrared spectra were measured as Nujol or Fluorolube mulls on a Perkin-Elmer 237-B grating spectrometer; mass spectra were measured using a Varian CH-7 mass spectrometer; nmr spectra were measured using either a Varian A-60A or a Varian EM-60 spectrometer. Benzene and tetrahydrofuran were dried over sodium ribbon and distilled prior to use. Phosgene (12.5% solution in benzene) and thionyl chloride were purchased from Matheson Coleman and Bell and used without further purification.

Nitrones. All nitrones were prepared according to the standard procedure as follows.[16] Equal molar quantities of the aryl hydroxylamine and the aldehyde were mixed in benzene solution and refluxed, water being removed in a Dean-Stark apparatus. In general, these reactions went to completion in a very short time. The solvent was evaporated and the crude nitrone was recrystallized from a 1:1 mixture of low-boiling petroleum ether and benzene. All of the nitrones utilized in this investigation have been reported in the literature[16,17] with the exception of **16**. This was isolated in 80% yield (mp 141–142°) by the above procedure. Compound **16** exhibited a mass spectrum in accord with the nitrone structure[18] (M^+, *m/e* 269; base peak, $[M - 28]^+$, *m/e* 241). Other analytical data are as follows: ir ($CHCl_3$) 3.32, 5.78, 6.14, 6.84, 6.95, 7.09, 7.22, 7.75, 8.13, 8.33, 8.48, 8.93, 9.09, 9.18, 9.71, 11.11, 11.37, 14.39, 14.82

Table II



Compd	Ar	Ar′	Mp, °C	Mass spectral data[a] $M^{+\,b,c}$	Mass spectral data[a] Base peak	Ir frequencies, μ
2	C_6H_5	2-ClC_6H_4	215 dec	215, 217	215	3.85, 4.28, 5.05, 6.10
3	C_6H_5	4-ClC_6H_4	189–191	215, 217	215	3.90, 4.30, 6.15
5	C_6H_5CHCH	2-ClC_6H_4	148 dec	241, 243	240	4.30, 5.08, 6.12, 6.23
6	C_6H_5CHCH	4-ClC_6H_4	167–169	241, 243	240	4.25, 5.00, 6.15, 6.28
8	4-$NO_2C_6H_4$	2-ClC_6H_4	188–190 dec	260, 262	51	3.88, 5.02, 6.32
11	C_6H_5	2-Cl-4-$CH_3C_6H_3$	194–197	229, 231	77	3.85, 5.00, 6.32
13	C_6H_5	2,4-$Cl_2C_6H_3$	20–205	249, 251, 253	161	3.90, 4.30, 6.25
15	4-$CH_3OC_6H_4$	2,4-$Cl_2C_6H_3$	182–185	279, 281 283	245	3.90, 6.24
17	C_6H_5	2-Cl-4-$H_5C_2O_2CC_6H_3$	163–166	287, 289	154	3.88, 5.78, 6.25

[a] All mass spectra were observed at 70 eV with a trap current of 100 μA. [b] As is common with hydrochlorides, the highest *m/e* peak observed involves loss of HCl from the parent molecule. [c] Appropriate Cl isotope patterns were observed in all cases.

μ; nmr ($CDCl_3$) δ 1.40 (t, 3 H), 4.38 (q, 2 H), 7.2–8.5 (m, 10 H). *Anal.* Calcd for $C_{16}H_{15}NO_3$: C, 71.37; H, 5.58. Found: C, 71.62; H, 5.86.[19]

General Procedure for the Reaction of Nitrones with Thionyl Chloride (or Phosgene). The aryl nitrone was dissolved in benzene and to it was added thionyl chloride (phosgene in benzene, 12.5%) dropwise in 10% molar excess. The precipitate which immediately formed was collected and washed with pentane. Rigorous purification was effected by vacuum sublimation. The product substituted imine hydrochlorides were compared with authentic materials synthesized by a standard independent means from the appropriate amines and aldehydes *via* azeotropic distillation using a Dean-Stark apparatus.[20] The isolated imines were dissolved in benzene and treated with anhydrous HCl to yield the imine hydrochlorides necessary for product comparison. Such comparisons were made in the usual manner by mixture melting points and by matching infrared and mass spectra. In all cases no depression of melting points was observed and excellent spectral matches were obtained.

Imine hydrochlorides are reasonably stable when stored in a dry atmosphere, but hydrolyze rapidly when exposed to moisture, precluding in some cases satisfactory combustion analysis. Compounds **2**[21] and **3**[22] have been previously reported. Satisfactory combustion analyses were obtained for **9**, **10**, and **17** (**9** and **10** as dihydrates). Compounds **11**, **15**, **13**, and **8** gave unsatisfactory analytical data, presumably owing to rapid hydrolysis. However, this phenomenon of rapid hydrolysis can be exploited to obtain the absolute proof of structure required in the absence of satisfactory analytical data. To this end, the products of the nitrone–phosgene reactions were degraded by hydrolysis to the parent aldehydes and amines, which were then analyzed. The following procedure was followed in all cases. The imine hydrochlorides resulting from the nitrone reactions were dissolved in tetrahydrofuran, and dilute hydrochloric acid was added. The liberated aldehyde component of the imine was extracted into ether and identified by infrared spectroscopy and prepation of its 2,4-dinitrophenylhydrazonederivatives (anisaldehyde 2,4-dinitrophenylhydrazone, mp 252–254°; benzaldehyde 2,4-dinitrophenylhydrazone, mp 236–237°; *p*-nitrobenzaldehyde 2,4-dinitrophenylhydrazone, mp 320°; no depression of melting point was observed on admixture with authentic samples). After extraction of the aldehyde, the remaining reaction mixture was made basic, and the liberated amine was extracted into ether and isolated by evaporation. Structure verification was obtained through comparison of the spectroscopic properties and/or melting points of authentic materials, and also by combustion analysis of the derived amine hydrochlorides, prepared by passing hydrogen chloride into an ethereal solution of the amine. 2,4-Diloroaniline hydrochloride (**29**) had mp 216°. *Anal.* Calcd for $C_6H_6NCl_3$: C, 36.27; H, 3.02. Found: C, 36.50; H, 3.15. 2-Chloro-4-methylaniline hydrochloride (**30**) sublimed at 240–245°. *Anal.* Calcd for $C_7H_9NCl_2$: C, 47.19; H, 5.06. Found: C, 47.42; H, 5.07. 2-Chloroaniline hydrochloride (**31**) sublimed at 200–205°. *Anal.* Calcd for $C_6H_7NCl_2$: C, 43.90; H, 4.27. Found: C, 44.02; H, 4.44.

All the amines derived from the imine hydrochlorides have been reported previously, except that derived from compound **17**, *via* 4-amino-3-chlorobenzoic acid ethyl ester (**27**). Thus, compound **27** was further hydrolyzed with 40% aqueous sodium hydroxide solution at reflux temperature for 15 min. The solution was allowed to cool and the pH was adjusted to 4.5. The 4-amino-3-chlorobenzoic acid (**28**) which precipitated was recrystallized from 85% aqueous tetrahydrofuran, mp 222–224°.[23] Mass spectral and ir data for **17** are given in Table II. *Anal.* Calcd for $C_{16}H_{15}NO_2Cl_2$ (**17**): C, 59.26; H, 4.63. Found: C, 59.39; H, 4.88.

General Procedure for the Reaction of *N*,*N*-Dimethylaniline *N*-Oxide (19) with Thionyl Chloride. Compound **19** was prepared according to a method described previously.[13] It was dried through azeotropic distillation with benzene, then filtered in a nitrogen atmosphere in a glove bag. A 10% molar excess of thionyl chloride was then added dropwise to a solution of **19** in various solvents (chloroform, tetrahydrofuran, benzene, and petroleum ether were tried in different runs). After the addition was complete, the solution was made basic with aqueous sodium hydroxide and the organic fraction was collected, dried ($MgSO_4$), and evaporated. The crude products obtained in each run were examined by gas–liquid chromatography (30% Carbowax on Chromosorb P, 180°) and by mass spectrometry. Unless dilute solutions (*e.g.*, 1%) of **19** were used, significant quantities of *N*,*N*-dimethylaniline (**20**) were formed along with 2-chloro-*N*,*N*-dimethylaniline (**21**), *sym*-trinitrobenzene adduct, mp 108.5–109° (lit. mp 110–111°),[24] *m/e* 154, 156. With dilute solutions of **19** in tetrahydrofuran or petroleum ether, **21** was obtined as the only significant product.

General Procedure for the Reaction of Nitrosobenzene (23) with Thionyl Chloride. Nitrosobenzene (**23**) was dissolved in benzene, and thionyl chloride was added dropwise in 10% molar excess. An immediate reaction occurred. The product was isolated by bringing the reaction mixture to pH 11, extracting with ether, drying the organic material ($MgSO_4$), and evaporating the solvent. The product was proven to be 2,4-dichloroaniline (**24**) by mass spectrometry, *m/e* 161 (100%), 163, 91, preparation of its benzylidene derivative, mp 84° (lit. mp 84°),[25] and by comparison of its ir spectrum with one reported in the literature.[26]

Reaction of Nitrobenzene with Thionyl Chloride. Nitrobenzene (**22**) was refluxed with a 10% molar excess of thionyl chloride for 1 week. After this time the solution had a distinctly purple color. However, it proved impossible to isolate any organic material other than nitrobenzene in quantities sufficient for analysis.

Reaction of Iodosobenzene with Thionyl Chloride. The procedure is exactly the same as that used for nitrosobenzene. The product was identified by comparison with iodobenzene dichloride (**26**), mp 110–111°, which was independently synthesized.

Registry No.—**28**, 2486-71-7; **29**, 29084-76-2; **30**, 51085-51-9; **31**, 137-04-2; thionyl chloride, 7719-09-7; phosgene, 75-44-5.

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(9) Subsequent treatment of the filtrate with hydrogen chloride caused precipitation of the remainder of imines in solution as their hydrochlorides. These were shown to be, again, an approximately equal mixture of benzylideneaniline hydrochloride and benzylidene-*p*-chloroaniline hydrochloride.

(10) Whether intermediate II exists in the form shown or as PhCH(Cl)N(Cl)Ph is irrelevant. The same chlorinated imine hydrochloride should be formed as α-chloroamines readily isomerize to imine hydrochlorides.

(11) (a) P. Haberfield and D. Paul, *J. Amer. Chem. Soc.*, **87**, 5502 (1965); (b) another example is given by R. S. Neale, R. G. Schepers, and M. R. Walsh, *J. Org. Chem.*, **29**, 3390 (1964).

(12) The small amount of para isomer observed in some cases can be accounted for by an S_N2' type process to which intermediate II might be subject.

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1,3-Oxathiole 3,3-Dioxides and Benzoyl-Substituted Thiirane 1,1-Dioxides

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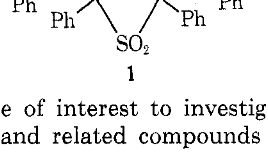
Bis(phenacyl) sulfone on bromination to bis(α-bromophenacyl) sulfone (**2**) and then treatment with base yielded 2-benzoyl-4-bromo-5-phenyl-1,3-oxathiole 3,3-dioxide (**5**). Reduction of **5** with triphenylphosphine in methanol gave 2-benzoyl-5-phenyl-1,3-oxathiole 3,3-dioxide (**10**), which can be degraded with base to the known 5-phenyl-1,3-oxathiole 3,3-dioxide (**7**). The structural assignments for the compounds previously ascribed to be 2,3-dibenzoyl-2,3-diphenylthiirane (**15**) and the corresponding thiirane 1-oxides and 1,1-dioxide are revised. It is suggested that the compounds are 2-benzoyl-2,4,5-triphenyl-1,3-oxathiole (**14**), and the corresponding 3-oxides **18a** and **18b** and 3,3-dioxide **12**, respectively. The reactions and properties of these compounds will be discussed in terms of the new structural assignments. 2-Benzoyl-5-phenyl-1,3-oxathiole 3,3-dioxide (**10**) can be specifically deuterated in the 2 and 4 positions. There is no deuterium exchange between the two positions at room temperature, or at the melting point (150°). Rearrangement between 1,3-oxathiole 3,3-dioxides and 2,3-dibenzoylthiirane 1,1-dioxides is therefore negligible under these conditions.

Thiirane 1,1-dioxides easily undergo thermal decomposition to yield alkenes and sulfur dioxide. 2,3-Dibenzoyl-2,3-diphenylthiirane 1,1-dioxide (**1**) is, however, reported to be unusually thermostable.[1]



1

It was therefore of interest to investigate the possible synthesis of this and related compounds from the corresponding α-halo sulfones, thus for the first time being able to trap an intermediate thiirane 1,1-dioxide in a Ramberg–Bäcklund rearrangement.[2] However, efforts to prepare 2-bromo-2,3-dibenzoylthiirane 1,1-dioxide (**3**) or the corresponding thiirene 1,1-dioxide **4** from bis(α-bromophenacyl) sulfone (**2**) failed. Instead 2-benzoyl-4-bromo-5-phenyl-1,3-oxathiole 3,3-dioxide (**5**) was formed in a high yield, which is in agreement with a previous synthesis of 5-phenyl-1,3-oxathiole 3,3-dioxide (**7**) from the α-halo keto sulfone **6**.[3]

The present paper describes the synthesis and properties of some 1,3-oxathiole 3,3-dioxides. Furthermore, the structure of the compound previously assigned to be 2,3-dibenzoyl-2,3-diphenylthiirane 1,1-dioxide (**1**) will be questioned, and evidence for the 1,3-oxathiole 3,3-dioxide structure **12** will be presented. In view of this new structural assignment the previously reported reactions of this[1] and related compounds[4,5] will be discussed.

Bis(phenacyl) sulfone was prepared from bis(phenacyl) sulfide[6] by oxidation with 3-chloroperbenzoic acid in chloroform. The sulfone was brominated with 2 equiv of bromine in chloroform to yield bis(α-bromophenacyl) sulfone[7] (**2**), which precipitated from the reaction mixture. The compound was almost insoluble in most solvents and was therefore difficult to obtain chromatographically pure (tlc). Treatment of the crude compound with triethylamine in methylene chloride at room temperature gave 2-benzoyl-4-