mechanisms cannot apply generally, of course, since a mobile group such as hydrogen is essential. Realistically, we believe we are left with steps a or c and i in Scheme I as alternate mechanisms in this system.

Rate Comparisons.—In Table II we have collected rate data for Menschutkin substitutions of differing types of organic bromides. Were it necessary, one could estimate the rate constant for triethylamine with ethyl bromide in DMF.[13,15] It should be appreciated that any comparison of reactivity of saturated with unsaturated centers involves a comparison of an SN2 with an AdN2 process. Our preliminary and generally qualitative comparisons[6] stand up here: k (alkyl) $\cong$ k (ethynyl) $\gg$ k (vinyl) $\gg$ k (aryl).

Registry No.—1, 593-61-3; 2, 31883-95-1; triethylamine, 121-44-8; dimethylformamide, 68-12-2; tetraethylammonium bromide, 71-91-0.

Carbodiimide–Sulfoxide Reactions. XIII.[1] Reactions of Amines and Hydrazine Derivatives

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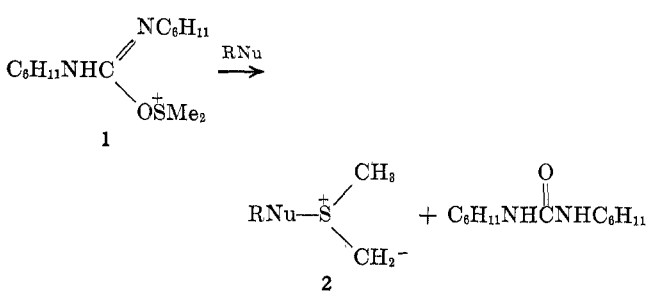
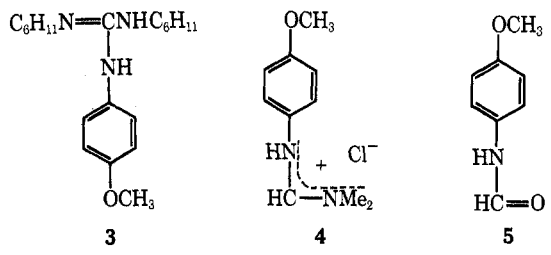
The acid-catalyzed reactions of a variety of amines and hydrazine derivatives with DMSO and DCC have been examined. Mildly basic aromatic amines such as nitroanilines readily react to form *N*-aryl-*S*,*S*-dimethylsulfilimines in high yield. The reaction of 2,4-dinitrophenylhydrazine leads to a variety of products arising *via* initial formation of the corresponding aryldiimide and aryldiazonium salt. Some reactions of methylthio(2,4-dinitrophenyl)diimide are reported. Acylhydrazides are largely converted into *N*,*N*′-diacylhydrazines, probably *via* the acyldiimides. A more complex array of products results from the reaction of an acylhydrazide with DMSO and phosphorus pentoxide. Sulfonylhydrazides lead ultimately to the formation of thiolsulfonates presumably *via* disproportionation of an intermediate sulfinic acid. The reaction of benzophenone hydrazone leads to the formation of diphenyldiazomethane which subsequently reacts further to give a number of products. Benzil dihydrazone gives as its major product diphenylacetylene. Indole slowly gives 3-(methylthiomethyl)indole which is partially converted into 3,3′-bisindolylmethane. Mechanisms are considered for all these types of reactions.

Previous papers in this series have described the mild, acid-catalyzed reactions of alcohols,[3] phenols,[4] enols,[5] oximes,[6] carboxylic and hydroxamic acids,[7] carboxylic acid amides,[7] and sulfonamides[1] with dimethyl sulfoxide (DMSO) and dicyclohexylcarbodiimide (DCC). These varied types of reactions can all be explained by initial formation of a DMSO–DCC adduct (**1**) which undergoes reaction with the appropriate nucleophile to form a sulfonium ylide (**2**) which can subsequently collapse or rearrange in a number of ways. Formation of the ylide **2** can occur either directly *via* a concerted cyclic process[8] or in two steps by facile loss of a proton from the corresponding sulfonium compound.



Since all the DMSO–DCC reactions we have examined have been found to require acidic catalysis, we felt that an extension of the above studies to amines as the reactive nucleophile might be difficult. This seemed particularly so since at an early stage we examined the reaction with 2,4-dinitroaniline, an amine that we felt might be sufficiently weakly basic to not block the acid-catalyzed formation of **1**. This compound showed no reaction whatsoever by tlc and an essentially quantitative yield of unreacted amine was recovered in crystalline form. A more strongly basic amine, *p*-anisidine, also failed to undergo any interesting reaction and was instead shown to undergo simple addition to DCC forming 1,3-dicyclohexyl-2-(4-methoxyphenyl)guanidine (**3**). The formation of **3** was



previously observed during preparation of nucleoside 5′-phosphoroanisidates, the latter compounds being isolated as their salts with this guanidine.[9] Since DMSO did not appear to be involved in the formation of **3**, a comparable reaction was carried out between *p*-anisidine, DCC, and anhydrous phosphoric acid in dimethylformamide (DMF). A totally different reaction then occurred giving *N*-(4-methoxyphenyl)-*N*′,*N*′-dimethylformamidine, which was isolated as its

(1) For Part XII, see U. Lerch and J. G. Moffatt, *J. Org. Chem.*, **36**, 7314 (1971).

(2) Syntex Postdoctoral Fellow, 1966–1968.

(3) (a) K. E. Pfitzner and J. G. Moffatt, *J. Amer. Chem. Soc.*, **87**, 5661, 5670 (1965). (b) For a review see J. G. Moffatt in "Techniques and Applications in Organic Synthesis: Oxidation," Vol. 2, R. Augustine and D. J. Trecker, Ed., Marcel Dekker, New York, N. Y., 1971 p1.

(4) (a) M. G. Burdon and J. G. Moffatt, *J. Amer. Chem. Soc.*, **88**, 5855 (1966); (b) M. G. Burdon and J. G. Moffatt, *ibid.*, **89**, 4725 (1967).

(5) A. F. Cook and J. G. Moffatt, *ibid.*, **90**, 740 (1968).

(6) A. H. Fenselau, E. H. Hamamura, and J. G. Moffatt, *J. Org. Chem.*, **35**, 3546 (1970).

(7) U. Lerch and J. G. Moffatt, *ibid.*, **36**, 3686 (1971).

(8) J. G. Moffatt, *ibid.*, **36**, 1909 (1971).

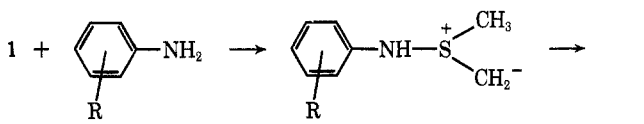
(9) J. G. Moffatt and H. G. Khorana, *J. Amer. Chem. Soc.*, **83**, 649 (1961).

crystalline hydrochloride **4** in 88% yield. During attempted crystallization of the free base of **4** from aqueous methanol, considerable hydrolysis occurred giving 4-methoxyformanilide (**5**).

The formation of formamidines through condensations of DMF with amines in the presence of phosphorus oxychloride,[10] sulfonyl chlorides,[11] etc., is well known and the present experiment suggests that DMF can also be activated by reaction with DCC.

While the results with both 2,4-dinitroaniline and *p*-anisidine were disappointing, other aromatic amines of intermediate basicity reacted quite differently. Thus, *p*-nitroaniline, *m*-nitroaniline, and 3,5-dinitroaniline all reacted rapidly with DMSO, DCC, and anhydrous phosphoric acid at room temperature to give the corresponding crystalline *S,S*-dimethyl-*N*-arylsulfilimines (**7a–c**) in 74–85% yields. This type of compound has only recently become known through the work of Claus and Vycudilik,[12] who have reacted a number of aromatic amines with DMSO and phosphorus pentoxide in the presence of triethylamine. Both the *m*-nitro- and *p*-nitrophenylsulfilimines (**7a,b**) were prepared by this route, but the isolated yields of 37 and 35% are much lower than those using DMSO and DCC. By tlc examination it is clear that other aromatic amines such as α-naphthylamine also react with DMSO and DCC to form sulfilimines, but these compounds are rather unstable and undergo partial decomposition to the parent amine during work-up.

The formation of sulfilimines no doubt occurs *via* attack of the amine on **1** to form the sulfonium ylide **6**, which then undergoes a proton shift to form the more stable product **7**. Once again, we cannot at this time rule out the alternative possibility that concerted reaction of the amine with **1** gives a sulfonium salt rather than the ylide **6**, facile loss of an NH proton then giving the sulfilimine.



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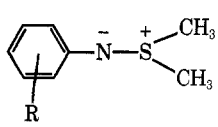
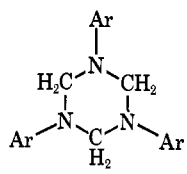
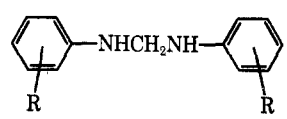


7a, R = *p*-NO_2
b, R = *m*-NO_2
c, R = 3,5-diNO_2^-

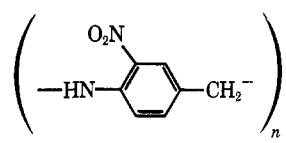
It is interesting to note that we too had examined the reactions of several aromatic amines with DMSO and phosphorus pentoxide, only without the addition of triethylamine. Under these conditions sulfilimines were not formed. Thus, reaction of *p*-nitroaniline with DMSO and phosphorus pentoxide at room temperature gave a highly insoluble, crystalline product which appears to be a polymer resulting from condensation of the amine with formaldehyde. The presence of an $-NCH_2N-$ grouping was clearly apparent from the nmr spectrum of the product, and its mass spectrum showed the monomeric unit $NO_2C_6H_4NCH_2$ as its largest fragment. Since the product shows no NH stretching vibrations in its infrared spectrum, we suggest that it is the cyclic trimer **8**, although we cannot exclude a linear polymer. As early as 1892 Pulvermacher[13] reported that condensation of *p*-nitroaniline with formaldehyde in ethanol gives *N,N'*-bis(*p*-nitrophenyl)methylenediamine (**9a**) with mp 232°, and this same product has also been obtained by different routes.[14,15] We have repeated and confirmed the original preparation,[13] obtaining analytically pure **9a** that was clearly different from the product from the DMSO–P_2O_5 reaction, particularly by the presence of an intense NH stretching band at 3500 cm^{-1} in its infrared spectrum. Similarly, the reaction of *o*-nitroaniline with DMSO and phosphorus pentoxide gave a polymeric material that was identical with the "polymeric anhydro-3-nitro-4-aminobenzyl alcohol" (**10**) prepared according to Meyer and Rohmer.[16] The structure of this compound has been deduced by its hydrolysis with strong acid to 3-nitro-4-aminobenzyl alcohol[16] and is consistent with its nmr spectrum in which the aromatic proton adjacent to the nitro group appears as a doublet showing only meta coupling. The absence of ortho coupling clearly shows that the aromatic ring is substituted at the 4 position. Finally, the reaction of 2,4-dinitroaniline with DMSO and P_2O_5 gives, in 82% yield, a crystalline product which from its elemental analysis must be *N,N'*-bis(2,4-dinitrophenyl)methylenediamine (**9b**).



8, Ar = *p*-$NO_2C_6H_4$



9a, R = *p*-NO_2
b, R = 2,4-diNO_2



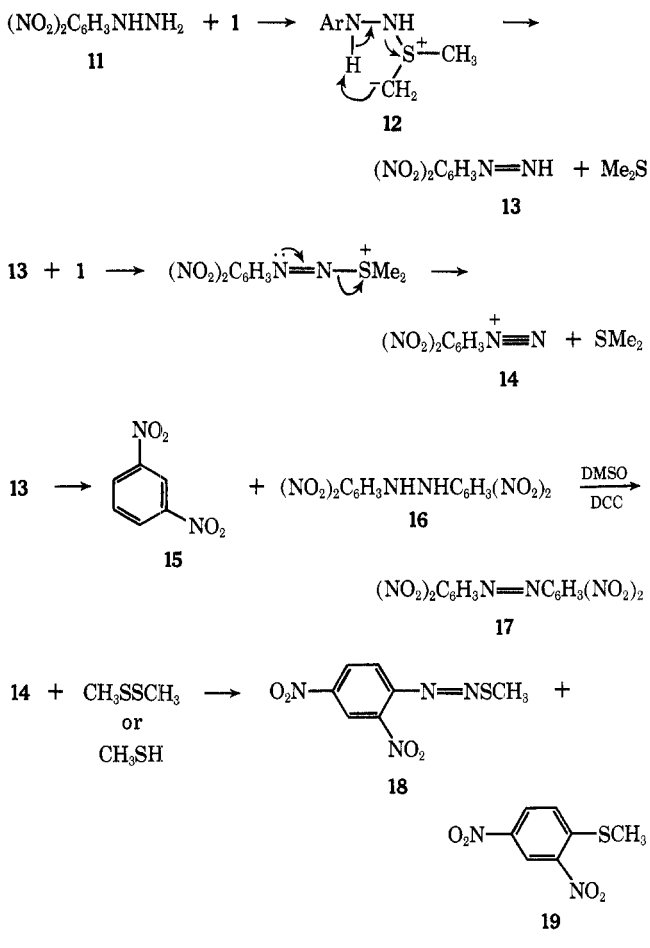
10

The formation of **8**, **9**, and **10** must be a consequence of the decomposition of DMSO to formaldehyde in the presence of phosphorus pentoxide. It is not clear, however, why the three nitroanilines above should give different types of formaldehyde adducts. The totally different reaction path observed in the presence of triethylamine[12] is probably due to both the absence of protonation of the aniline amino group and a suppression of the decomposition of DMSO to formaldehyde.

We next turned our attention to the reactions of hydrazine derivatives and found that 2,4-dinitrophenylhydrazine (**11**) rapidly reacted with DMSO, DCC, and anhydrous phosphoric acid with evolution of

(10) H. Bredereck, R. Gompper, K. Klemm, and H. Rempfer, *Chem. Ber.*, **92**, 837 (1959).
(11) N. Steiger, U. S. Patent 3,184,482 (1965); *Chem. Abstr.*, **63**, 5564 (1965).
(12) (a) P. Claus and W. Vycudilik, *Tetrahedron Lett.*, 3607 (1968); (b) P. Claus and W. Vycudilik, *Monatsh. Chem.*, **101**, 396, 405 (1970).
(13) G. Pulvermacher, *Ber.*, **25**, 2762 (1892).
(14) C. J. Pederson, *J. Org. Chem.*, **23**, 255 (1958).
(15) H. Zinner and H. Wigert, *Chem. Ber.*, **94**, 2209 (1961).
(16) J. Meyer and M. Rohmer, *Ber.*, **33**, 250 (1900).

nitrogen. From the complex mixture of products three crystalline substances were isolated and shown to be *m*-dinitrobenzene (**15**, 29%), 2,4-dinitrophenyl methylsulfide (**19**, 11%),[17] and 2,2′,4,4′-tetranitroazobenzene (**17**, 2%).[18] A similar reaction between **11**, DMSO, and phosphorus pentoxide also gave **15** (5%) and **19** (31%) and, in addition, a 13% yield of a crystalline compound identified as methylthio(2,4-dinitrophenyl)diimide (**18**). All of these compounds could arise *via* the intermediacy of either 2,4-dinitrophenyldiimide (**13**) or 2,4-dinitrophenyldiazonium ion (**14**) and formation of the latter compounds can be rationalized as follows.



In the above sequence, intramolecular proton abstraction and collapse of the intermediate sulfonium ylide **12** leads directly to 2,4-dinitrophenyldiimide (**13**). Based upon the work of Kosower, *et al.*,[19] upon the reactions of aryldiimides, **13** would be expected to spontaneously decompose to **15** and 2,2′,4,4′-tetranitrohydrazobenzene (**16**), probably *via* radical processes. As will be seen later, the hydrazobenzene **16** would be rapidly oxidized to **17** by DMSO and DCC. The oxidation of phenylhydrazine to phenyldiimide, and decomposition of the latter, has been achieved using lead tetraacetate and other reagents.[20]

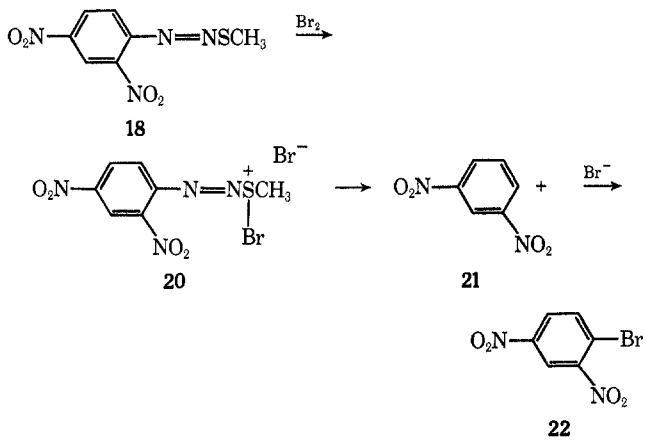
On the other hand, the diazosulfide **18**, and perhaps the sulfide **19**, would appear more likely to arise from the diazonium salt **14**. As early as 1884 Stadler[21] demonstrated the formation of diazosulfides from aryldiazonium salts and mercaptans, and subsequently these compounds have been further studied.[22] The presence of the diazonium ion **14** during reaction of **11** with DMSO and phosphorus pentoxide was supported by the isolation, in 39% yield, of the known azo dye, 4-(2,4-dinitrophenylazo)-1-naphthol,[23] in the presence of 1-naphthol. The diazosulfide **18** was independently prepared by reaction of 2,4-dinitrophenyldiazonium fluoroborate[24] with dimethyl disulfide, and **19** was chromatographically identified as another major product. The disulfide was used in this reaction since mercaptans are known to be very rapidly oxidized to the corresponding disulfides by DMSO and DCC.[3b,25] Since the decomposition of DMSO to methyl mercaptan and formaldehyde seems to be promoted much more readily by phosphorus pentoxide than by DCC, the absence of **18** in the reaction of **11** with DMSO and DCC is probably due to a shortage of the mercaptan. In support of this it was shown that addition of excess dimethyl disulfide to a reaction as above with DCC led to the isolation of **18** in 20% yield. Similarly, the yield of **18** was raised to 43% in the phosphorus pentoxide reaction by addition of dimethyl disulfide, while dimethyl sulfide had no effect. Treatment of 2,4-dinitrophenyldiazonium tetrafluoroborate with DMSO and phosphorus pentoxide was shown by tlc to give the methyl sulfide **19** as the major product.

Several simple reactions of the diazosulfide **18** were also examined. In the presence of acid, **18** appears to decompose with formation of the diazonium ion **14**. Thus, treatment of **18** at room temperature with a solution of hydrogen chloride in dioxane in the presence of 1-naphthol gave 4-(2,4-dinitrophenylazo)-1-naphthol in 78% yield. Thermal decomposition of **18** took place upon heating without solvent at 140° and gave the methyl sulfide **19** in 72% yield together with smaller amounts of **15** (3%) and bis(2,4-dinitrophenyl)-sulfide (5%).[26] Smooth decomposition of **18** with loss of nitrogen also occurred upon heating its solution in dimethylformamide at 160° but under these conditions the yield of **19** was reduced to 25 and 27% of **15** was isolated. Thermal decomposition of aryldiazosulfides has previously been shown to lead to aromatic hydrocarbons, sulfides, and disulfides, presumably *via* radical pathways.[22]

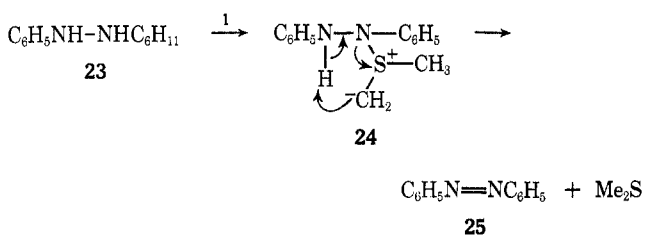
Addition of a slight excess of bromine to a solution of **18** in chloroform at 0° led to almost instantaneous decolorization and evolution of nitrogen. From this reaction crystalline 2,4-dinitrobromobenzene (**22**)[27] was isolated in 96% yield. It is likely that this reaction proceeds *via* initial formation of the bromosulfonium compound **20** followed by dissociation into nitrogen and the aryl cation **21** and recombination with bromide ion.

Hydrazobenzene (**23**) reacted rapidly with DMSO

(17) R. W. Bost, J. O. Turner, and R. D. Norton, *J. Amer. Chem. Soc.*, **54**, 1985 (1932).
(18) A. S. Bailey, M. Maung, G. W. F. Orpwood, and J. E. White, *Tetrahedron*, **22**, 995 (1966).
(19) (a) E. M. Kosower, P. C. Huang, and T. Tsuji, *J. Amer. Chem. Soc.*, **91**, 2325 (1969); (b) P. C. Huang and E. M. Kosower, *ibid.*, **90**, 2367 (1968).
(20) J. B. Aylward, *J. Chem. Soc. C*, 1663 (1969), and references cited therein.
(21) O. Stadler, *Ber.*, **17**, 2075 (1884).
(22) H. Van Zwet and E. C. Kooyman, *Recl. Trav. Chim. Pays-Bas*, **86**, 993, 1143 (1967).
(23) K. H. Meyer, A. Irschick, and H. Schlosser, *Ber.*, **47**, 1741 (1913).
(24) J. C. Brunton and H. Suschеitzky, *J. Chem. Soc.*, 1035 (1955).
(25) J. B. Jones and D. C. Wigfield, *Can. J. Chem.*, **44**, 2517 (1966).
(26) H. W. Talen, *Recl. Trav. Chim. Pays-Bas*, **47**, 782 (1928).
(27) A. G. Kekule, *Justus Liebigs Ann. Chem.*, **137**, 167 (1866).



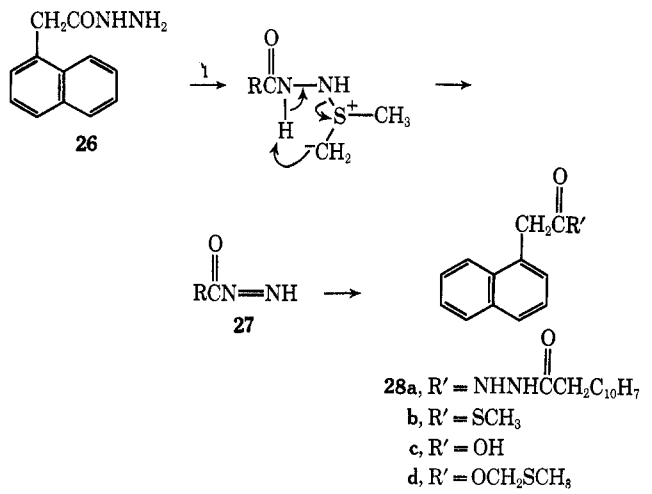
and DCC to give crystalline azobenzene (**25**) which was isolated in 94% yield. The same reaction using DMSO and phosphorus pentoxide gave **25** in 64% yield and in this case also produced some dark-colored, unidentified by-products. Formation of azobenzene presumably involves intramolecular proton abstraction and collapse of the initial sulfonium ylide **24**.



The reaction of 1-naphthylacetylhydrazide (**26**) with DMSO and phosphorus pentoxide was accompanied by nitrogen evolution and led to the isolation of four products. These were identified as *N*,*N*′-bis(1-naphthylacetyl)hydrazine (**28a**, 5%), methyl 1-naphthylthiolacetate (**28b**, 26%), 1-naphthylacetic acid (**28c**, 28%), and methylthiomethyl 1-naphthylacetate (**28d**, 2%). The formation of all of these compounds could be explained by a pathway involving initial oxidation of **26** to the acyldiimide **27**. Subsequent acid-catalyzed reactions of the latter with the available nucleophiles **26**, methyl mercaptan, phosphoric acid, and DMSO would then lead to the observed products (**28a–d**), the latter *via* the mechanism described earlier for reactions of carboxylic acids with DMSO and DCC. These reactions could, of course, all proceed *via* initial acid-catalyzed heterolysis to the acyl cation rather than being truly concerted. Previous work by Cohen and Nicholson[28] and by Kelly[29] has demonstrated both the oxidation of *N*-acyl-*N*′-arylhydrazines with manganese dioxide or lead tetraacetate to the corresponding diimides and nucleophilic decomposition of the latter to acyl derivatives.

The reaction of **26** with DMSO and DCC led predominantly to the diacylhydrazine **28a** and was complicated by the extreme insolubility of this compound, which crystallized from the reaction mixture with the dicyclohexylurea. By using diisopropylcarbodiimide in place of DCC, the much more soluble urea by-product could be readily removed with hot methanol, leaving pure **28a** in 58% yield.

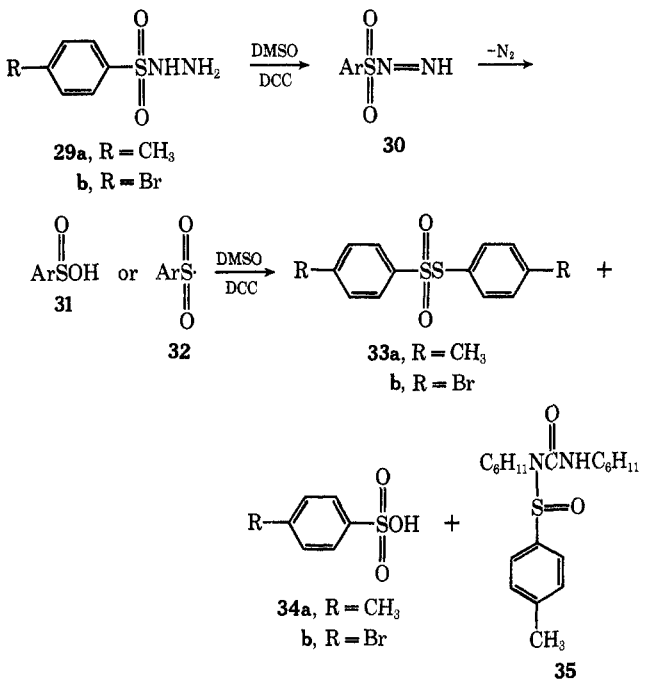
(28) S. G. Cohen and J. Nicholson, *J. Org. Chem.*, **30**, 1162 (1965).
(29) (a) R. B. Kelly, *ibid.*, **28**, 453 (1963); (b) *ibid.*, **29**, 1273 (1964).



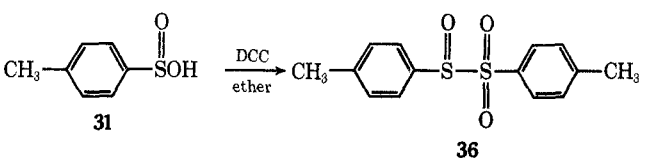
The reaction of sulfonyl hydrazides took a somewhat different course. Treatment of *p*-toluenesulfonyl hydrazide (**29a**) with DMSO, DCC, and anhydrous phosphoric acid led to immediate evolution of nitrogen and the formation of several products. The aqueous extracts were shown by paper chromatography, paper electrophoresis, and ultraviolet spectra to contain roughly 70% of *p*-toluenesulfonic acid (**34a**). The organic phase contained two major products, both of which were isolated in crystalline form by preparative tlc. The less polar product (24%) was shown to be the known *p*-tolyl *p*-toluenethiolsulfonate (**33a**)[30] while the other substance (7%) was an adduct of toluenesulfinic acid and DCC for which we tentatively suggest the structure **35**. This structure is supported by the similarity of its intense infrared absorption band at 1685 cm^{-1} to that in *N*-acylureas and by the ready decomposition of **35** to, *inter alia*, **33a**, upon heating. The presence of a peak at *m/e* 139 ($CH_3C_6H_4SO$) in its mass spectrum also suggests a sulfinyl structure but is not compelling.

Thiolsulfonates and sulfonic acids are known to result from the disproportionation of sulfinic acids[31] or of sulfonyl radicals.[32] We suggest that the present reaction leads (as in **26** → **27**) initially to the sulfonyldiimide **30**, which then loses nitrogen to form the sulfinic acid **31**. Indeed, reaction of *p*-toluenesulfinic acid (**31**)[31] with DMSO, DCC, and phosphoric acid leads to the same two products, **33a** and **35**, in modest yield although in this case, the urea adduct preponderates. Since no **33a** is formed upon short storage of the sulfinic acid **31** in DMSO either alone or in the presence of anhydrous phosphoric acid, we must conclude that, if the free sulfinic acid is an intermediate in the DMSO–DCC reaction, it must undergo further activation prior to disproportionation. Collapse of the diimide **30** to a sulfonyl radical **32** could also explain the formation of **33** and *p*-toluenesulfonic acid.[32] *p*-Bromobenzenesulfonylhydrazide (**39b**) appears to react in a similar way with DMSO–DCC, and the thiolsulfonate **33b** and bis(4-bromophenyl)disulfide were isolated in crystalline form.

(30) P. Karrer, W. Wehrli, E. Biedermann, and M. Vedova, *Helv. Chim. Acta*, **11**, 233 (1928).
(31) J. L. Kice, G. Guaraldi, and C. G. Venier, *J. Org. Chem.*, **31**, 3561 (1966), and references cited therein.
(32) C. M. M. da Silva Correa and W. A. Waters, *J. Chem. Soc. C*, 1874 (1968).

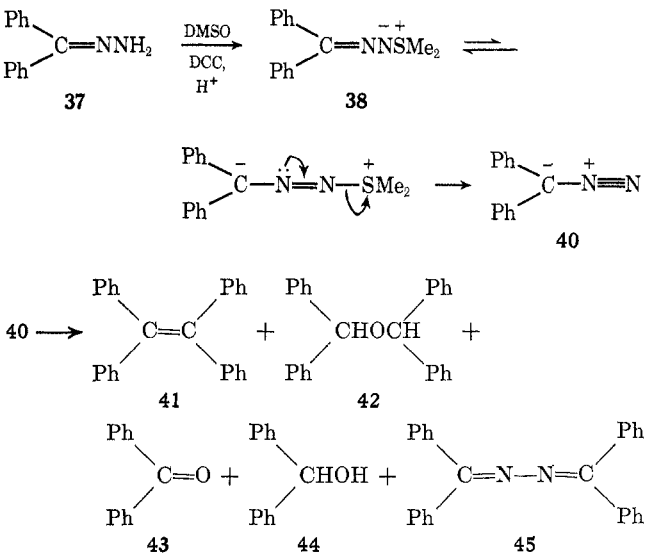


The reaction of **31** with DCC in ether or methylene chloride gave only small amounts of **33a** and **35**, the major product being *p*-toluenesulfinyl *p*-tolylsulfone (**36**), which was isolated in 82% yield. This compound was previously obtained from reaction of **31** with acetic anhydride and sulfuric acid and was at that time considered to be the symmetrical sulfinic anhydride.[33] The structure of **36** was clarified by Bredereck, *et. al.*,[34] who provided an alternative synthesis. The exact mechanism of the formation of **36** from **31** with DCC is not clear, as is the question of whether **36** could be an intermediate in the formation of **33a**.[31]



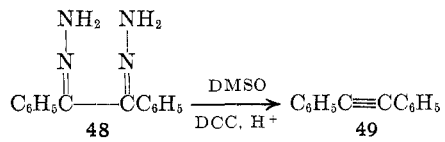
The reaction of benzophenone hydrazone (**37**) with DMSO and DCC led to rapid nitrogen evolution and formation of a dark red color. Preparative tlc of the reaction mixture led to the isolation of tetraphenylethylene (**41**, 5%), dibenzhydryl ether (**42**, 12%), benzophenone (**43**, 24%), and benzhydrol (**44**, 19%), the latter as its acetate, presumably due to transesterification with ethyl acetate during the work-up. These products can all arise from diphenyldiazomethane (**40**) and, indeed, immediate extraction of a reaction mixture with hexane removed a red substance with an ultraviolet spectrum identical with that of authentic **40**.[35] Similar treatment of crystalline **40** with DMSO, DCC, and anhydrous phosphoric acid gave **41** (16%), **42** (17%), **43** (15%), **44** (16%), and in addition a 6% yield of benzophenoneazine (**45**) which was probably also formed from **37** but not isolated.

Formation of diphenyldiazomethane from **37** can be rationalized by the scheme below (**37** → **40**) with initial formation of the iminosulfilimine intermediate **38** being similar to what was previously described for the reactions of amides.[1,7]



The reaction of **37** with DMSO and phosphorus pentoxide was somewhat different since neither **41** nor **42** was isolated. The major product was benzhydrol (**44**) in 42% yield, and in addition, benzophenone (**48**), the azine **45**, and benzhydryl methyl sulfide (**47**) were isolated in yields of 19, 9, and 10%, respectively. From the color of the reaction mixture, **40** was probably once again formed but due to the much more acidic nature of the medium, this compound would decompose to the benzhydryl cation. Reaction of the latter with DMSO would give the oxysulfonium salt **46**, which would lead to **43** and **44**, while reaction with methyl mercaptan would form the sulfide **47**.

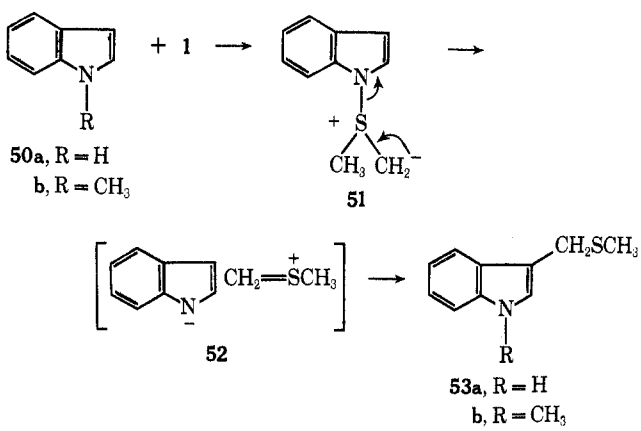
The only other hydrazone examined was benzil dihydrazone (**48**), which reacted with vigorous evolution of nitrogen. In addition of 15% of benzil, the only pure product isolated was diphenylacetylene (**49**) which was obtained in 21% yield. Conversion of **48** to **49** has previously been achieved using oxidants such as mercuric oxide.[36] In the present case, the reaction clearly involves diazo intermediates formed as above, and a variety of tentative mechanisms can be drawn. All are fairly complex, however, and in the absence of any compelling evidence in favor of one or the other, we prefer not to make any precise suggestion.



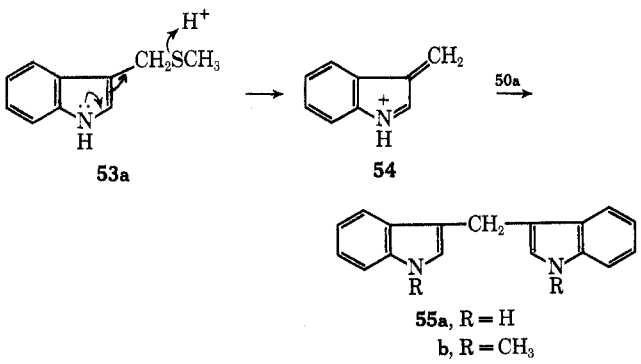
Finally, we mention the results of a few experiments with indole derivatives. Thus, it was found that indole (**50a**) itself reacts very slowly with DMSO and

(33) E. Knoevenagel and L. Pollack, *Ber.*, **41**, 3323 (1908).
(34) H. Bredereck, A. Wagner, H. Beck, and R.-J. Klein, *ibid.*, **93**, 2736 (1960).
(35) J. B. Miller, *J. Org. Chem.*, **24**, 560 (1959).
(36) A. C. Cope, D. S. Smith, and R. J. Cotter, "Organic Syntheses," Collect. Vol. IV, N. Rabjohn, Ed., Wiley, New York, N. Y., 1963, p 377.

DCC under the usual conditions. Even after 9 days at room temperature 33% of unreacted **50a** was recovered and two new products were isolated in modest yield. These proved to be 3-(methylthiomethyl)-indole (**53a**, 10%) and 3,3′-bisindolylmethane (**55a**, 6%), the latter being a known coumpound[37] and the former being readily identified by its nmr spectrum.[38] The spectrum of **53a** clearly shows that C_2–H is coupled only to NH, thus confirming the point of alkylation as C_3. Compound **53a** would appear most likely to arise through condensation of **50a** with the methylmethylene sulfonium ion (**52**). The latter ion has been encountered many times in our work and is considered to generally arise by dissociation of any ylide such as **51**. Recombination of the ion pair would be expected to lead to alkylation at C_3.



The dimer **55a** has previously been prepared both by condensation of indole with formaldehyde and zinc chloride and by treatment of 3-(hydroxymethyl)- or 3-(ethoxymethyl)indole with base.[37] In the present reaction it could arise by acid-catalyzed decomposition of **53a** to the ion **54**, which then couples with indole. To test this a mixture of **50a** and **53a** was treated with anhydrous phosphoric acid in DMSO and it was shown by tlc and vpc that **55a** was formed in 10% yield.



Treatment of *N*-methylindole (**50b**)[39] with DMSO and DCC also led to a very slow reaction from which only the dimer **55b** (8%) could be isolated in addition to unreacted **50b**. The absence of the methylthiomethyl derivative **53b** is to be expected if the formation **53a** is indeed *via* dissociation of the ylide **51**, and we have previously provided evidence that the ion **52** does not arise to any extent by decomposition of of ylides related to **1**.[4b] The formation of **55b** may be a consequence of condensation of **50b** with formaldehyde resulting from slow decomposition of DMSO.

From this and several previous papers[1,7] it is clear that many types of nitrogenous functional groups undergo interesting acid-catalyzed reactions with DMSO and DCC. In a future publication the reactions of some sulfur-containing groups will be considered.[40]

(37) E. E. Leete and L. Marion, *Can. J. Chem.*, **31**, 775, 1195 (1953).

(38) For the nmr spectra of indole derivatives, see L. A. Cohen, J. W. Daly, H. Kny, and B. Witkop, *J. Amer. Chem. Soc.*, **82**, 2184 (1960).

(39) K. T. Potts and J. E. Saxton, *J. Chem. Soc.*, 2641 (1954).

Experimental Section

General Methods.—The general methods employed are similar to those described previously.[1] Unless otherwise stated, mass spectra were obtained at an ionizing voltage of 70 eV. We are particularly indebted to Dr. M. L. Maddox and Mrs. J. Nelson and to Dr. L. Tokes for their continuous help in obtaining the reported nmr and mass spectral data.

***S,S*-Dimethyl-*N*-*p*-nitrophenylsulfilimine (7a).**—A solution of *p*-nitroaniline (1.39 g, 10 mmol), DCC (6.18 g, 30 mmol), and anhydrous phosphoric acid (15 mmol) in DMSO (10 ml) and benzene (10 ml) was kept overnight at room temperature. Ether (100 ml) and water (100 ml) were added and the mixture was filtered. The ether phase was extracted three times with water and the combined aqueous extracts were adjusted to pH 12 with sodium hydroxide giving yellow needles of **7a** (0.90 g).

The mother liquors were extracted three times with methylene chloride and the organic phase was dried ($MgSO_4$) and evaporated, leaving 1.43 g of needles. This was combined with the first crystalline product and recrystallized from methylene chloride–ether giving 1.63 g (82%) of **7a**: mp 163–165° (lit.[12b] mp 148–151°); λ_{max}^{MeOH} 234 mμ (ε 6200), 386 (16,700); nmr ($CDCl_3$) 2.72 (s, 6, SMe), 6.72 and 8.00 ppm (d, 2, J = 9 Hz, Ar); mass spectrum m/e 198 (M^+), 183 ($M - CH_3$), 153, 138 ($NO_2C_6H_4NH_2$), 62 (Me_2S), 61 ($CH_3S^+{=}CH_2$).

Anal. Calcd for $C_8H_{10}N_2O_2S$: C, 48.48; H, 5.09; N, 14.14; S, 16.17. Found: C, 48.33; H, 5.08; H, 14.21; S, 16.07.

1,3,5-Tris(4-nitrophenyl)hexahydro-*s*-triazine (8).—Phosphorus pentoxide (3.6 g) was added, with cooling, to anhydrous DMSO (15 ml). After 15 min *p*-nitroaniline (2.76 g, 20 mmol) was added, giving a clear solution. The solution was stirred for 48 hr during which time a solid material separated. The mixture was diluted with methanol and the chromatographically homogeneous product (**8**, 1.43 g, 48%) was collected. After recrystallization from pyridine this material turned orange above 250° and melted with decomposition at 286–287°: $\lambda_{max}^{dioxane}$ 355 mμ; ir (KBr) no NH; nmr (DMSO-d_6) 5.36 (s, 2, NCH_2N), 7.23 and 8.09 ppm (d, 2, J = 8 Hz, Ar); mass spectrum m/e 150 ($NO_2C_6H_4NCH_2$), 120 (m/e 150 − NO).

Anal. Calcd for $C_{21}H_{18}N_6O_6$: C, 56.00; H, 4.03; N, 18.66; O, 21.30. Found: C, 56.20; H, 3.99; N, 18.49; O, 21.50.

Reaction of *o*-Nitroaniline with DMSO and Phosphorus Pentoxide.—*o*-Nitroaniline (2.76 g, 20 mmol) was added to a premixed solution of phosphorus pentoxide (3.6 g) in DMSO (15 ml) and the resulting solution was stirred at 23° for 3 days. The resulting precipitate was collected and washed thoroughly with methanol, giving 1.87 g of a yellow solid that was crystallized from pyridine with mp 238–240° (gas evolution). This material was identical with the polymer (**10**) prepared from *o*-nitroaniline, formaldehyde, and hydrochloric acid:[16] $\lambda_{max}^{dioxane}$ 424 mμ ($\epsilon_{1\%}$ 281), 238 (935); ir (KBr) 3390, 1635, 1570, 1525 cm^{-1}; nmr (DMSO-d_6 4.50 (br s, 2, NCH_2N), 6.93 (q, 1, J_o = 9 Hz, J_m = 2 Hz, C_6H), 7.56 (br q, 1, J_o = 9, J_m = 2 Hz, C_5H), 8.07 (d, 1, J_m = 2 Hz, C_3H).

Anal. Calcd for $(C_7H_6N_2O_2)_n$: C, 56.00; H, 4.03; N, 18.66; O, 21.31. Found: C, 56.03; H, 4.39; N, 18.83; O, 21.44.

***N,N′*-Bis(2,4-dinitrophenyl)methylenediamine (9b).**—2,4-Dinitroaniline (2.74 g, 20 mmol) was added to a premixed solution of phosphorus pentoxide (2.6 g) in DMSO (10 ml). A yellow precipitate slowly separated and the mixture was stirred for 5 days. The precipitate was filtered, thoroughly washed with DMSO and chloroform, and dried, giving 2.41 g (82%) of chromatographically homogeneous **9b** with mp 275–277° (dec with gas evolution) from pyridine: $\lambda_{max}^{dioxane}$ 260 mμ (ε 18,900), 338 (30,200); mass spectrum m/e 195 [$(NO_2)_2C_6H_3N{=}CH_2$], 183

(40) Unpublished work by J. G. Moffatt.

$[(NO_2)_2C_6H_3NH_2]$, 167 (*m/e* 183 − O), 153 (*m/e* 183 − NO), 137 (*m/e* 183 − NO_2).

Anal. Calcd for $C_{13}H_{10}N_6O_8$: C, 41.28; H, 2.66; N, 22.22; O, 33.84. Found: C, 41.33; H, 2.88; N, 22.31; O, 33.89.

S,S-Dimethyl-N-m-nitrophenylsulfilimine (7b).—A solution of *m*-nitroaniline (1.39 g, 10 mmol), DCC (6.18 g, 30 mmol), and anhydrous phosphoric acid (15 mmol) in DMSO (10 ml) and benzene (10 ml) was kept at 23° for 2 hr. The mixture was diluted with ether and extracted three times with water. The aqueous extracts were made alkaline with sodium hydroxide and extracted with methylene chloride. Evaporation of the organic extracts and crystallization from carbon tetrachloride gave 1.68 g (85%) of **7b** as dark red needles with mp 100–101° (lit.[12b] mp 96–98°): λ_{max}^{MeOH} 260 mμ (ε 15,100), 394 (1200); nmr ($CDCl_3$) 2.68 (s, 6, SMe_2), 7.0–7.7 (m, 4, Ar); mass spectrum *m/e* 198 (M^+), 183 (M − CH_3), 168 (M − 2 CH_3 or M − CH_3 and NO), 136 (M − SMe_2), 122 ($NO_2C_6H_4^+$), 62 (Me_2S).

Anal. Calcd for $C_8H_{10}N_2O_2S$: C, 48.48; H, 5.09; N, 14.14; S, 16.17. Found: C, 48.29; H, 4.99; N, 14.17; S, 16.06.

S,S-Dimethyl-N-(3,5-dinitrophenyl)sulfilimine (7c).—A reaction between 3,5-dinitroaniline (1.83 g, 10 mmol), DCC (6.18 g, 30 mmol), and anhydrous phosphoric acid (15 mmol) in DMSO (10 ml) and benzene (10 ml) for 1 hr was worked up exactly as above for **7b**. Crystallization of the crude product from chloroform–carbon tetrachloride gave **7c** (1.80 g, 74%) as orange needles with mp 168–170° unchanged on recrystallization from ethanol: λ_{max}^{MeOH} 227 mμ (ε 18,500), 260 (20,700), 350 (1600), 410 (1500); nmr (DMSO-d_6) 2.77 ppm (s, 6, SMe_2), 7.5–7.8 (m, 3, Ar); mass spectrum *m/e* 243 (M^+), 228 (M − CH_3), 62 (Me_2S).

Anal. Calcd for $C_8H_9N_3O_4S$: C, 39.51; H, 3.73; N, 17.28; S, 13.17. Found: C, 39.35; H, 3.88; N, 17.05; S, 12.95.

Reactions of *p*-Anisidine. A. With DMSO–DCC.—Anhydrous phosphoric acid (15 mmol) and DCC (6.18 g, 30 mmol) were added to a solution of *p*-anisidine (1.23 g, 10 mmol) in DMSO (10 ml) and benzene (10 ml) under argon. After 20 min the mixture was partitioned between water and ether and the water was washed with methylene chloride. The aqueous solution was made alkaline with sodium hydroxide and extracted with methylene chloride. The organic extracts were washed with water, dried, and evaporated, giving 1.76 g of a semicrystalline oil. Crystallization from ether at −15° after charcoal treatment gave 610 mg (19%) of 1,3-dicyclohexyl-2-(4-methoxyphenyl)-guanidine (**3**) as white needles with mp 142–144°;[41] λ_{max}^{MeOH} 233 mμ (ε 9400); nmr ($CDCl_3$) 0.8–2.3 (m, 20 H, cyclohexyl), 3.5 (m, 4, >CHN and NH), 3.75 (s, 3, OCH_3), 6.79 ppm (s, 4, Ar); mass spectrum *m/e* 329 (M^+), 247 (M − C_6H_{10}), 123 ($MeOC_6H_4NH_2$).

Anal. Calcd for $C_{20}H_{31}N_3O$: C, 72.90; H, 9.48; N, 12.76. Found: C, 72.81; H, 9.39; N, 12.92.

B. With DMF–DCC.—A reaction was carried out exactly as in A except that the DMSO was replaced by dimethylformamide (20 ml). After 4 hr it was worked up as above, evaporation of the extracts following basification giving 1.60 g of a chromatographically homogeneous, clear syrup that could not be crystallized. An ether solution of one half of this was treated with an excess of hydrogen chloride in dioxane, giving 0.94 g (88%) of *N*-(4-methoxyphenyl)-*N'*,*N'*-dimethylformamidinium chloride (**4**)[42] which was readily recrystallized from ethanol with mp 207–212° dec: λ_{max}^{MeOH} 265 mμ (ε 1300); nmr (D_2O) 3.27 and 3.43 (s, 3, N^+Me),[43] 3.87 (s, 3, OMe), 7.2 (m, 4, Ar), 8.25 ppm (s, 1, $NCH{=}N^+<$).

Anal. Calcd for $C_{10}H_{15}N_2OCl$: C, 55.96; H, 7.04; N, 13.05. Found: C, 55.59; H, 7.02; N, 13.02.

During attempted crystallization of the free base of **4** from aqueous methanol considerable hydrolysis occurred. Subsequent crystallization from ether gave 4-methoxyformanilide (**5**) with mp 80–81.5° (lit.[44] mp 80–81°) and in all ways identical with an authentic sample from anisidine, acetic anhydride, and formic acid:[45] λ_{max}^{MeOH} 250 mμ (ε 14,500); nmr ($CDCl_3$) 3.78 (s, 3 OCH_3), 6.7–7.6 (m, 4, Ar), 8.27 and 8.57 ppm (br s, total 1 H, CHO);[46] mass spectrum *m/e* 151 (M^+), 122 (M − CHO), 108 ($C_6H_5OCH_3$).

Reaction of 2,4-Dinitrophenylhydrazine (11). A. With DMSO–DCC.—A solution of **11** (1.98 g, 10 mmol), DCC (5.8 g, 28 mmol), and anhydrous phosphoric acid (5 mmol) in DMSO (10 ml) was kept at room temperature with occasional cooling (gas evolution) for 1 hr. The mixture was diluted with ethyl acetate and water and filtered, and the organic phase was washed three times with water. Evaporation of the dried solution followed by preparative tlc on three plates using three developments with benzene–CCl_4 (1:1) gave three major bands as well as a complex mixture on the origin. Elution of the fastest band gave 480 mg (29%) of *m*-dinitrobenzene with mp 90–91° from ethanol and identical with an authentic sample: nmr ($CDCl_3$) 7.90 (AB_2 q, 1, J = 8.5 Hz, C_5H), 8.66 (q, 2, J_o = 8.5, J_m = 2 Hz, C_4H, C_6H), 9.10 ppm (t, 1, J_m = 2 Hz, C_2H).

Elution of the middle band followed by rechromatography using CCl_4–MeOH (99:1) gave 232 mg (11%) of 2,4-dinitrophenyl methylsulfide (**19**) with mp 125–127° from ethanol (lit.[17] mp 128°): λ_{max}^{MeOH} 269 mμ (ε 5300), 332 (10,200); nmr ($CDCl_3$) 2.60 (s, 3, SMe), 7.40 (d, 1, J_o = 9 Hz, C_6H), 8.35 (q, 1, J_o = 9, J_m = 2 Hz, C_5H), 9.06 ppm (d, 1, J_m = 2 Hz, C_3H); mass spectrum *m/e* 214 (M^+), 199 (M − CH_3), 184 (M − NO), 151 (*m/e* 184 − SH), 121 (*m/e* 154 − NO).

Elution of the slowest band and crystallization from acetone gave 32 mg (2%) of 2,2',4,4'-tetranitroazobenzene: mp 223–225° (lit.[18] mp 221°); λ_{max}^{MeOH} 304 mμ (ε 18,900); mass spectrum *m/e* 362 (M^+), 195 [M − $C_6H_3(NO_2)_2$].

Anal. Calcd for $C_{12}H_6N_6O_8$: C, 39.79; H, 1.67; N, 23.20. Found: C, 39.99; H, 1.79; N, 23.17.

B. With DMSO–P_2O_5.—Phosphorus pentoxide (2.5 g) was added portionwsie to DMSO (30 ml), followed, after 20 min, by **11** (3.97 g, 15 mmol). After 16 hr at 23° the mixture was partitioned between chloroform and water and 490 mg of a highly insoluble unidentified material (polymer?) was removed by filtration. The organic phase was purified by preparative tlc on three plates using two developments with benzene–CCl_4 (3:2) giving three bands and an intractable streak near the origin. Elution of the fastest band and crystallization from methanol gave 473 mg (13%) of methylthio(2,4-dinitrophenyl)diimide (**18**) as long yellow needles with mp 107.5–108°: λ_{max}^{MeOH} 250 mμ (ε 9100), 342 (15,200); nmr ($CDCl_3$) 2.85 (s, 3, SMe), 7.60 (d, 1, J_o = 9 Hz, C_6H), 8.47 (q, 1, J_o = 9, J_m = 2 Hz, C_5H), 8.73 ppm (d, 1, J_m = 2 Hz, C_3H); mass spectrum *m/e* 242 (M^+), 195 (M − SCH_3), 75 [$C_6H_3(NO_2)_2$].

Anal. Calcd for $C_7H_6N_4O_4S$: C, 34.71; H, 2.50; N, 23.13; S, 13.24. Found: C, 34.83; H, 2.97; N, 22.90; S, 13.01.

Elution of the second band and crystallization from ethanol gave 126 mg (5%) of *m*-dinitrobenzene (mp 90–91°) while elution of the slower band and crystallization from methanol gave 989 mg (31%) of **19** with mp 125–127°.

C. With DMSO–P_2O_5 in the Presence of 1-Naphthol.—Phosphorus pentoxide (3.2 g) was slowly added to DMSO (20 ml) followed by 1-naphthol (4.32 g, 30 mmol) and 2,4-dinitrophenylhydrazine (2.97 g, 15 mmol). A crystalline product separated and after 2.5 hr the mixture was diluted with methanol and filtered, giving 1.95 g (39%) of 4-(2,4-dinitrophenylazo)-1-naphthol, which was recrystallized from pyridine with mp 276–278° (lit.[23] mp 278°): $\lambda_{max}^{OH^-}$ 245 mμ (sh, ε 15,100), 314 (10,000).

D. With DMSO–P_2O_5 and Dimethyl Disulfide.—Phosphorus pentoxide (16 g) was added slowly at 0° to a mixture of DMSO (75 ml) and dimethyl disulfide (20 ml). 2,4-Dinitrophenylhydrazine (15 g) was then added and the mixture was stirred at −10° for 1 hr, at 0° for 2 hr, and at 23° for 1 hr. The red mixture was then partitioned between chloroform and water and filtered, and the organic phase was washed with aqueous bicarbonate, dried, and evaporated. The residue was applied to a 6 × 50 cm column of silicic acid and eluted with benzene–CCl_4 (1:1), giving 7.8 g (43%) of crystalline **18** which was recrystallized from methanol with mp 107–108°.

E. With DMSO–DCC–Dimethyl Disulfide.—Anhydrous phosphoric acid (6 mmol) was added to a solution of **11** (1.98 g, 10 mmol), DCC (5.89, 28 mmol), and dimethyl disulfide (5 ml) in DMSO (10 ml). After 16 hr at 2°, the mixture was worked up as in A, giving 493 mg (20%) of the diazosulfide **18**, 179 mg (11%) of *m*-dinitrobenzene, and 682 mg (32%) of **19**.

Methylthio(2,4-dinitrophenyl)diimide (18).—2,4-Dinitrophen-

(41) The reaction was nearly quantitative by tlc but crystallization of **3** was difficult and accompanied by some decomposition.

(42) The perchlorate of **4** has been described: D. Duerr, H. Aebi, and L. Ebner, U. S. Patent 3,284,289 (1966); *Chem. Abstr.*, **66**, 28499 (1967).

(43) Magnetic nonequivalence of the methyl groups in *N,N*-dimethylformamidines has been described by J. P. Marsh and L. Goodman, *Tetrahedron Lett.*, 683 (1967).

(44) C. W. Huffman, *J. Org. Chem.*, **23**, 727 (1958).

(45) H. Susagawa and H. Shigehara, *J. Pharm. Soc. Japan*, **62**, 531 (1942).

(46) Restricted rotation in para-substituted formanilides has been noted by R. E. Carter, *Acta Chem. Scand.*, **22**, 2643 (1968).

yldiazonium fluoroborate[24] (500 mg, 1.78 mmol) was added with stirring at 0° to a solution of dimethyl disulfide (1 ml) and anhydrous phosphoric acid (4 mmol) in DMSO (3 ml). After 2 hr at 0°, the mixture was diluted with chloroform, extracted several times with water, dried, and evaporated. Preparative tlc using benzene–CCl_4 (1:1) followed by crystallization from methanol gave 121 mg (28%) of **18** identical with that above.

Thermal Decomposition of 18. A. Without Solvent.—Dry **18** (700 mg) was heated at 140° for 3 hr, during which time there was continuous gas evolution.[47] The temperature was raised to 160° for 30 min and the cooled residue was purified by preparative tlc using two developments with CCl_4–benzene (7:3), giving four bands. Elution of the fastest band gave 109 mg (16%) of unreacted **18**. The second band contained 13 mg (3%) of *m*-dinitrobenzene, while elution of the third band gave 446 mg (72%) of crystalline **19** identical with that above. Elution of the slowest band and crystallization from methanol gave 27 mg (5%) of bis(2,4-dinitrophenyl)sulfide with mp 196.5–198° (lit.[26] mp 196°); mass spectrum *m/e* 366 (M^+).

Anal. Calcd for $C_{12}H_6N_4O_8S$: C, 39.35; H, 1.65; N, 15.30; S, 8.76. Found: C, 39.31; H, 1.72; N, 15.11; S, 8.92.

B. In Dimethylformamide.—A solution of **18** (700 mg) in dimethylformamide (2 ml) was heated at 160° for 6 hr. It was then diluted with chloroform, extracted several times with water, evaporated, and purified by preparative tlc as above giving 6% of unreacted **18**, 27% of *m*-dinitrobenzene, and 25% of **19**.

Reaction of 18 with Acid and 1-Naphthol.—1-Naphthol (100 mg, 0.7 mmol) and **18** (121 mg, 0.5 mmol) were dissolved in a 3.8 *M* solution of hydrogen chloride in dioxane and kept at room temperature for 30 hr. After addition of ether (5 ml) the crystalline product was collected and washed, giving 131 mg (78%) of 4-(2,4-dinitrophenylazo)-1-naphthol, which was recrystallized from pyridine with mp 276–278° identical with that above.

Reaction of 18 with Bromine.—A 1 *M* solution of bromine in chloroform (2.3 ml) was added to an ice-cooled solution of **18** (500 mg, 2.07 mmol) in chloroform (4 ml). After nitrogen evolution had ceased, the mixture was evaporated and purified by preparative tlc using hexane–benzene (2:1). Elution of the major band gave 487 mg (96%) of crystalline 2,4-dinitrobromobenzene (**22**) with mp 72–73° after recrystallization from methanol (lit.[27] mp 72°): λ_{max}^{MeOH} 206 mμ (ε 15,300), 266 (12,100); nmr ($CDCl_3$) 8.07 (d, 1, J_o = 9 Hz, C_6H), 8.38 (q, 1, J_o = 9 Hz, J_m = 2 Hz, C_5H), 8.70 ppm (d, 1, J_m = 2 Hz, C_3H); mass spectrum *m/e* 246 and 248 (M^+).

Reaction of *p*-Toluenesulfonyl Hydrazide (29a).—Anhydrous phosphoric acid (5 mmol) was added to a solution of **29a** (1.86 g, 10 mmol) and DCC (5.8 g, 28 mmol) in DMSO (10 ml) and benzene (5 ml). Nitrogen evolution was almost immediate, and after 1 hr with periodic cooling the mixture was diluted with ethyl actate and water, filtered, washed with water, and purified by preparative tlc using CCl_4–ethyl acetate (19:1). A very fast band containing an unidentified, volatile material and two slower bands resulted. Elution of the faster band gave 326 mg (24%) of crystalline *p*-tolyl *p*-toluenethiolsulfonate (**33a**) with mp 75–78° from hexane (lit.[30] mp 76°): λ_{max}^{MeOH} 236 mμ (ε 19,800), 270 (sh, 6400); nmr 2.36 and 2.40 (s, 3, $ArCH_3$), 7.0–7.6 (m, 8, Ar); mass spectrum *m/e* 278 (M^+), 139 ($CH_3C_6H_4SO$), 123 ($CH_3C_6H_4S$).

Anal. Calcd for $C_{14}H_{14}S_2O_2$: C, 60.42; H, 5.07; S, 23.01. Found: C, 60.54; H, 5.07; S, 23.08.

Elution of the slower band gave 270 mg (7%) of crystalline **35** that was recrystallized from hexane with mp 89–91° (sensitive to rate of heating) with partial resolidification: λ_{max}^{MeOH} 222 mμ (ε 9700), 239 (9600); ν_{max} (KBr) 3340, 1685, 1540 cm^{-1}; nmr ($CDCl_3$) 0.9–2.2 (m, 20, cyclohexyl), 2.40 (s, 3, $ArCH_3$), 3.3 and 4.1 (m, 1, >CHN), 7.26 and 7.52 (d, 2, J = 8 Hz, Ar); mass spectrum *m/e* 362 (M^+), 280 ($M - C_6H_{10}$), 220, 139 (MeC_6H_4SO), 98 ($C_6H_{11}NH$).

Anal. Calcd for $C_{20}H_{30}N_2O_2S$: C, 66.27; H, 8.34; N, 7.73. Found: C, 66.21; H, 8.27; N, 7.74.

The aqueous extracts were shown by paper chromatography and electrophoresis to contain roughly 7 mmol (70%) of *p*-toluenesulfonic acid based upon ultraviolet spectra.

***p*-Toluenesulfinyl *p*-Tolyl Sulfone (36).**—DCC (1.03 g, 5 mmol) was added to a solution of *p*-toluenesulfinic acid (1.56 g, 10 mmol)[31] in methylene chloride (25 ml). After 10 min the mixture was filtered, giving 0.93 g of dicyclohexylurea, and the filtrate was concentrated to about 5 ml. Gradual addition of hexane (10 ml) led to crystallization of 1.21 g (82%) of **36** with mp 83–85°, unchanged upon recrystallization (lit.mp 75°,[33] 76°,[48] 87°[34]): ir identical with that reported;[34] λ_{max}^{MeOH} 222 mμ (ε 19,800), 244 (8700) and changing with time; nmr ($CDCl_3$) 2.47 (s, 6, $ArCH_3$), 7.2–7.7 (m, 8, Ar).

Anal. Calcd for $C_{14}H_{14}S_2O_3$: C, 57.14; H, 4.80. Found: C, 57.19; H, 4.78.

Reaction of *p*-Bromobenzenesulfonyl Hydrazide (29b).—A reaction between **29b** (2.51 g, 10 mmol), DCC (5.8 g, 28 mmol), and anhydrous phosphoric acid (5 mmol) in DMSO (10 ml) and benzene (10 ml) was kept for 16 hr with cooling during the early stages. It was worked up in the usual way with ethyl acetate and purified by preparative tlc using CCl_4–benzene (4:1). Elution of a very fast band and crystallization from methanol gave 67 mg (2%) of bis(4-bromophenyl)disulfide with mp 90.5–92° (lit.[49] mp 93–94°): nmr ($CDCl_3$) 7.2–7.5 ppm (m, 8, Ar); mass spectrum *m/e* 372, 374, 376 (M^+), 295, 297 ($M - Br$), 216 ($M - 2Br$), 187, 189 (BrC_6H_4S), Elution of the slower band followed by crystallization from ether–hexane gave 235 mg (12%) of 4-bromophenyl 4-bromobenzenethiolsulfonate (**33b**) with mp 160–161°: λ_{max}^{MeOH} 243 mμ (ε 23,100); nmr ($CDCl_3$) 7.1–7.8 (m, 8, Ar).

Anal. Calcd for $C_{12}H_8Br_2O_2S_2$: C, 35.12; H, 1.96; S, 15.70. Found: C, 35.46; H, 1.73; S, 15.69.

Reaction of Hydrazobenzene (23). A. With DMSO–DCC.—A solution of **23** (1.84 g, 10 mmol), DCC (5.8 g, 28 mmol), and anhydrous phosphoric acid was allowed to react in DMSO (5 ml) and benzene (5 ml) for 4 hr and then worked up with ethyl acetate. Preparative tlc using two developments with CCl_4–$CHCl_3$ (4:1) gave essentially a single product that was eluted giving 1.72 g (94%) of crystalline azobenzene (**25**) with mp 68–69° and λ_{max}^{MeOH} 316 mμ (ε 17,700), 229 (13,700), both identical with those of an authentic sample.

B. With DMSO–P_2O_5.—Hydrazobenzene (2.76 g) was added to a mixture of phosphorus pentoxide (3 g) in DMSO (15 ml) and stirred for 1 hr. The mixture was worked up with ether, giving some dark-colored, insoluble material. Preparative tlc as above gave 1.75 g (64%) of crystalline azobenzene.

Reaction of 1-Naphthylacetyl Hydrazide (26). A. With DMSO–P_2O_5.—1-Naphthylacetylhydrazide (3.0 g, 15 mmol) was added with stirring and periodic cooling to a solution of phosphorus pentoxide (2.5 g) in DMSO (20 ml). After 1 hr the mixture was diluted with chloroform and extracted three times with water with removal of 145 mg (5%) of crystalline *N,N'*-bis(1-naphthylacetyl)hydrazine (**28a**) of mp 290–292° dec, unchanged upon recrystallization from dimethylformamide–methanol: nmr (DMSO-d_6) 4.00 (s, 4, CH_2CO), 7.4–8.3 (m, 14, Ar), 10.25 ppm (s, 2, NH); mass spectrum *m/e* 368 (M^+), 168 ($C_{10}H_7CH{=}C{=}O$) 141 ($C_{10}H_7CH_2^+$).

Anal. Calcd for $C_{24}H_{20}N_2O_2$: C, 78.24; H, 5.47; N, 7.61. Found: C, 78.03; H, 5.74; N, 7.65.

Extraction of the chloroform solution with aqueous bicarbonate followed by acidification gave 783 mg (28%) of crystalline 1-naphthylacetic acid (**28c**) of mp 130–132° and identical with an authentic sample. Preparative tlc of the dried organic phase using CCl_4–acetone (19:1) gave two major bands. Elution of the faster band and short path distillation [bath temperature 90° (0.1 mm)][50] gave 853 mg (26%) of methyl 1-naphthylthioacetate (**28b**) as an oil: λ_{max}^{MeOH} 222 mμ (ε 77,000), 284 (7500); nmr ($CDCl_3$) 2.17 ppm (s, 3, SCH_3), 4.23 (s, 2, CH_2CO), 7.3–8.2 (m, 7, Ar); mass spectrum *m/e* 216 (M^+), 141 ($C_{10}H_7CH_2^+$).

Anal. Calcd for $C_{13}H_{12}OS$: C, 72.18; H, 5.59; (S, 14.83. Found: C, 71.73; H, 5.51; S, 14.76.

Elution of the slower band gave 81 mg (2%) of methylthiomethyl 1-naphthylacetate (**28d**), which could be distilled in a short path apparatus [bath temperature 95° (0.1 mm)]: nmr ($CDCl_3$) 1.96 (s, 3, SCH_3), 4.00 (s, 2, $ArCH_2CO$), 5.05 (s, 2, OCH_2S), 7.3–8.2 ppm (m, 7, Ar); mass spectrum *m/e* 246 (M^+), 141 ($C_{10}H_7CH_2^+$), 61 ($CH_3S^+{=}CH_2$). An acceptable elemental analysis was not obtained. Rechromatography of a band on the origin gave a complex mixture that was not examined further.

B. With DMSO–Diisopropylcarbodiimide.—Anhydrous phosphoric acid (2.5 mmol) was added to a solution of **26** (1.0 g, 5 mmol) and diisopropylcarbodiimide (1.89 g, 15 mmol) in DMSO (5 ml). Gas evolution and separation of crystals started after a few minutes and after 1 hr the mixture was diluted with methanol and filtered. The crystalline product was extracted twice with

(47) A sample heated directly to 150° decomposed quite violently.

(48) J. L. Kice and K. W. Bowers, *J. Amer. Chem. Soc.*, **84**, 605 (1962).

(49) L. Field, *ibid.*, **74**, 394 (1952).

(50) R. Graeve and G. H. Wahl, *J. Chem. Educ.*, **41**, 279 (1964).

hot methanol, leaving pure **24a** (0.52 g, 58%) identical with that above. The other products were not examined.

Reaction of Benzophenone Hydrazone (37). A. With DMSO–DCC.—The reaction of **37** (1.96 g, 10 mmol), DCC (6.18 g, 30 mmol), and anhydrous phosphoric acid (5 mmol) in DMSO (10 ml) and benzene (5 ml) led to rapid gas evolution and became a dark red color.[51] After 24 hr the mixture was worked up in the usual way using ethyl acetate and the organic phase was separated into three major and several minor bands by preparative tlc using CCl_4–benzene (4:1). Elution of the fastest band and crystallization from hexane gave 86 mg (5%) of tetraphenylethylene (**41**) with mp 222–224° (lit.[52] mp 223–224°): λ_{max}^{MeOH} 238 mμ (ε 13,100), 380 (7800); nmr ($CDCl_3$) 7.05 ppm (s, 20, Ar); mass spectrum *m/e* 332 (M^+), 255 ($M - C_6H_5$).

Anal. Calcd for $C_{26}H_{20}$: C, 93.94; H, 6.06. Found: C, 94.05; H, 6.02.

Elution of the second band and crystallization from hexane gave 204 mg (12%) of dibenzhydryl ether (**42**) of mp 107–108.5° (lit.[53] mp 109°): λ_{max}^{MeOH} 253 mμ (ε 770), 259 (960), 265 (720); nmr ($CDCl_3$) 5.42 (s, 2, Ar_2CHO), 7.30 ppm (s, 20, Ar); mass spectrum *m/e* 350 (M^+), 272 ($M - C_6H_6$), 183 (Ar_2CHO^+), 167 (Ar_2CH^+), 152.

Anal. Calcd for $C_{26}H_{22}O$: C, 89.11; H, 6.33. Found: C, 88.97; H, 6.15.

Elution of the major slow spot and short path distillation [bath temperature 105° (0.07 mm)] gave 860 mg (~43%) of a colorless oil that could not be further separated by tlc in several solvents but was shown by vpc (5-ft column of NPGS on Gas-Chrom Q[54] at 150°) and nmr to be a 3:2 mixture of benzophenone and benzhydrol acetate, both being compared with authentic samples.

B. With DMSO–P_2O_5.—Phosphorus pentoxide (2.5 g) was carefully added to DMSO (20 ml) and after 20 min **37** (2.94 g, 15 mmol) was added portionwise with stirring. The mixture, which evolved nitrogen, was kept at 23° for 3 hr, diluted with chloroform, and washed with aqueous bicarbonate and water. The dried and evaporated organic phase was examined by quantitative vpc using a 5-ft column of NPGS on Gas-Chrom Q[54] at 150° which showed the two major products to be benzhydrol (42%) and benzophenone (19%). Preparative tlc using CCl_4–benzene (4:1) separated these compound as well as several other bands. Elution of the fastest band followed by rechromatography using hexane–CCl_4 (7:3) and short path distillation [bath temperature 85° (0.2 min)] gave 268 mg of benzhydryl methylsulfide (**47**) of mp 30–32° (lit.[55] mp 33°): λ_{max}^{MeOH} 248 mμ (sh, ε 1200), 260 (sh, 950); nmr ($CDCl_3$) 1.99 (s, 3, SMe), 5.10 (s, 1, Ar_2CHS), 7.2–7.7 ppm (m, 10, Ar); mass spectrum *m/e* 214 (M^+), 167 ($M - SCH_3$), 165, 152.

Anal. Calcd for $C_{14}H_{14}S$: C, 78.45; H, 6.58; S, 14.96. Found: C, 78.77; H, 6.60; S, 14.70.

The band which consisted mainly of benzophenone was rechromatographed using CCl_4–acetone (9:1) which barely resolved a faster moving substance. Crystallization of this material from hexane–ethyl acetate gave 232 mg (9%) of benzophenone azine (**45**) with mp 163–164° (lit.[56] mp 164°) that was identical with an authentic sample.

Reaction of Diphenyldiazomethane (40).—A solution of freshly prepared **40** (1.94 g, 10 mmol),[35] DCC (1.5 g), and anhydrous phosphoric acid (5 mmol) in DMSO (5 ml) and benzene (5 ml) was kept at room temperature for 24 hr. The mixture was worked up in the usual way with ethyl acetate and the organic phase was separated into five compounds by preparative tlc on three plates using carbon tetrachloride. Elution of the bands and purification as described above gave tetraphenylethylene, 266 mg (16%), mp 223–225°; dibenzhydryl ether, 301 mg (17%), mp 107–109°; benzophenone, 277 mg (15%); benzophenone azine, 107 mg (6%), mp 163–164°; and benzhydrol, 293 mg (16%), mp 66–68°.

Reaction of Benzil Dihydrazone (48).—Anhydrous phosphoric acid (20 mmol) was added to a stirred, ice-cooled solution of **48** (2.38 g, 10 mmol) and DCC (8.5 g, 41 mmol) in DMSO (5 ml) and benzene (10 ml). The temperature was slowly raised (15–20°) until a controlled evolution of nitrogen resulted. The mixture was finally kept at room temperature for 3 hr and then worked up in the usual way using ethyl acetate. The organic phase was purified by preparative tlc on three plates using benzene–chloroform (85:15). Elution of the fastest band and crystallization from ethanol gave 376 mg (21%) of diphenylacetylene (**49**) with mp 61–62° (lit.[36] mp 60–61°) that was identical (ir, tlc, and melting point) with an authentic sample. Elution of the second band and crystallization from hexane gave 318 mg (15%) of benzil with mp 96–97° and identical with an authentic sample. Elution of a band near the origin gave a complex mixture of products that was not studied further.

Reaction of Indole (50a).—A solution of anhydrous orthophosphoric acid in DMSO (2 ml of 5 *M*, 10 mmol) was added to a solution of indole (2.34 g, 20 mmol) and DCC (11.6 g, 56 mmol) in a mixture of DMSO (5 ml) and benzene (15 ml). The mixture was kept at 23° for 9 days and then diluted with ethyl acetate, and excess DCC was destroyed by addition of a solution of oxalic acid (5.0 g, 40 mmol) in methanol. After 30 min the mixture was filtered, made alkaline with sodium hydroxide, extracted three times with water, dried ($MgSO_4$), and evaporated to dryness. The residue was purified by preparative tlc using two developments with hexane–benzene (1:1), giving unreacted **50a** (770 mg, 33%) and two slower bands. Elution of the faster of these gave 350 mg (10%) of 3-(methylthiomethyl)indole (**53a**) with mp 90–91° from benzene–hexane: λ_{max}^{MeOH} 221 mμ (ε 34,300), 274 (5600), 281 (6000), 289 (5100); nmr ($CDCl_3$) 1.95 (s, 3, SCH_3), 3.83 (s, 2, In CH_2S), 6.85 (d, 1, J = 2 Hz, C_2H), 7.2 (m, 3, Ar), 7.7 ppm (m, 2, NH and C_7H); mass spectrum *m/e* 177 (M^+), 130 ($M - SCH_3$).

Anal. Calcd for $C_{10}H_{11}NS$: C, 67.75; H, 6.26; N, 7.90. Found: C, 67.82; H, 6.21; N, 7.96.

Elution of the slower band and crystallization from benzene–hexane gave 158 mg (6%) of 3,3′-bisindolylmethane with mp 163–165° (lit.[37] mp 164–165°): λ_{max}^{MeOH} 226 mμ (ε 60,300), 276 (9900), 284 (10,800), 292 (9500); nmr ($CDCl_3$) 4.22 (d, s, 2, $J_{allylic}$ = 1 Hz, CH_2), 6.86 (br d, 2, J = 2 Hz, C_2H and $C_{2'}H$), 7.0–7.35 (m, 6, Ar), 7.58 (q, 2, J_0 = 7 Hz, J_m = 2 Hz, C_7H and $C_{7'}H$), 7.78 ppm (br s, 2, NH); mass spectrum *m/e* 246 (M^+), 245 (M − H), 218 (*m/e* 245 − HCN), 217 (*m/e* 218 − H).

In a separate experiment a solution of **53a** (29 mg), indole (50 mg), and anhydrous phosphoric acid (1 mmol) in DMSO (0.25 ml) was kept at 23° for 4 days. After neutralization with sodium hydroxide the mixture was diluted with ethyl acetate, extracted three times with water, dried, and evaporated. The presence of a roughly 10% yield of **55a** was shown by both tlc using chloroform–hexane (7:3) and vpc using a silicone oil column at 220°.

3,3′-Bis(*N*-methylindolyl)methane (55b).—A solution of *N*-methylindole (2.62 g, 20 mmol),[39] DCC (11.6 g, 56 mmol), and anhydrous phosphoric acid (11 mmol) in anhydrous DMSO (10 ml) and benzene (10 ml) was kept at 23° for 6 days. The reaction was worked up as described above for indole and purified by preparative tlc on three plates using benzene–hexane (7:13). The major band was unreacted (**50b**) while elution of the slower band gave 0.5 g of a semicrystalline yellow oil that was distilled in a Kugelrohr apparatus.[50] Crystallization from ethanol gave 212 mg (8%) of **55b** with mp 108–110°: λ_{max}^{MeOH} 228 mμ (ε 12,700), 290 (br, 2100); nmr ($CDCl_3$) 3.30 (s, 6, NMe), 4.15 (s, 2, CH_2), 6.58 (s, 2, C_2H and $C_{2'}H$), 7.1 (m, 6, Ar), 7.57 (q, 2, J_0 = 7, J_m = 2 Hz, C_7H and $C_{7'}H$); mass spectrum *m/e* 274 (M^+), 273 (M − H), 259 ($M - CH_3$), 144 ($M^+ - N$-Me-indole).

Anal. Calcd for $C_{19}H_{18}N_2$: C, 83.18; H, 6.61; N, 10.21. Found: C, 83.25; H, 6.82; N, 9.94.

Registry No.—DMSO, 67-68-5; DCC, 538-75-0; **3**, 31896-55-6; **4**, 1202-63-7; **7a**, 31896-57-8; **7b**, 31899-31-7; **7c**, 31896-59-0; **8**, 7507-66-6; **9b**, 31896-61-4; **10**, 31872-13-6; **18**, 31899-35-1; **19**, 2363-23-7; **22**, 584-48-5; **25**, 103-33-3; **28a**, 31896-65-8; **28b**, 31896-66-9; **28d**, 31896-67-0; **33a**, 2943-42-2; **33b**, 3347-03-3; **35**, 31896-70-5; **36**, 788-86-3; **41**, 632-51-9; **42**, 574-42-5; **44**, 91-01-0; **45**, 983-79-9; **47**, 15733-08-1; **53a**, 31899-46-4; **55a**, 1968-05-4; **55b**, 31896-75-0; *m*-dinitrobenzene, 99-65-0; 2,2′,4,4′-tetranitroazobenzene, 5267-25-4; 4-(2,4-dinitrophenylazo)-1-naphthol, 3468-62-0; bis(2,4-dinitrophenyl) sulfide, 2253-67-0; bis(4-bromophenyl) disulfide, 5335-84-2.

(51) In a separated reaction omitting the benzene, the red material was immediately extracted into hexane and showed λ_{max}^{hexane} 524 mμ, identical with that of an authentic sample of diphenyldiazomethane.[35]

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