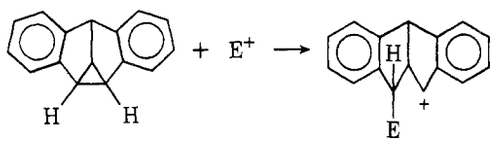
The effect is observed whether the two aromatic rings are cis to one another or trans, and thus cannot be due to a steric relief of strain. We do not have any stereochemical results in a diphenyl system, so we cannot say whether the electrophile is entering with retention or inversion, but in the system studied by Cristol and coworkers[14] ring opening always occurred on the bond between the aromatic rings and with retention (eq 11). It will be interesting to see if this stereochemistry will hold for simple cyclopropanes.



(11)

The independence of product composition with cyclopropane stereochemistry is also clearly shown by the reactions of *cis*- and *trans*-2-phenyl-1-methylcyclopropanols, and the product composition is also unchanged when the much less reactive methyl ethers are used in place of the alcohols. Additional work is now in progress which may shed light on some of these puzzling observations.

Acknowledgment. The authors wish to thank the National Science Foundation for support of this research by Grant GP 13783X.

Registry No.—Ia, 52306-22-6; Ib, 52438-83-2; IIa, 52306-23-7; IIb, 10606-71-0; *cis*-III, 52306-24-8; *trans*-III, 52306-25-9; (+)-IV, 52306-26-0; Va, 43187-69-5; Vb, 43187-79-7; *cis*-VI, 52374-29-5; *trans*-VI, 52306-27-1; VII, 495-41-0; VIII, 769-60-8; benzalacetone, 122-57-6; hydrazine, 302-01-2; 3-methyl-5-phenyl-2-pyrazoline, 939-03-7; 3-acetoxy-3-methyl-5-phenyl-1-pyrazoline, 52306-28-2; *N*-bromosuccinimide, 128-08-5; mercuric acetate, 1600-27-7; *tert*-butyl hypochlorite, 507-40-4; ferric chloride, 7705-08-0; 4-chloro-4-phenyl-2-butanone, 52306-29-3; 4-bromo-4-phenyl-2-butanone, 52306-30-6; *cis*-1,2-diphenylcyclopropyl acetate, 43187-69-5; *trans*-1,2-diphenylcyclopropyl acetate, 43187-79-7; β-bromo-β-phenylpropiophenone, 52306-31-7; α-phenylpropiophenone, 2042-85-5; 2-phenylpropionaldehyde, 93-53-8; 1,2-diphenyl-1-propanol, 28795-94-0; β-chloro-β-methylpropiophenone, 34880-85-8; isobutyraldehyde, 78-84-2; isopropylphenylcarbinol, 611-69-8; isobutyrophenone, 611-70-1; α-bromo-α-methylpropiophenone, 10409-54-8.

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Activation of Dimethyl Sulfoxide by Electrophiles and Use of the Reactive Intermediates in the Preparation of Iminosulfuranes[1a]

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Dimethyl sulfoxide (DMSO) reacts at oxygen with SO_3, P_4O_{10}, BF_3, and H_2SO_4 at or below room temperature. With the first two electrophiles, intermediates are obtained that generally react readily with sulfonamides, amides, and aromatic amines to give iminosulfuranes in good to excellent yields (60–90%). Although intermediate complex formation is necessary for the formation of iminosulfuranes, it is not a sufficient condition for successful reaction, as a good leaving species must also be provided to facilitate cleavage of the S–O bond of DMSO. Acetic anhydride does not form significant quantities of "activated" intermediate with DMSO at room temperature but does at elevated temperatures and, if sulfonamides or carboxamides are present, iminosulfuranes are obtained. The activation of DMSO with SO_3 has received detailed study; SO_3 is especially useful in the preparation of iminosulfuranes from DMSO and aromatic amines; and it can also be used with the other nitrogen compounds. Salts have been prepared from selected iminosulfuranes and hydrogen chloride. Mechanistic considerations are also discussed.

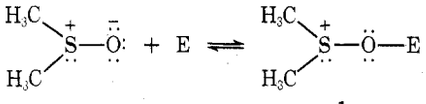
In this paper we are reporting (a) the "activation" of DMSO by liquid SO_3 and, for comparison, P_4O_{10}, acetic anhydride, concentrated sulfuric acid, and boron trifluoride; (b) the scope and limitations of the reaction of "activated" DMSO with a variety of nitrogen compounds (sulfonamides, amides, and aryl amines) to prepare iminosulfuranes with a wide range of structures (R_2S^+–N^-–R'); (c) certain mechanistic aspects of the iminosulfurane preparative reaction; and (d) some spectral and other miscellaneous characteristics of iminosulfuranes. As a corollary of (a),

we were also interested in knowing if complex formation between DMSO and any electrophile followed by reaction with an appropriate nitrogen compound as the nucleophile is a sufficient condition to ensure iminosulfurane formation.

Various electrophiles have been used to "activate" DMSO;[2] these include, among others, dicyclohexylcarbodiimide + acid,[3] acetic anhydride,[4] acetyl chloride,[5] phosphorus pentoxide,[6] polyphosphoric acid,[7] sulfur trioxide–pyridine,[8] and diphenylketene-*p*-tolylimine + acid.[9] In most instances, alcohols have been the nucleophiles,[2-4] but in a limited number of cases phenols,[10] enols,[11] oximes,[12] and amines[6,13] have also been used.

Results and Discussion

A. "Activation" of DMSO by Electrophiles. Nuclear magnetic resonance spectroscopy is an excellent microtechnique for *in situ* observation of complex formation between DMSO and electrophiles without the need to isolate and handle extremely labile and hygroscopic intermediates. DMSO shows a sharp singlet at *ca.* δ 2.6 (TMS O), but upon the addition of certain electrophiles, usually with cooling, a new downfield singlet appears immediately at *ca.* δ 3.0. A downfield shift would be expected if a DMSO–electrophile complex (**1**) had formed owing to the greater deshielding of the $S(CH_3)_2$ protons as a result of the development of a full positive charge on sulfur. Such a downfield shift is observed upon addition to DMSO of BF_3, P_4O_{10}, SO_3, or concentrated sulfuric acid but not acetic anhydride at room temperature.



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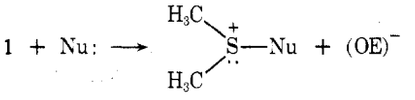
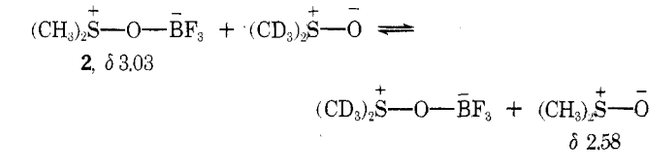
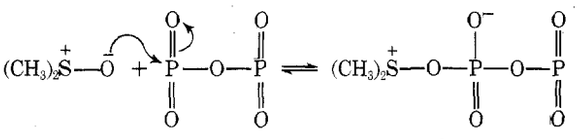


To be certain that the new signal was, in fact, derived from the complex (**1**) and was not an artifact, we isolated the intermediates in some cases and examined their nmr spectra. The nmr spectrum of the isolated (very hygroscopic) DMSO–BF_3 complex (**2**), mp 51° (lit.[14a] mp 53°), in acetone-d_6 shows a sharp singlet at δ 3.08; in DMSO-d_6, in which the complex is more soluble, two sharp singlets are observed at δ 3.03 and 2.58 suggesting that the following equilibrium exists.



2, δ 3.03 δ 2.58

Interaction of DMSO with P_4O_{10} in chloroform at room temperature immediately yields an extremely hygroscopic white precipitate whose nmr spectrum in acetone-d_6 shows only one sharp singlet at δ 2.96. We visualize the formation and structure of the complex (**3**) as follows (P_2O_5 is used



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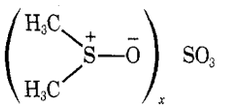
for convenience in the equation). As with the DMSO–BF_3 complex, **3** also shows two sharp singlets at δ 2.87 and 2.61 in DMSO-d_6 suggesting an equilibrium exchange process.

A solid DMSO–SO_3 complex having the formula **4**, where x ranges from 1 to 3, has been reported recently by Pet-



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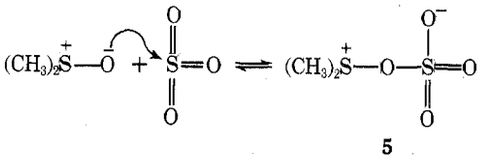
titt.[15] We find that reaction of DMSO with liquid SO_3 yields an immediate white precipitate (**5**) but we have been unable to isolate it without decomposition as it is extremely sensitive to moisture. A DMSO solution of this complex, however, shows the anticipated sharp singlets at δ 3.06 and 2.6.



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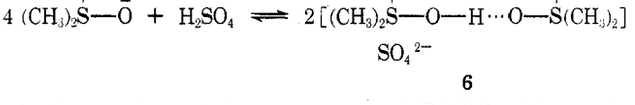
In contrast, no changes are observed in the nmr spectrum of a solution of DMSO and acetic anhydride at room temperature over several hours; two singlets are seen at δ 2.51 and 2.2 corresponding to the methyl protons of DMSO and acetic anhydride, respectively, with no peaks farther downfield. DMSO reacts slowly with acetic anhydride at room temperature,[16] a result that is not surprising, as bond breaking is first required. Upon heating the solution, however, the Pummerer rearrangement occurs rapidly and is easily observed by nmr.

A solution of DMSO in concentrated sulfuric acid (4:1 molar ratio) exhibits two singlets at *ca.* δ 3.2 and 11.32. Since no DMSO signal is observed at δ 2.6 it is assumed that all of the DMSO is bound as a rapidly equilibrating hydrogen-bonded complex **6**. The proposed structure is



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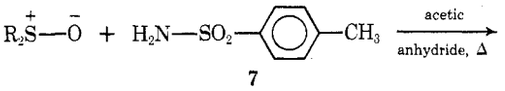
similar to that of the complexes of DMSO with methanesulfonic acid[17] and 2,4,6-trinitrobenzenesulfonic acid.[18]

B. "Activated" DMSO Reaction with *p*-Toluenesulfonamide. We next directed our attention to the question of whether complex formation between DMSO and the electrophiles is a sufficient condition to ensure iminosulfurane formation on reaction of the complexes with an appropriate nitrogen compound as the nucleophile. We chose *p*-toluenesulfonamide (**7**) as the standard nucleophile because Tarbell and Weaver[19] had shown that certain sulfoxides condense with **7** on heating a chloroform solution in the presence of acetic anhydride or phosphorus pentoxide to give low to modest yields of crystalline iminosulfuranes (dimethyl sulfoxide was not studied by Tarbell and Weaver). The condensation was apparently viewed as a simple dehydration reaction with the P_4O_{10} or acetic anhydride functioning as the dehydrating agent; no suggestion of complex formation was offered.[19]



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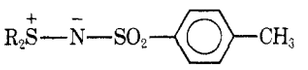


As a control, DMSO and *p*-toluenesulfonamide (**7**) were shown to be unreactive at room temperature for 72 hr (nmr, tlc). In contrast, reaction of **7** with excess DMSO containing sulfur trioxide or phosphorus pentoxide at room

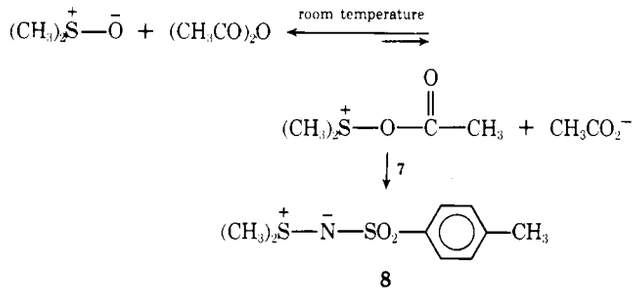
Table I
***N*-Sulfonyliminosulfuranes from "Activated" DMSO and Sulfonamides**

Sulfonamide	Registry no.	Activator	Reaction conditions Temp, °C	Time, hr	Product	Yield,[a] %	Mp,[a] °C	Lit. mp, °C	Ref
p-Toluenesulfonamide 7	70-55-3	SO_3	15–25	10	*p*-H_3C—$C_6H_4SO_2\bar{N}$—$\dot{S}(CH_3)_2$ 8	60–80	156–158	158–159	20
		P_4O_{10}	15–25	1.5		60–75	156–158		
		Ac_2O	85–90	1.5		60–75	156–158		
Benzenesulfonamide 9	98-10-2	SO_3	15–25	20	$C_6H_5SO_2\bar{N}$—$\dot{S}(CH_3)_2$ 10	65	128–130.5	131	21
		Ac_2O	90	4		60–75	124–126		
p-Nitrobenzenesulfonamide 11	6325-93-5	SO_3	15–25	27	*p*-O_2N—$C_6H_4SO_2\bar{N}$—$\dot{S}(CH_3)_2$ 12	>75	183–185	186	22
		Ac_2O	95	2.5		>90	183–185		
p-Chlorobenzenesulfonamide 13	98-64-6	SO_3	15–25	5	*p*-Cl—$C_6H_4SO_2\bar{N}$—$\dot{S}(CH_3)_2$ 14[c]	70–90	110–113	116–117[b]	
Methanesulfonamide 15	3144-09-0	Ac_2O	85–90	4	$CH_3SO_2\bar{N}$—$\dot{S}(CH_3)_2$ 16	30–40	111–117	122–123	23

[a] Crude reaction product. [b] New compound purified by crystallization successively from methylene chloride and then acetone. *Anal.* Calcd for $C_8H_{10}NO_2S_2Cl$: C, 38.16; H, 4.00; N, 5.56; S, 25.47; Cl, 14.08. Found: C, 38.45; H, 4.03; N, 5.68; S, 25.26; Cl, 14.30. [c] Registry no., 52259-84-4.

temperature for 10 or 1.5 hr, respectively, followed by dilution of the reaction mixture with 10% aqueous sodium hydroxide gave 60–80% yields of the iminosulfurane, *S,S*-dimethyl-*N*-*p*-toluenesulfonyliminosulfurane (8). Dilution of the reaction mixture with water rather than with base gave substantially lower yields of 8 contaminated with adhering sulfuric or phosphoric acids. Solvents, such as chloroform used by Tarbell and Weaver,[19] are undesirable as lower yields are obtained.

Although we had shown earlier that complex formation could not be detected after several hours (by nmr) between DMSO and acetic anhydride at room temperature, if 7 (1 mol) is dissolved in a DMSO–acetic anhydride solution (5:1.02 molar ratio) for 28 hr at room temperature, nmr shows that some reaction has taken place but most of the amide (7) is unchanged. On work-up, an approximately 20% yield of iminosulfurane 8 is isolated and almost 60% of the starting material 7 is recovered. We conclude that the initial reaction at room temperature between DMSO and acetic anhydride is an equilibrium process which highly favors reactants and the small quantity of complex present cannot be detected by ordinary nmr monitoring. In the presence of 7, however, the intermediate complex is drained off, the equilibrium is reestablished, and some iminosulfurane 8 (20%) is slowly formed. If a solution of 7 in DMSO–acetic



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anhydride is heated at about 85° for 1.5 hr all the amide 7 reacts and a 75% yield of 8 is obtained. In the absence of 7, heating a solution of DMSO–acetic anhydride yields Pummerer rearrangement product.

Although "activation" of DMSO by electrophilic reagents is essential for iminosulfurane formation, certain complexes do not yield iminosulfuranes on reaction with *p*-toluenesulfonamide (7). Thus, DMSO forms complexes with boron trifluoride and concentrated sulfuric acid but no reaction is observed between those complexes and 7 for up to 72 hr (80–85% of 7 is recovered). In the sulfuric acid case, reaction temperatures up to 85° were studied.

C. Scope of the Reaction of "Activated" DMSO with Nitrogen Compounds. *N*-Sulfonyliminosulfuranes. Table I lists sulfonyliminosulfuranes (**8, 10, 12, 14, 16**) prepared from sulfonamides (**7, 9, 11, 13, 15**) (1 mol), DMSO (5 mol), and the three electrophilic activating agents (1.1 mol) that had proven to be successful in the earlier control studies. The sulfonyliminosulfuranes are white solids with the exception of ylide **12** [from *p*-nitrobenzenesulfonamide (**11**)] which is pale yellow. They are nonhygroscopic compounds, stable at room temperature without special precautions.

***N*-Acyliminosulfuranes.** In view of the uncertainty and sparsity of the earlier work, we next examined the reaction of DMSO with a series of amides. Table II summarizes the results. With the exception of **22** which is pale yellow, all the other *N*-acyliminosulfuranes, including those previously reported by us,[28] are white, crystalline, nonhygroscopic, stable solids at room temperature.

***N*-Arylliminosulfuranes.** When this study was initiated, *N*-aryliminosulfuranes had not yet been described in the literature. The first preparation was reported by Claus and Vycudilik[6] from aromatic amines and DMSO in chloroform solution for 2–24 hr in the presence of phosphorus pentoxide–triethylamine. If triethylamine is omitted, bismethylene derivatives of the amine or polymers are obtained.[13] Subsequently, Lerch and Moffatt[13] obtained *N*-aryliminosulfuranes in 75–85% yields only from *m*- and *p*-nitro- and 3,5-dinitroaniline on reaction with DMSO, dicyclohexylcarbodiimide, and anhydrous phosphoric acid; 2,4-dinitroaniline did not react and was recovered. Acetic anhydride acetylates the amines and thus is not a suitable activator. Our study of the preparation of *N*-aryliminosulfuranes, therefore, focussed exclusively on sulfur trioxide activation; results are summarized in Table III.

The *N*-aryliminosulfuranes with a powerful electron-withdrawing group (CN or NO_2) on the ring (**40, 42, 48, 50, 52, 58**) are fairly stable; they have been stored for 1–12 months at room temperature with no observable change, and appear to be stable indefinitely at −20°. In contrast, the iminosulfuranes obtained from the haloanilines (**28, 30, 32, 34, 36, 38, 44**) are hygroscopic and decompose within a few days to a few weeks at room temperature but they can be stored for at least 1 month at 0° and up to 6 months at −30°. The least stable iminosulfurane (**54**), prepared from

Table II
***N*-Acyliminosulfuranes from "Activated" DMSO and Amides**

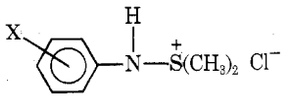
Amide	Registry no.	Activator	Reaction conditions: Temp, °C	Time, hr	Product	Yield,[a] %	Mp,[b] °C	Lit. mp, °C	Ref
Dichloroacetamide **17**	683-72-7	SO_3	15–25	46	$Cl_2CH-C(=O)-\bar{N}-\overset{+}{S}(CH_3)_2$ **18**	25–35	84–89		
		Ac_2O	80–95	9.5		25–30	(101–102) 95–98 (101–102)	101–102	24
Trichloroacetamide **19**	594-65-0	Ac_2O	90	3	$Cl_3C-C(=O)-\bar{N}-\overset{+}{S}(CH_3)_2$ **20**	4	86–87 (91–92)	78–79	25
p-Nitrobenzamide **21**	619-80-7	SO_3	15–25	24	*p*-$O_2N-C_6H_4-C(=O)-\bar{N}-\overset{+}{S}(CH_3)_2$ **22**[f]	80–85	202–206		
		P_4O_{10}	15–25	24		70–75	184–200	220–222[d]	
		Ac_2O	95–100	3.5		0[c]			
Benzamide **23**	55-21-0	SO_3	15–25	45	$\left(C_6H_5-C(=O)-NH-\right)_2CH_2$ **24**	22–26[e]	216 (219)	219	26
$NCNH_2$ **25**	420-04-2	Ac_2O	25	44	$NC-\bar{N}-\overset{+}{S}(CH_3)_2$ **26**	28	63–70	82–83	27
		SO_3	<25	4		0	(74–78)		

[a] Crude reaction product. [b] Crude (pure). [c] **21** (85%) was recovered. [d] New compound. *Anal.* Calcd for $C_9H_{10}N_2O_3S$: C, 47.78; H, 4.46; N, 12.38; S, 14.17. Found: C, 48.06; H, 4.56; N, 12.44; S, 13.96. [e] **23** (58%) was recovered. [f] Registry no., 52259-85-5.

p-toluidine, turns black within several days at room temperature but it can be stored at −30°.

In the reaction of aromatic amines and amides with DMSO–SO_3 two points are noteworthy: (1) some amines react rapidly and quite exothermically, and require careful temperature control, whereas sulfonamides and carboxamides react slowly and only slightly exothermically; and (2) in the reaction of sulfonamides, a portion of the iminosulfurane precipitates during the reaction but the best yields are obtained only if the reaction mixture is diluted with aqueous base. With the amines, dilution of the reaction mixture with water gives no precipitate of iminosulfurane (water-insoluble), suggesting that the reaction product is a (bisulfate?) salt; base is required to obtain the ylide from the salt and solvent extraction of the aqueous DMSO solution is often needed to obtain the best yields (up to 90%).

D. Salts of Iminosulfuranes with Hydrogen Chloride. Iminosulfuranes are basic and form salts with hydrogen chloride but, in the cases studied, the salts were unstable and hygroscopic and lost hydrogen chloride readily, thereby precluding correct elemental analyses. The salts are easily precipitated by treating a cold ether solution of iminosulfurane with a hydrogen chloride–ether solution. Rapid work-up and solvent evaporation permits isolation of salts that are fairly pure as shown by titrimetric analysis. The following salts were prepared.



X=3-Cl, 4-Cl, 3-Br, 4-NO_2, 4-CN

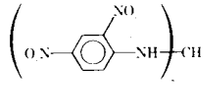
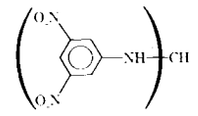
All salts have strong ir absorptions at 3500–3000 cm^{-1} (NH). The salts in which X = 4-NO_2 and 4-Cl have been reported by Vilsmaier and Sprügel,[31] but in the latter case we obtain mp 113–114° dec (lit. mp 103–104°).

E. Mechanistic Considerations. "Activation" of DMSO by an electrophilic reagent which converts it to an intermediate with a good leaving group is an essential condition for successful preparation of iminosulfuranes from DMSO and the nitrogen compounds discussed in this paper. In the initial stages of our study, when we had examined only a few sulfonamides, carboxamides, and aromatic amines, and based also on the literature,[6,19,32] we tentatively concluded that the acidity of the N–H proton was the most important structural feature for the successful preparation of iminosulfuranes from "activated" DMSO.[33] That conclusion was based on the higher yields obtained when the amino compounds contained a good electron-withdrawing group either on the aromatic ring (*p*-nitroaniline and *p*-nitrobenzamide, for example) or attached to the nitrogen function (*p*-toluenesulfonamide, for example). With improved monitoring and work-up techniques and better handling of liquid sulfur trioxide to prevent the entry of water, it was shown that proton acidity is not the crucial factor in the yields obtained. The acidity of the N–H proton of the nitrogen component, however, is important in facilitating the removal of the second proton from the intermediate iminosulfonium salt. The nucleophilicity of the nitrogen component is important in controlling the time required for reaction, although the effects have not been quantitated nor are they very large.

Aromatic amines fall into three groups: (a) those with electron-donor or weak electron-withdrawing groups on the ring are usually completely consumed after addition to the reaction mixture is complete (very exothermic reaction); (b) those with one powerful electron-withdrawing group require 1.5–2 hr (slight exothermicity); and (c) those with more than one electron-withdrawing group require up to 5 hr. The reaction rates do not differ by the orders of magnitude that might be expected in comparing *p*-toluidine, for example, with *p*-nitroaniline (rate ratio approximately 5:1). We believe that the relatively small rate differences among the amines are due to a "leveling" effect caused by the facile departure of an effective leaving group from the DMSO–SO_3 intermediate. In transition-state terms, bond breaking in the highly polar DMSO medium is expected to be an energetically favorable process and should be farther advanced than bond making. The reaction may thus be viewed as a solvolytically assisted nucleophilic displacement reaction.

Although we have not attempted a systematic study of

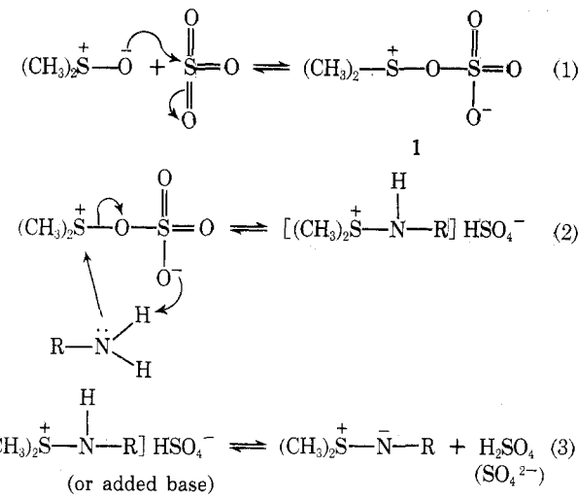
Table III
N-Aryliminosulfuranes from Aromatic Amines and DMSO "Activated" by SO_3[a]

Aromatic amine	Registry no.	Reaction time, min	Product[b]	Yield,[c] %	Mp,[d,e] °C	Lit. mp, °C	Ref
o-Chloroaniline **27**	95-51-2	15	*o*-Cl—C_6H_4—$\bar{N}$—$\overset{+}{S}(CH_3)_2$ **28**	70	73–75 (74–75)	58–60	6b
m-Chloroaniline **29**	108-42-9	10	*m*-Cl—C_6H_4—$\bar{N}$—$\overset{+}{S}(CH_3)_2$ **30**	75–100	53–55 (55.5–56.5)	50–52	6b
p-Chloroaniline **31**	106-47-8	40	*p*-Cl—C_6H_4—$\bar{N}$—$\overset{+}{S}(CH_3)_2$ **32**	50–75	65–66 (66.5–67.5)	64–66 66–67	6b 30
o-Bromoaniline **33**	615-36-1	90	*o*-Br—C_6H_4—$\bar{N}$—$\overset{+}{S}(CH_3)_2$ **34**	60–70	61.5–62.5 (62–63)		
m-Bromoaniline **35**	591-19-5	10–15	*m*-Br—C_6H_4—$\bar{N}$—$\overset{+}{S}(CH_3)_2$ **36**	60–90	55–58 (58.5–59.5)		
p-Bromoaniline **37**	106-40-1	10–15	*p*-Br—C_6H_4—$\bar{N}$—$\overset{+}{S}(CH_3)_2$ **38**	50–70	73.5–74.5 (74–75)	72–74	6b
o-Cyanoaniline **39**	1885-29-6	100	*o*-NC—C_6H_4—$\bar{N}$—$\overset{+}{S}(CH_3)_2$ **40**	80–90	94–95.5 (95–96)		
p-Cyanoaniline **41**	873-74-5	90	*p*-NC—C_6H_4—$\bar{N}$—$\overset{+}{S}(CH_3)_2$ **42**	70–85	104–108 (111–112)	108–112	30
p-Fluoroaniline **43**	371-40-4	45	*p*-F—C_6H_4—$\bar{N}$—$\overset{+}{S}(CH_3)_2$ **44**	50–85	106–108 (109–110)		
2,4,6-Tribromoaniline **45**	147-82-0	300	2,4,6-$Br_3C_6H_2$—$\bar{N}$—$\overset{+}{S}(CH_3)_2$ **46**	65–75	76–79 (79–81)	78–80	6b
m-Nitroaniline **47**	99-09-2	180	*m*-O_2N—C_6H_4—$\bar{N}$—$\overset{+}{S}(CH_3)_2$ **48**	60–75	96–98 (97.5–99)	100–101	13
p-Nitroaniline **49**	100-01-6	165	*p*-O_2N—C_6H_4—$\bar{N}$—$\overset{+}{S}(CH_3)_2$ **50**	70–90	169–170 (172–174)	148–151 163–165	6b 13
2-Methyl-5-nitroaniline **51**	99-55-8	120	2-CH_3—5—O_2N—C_6H_3—$\bar{N}$—$\overset{+}{S}(CH_3)_2$ **52**	85	92–95 (100.5–101.5)		
p-Toluidine **53**	106-49-0	30	*p*-H_3C—C_6H_4—$\bar{N}$—$\overset{+}{S}(CH_3)_2$ **54**		49–52 (55–56)	45 40–45	6b 30
2,4-Dinitroaniline **55**	97-02-9	1560	 **56**	>90	277–279 (286–286.5)	275–277	13
3,5-Dinitroaniline **57**	618-87-1	270	2,3-$(O_2N)_2C_6H_3$—$\bar{N}$—$\overset{+}{S}(CH_3)_2$ **58**	65–70	166–168 (169–170)	168–170	13
			 **59**	25–35	197–200 (253–254)		

[a] Mole ratios of DMSO:SO_3:amine were approximately 5:1.2:1 in most cases (consult Experimental Section for variations); reaction temperature 10–20°; reaction time determined by disappearance of amine (tlc). [b] Registry no.: **28**, 20094-93-3; **34**, 52259-86-6; **36**, 52259-87-7; **40**, 52259-88-8; **44**, 52259-89-9; **50**, 27691-52-7; **52**, 52259-90-2; **54**, 27691-50-5; **56**, 31896-61-4; **59**, 52259-91-3. [c] Crude reaction product. [d] Crude (pure). [e] Satisfactory analytical data (±0.3% for C, H, N, S, and halogen when present) were reported for **28**, **34**, **36**, **40**, **44**, **50**, **52**, **54**, **56**, and **59**: Ed.

steric effects on iminosulfurane formation, a large ortho substitutent in the aromatic amines seems to slow down the reaction markedly (Table III).

A reaction pathway which accounts for all the facts is shown below, using SO_3 as the activating agent for illustrative purposes as it is the most generally useful of the electrophiles studied taking into account not merely overall reaction times but ease of handling as well.



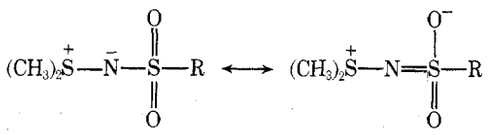
The first step is the formation by the equilibrium process shown of the DMSO–SO_3 intermediate (**1**, E = SO_3) which undergoes nucleophilic attack by amine (sulfonamide or carboxamide). Step 2 is rapid with amines and slow with sulfonamides and carboxamides (the role of electron-withdrawing substituents in reducing the overall reaction rate has already been noted). The equilibrium in step 3 is disfavored (far to the left) with aromatic amines owing to the lower acidity of the remaining N–H proton but the forward reaction is favored with sulfonamides and *p*-nitrobenzamide. With amines, no iminosulfurane can be detected until strong base is added, which forces step 3 to the right. With sulfonamides and *p*-nitrobenzamide the higher acidity of the remaining N–H proton permits its facile removal either by the excess DMSO present or even to some extent by HSO_4^-. Iminosulfurane is present in substantial amounts in these cases even before strong aqueous base is added and it precipitates upon addition of water or spontaneously.

The formation of bis(amino)- [or bis(amido)-] methanes in the DMSO–SO_3 reactions is a side reaction that occurs only when the longest reaction times are required. In the case of 2,4-dinitroaniline, the bis(amino)methane is the major (sole?) product. In the one case studied, we have shown that the bis(amino)methane (**59**, Table III) can be formed from preformed iminosulfurane, *S,S*-dimethyl-*N*-3,5-dinitrophenyliminosulfurane (**58**), by dissolving it in DMSO–SO_3 reaction mixture overnight. This experiment leads us to believe that iminosulfuranes or their bisulfate salts may be the precursors of the bis(amino)methanes, but whether that is the exclusive pathway is uncertain.

F. Spectral Characteristics of Iminosulfuranes.[34-37] Nmr spectra show no unexpected features and are readily interpreted by first-order analysis. The singlet observed for the $S^+(CH_3)_2$ protons indicates that (a) resonance contribution to the ylide structure of the S=N form (3d–2p overlap) is minor or (b) if cis–trans isomerism does exist interconversion of isomers is rapid on the nmr time scale.

Ir spectra of iminosulfuranes are considerably more complex than those of the starting amines or amides. No characteristic absorptions are observed between 3600–3100 and 2900–1620 cm^{-1} in the iminosulfuranes. They show weak to medium absorptions in the 3100–2900-cm^{-1} region assigned to the C–H stretching frequency of the SCH_3 group, and strong absorptions in the 1100–770-cm^{-1} region assigned to the N–S stretch.

The SO_2 stretching frequencies of the *N*-sulfonyliminosulfuranes (**8, 10, 12, 14, 16**) are significantly lower than those of the sulfonamides (**7, 9, 11, 13, 15**) from which they are derived. The ν_{SO_2} (unsym) is shifted by about 40–70 cm^{-1} and the ν_{SO_2} (sym) by 30–60 cm^{-1}. This shift suggests that there is substantial delocalization of the negative charge on nitrogen into the SO_2 group as shown.



N-Acyliminosulfuranes (**18, 20, 22**) show strong absorption bands in the region of 770–840 and 945–1000 cm^{-1}, not present in the amide starting materials (**17, 19, 21**). In *N*-acyliminosulfuranes, carbonyl stretching absorptions (1550–1600 cm^{-1}) are also strong and shifted to lower frequencies (*ca.* 90–130 cm^{-1}) than those of the amides from which they are derived. The shift to lower frequencies is attributed to extensive charge delocalization from nitrogen to oxygen. A similar shift to lower frequency (110 cm^{-1}) is observed in the C≡N group of *S,S*-dimethyl-*N*-cyanoiminosulfurane (**26**) compared to that of cyanamide (**25**).

N-Aryliminosulfuranes (**28, 30, 32, 34, 36, 38, 40, 42, 44, 46, 48, 50, 52, 54, 58**) show weak to moderate absorption around 1020 cm^{-1} and several moderate to strong bands between 990 and 890 cm^{-1}.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 137B or Pye Unicam SP-1000. Nmr spectra were obtained on Varian Models A-60A or XL-100, with TMS as internal standard. Melting points (uncorrected) were obtained using a Thomas-Hoover capillary apparatus. Tlc was conducted on Eastman silica gel chromagrams with fluorescent indicator; visualization was conducted either with uv light or by development in a chamber containing iodine crystals. All reagents were the purest obtainable; in all cases purity exceeded 97%. Solvents were the best commercial grades and were used as received. DMSO was distilled under reduced pressure from calcium hydride and stored in a nitrogen atmosphere over Linde molecular sieve, Type 4A. Sulfan (stabilized SO_3) and phosphorus pentoxide were obtained from Allied Chemical Co. Elemental analyses were done by Micro-Analysis, Inc., Wilmington, Del.

"Activation" of DMSO by Electrophiles. DMSO–BF_3 Complex (2).[14a] Boron fluoride–diethyl ether complex (27.2 g, 0.192 mol) was placed in a 100-ml three-neck flask equipped with a magnetic stirrer, thermometer, addition funnel, and drying tube. The contents of the flask were cooled to 20° and DMSO (15.0 g, 0.192 mol) was added dropwise with stirring and cooling over 20–35 min. The reaction was strongly exothermic and a white precipitate formed. It was filtered, washed with dry ether, and dried under vacuum; the yield of **2** (very hygroscopic) was 81% (23.5 g, mp 50–51°) (lit.[14a] mp 53°). Compound **2** is insoluble in chloroform but slightly soluble in acetone: nmr (acetone-d_6) δ 3.08 (s); nmr (DMSO-d_6) δ 3.30 (s) and 2.58 (s).

DMSO–P_4O_{10} Complex (3). As described above, DMSO (1.4 g, 0.018 mol) was added to a stirred suspension of phosphorus pentoxide (2.5 g, 0.018 mol) in dry chloroform. The white precipitate was filtered, washed with dry ether, and dried under vacuum. The product was exceedingly hygroscopic and quickly liquefied: nmr (acetone-d_6) δ 2.96 (s); nmr (DMSO-d_6) δ 2.87 (s) and 2.61 (s).

DMSO–SO_3 Complex (5). Although **5** was prepared by the method of Pettit,[15] we were unable to isolate it without decomposition as it is extremely moisture sensitive: nmr (DMSO) δ 3.06 (s) and 2.6 (s). Reaction of SO_3 with DMSO is exothermic.

Reaction of *p*-Toluenesulfonamide (7) with DMSO. A. SO_3 Activation. DMSO (34.0 g, 0.436 mol) was cooled to 20° in a 100-ml three-neck flask fitted with a thermometer, stirrer, addition

funnel, and drying tube. Sulfur trioxide (7.1 g, 0.089 mol) was slowly added (40 min) while maintaining the temperature of the well-stirred DMSO below 20°. Compound 7 (15.0 g, 0.088 mol) was added in one portion with stirring; a precipitate began to form within a few minutes at 15–25°. Tlc monitoring showed that all of 7 had been consumed after about 10 hr. Addition of water (80 ml) followed by 10% aqueous NaOH (80 ml) to pH 12 precipitated the product, *S,S*-dimethyl-*N*-*p*-toluenesulfonyliminosulfurane (8), 14.2 g, mp 156–158.5° (lit.[25] mp 158–159°). The aqueous filtrate was extracted with methylene chloride (3 × 200 ml), washed with water, and dried to yield additional 8 (2.0 g, mp 156–158°) after solvent evaporation. The ir spectra of the two portions of 8 were identical, as were their nmr spectra, and consistent with the proposed structure. The total yield of 8 in a replicate experiment was 60–80%. Analytically pure 8 (recrystallized from methylene chloride) had mp 158.5–159.5°.

B. P_4O_{10} Activation. As described in A above but using P_4O_{10} instead of SO_3, 7 was consumed in less than 2 hr and a 70% yield of 8, mp 157–158.5°, was obtained; its ir and nmr spectra were identical with those of 8 prepared as in A.

C. Acetic Anhydride Activation. Acetic anhydride (2.75 g, 0.027 mol) was added to DMSO (10.3 g, 0.132 mol) followed by *p*-toluenesulfonamide (4.5 g, 0.026 mol). The solution was heated on the steam bath (85–90°) for 1.5 hr, at which time tlc showed that all of 7 had disappeared. The cooled reaction mixture was then diluted with cold water (200 ml) and made basic to pH 12 with 10% aqueous sodium hydroxide (30 ml). The precipitate was filtered, washed with water until free of base, and dried (yield 1.1 g, mp 156–158°). The aqueous filtrate was extracted with methylene chloride (3 × 200 ml) and the combined extracts were washed with aqueous sodium hydroxide (60 ml) and then with water (2 × 100 ml) and dried. Solvent evaporation yielded additional 8 (3.4 g, mp 156–158°). The ir spectra of both precipitates were identical, as were their nmr spectra, and identical with the corresponding spectra of authentic 8. The total yield of 8 in replicate experiments was 60–75%.

Repetition of this experiment at room temperature for 28 hr with tlc monitoring showed a small spot due to 8 but most of 7 remained unreacted. Nmr also suggested the presence of 8. Dilution with cold water (120 ml) caused unreacted 7, mp 136–138°, to precipitate (56% recovery). The filtrate was made basic (pH 12) with 10% sodium hydroxide; no precipitation occurred. The basic solution was extracted with methylene chloride (3 × 100 ml) and the combined extracts were dried and then evaporated under vacuum. The white solid residue (1.0 g, 19% yield, mp 156–158°) had the same ir and nmr spectra as authentic 8.

D. BF_3 Activation. *p*-Toluenesulfonamide (7, 3.2 g, 0.019 mol) was added to a stirred solution of DMSO (8.8 g, 0.11 mol) and boron fluoride–diethyl ether complex (2.9 g, 0.02 mol); the reaction system was monitored by nmr and tlc. Nmr showed the formation of the DMSO–BF_3 complex but no other spectral changes were observed over 3 days at room temperature (except for disappearance of the ether signals). Tlc showed no diminution in 7 nor the appearance of any new spots. Dilution with water yielded unreacted 7 (2.0 g, mp 136–138°) whose melting point and ir were identical with those of authentic 7. Extraction of the aqueous filtrate with methylene chloride (3 × 200 ml) yielded additional 7 but no 8.

E. H_2SO_4 Activation. Similarly, 65–82% of 7 was recovered from a reaction system consisting of concentrated H_2SO_4 (1.2 g, 0.013 mol), DMSO (4.4 g, 0.056 mol), and 7 (1.7 g, 0.01 mol) held at room temperature for 48 hr or at 85° for 3 hr.

Preparation of Iminosulfuranes. *N*-Sulfonyliminosulfuranes (Table I). A. SO_3 Activation. The procedure described above for the reaction of *p*-toluenesulfonamide (7) with DMSO–SO_3 was used with minor modifications. Reaction time was determined by tlc. If the sulfonyliminosulfurane did not precipitate (10) when the reaction mixture was made basic it was extracted with methylene chloride. If the sulfonyliminosulfurane was particularly insoluble on basification (12), the alkaline aqueous filtrate was discarded. When methylene chloride was not suitable as the extraction solvent (14), benzene was used. About 50% of 14 precipitated from the reaction mixture before addition of aqueous base and the remainder was isolated by benzene extraction of the aqueous phase.

B. Acetic Anhydride Activation. The procedure described above for the reaction of 7 with DMSO–acetic anhydride was used with minor modifications as mentioned in A. Compound 12 precipitated almost completely from the reaction mixture (>90% yield) but an additional quantity (*ca.* 1.5%) could be obtained by the usual work-up of the aqueous alkaline filtrate. In the reaction of methanesulfonamide (15), excess DMSO and acetic anhydride were largely removed by distillation under reduced pressure (maximum temperature *ca.* 60°). The yellow oily residue (16 + DMSO) was washed with cold ether and the white precipitate (crude 16) was filtered and dried (4.2 g, mp 111–117°, 25%). The oily residue from the filtrate was dissolved in a minimum quantity of acetone and hexane was added until the solution was turbid. Upon cooling to 0°, white crystals of pure 16 were obtained (2.9 g, mp 122–123°, 18%). Both the crude and pure 16 had identical ir spectra and nmr spectra.

***N*-Acyliminosulfuranes (Table II). *S,S*-Dimethyl-*N*-*p*-nitrobenzoyliminosulfurane (22). A. SO_3 Activation.** *p*-Nitrobenzamide (21, 7.0 g, 0.042 mol) was added to a stirred solution of DMSO (11.3 g, 0.145 mol) and SO_3 (4.1 g, 0.051 mol). After 24 hr at room temperature, tlc showed that all of the 21 had disappeared. The reaction mixture was diluted with water (100 ml), precipitating 22 in 75% yield (7.2 g, mp 202–206°); its ir and nmr spectra were consistent with its structure. Recrystallization from methanol gave analytically pure 22, mp 220–222°. The original aqueous filtrate was made basic to pH 12 with 10% aqueous sodium hydroxide (80 ml) when an additional quantity of 22 precipitated (0.7 g, 8% yield, mp 218–219°); its spectra were identical with those of analytically pure 22.

B. P_4O_{10} Activation. Compound 22 was prepared from 21 (4.6 g, 0.028 mol), DMSO (22.2 g, 0.29 mol), and P_4O_{10} (4.3 g, 0.03 mol); the reaction time was 24 hr. Dilution of the reaction mixture with water yielded crude 22 (4.3 g, 70%, mp 184–200°); it consisted largely of 22 contaminated with a small quantity of 21.

C. Acetic Anhydride Activation. Compound 21 was recovered in 85% yield upon dilution of the reaction mixture. No 22 could be detected during the reaction nor could any be isolated from the aqueous filtrate upon basification to pH 12.

***S,S*-Dimethyl-*N*-dichloroacetyliminosulfurane (18). A. SO_3 Activation.** After 46 hr, the reaction mixture of DMSO (27.4 g, 0.35 mol), SO_3 (5.5 g, 0.069 mol), and dichloroacetamide (17, 8.7 g, 0.068 mol) still showed unreacted 17. Dilution with water (50 ml) followed by addition of 10% aqueous sodium hydroxide (50 ml) to pH 12 gave a turbid solution which was extracted with methylene chloride (3 × 150 ml) and washed with water. Evaporation of the dried methylene chloride solution yielded a white solid which was moderately pure 18 (4.2 g, 34%, mp 84–89°) contaminated with a trace of DMSO (ir and nmr). Recrystallization from methylene chloride yielded analytically pure 18 (3.2 g, 28%, mp 101–102°) which showed no depression in melting point on admixture with authentic 18.[24] A reported[25] melting point of 46–47° for 18 appears to be in error.

B. Acetic Anhydride Activation. Similar results were obtained upon heating a solution of DMSO (17.1 g, 0.22 mol), acetic anhydride (16.8 g, 0.165 mol), and 17 (13.8 g, 0.108 mol) for 9.5 hr followed by evaporation of volatiles at 65° under high vacuum. The brown solid residue was washed with ether (25 ml) which removed the color and residual DMSO; the residue was moderately good quality 18 (5.6 g, 28% yield, mp 95–98°). Recrystallization from methylene chloride yielded pure 18, mp 101–102° (mixture melting point with authentic 18 was undepressed).

***N*-Aryliminosulfuranes (Table III).** For the highest yields and purity of crude reaction products in the shortest reaction times, the molar ratio of DMSO:SO_3:aromatic amine was 4–6:1:0.6–0.9. A DMSO:SO_3 ratio as low as 2–3:1 was sometimes used but those ratios were atypical and are not recommended. For convenience, high-melting amines were sometimes added in solution in a portion of the total DMSO. In some cases, the crude reaction products precipitated when the reaction solution was made basic but extraction with benzene or methylene chloride was usually required.

Typical Procedures. *S,S*-Dimethyl-*N*-2-chlorophenyliminosulfurane (28). DMSO (14.5 g, 0.19 mol) was cooled to 20° and SO_3 (4.0 g, 0.05 mol) was added with stirring while maintaining the reaction temperature between 15–20°. When addition was complete the reaction mixture was cooled to 10° and *o*-chloroaniline (27, 3.0 g, 0.024 mol) was added; 15 min after addition was complete tlc showed that all of the 27 had been consumed. The reaction mixture was diluted with ice-cold water (80 ml) and then made basic with 10% aqueous sodium hydroxide (45 ml), followed by multiple extraction with benzene (3 × 150 ml) or ether. The combined extracts were evaporated to dryness and the brown oily residue (4.0 g) was dissolved in ether. Hexane was added to the ether solution until it was turbid and the mixture was cooled to 0°. Compound 28 was obtained as a white, crystalline solid (3.1 g, 71% yield, mp 73–75°). The sample for analysis, mp 74–75°, was ob-

tained by recrystallization from ether–hexane. (The melting point reported[6b] for **28** is 58–60°).

S,S-**Dimethyl-*N*-4-nitrophenyliminosulfurane (50).** This was prepared from DMSO (10.2 g, 0.13 mol), SO_3 (2.1 g, 0.026 mol), and *p*-nitroaniline (**49,** 2.6 g, 0.019 mol); reaction time 165 min. Crude **50** (3.3 g, 90%, mp 169–170°) precipitated cleanly from the diluted alkaline reaction mixture and was virtually pure upon drying. The sample for analysis, mp 172–174° (yellow needles), was obtained by recrystallization from benzene (literature melting points reported for **50** are 163–165[13] and 148–151°.[6b]): uv spectrum λ_{max} (CH_3OH) 386 mμ (ε 17,900), 234 (6700), 201 (16,500) (*c* 1.06 × 10^{-4} mol/l.) [lit.[13] λ_{max} (CH_3OH) 386 mμ (16,700), 234 (6200)]. In a duplicate experiment, base was not added to the diluted reaction mixture, which was extracted directly with CH_2Cl_2 (2 × 125 ml). The product obtained (0.3 g) had ir and nmr spectral characteristics suggestive of a mixture of **50** and its bisulfate salt; it was not studied further. When the aqueous layer was made basic to pH 12 with 10% sodium hydroxide, **50** (3.0 g, 67%, mp 168–170°) precipitated; its ir and nmr spectra were identical with those of pure **50.**

S,S-**Dimethyl-*N*-3,5-dinitrophenyliminosulfurane (58) and Bis(3,5-dinitrophenylamino)methane (59).** To the stirred DMSO (10.4 g, 0.13 mol)–SO_3 (4.2 g, 0.053 mol) mixture, a solution of 3,5-dinitroaniline (**57,** 4.8 g, 0.026 mol) dissolved in DMSO (14.9 g, 0.19 mol) was added. After 30 min, a yellow precipitate began to form. After 4.5 hr, all of the **57** had been consumed (tlc). The yellow precipitate (1.6 g, 33%, mp 195–197°) was filtered, washed with water until free of acid and adhering DMSO, and dried. Three crystallizations from pyridine yielded pure **59:** mp 253–254°; ir (KBr) 3500–3350 (s), 3150 (w), 2350 (w), 1620 (m), 1520 (vs), 1343 (vs), 1270 (s), 1120 (s), 1080 (w), 1050 (w), 980 (w), 920 (m), 875 (m), 808 (m), and 728 cm^{-1} (vs).

The DMSO filtrate after filtration of **59** was diluted with cold water, and 10% aqueous sodium hydroxide (45 ml) was added to pH 12. An orange precipitate formed; it was filtered, washed with water until free of base, and dried (4.3 g, 67%, mp 164–165°). It was virtually pure **58.** Recrystallization from methylene chloride gave orange needles, mp 169–170° (lit.[13] mp 168–170°).

Bis(2,4-dinitrophenylamino)methane (56). In the reaction of DMSO (15.2 g, 0.19 mol), SO_3 (3.4 g, 0.0425 mol), and 2,4-dinitroaniline (**55**), a yellow precipitate started to form after about 3 hr but it required 26 hr for all of the **55** to be consumed (tlc). The reaction mixture was filtered and the yellow solid precipitate was washed several times with water and dried (4.9 g, 92%, mp 277–279°). Two crystallizations from pyridine yielded pure **56:** mp 285–286° (lit.[13] mp 275–277°); ir (KBr) 3450–3300 (m), 1600 (s), 1510 (m), 1420 (w), 1340 (m), 1320 (m), 1160 (w), 1140 (w), 1085 (m), 1030 (w), 920 (w), 830 (m), 740 (m), and 700 cm^{-1} (w).

S,S-**Dimethyl-*N*-2,4-dinitrophenyliminosulfurane** was prepared by a modification of the method of Yamamoto, *et al.*[29,32]

Hydrochlorides of *N*-Aryliminosulfuranes. It is important to work up the salts promptly and analyze them immediately owing to their instability and hygroscopicity.

Typical Procedure. *S,S*-Dimethyl-*N*-*p*-chlorophenyliminosulfurane (**32,** 1.0 g, 0.0053 mol) was dissolved in dry ether (15 ml) and the solution was cooled to 0°. A 0.5 *N* solution of anhydrous HCl in ether (11 ml) was added dropwise and the precipitated salt was filtered under dry nitrogen, washed with ether, and dried under vacuum, 0.9 g (75%), mp 113–114° dec (lit.[30] mp 103–104°), calcd neut equiv 224, found 227. The salt is very hygroscopic: ir (KBr) 3100 (s), 2900–2800 (s), 1595 (m), 1480 (s), 1420–1395 (m), 1292 (w), 1263 (m), 1200 (s), 1175 (w), 1112 (w), 1095 (m), 1020 (w), 995 (s), 965 (w), 930 (w), 905 (m), 847 (w), 825 (s), 805 (m), and 725 cm^{-1} (m).

The *m*-chlorophenyl, *m*-bromophenyl, *p*-nitrophenyl, and *p*-cyanophenyl analogs, obtained in 65–75% yields, had the following melting points respectively: 115–120, 95–102, 115–116, and 202–203°.

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Registry No.—**30** HCl, 52259-92-4; **32** HCl, 52259-93-5; **36** HCl, 52259-94-6; **42** HCl, 52259-95-7; **50** HCl, 52259-96-8; DMSO, 67-68-5.

Supplementary Material Available. Full ir and nmr data will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-74-3365.

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