azocarbonyl amino acids by the method of Pieroni.[5] Their properties and analyses are shown in Table IV.

The N-carboxyphenylhydrazidoamino acid (0.01 mole) and 0.01 mole of sodium bicarbonate were dissolved in 80 ml. of water. This solution was added to a solution of potassium permanganate (0.005 mole) in 20 ml. of water, and the resulting solution was stirred for 9 min. Oxalic acid (0.01 mole, dissolved in 50 ml. of water) was added to the above solution, and this was then made acidic by the dropwise addition of dilute sulfuric acid. The acidic solution was extracted with five 25-ml. portions of ether. The ether extract was dried over anhydrous magnesium sulfate, and the solvent was evaporated to yield a red-orange solid which was recrystallized from the solvent indicated in Table IV.

The infrared spectra of the N-phenylazocarbonylamino acids (films deposited from methanol) showed the following maxima: N–H stretch at 3.08 μ was reduced as compared with the starting material; C=O stretch [NHC(O)NH] was shifted from 6.01 to 5.90 μ; N–H deformation at 6.23 μ disappeared, and a new peak appeared at 8.38 μ. The ultraviolet spectra (dichloromethane solutions) showed peaks at $\lambda_{\max}$ 450.0 mμ (ϵ 112) and 297.5 mμ (ϵ 12,500).

Enzymatic Syntheses of N-Carboxyphenylhydrazidoamino Acid Phenylhydrazides.—The N-carboxyphenylhydrazidoamino acid phenylhydrazides were prepared enzymatically by the method reported previously.[11] Their physical properties are listed in Table V and their analyses are given in Table VI.

The infrared spectra of N-carboxyphenylhydrazidoamino acid phenylhydrazides (films deposited from dioxane) showed maxima at N–H stretch, 3.08; C=O stretch, 6.00; N–H deformation, 6.30; and C–H out-of-plane deformation, 13.25 and 14.40 μ. The ultraviolet spectra of these compounds (absolute ethanol solutions) showed peaks at $\lambda_{\max}$ 235 mμ (ϵ 21,200) and 282 mμ (ϵ 3000). Although all N-carboxyphenylhydrazidoamino acids used were optically inactive, the products (excepting the glycine derivative) were strongly dextrorotatory.

Enzymatic Synthesis of N-Carboxyphenylhydrazido-L-leucine Phenylhydrazide.—N-Carboxyphenylhydrazido-DL-leucine (3.0 g., 0.011 mole) was dissolved in 100 ml. of water with an equivalent amount of sodium hydroxide, and this solution was added to a solution of 14.4 g. (9.1 mole) of phenylhydrazine hydrochloride, 4 g. of L-cysteine hydrochloride, and 3 g. of sodium versenate in 100 ml. of water. The volume of the solution was brought to 500 ml. with 2 M sodium acetate–acetic acid buffer (pH 4.7), 5 g. of papain was added, and the solution was saturated with nitrogen and incubated at 40°. At intervals the solid product was collected by filtration, and the filtrate was incubated further. The melting point and specific rotation of each sample of precipitate were determined. The results are shown in Table VII.

N-Phenylazocarbonyl-L-leucine.—N-Carboxyphenylhydrazido-L-leucine phenylhydrazide (1 g., 0.0028 mole), $[\alpha]^{25}{}_{\mathrm{D}}$ +39.2° (c 1.3, glacial acetic acid), was dissolved in 100 ml. of acetone, the solution was heated to 40°, and a solution of ferric chloride hexahydrate (8 g., 0.03 mole, in 30 ml. of water) was added dropwise over a period of 40 min. The acetone was removed with a rotary evaporator, and the remaining oily aqueous layer was extracted with three 50-ml. portions of ether. The ether solution was dried over anhydrous magnesium sulfate, and the ether was evaporated to give an oil. The oil did not crystallize, but it had an infrared spectrum identical with that of a sample of N-phenylazocarbonyl leucine prepared by oxidizing N-carboxyphenylhydrazido-DL-leucine. The yield was 0.4 g. (54%), $[\alpha]^{25}{}_{\mathrm{D}}$ −33.9° (c 1.78, methanol).

N-Phenylazocarbonyl-L-leucine as Substrate in Enzymatic Synthesis.—N-Phenylazocarbonyl-L-leucine (0.34 g., 0.0013 mole), $[\alpha]^{25}{}_{\mathrm{D}}$ −33.9° (c 1.78, methanol), was dissolved in 25 ml. of dilute sodium hydroxide solution, and this was added to a solution of phenylhydrazine hydrochloride (5 g., 0.035 mole) and 2 g. of L-cysteine hydrochloride in 50 ml. of water, and the volume of the solution was brought to 275 ml. The solution was buffered at pH 4.7 with approximately 1 M sodium acetate and acetic acid; 1 g. of versene and 1 g. of papain were added, and the solution was saturated with nitrogen and incubated at 40°. The product was isolated after 4 days and recrystallized from acetone–ether. The yield was 0.2 g. (43.5%), m.p. 186–188.5°, $[\alpha]^{25}{}_{\mathrm{D}}$ +46.97° (c 1.88, glacial acetic acid). The infrared spectrum was identical with that of a sample of N-carboxyphenylhydrazido-L-leucine phenylhydrazide prepared from N-carboxyphenylhydrazido-DL-leucine.

Phenylhydantoic Acid.—N-Carbobenzoxyglycine anilide (2.84 g., 0.01 mole) was refluxed in 50 ml. of 0.2 N alcoholic potassium hydroxide, under a nitrogen atmosphere, for 4 hr. The solvent was removed with a rotary evaporator, the remaining oil was dissolved in 25 ml. of water, and the product was precipitated by acidification and recrystallized from ethanol; the yield was 1.8 g. (95%), m.p. 186–188°. A mixture (m.p. 187–189°) showed no depression, and the infrared spectrum was identical with that for an authentic sample of phenylhydantoic acid.

Potassium N-Carboxyhydrazidoglycinate.—N-Carboethoxyglycine (15 g., 0.1 mole) was dissolved in 150 ml. of absolute methanol, and the solution was saturated with dry hydrogen chloride gas and stored at room temperature for 4 days. The solvents were removed, and the resulting oil was dissolved in 25 ml. of absolute ethanol; 5 ml. (0.08 mole) of 85% hydrazine hydrate was added, and the resulting solution was stored for 3 days at room temperature. The solvents were removed, and the resulting oil was treated three times, by the addition and subsequent evaporation under vacuum, of three portions of 15–20 ml. of absolute ethanol. The resulting oil was dissolved in 100 ml. of ethanol, and 5.6 g. (0.1 mole) of potassium hydroxide was added. This solution was refluxed, for 4 hr., and then cooled, and the salt was separated by filtration and washed with hot methanol; the yield was 11.3 g. (65%), m.p. 212–214°.

Anal. Calcd. for $C_3H_6KN_3O_3$: C, 21.05; H, 3.55; N, 24.54. Found: C, 21.20; H, 3.57; N, 24.84.

The Reaction of 1,1-Bis(diethylamino)ethene with Phenylmethanesulfonyl Chloride

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Received July 20, 1964

Phenylmethanesulfonyl chloride reacts with 1,1-bis(diethylamino)ethene to give a substitution product, whereas ketene diethyl acetal yields a cycloadduct. Some of the factors which appear to be involved in determining the nature of products are discussed.

In the presence of base, various sulfonyl chlorides react with ketene diethyl acetal to give thietane dioxides (referred to hereafter as cycloadducts).[1] However, under similar conditions, ketene aminals yield either a cycloadduct or a substitution product depending on the nature of the reactants and the reaction media.[2,3] This paper attempts to describe some factors which bring about the substitution products.

In tetrahydrofuran, 1,1-bis(diethylamino)ethene reacted with phenylmethanesulfonyl chloride in the presence of triethylamine, to produce a substitution

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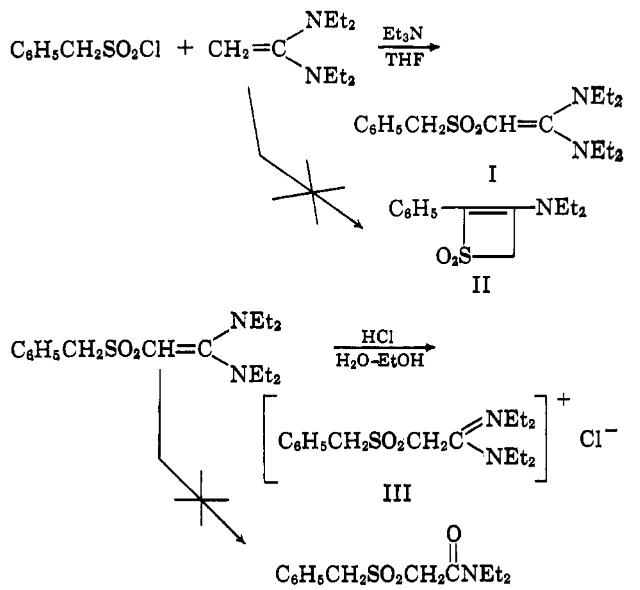
(1) W. E. Truce and J. R. Norell, *J. Am. Chem. Soc.*, **85**, 3231 (1963).

(2) R. H. Hasek, P. G. Gott, R. H. Meen, and J. C. Martin, *J. Org. Chem.*, **28**, 2496 (1963).

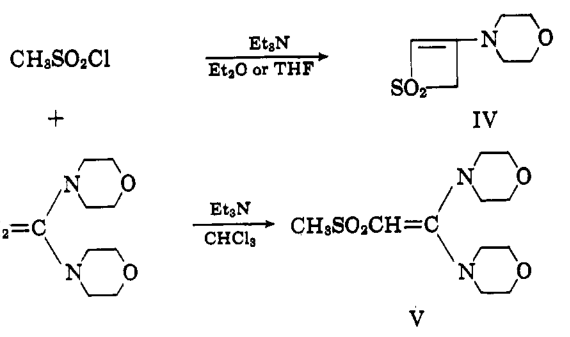
(3) G. Optiz and H. Schempp, *Z. Naturforsch.*, **19b**, 78 (1964).

product, 1,1-bis(diethylamino)-2-(phenylmethanesulfonyl)ethene (I), in 67% yield; none of the cycloadduct was found. Acid-catalyzed hydrolysis of I failed to yield the expected corresponding amide; instead, the amidinium chloride salt III was isolated.

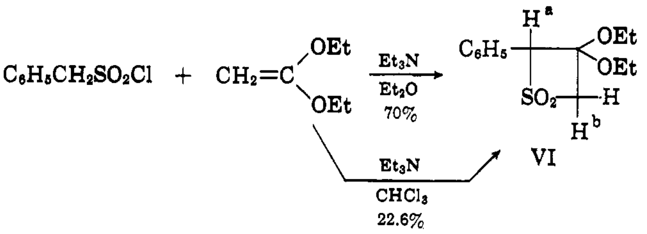


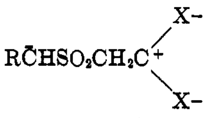
The absence of cycloadduct and the resistance of the substitution product toward hydrolysis are attributable to crowding at the vinylic carbon atom, which bears the *gem*-diethylamino groups. The scale model exhibits a convincing picture of this phenomenon. Even with the least likely conformation of the two amino groups, which provides a maximum space for the incoming nucleophile toward the disubstituted vinylic carbon atom, the hydrogen atoms of the methylenic groups adjacent to the nitrogen atoms completely shield the carbon atom in question.

In contrast to these results, Opitz and Schempp[3] and Hasek, *et al.*,[2] found that 1,1-bis(dimorpholino)ethene reacted with methanesulfonyl chloride in ether and tetrahydrofuran to give 3-morpholinothietane 1,1-dioxide (IV) in good yields, whereas in chloroform only substitution product, 1,1-bis(dimorpholino)-2-methanesulfonylethene (V), resulted. Here the methylene groups adjacent to the nitrogen atoms are tied back by the ring and the steric factor discussed in the preceding paragraph is greatly reduced.



In the system studied by Opitz and Schempp, solvent appears to determine the nature of the product. Unlike the ethers, chloroform dissolves triethylamine hydrochloride (by-product of the reaction), thereby providing a ready source of protons. When ketene diethylacetal was employed in the place of the ketene aminal, however, we observed no such solvent effect. Only a reduced yield of cycloadduct and a small amount of by-product, triethylammonium phenylmethanesulfonate were obtained in chloroform. This difference between the ketene acetal and the ketene aminal (where N is a part of the ring system) can be rationalized by assuming a difference in degree of stabilization of positive charge being developed at the carbon atom, which is substituted either by alkoxyl groups or by amino groups. The latter being more effective in stabilization of positive charge, the postulated zwitterion (probably formed by the addition of sulfene[4,5]) would have a longer lifetime for picking up a proton to give rise to a substitution product.

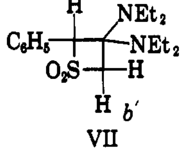



$\overset{-}{R}CHSO_2CH_2C^{+}(X-)_2$

X = O or N–
R = alkyl or aryl

The reason for formation of 1,1-bis(dimorpholino)-2-(β-phenylethanesulfonyl)ethene[3] from the appropriate sulfonyl chloride and ethene in ether solution (whereas methanesulfonyl chloride yields cycloadduct) may be due to an electronic as well as a steric factor. One might argue that stabilization of the negative charge of the postulated zwitterion is also important. Further investigation is imperative, however, before one can confirm the existence of the zwitterion and its role in determining the nature of the products hitherto observed.

The assigned structure of 1,1-bis(diethylamino)-2-(phenylmethanesulfonyl)ethene (I) has been verified on the basis of elemental analysis, molecular weight determination, and infrared and n.m.r. spectra. The structure I is preferred over the alternative cyclic structure VII, for in interactions of "sulfenes" with ketene aminals no cycloadducts, without an elimination of one of the two amino groups, have been observed.[2,3] Such elimination is believed to be due to steric interactions between the two amino groups attached to the same carbon atoms. The same is true for the less hindered ketene O,N-acetal[2] (here the alkoxyl group is eliminated). Thus, it is very unlikely that the more sterically hindered ketene aminal, 1,1-bis(diethylamino)-ethene, should give the cycloadduct VII without an elimination of a diethylamino group (which would lead



VII

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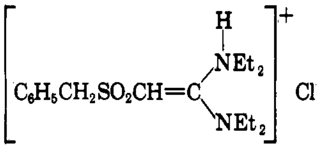
(4) J. F. King and T. Durst, *J. Am. Chem. Soc.*, **86**, 287 (1964).

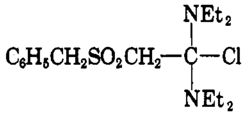
(5) W. E. Truce, R. W. Campbell, and J. R. Norell, *ibid.*, **86**, 288 (1964).

to II). Secondly, the infrared spectrum (Nujol mull) shows strong bands at 7.86 and 8.69 ($-SO_2-$) and also at 6.50 μ, the latter being attributed to the olefinic double bond.[6] The n.m.r. spectrum ($CDCl_3$) is also in harmony with the suggested structure I. A triplet at δ 1.00 and a sextet[7a] at 3.08 with ratio of 12:8 represents the protons of four ethyl groups attached to the two nitrogen atoms in pairs. A singlet at δ 7.29, with an area equivalent to five protons, was attributed to the protons of the phenyl group. Two singlets at δ 3.83 and 4.17 (1:2 area ratio) were assigned to a vinylic proton and to the two protons of the benzylic methylene group, respectively. The abnormal chemical shift of the vinylic proton to the higher field is considered to be a result of the polarization of the double bond by the two strong electron-donating diethylamino groups.[7b] For the alternative structure VII one would expect the signal due to proton a′ to appear at lower field than that of the two b′ protons (the proton a′ is subjected to the inductive effect by two strong election-withdrawing groups, phenyl and sulfone, whereas the proton b′, only by the sulfone group). This argument is consistent with the reported assignments[1] of the protons of a and b for the cycloadduct VI and its analogs.



$$\left[C_6H_5CH_2SO_2CH{=}C\begin{array}{l}\overset{\displaystyle H}{\overset{|}{N}}Et_2\\ NEt_2\end{array}\right]^{+}Cl^{-}$$

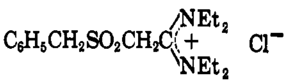
VIII



$$C_6H_5CH_2SO_2CH_2{-}\underset{\displaystyle NEt_2}{\overset{\displaystyle NEt_2}{C}}{-}Cl$$

IX

The structure of the amidinium salt III has been deduced by similar physicochemical methods. On the basis of elemental analysis and molecular weight determination, the following two possible structures were considered besides the suggested structure III. The isomer in which the chlorine atom is attached by a covalent bond IX is unlikely owing in part to its high melting point. The other alternative ammonium salt VIII was precluded largely on the basis of the lack of an $^{+}NH\lessdot$ infrared absorption band at 3.66 μ (2735 cm.$^{-1}$)[8] and its inconsistency with n.m.r. data. The n.m.r. spectrum (in $CDCl_3$) shows a triplet at δ 1.25 and a quartet at 3.62 (12:8) which corresponds to protons of four ethyl groups attached to the two nitrogen atoms. Two singlets at δ 5.00 and 5.55 (2:2) are responsible for the protons of the methylenic and benzylic groups, respectively.[9] Five protons of the phenyl group show multiple peaks around δ 7.2–7.8. It is noteworthy that the protons of the ethyl groups attached to the two nitrogen atoms show no chemical shift relative to each other. This indicates that the two amino groups are equivalent. The equivalence of the two amino groups would be expected on the basis of the following resonance hybrid for compound III. Additional evidence in favor of structure III has been obtained from the infrared spectrum (Nujol mull). The shift of the absorption band of the double bond stretching toward higher frequency going from a *gem*-diaminoethene (I, 6.50 μ or 1538 cm.$^{-1}$) to its salt (III, 6.33 μ or 1580 cm.$^{-1}$), is in excellent agreement with what Leonard and Gash[10] observed in the transformation of an unsaturated amine into its salt.



$$C_6H_5CH_2SO_2CH_2C\left(\begin{array}{l}NEt_2\\ +\\ NEt_2\end{array}\right.\;Cl^{-}$$

Experimental[11]

Materials.—Ketene diethylacetal was prepared by the procedure of McElvain and Kundiger.[12] Triethylamine (Matheson Coleman and Bell) had b.p. 88–90°. Mallinckrodt anhydrous diethyl ether and tetrahydrofuran were used as obtained. Phenylmethanesulfonyl chloride, m.p. 87–91°, was purchased from Aldrich Chemical Co.

1,1-Bis(diethylamino)ethene.[13]—To 23 g. (0.23 mole) of diethylamine was added 55.5 g. (0.48 mole) of ketene diethyl acetal. The mixture was allowed to stir for 12 hr. and was then heated in a sealed tube at 120° for 5.5 hr. The tube was cooled and the pale yellow liquid was fractionated through a Fenske column packed with glass helices; 5.3 g. of pure 1,1-bis(diethylamino)ethene was obtained, b.p. 92–93° at 40 mm., $n^{20}{}_D$ 1.4519 (lit.[13] $n^{20}{}_D$ 1.4520).

1,1-Bis(diethylamino)-2-(phenylmethanesulfonyl)ethene (I).—A solution of 5.93 g. (0.031 mole) of phenylmethanesulfonyl chloride in 50 ml. of tetrahydrofuran was added dropwise to the mixture of 5.30 g. (0.031 mole) of 1,1-bis(diethylamino)ethene, 3.15 g. (0.031 mole) of triethylamine, and 80 ml. of tetrahydrofuran. A white precipitate formed immediately. The reaction mixture was stirred overnight. After filtration crude triethylamine hydrochloride was collected, 3.7 g. (86.1% yield), m.p. 248–254° dec. The filtrate was evaporated *in vacuo*, leaving a brown semisolid in the flask. It was recrystallized five times from hexane and gave a total of 6.6 g. (67.1%) of the substitution product, m.p. 75–77°.

Anal. Calcd. for $C_{17}H_{28}N_2O_2S$: C, 62.93; H, 8.56; N, 8.63; S, 9.88. Found: C, 62.76; H, 8.67; N, 8.93; S, 10.06.

Reaction of 1,1-Bis(diethylamino)-2-(phenylmethanesulfonyl)-ethene (I) with Aqueous Alcoholic Hydrochloric Acid.—In a 100-ml. flask, fitted with a reflux condenser, were placed 4.4 g. (0.014 mole) of I, 40 ml. of 2 *N* hydrochloric acid, and 15 ml. of ethanol. The above mixture was refluxed for 4.5 hr. and neutralized with 40 ml. of 2 *N* sodium hydroxide. The product was extracted with four 50-ml. portions of chloroform and then with three 50-ml. portions of dichloromethane. The solvents were removed from the combined extraction. The residual oil was crystallized on treatment with 80 ml. of hot ethyl acetate. Recrystallization from absolute ethanol and ethyl ether gave a total of 1.5 g. (31.2%) of amidinium chloride salt, m.p. 204–204.5°.

Anal. Calcd. for $C_{17}H_{29}ClN_2O_2S$: C, 56.57; H, 8.09; Cl, 9.83; N, 7.76; S, 8.90. Found: C, 56.69; H, 8.04; Cl, 10.10; N, 8.03; S, 9.10.

2-Phenyl-3,3-diethoxythietane 1,1-Dioxide.—A procedure like that used for the preparation of I was followed. When anhydrous diethyl ether was employed as solvent, a total yield of 18.9 g. (70%) of pure cycloadduct resulted, m.p. 91–92° (lit.[1] m.p. 89–90°). Hexane was used for recrystallization. When the reaction was carried out in chloroform solution, a reduced yield

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(6) This assignment is consistent with the observation by Opitz and Schempp that $>C{=}C<$ stretching occurs in 6.55-μ region for all the substitution products obtained from the reaction of the sulfene and ketene aminal.

(7) (a) The sextet is regarded as the result of the overlap of the two quartets, due to the small chemical shift (*ca.* δ 0.25) of the protons of the two methylene groups, which is in turn brought about by the crowding of the two amino groups. (b) D. H. Clemens, *et al.*, *J. Org. Chem.*, **29**, 2932 (1964).

(8) L. J. Bellamy, "Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1962, p. 260.

(9) These assignments are based on the same argument presented in the discussion of the n.m.r. spectrum of the substitution product I.

(10) N. J. Leonard and V. W. Gash, *J. Am. Chem. Soc.*, **76**, 2781 (1954).

(11) All melting points are uncorrected. The infrared spectra were run on a Perkin-Elmer Infracord or Perkin Model 21 spectrometer. The n.m.r. spectra were obtained with a Varian A-60 spectrometer at a sweep width of 500 c.p.s. with TMS as an internal standard. The molecular weights were determined with a Mechrolab vapor pressure osmometer.

(12) S. M. McElvain, "Organic Synthesis," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 506.

(13) S. M. McElvain and B. E. Tate, *J. Am. Chem.Soc.*, **67**, 202 (1945).

(6.1 g., 22.6%) of the cycloadduct as well as a small amount (1.61 g., 5.9%) of triethylammonium phenylmethanesulfonate (m.p. 114–115°) were isolated. The characterization of the products was accomplished by mixture melting points and by comparing infrared and n.m.r. spectra of the products with those of authentic samples.

Acknowledgment.—This investigation was supported by the U. S. Army Research Office (Durham) under Contract DA-31-124-ARO-D-211 and by Public Health Service Research Grant No. CA-04536-06 from the National Cancer Institute.

1,3-Dipolar Cycloadditions. XII.[1] The Synthesis of 1,3,4-Thiadiazolidine-5-thiones

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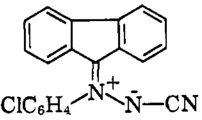
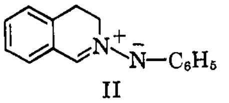
Received June 15, 1964

The reaction of N,N′-dialkylhydrazines with aromatic aldehydes and carbon disulfide affords a general synthesis of 3,4-dialkyl-1,3,4-thiadiazolidine-5-thiones. Instead of the first two components, hexasubstituted hexahydro-1,2,4,5-tetrazines may be used advantageously. Possible reaction mechanisms are discussed. Among the chemical and physical evidence which serves to establish the structure of the cyclic products, the n.m.r. spectra deserve attention owing to certain unusual features.

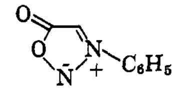
Azomethine imines have been recognized in recent years as a new class of 1,3-dipoles.[4] Those derived from diaryldiazomethanes and diazocyanides (I) are obtainable as stable, crystalline substances.[5] Upon warming with dipolarophiles, they readily undergo cycloaddition.[6] Still greater is the reactivity toward cycloaddition displayed by 3,4-dihydroisoquinoline-N-aryl imines (II). These 1,3-dipoles, however, are not stable, isolable substances, but exist in equilibrium with the head–tail dimeric form.[7] In the case of sydnones, (III), the azomethine imine system is incorporated in an aromatic nucleus and undergoes 1,3-dipolar cycloaddition with alkynes[8] and alkenes[9] followed by loss of carbon dioxide from the initially formed adduct.



I

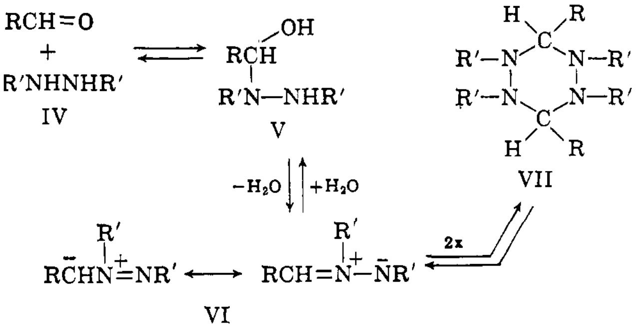


II



III

Since the azomethine imine systems discussed above yield rather specially substituted classes of compounds, we sought a more general synthesis and accordingly undertook an investigation of the reaction of N,N′-disubstituted hydrazines with carbonyl compounds. Rassow[10] had shown that N,N′-disubstituted hydrazines combine with aldehydes to form substituted hexahydro-1,2,4,5-tetrazines. These products, which have also been consider to possess the diaziridine structure, appear worthy of re-examination. The compounds which we isolated from the interaction of N,N′-dialkylhydrazines with aromatic aldehydes proved to be hexahydrotetrazines.



The formation of six-membered ring products may be viewed as proceeding *via* the carbonol–hydrazine V followed by dehydration to the azomethine imine VI. Dimerization of the latter proceeds by mutual neutralization of formal charges to yield VII. This reaction path is not unequivocal. However, it can be checked by trapping of the intermediate VI with dipolarophilic compounds. Such cycloadditions have indeed been accomplished with α,β-unsaturated esters and nitriles, as well as with acenaphthylene, isocyanates, isothiocyanates, and rhodanides.[11] In this paper we wish to report only on the reaction involving carbon disulfide as a dipolarophile.

Addition Reactions of Carbon Disulfide.—Mild warming of N,N′-dialkylhydrazines with aldehydes in carbon disulfide diluted with an inert solvent yields the corresponding 2,3,4-trisubstituted 1,3,4-thiadiazolidine-5-thiones (VIII–XIV) of Table I (method A). The nature of the aromatic aldehyde appears to have only a negligible effect upon the yield. N,N′-Dibenzylhydrazine, as well as the *p,p′*-dimethoxy derivative, and N,N′-dimethylhydrazine were used; hydrazobenzene proved unsuitable in this synthesis.

The conclusion that the intermediary azomethine imine VI adds more rapidly to the C=S double bond of carbon disulfide than it dimerizes to VII is not unambiguous. We have succeeded in achieving high yields of

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[1] Paper XI: G. Binsch, R. Huisgen, and H. König, *Chem. Ber.*, **97**, 2893 (1964).

[2] From the M.S. Thesis K. K. Sun, University of Munich, 1962.

[3] NATO Postdoctoral Fellow in Munich, 1959–1960.

[4] See R. Huisgen, *Proc. Chem. Soc.*, 357 (1961); *Angew. Chem., Intern. Ed. Eng.*, **2**, 565 (1963).

[5] R. Huisgen, R. Fleischmann, and A. Eckell, *Tetrahedron Letters*, **No. 12**, 1 (1960).

[6] R. Huisgen and A. Eckell, *ibid.*, **12**, 5 (1960).

[7] R. Huisgen, R. Grashey, P. Laur, and H. Leitermann, *Angew. Chem.*, **72**, 416 (1960); R. Grashey and K. Adelsberger, *ibid.*, **74**, 292 (1962); R. Grashey, H. Leitermann, R. Schmidt, and K. Adelsberger, *ibid.*, **74**, 491 (1962).

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