of removal of the solution from the palladium metal precipitate, extraction of organic products into ether, washing, drying, and evaporation of the ether. The products were analyzed by glpc on a 2-ft column of 20% SE-60 (silicon rubber) on Chromosorb W, at 100° + 15°/min to 290° with 30 cc of He/min. Samples of pure products (of Table III) were obtained by recrystallization, distillation, and/or preparative glpc and identified by melting point, ir and nmr spectra, and mass determination. The identity of chromatographically pure biaryls was confirmed by melting point, mixture melting point, ir and nmr spectra. In addition, the purity of *p,p'*-bitolyl was proved by glpc on a 15-ft column of 5% Apiezon N on Chromosorb W, operated at 225° with 60 cc of He/min, which separated all $C_{14}H_{14}$ isomers. Conversions were based on palladium salt and obtained from glpc peak areas.

Registry No.—$C_6H_5SO_2Na$, 873-55-2; *p*-$CH_3C_6H_4SO_2Na$, 824-79-3; Na_2PdCl_4, 13820-53-6; $Pd(OAc)_2$, 3375-31-3; $Na_2(PdBr_2Cl_2)$, 25637-01-8; Li_2PdCl_4, 15525-45-8.

Stereochemistry of Amine Additions to Acetylenic and Allenic Sulfones and Sulfoxides

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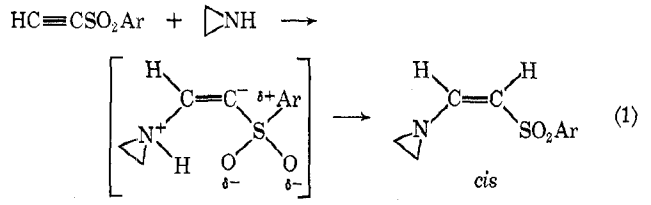
Additions of ethylenimine to *nonterminal* acetylenic sulfones and sulfoxides (RC≡CSO$_2$R' and RC≡CSOR') proceed nonstereoselectively to give mixtures of conjugated adducts. Allenic sulfones and sulfoxides react with ethylenimine to give the nonconjugated adducts, which do not isomerize under the reaction conditions to the conjugated adducts. A solvent effect and a temperature effect show the *trans* addition process to be kinetically favored and the *cis* process to give the more stable *trans* adduct. Both the R and R' groups in RC≡CSO$_2$R' affect the *cis–trans* ratio of adducts in the ethylenimine additions. Theories to explain these results are given.

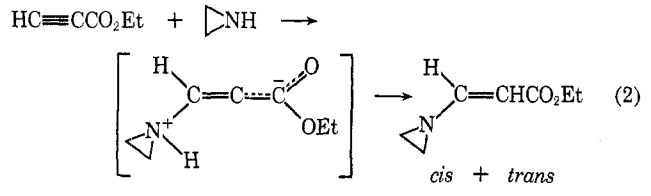
Several years ago, a study in this laboratory of the stereochemistry of additions of amines to acetylenic sulfones and carboxylic esters was reported.[1] This and other work in the area of amine additions to activated acetylenes registered over the last few years, was facilitated by the utility of nmr analysis for configurational determinations[1-3] and the unique advantage of ethylenimine as a nucleophile in producing adducts which resist *cis–trans* isomerization under the reaction conditions.[1,3,4] For example, ethylenimine adds to *p*-tolylsulfonylacetylene giving ≥95% *cis*-1-ethylenimino-2-(*p*-tolylsulfonyl)ethene (eq 1) while simple



(1)

secondary amines as well as primary amines give the *trans* adduct *via* isomerization of the initially produced *cis* isomer.

Ethyl and methyl propiolate undergo nonstereoselective addition with ethylenimine giving both *cis* and *trans* adducts.[1,3,4] It was suggested[1] that the ethyl propiolate–ethylenimine addition involves the formation of a dipolar intermediate which has a linear resonance stabilized carbanion center (eq 2). Protonation from

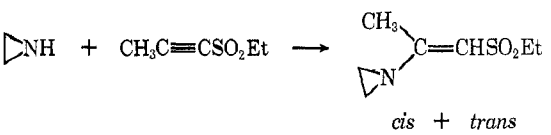


(2)

either side accounts for the nonstereoselectivity of the addition. It was proposed that the *p*-tolylsulfonyl-acetylene–ethylenimine intermediate has an angular carbanion center with the *cis* configuration being stabilized by electrostatic and/or hydrogen-bonding forces (eq 1), thereby accounting for predominant *trans* addition.

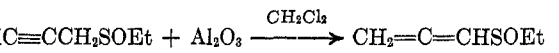
Results and Discussion

Amine additions to *nonterminal* acetylenes of the form RC≡CZ (where R = CH_3 and CH_2CH_3 and Z = SO_2Et, $SO_2C_6H_4CH_3$-*p*, and SOEt) needed careful examination and constitute part of the basis for this report. In the nonstereoselective reaction, there was the possibility that isomerization and subsequent addition to the allene, CH_2=C=$CHSO_2Et$, was competing



with addition to the conjugated acetylene.[1,2] Hence the nature of additions of ethylenimine to two allenic sulfones and an allenic sulfoxide as well as two propargyl sulfones and one propargyl sulfoxide was studied and is described herein.

Allenic sulfones have been prepared by isomerization of the propargyl sulfones with either triethylamine or basic alumina.[2,5] Allenic sulfoxides have not been reported, but we have found them to be accessible also in this manner (eq 3). The propargyl and 1-propynyl



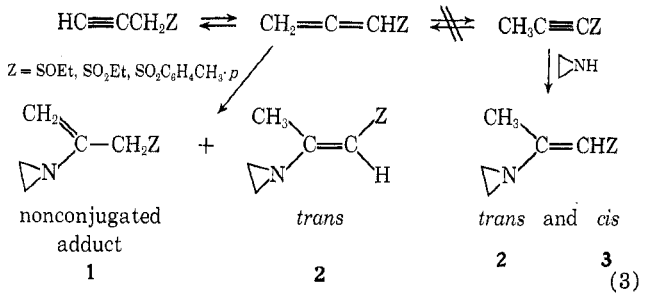
(3)

sulfoxides were prepared by oxidation of the corresponding sulfide with 1 equiv of sodium metaperiodate or 1 equiv of *m*-chloroperbenzoic acid.

Addition of ethylenimine to the allenic and propargylic sulfones and sulfoxides led to the formation of the nonconjugated adduct, by 1,2 addition to the allene directly or through initial isomerization of the

(1) W. E. Truce and D. G. Brady, *J. Org. Chem.*, **31**, 3543 (1966).
(2) C. J. M. Stirling, *J. Chem. Soc., Suppl. I*, 5863 (1964).
(3) J. E. Dolfini, *J. Org. Chem.*, **30**, 1298 (1965).
(4) R. Huisgen, B. Giese, and H. Huber, *Tetrahedron Lett.*, 1883 (1967).
(5) S. T. McDowell and C. J. M. Stirling, *J. Chem. Soc. B*, 351 (1967).

propargyl system to allene. In some systems small amounts of the *trans* conjugated adduct formed by 2,3 addition to the allene (eq 4) were obtained (allenic



(3)

nitriles have also been shown to add amines in both 1,2 and 2,3 fashion[6]). As shown in Table I, the ratio of

TABLE I

ADDITION OF ETHYLENIMINE TO CH_2=C=CHZ AND/OR HC≡CCH_2Z

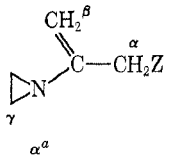
Z	Solvent	Reaction time, hr — Allene	Acetylene	% of 1	Mp or bp (mm) of 1, °C	% of 2
SOEt	C_6H_6	6	...[a]	77	81–84	23
	EtOH	24	24	100	(0.20)	
SO_2Et	C_6H_6	4[b]	4	100	64–65.5	
	EtOH	4[b]	4	100		
$SO_2C_6H_4CH_3$-*p*	C_6H_6	4	4	94	69.5–70.5	6
	EtOH	4	4	93		7

[a] The reaction was very slow. After 72 hr, there was only 6% of the product present. [b] A mixture of 78% ethylsulfonylpropadiene and 22% 3-ethylsulfonylpropyne was used.

nonconjugated to conjugated adducts is solvent dependent. The nmr spectra of the nonconjugated adducts given in Table II support the structural

TABLE II

NMR DATA FOR



Z	α[a]	β[a]	γ[a]
SOEt	3.55	4.57 and 4.63	1.92
SO_2Et	3.73	4.58 and 4.68	1.88
$SO_2C_6H_4CH_3$-*p*	3.87	4.38 and 4.45	1.75

[a] Positions given in parts per million (δ) in $CDCl_3$ relative to TMS. The α, β, and γ peaks all appeared as singlets.

assignments. In comparing the ir spectra of the conjugated and nonconjugated adducts, one finds as expected the olefinic stretching vibration shifted about 50 cm^{-1} lower in the conjugated isomers from that in the nonconjugated.

That the 2,3 adduct (**2**) does not arise by isomerization of the 1,2 adduct (**1**) was shown by treating the pure nonconjugated ethylenimine adducts with ethylenimine in both ethanol and benzene; the starting adducts **1** were recovered unchanged. Resistance of adducts **1** to isomerization under reaction conditions rules out an allenic intermediate in the addition of ethylenimine to *nonterminal* acetylenic sulfones and sulfoxides, which yield only conjugated adducts **2** and **3**. Also, this change in product composition indicates that, although ethylenimine can isomerize the propargyl systems to the allenes, further isomerization to the *nonterminal* 1-propynyl compounds does not compete with the addition process (eq 4).

Having ruled out an allene intermediate in the nonstereoselective addition of ethylenimine to 1-ethylsulfonylpropyne, it was of interest to study additions to other 1-propynyl sulfones and sulfoxides to gain more knowledge about the addition process. A temperature effect was found to be operative in the ethylenimine additions to *nonterminal* sulfones and sulfoxides and examples of such may be found in Tables III and IV.

TABLE III

TEMPERATURE EFFECT IN THE ADDITION OF ETHYLENIMINE TO CH_3C≡$CSOEt$ IN BENZENE

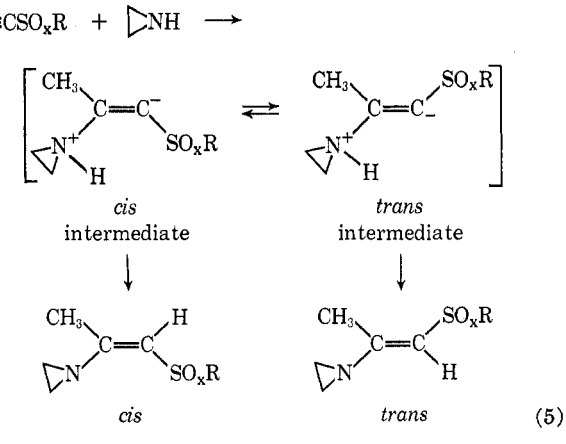
Temp, °C	Reaction time, hr	Configuration, % — *cis*	*trans*
53–54	6	22	78
26–27	6	40	60
3–5	96	66	34

TABLE IV

TEMPERATURE EFFECT IN THE ADDITION OF ETHYLENIMINE TO CH_3C≡$CSO_2C_6H_4CH_3$-*p* IN BENZENE

Temp, °C	Reaction time, hr	Configuration, % — *cis*	*trans*
53–54	4	31	69
24–25	4	80	20
2–5	96	83	17

Postisomerization does not account for the differences in product compositions, since treating the product mixture, obtained under one set of conditions, with ethylenimine in benzene at a different set of time and temperature conditions resulted in no change in the ratio of *cis*–*trans* isomers. These results suggest that the *trans* addition process giving *cis* adduct is the kinetically controlled process while *cis* addition yielding *trans* product is thermodynamically more favored. A mechanism incorporating these results involves formation of angular dipolar intermediates, one with a *cis* arrangement of amino and sulfonyl or sulfinyl groups and a second with a *trans* arrangement (eq 5). Protonation



(5)

of the *cis* intermediate gives the *cis* adduct and kinetic control. The *cis* intermediate may alternatively isomerize to the *trans* intermediate; subsequent protonation affords the *trans* adduct, which as will be shown later is the more stable of the two adducts.

(6) P. M. Greaves and S. R. Lander, *Chem. Commun.*, 322 (1966).

The formation of the *trans* intermediate occurs by one of two pathways, direct isomerization of the *cis* intermediate or equilibration of the *cis* intermediate with the starting acetylene and readdition to the acetylene.

Temperature and solvent dependent isomerization of vinyl carbanions has been found to occur in systems such as 1,2-diphenylvinyllithium where the *cis* isomer isomerizes to the more stable *trans* isomer. However, in other systems such as the *cis*- and *trans*-propenyllithiums, both isomers were shown to be quite stable.[7] Montanari and coworkers[8] have reported exchanging *cis*- and *trans*-β-arylsulfinyl- and β-arylsulfonylacrylic acid with sodium deuterioxide in deuterium oxide with complete retention of configuration, suggesting the arylsulfinyl- and arylsulfonylvinyl carbanions do not isomerize under the conditions employed. However, the conditions employed by Montanari would favor retention of configuration owing to facile deuteration of the vinyl carbanion formed and therefore it is not possible to favor one mode of isomerization over the other in the ethylenimine–acetylene additions with the data at hand.

The mechanism (eq 5) accounts not only for the temperature effect but also for an observed solvent effect. As shown in Tables V and VI, solvent effects

TABLE V

REACTION OF ETHYLENIMINE WITH $CH_3C{\equiv}CSO_2C_6H_4CH_3$-*p*

Solvent	Reaction time, hr	Temp, °C	Configuration, %[a] *cis*	*trans*
DMSO	4	24–25	68	32
Et_2O	4	24–25	74	26
C_6H_6	4	24–25	80	20
CCl_4	4	24–25	81	19
EtOH	4	24–25	58	42

[a] The ratios of *cis–trans* isomers were determined by nmr analysis on the crude reaction mixtures. The reactions were complete after 4 hr with quantitative yields of the adducts as shown by nmr.

TABLE VI

REACTION OF ETHYLENIMINE WITH $CH_3C{\equiv}CSOEt$

Solvent	Reaction time, hr	Temp, °C	Configuration, %[a] *cis*	*trans*
DMSO	6	26–27	16	84
Et_2O	6	26–27	31	69
C_6H_6	6	26–27	40	60
CCl_4	6	26–27	48	52
EtOH	24	24–26	86	14

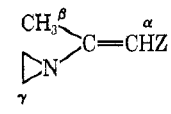
[a] The ratios of *cis–trans* isomers were determined by nmr analysis on both the crude reaction mixture and the purified liquid. There was no difference between the crude ratio and the purified. As shown by nmr, the reaction yields were quantitative.

were observed in the nonstereoselective additions of ethylenimine to 1-*p*-tolylsulfonylpropyne and 1-ethylsulfinylpropyne. Solvent effects were also observed in the additions of ethylenimine to 1-ethylsulfonylpropyne,[1] ethyl propiolate,[1,3] and methyl propiolate.[4] The mixture of adducts obtained in one solvent was treated with 1 equiv of ethylenimine in another solvent but there was no change in the ratio of *cis–trans* isomers showing there to be no postisomerization of the ethylenimine adducts as was observed with other secondary and primary amines.[1] In the aprotic solvents studied, the greatest amount of *trans* product (*cis* addition) was formed in dimethyl sulfoxide. This may be explained on the basis that dimethyl sulfoxide (having a high dielectric constant) can stabilize the zwitterionic intermediates best, and there is less stabilization of the ammonium moiety by the sulfonyl or sulfinyl groups in the *cis* intermediate shifting the equilibrium to the right in favor of the *trans* intermediate. In a protic solvent, ethanol, rapid proton abstraction from solvent giving kinetic control competes with the stabilization of the intermediates by this polar solvent.

The *cis* and *trans* configurations in the conjugated adducts were assigned on the basis of nmr analysis. The pertinent nmr data are given in Table VII and the

TABLE VII

NMR DATA FOR



Z	α[a] *cis*	α[a] *trans*	β[a] *cis*	β[a] *trans*	γ[a] *cis*	γ[a] *trans*
SOEt	5.40	5.55	2.00	2.20	2.05	1.90
SO_2Et	5.37	5.53	1.90	2.25	2.29	2.05
$SO_2C_6H_4CH_3$-*p*	5.51	5.68	1.85	2.20	2.24	1.95
$SO_2CH_2C_6H_5$	5.19	5.38	1.80	1.73	2.15	1.85
$SO_2CH_2CH_2C_6H_5$	5.35	5.47	1.85	2.22	2.25	1.91

[a] Positions given in parts per million (δ) in $COCl_3$ relative to TMS. The α, β, and γ peaks were all singlets.

chemical shifts are similar to those previously published.[1,2] With the 1-benzylsulfonyl-2-(ethylenimino)-propene isomers, the methyl propenyl protons are shifted upfield in the *trans* isomer from those in the *cis*. This may be due to shielding of these protons by the aromatic ring in the *trans* isomer shifting them upfield relative to the *cis*.[9]

Two isomeric intermediates are suggested for the ethylenimine additions to acetylenic sulfones and sulfoxides while a single intermediate has been proposed for the reactions of ethylenimine with methyl and ethyl propiolate (eq 2). If indeed such differences do exist, one would not expect to find a temperature effect on the ratio of *cis–trans* isomers in the addition of ethylenimine to methyl propiolate. As shown in Table VIII, there was no temperature effect observed.

TABLE VIII

REACTION OF ETHYLENIMINE WITH $HC{\equiv}CCO_2Me$ IN BENZENE

Temp, °C	Reaction time, hr	Configuration, % *cis*	*trans*
54–55	5	7	93
25–26	5	9	91
3–6	72	9	91

The temperature effect in the ethylenimine additions to *nonterminal* acetylenic sulfones and sulfoxides suggests that the *trans* adduct (*cis* addition) is the more stable isomer. It has been shown that other secondary

(7) (a) A. N. Nesmeyanov, A. E. Borisov, and N. A. Vol'kenau, *Izv. Akad. Nauk SSR, Otd. Khim. Nauk*, 992 (1954); (b) A. N. Nesmeyanov and A. E. Borisov, *Tetrahedron*, **1**, 158 (1957); (c) D. Y. Curtin, H. W. Johnson, Jr., and E. C. Steiner, *J. Amer. Chem. Soc.*, **77**, 4566 (1955); (d) D. Y. Curtin and J. W. Crump, *ibid.*, **80**, 1922 (1958).

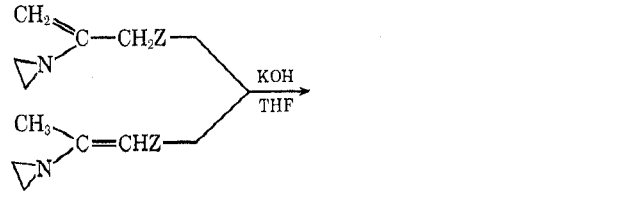
(8) H. Hogeveen, G. Maccagnani, F. Montanari, and F. Taddei, *Boll. Sci. Fac. Chem. Ind. Bologna*, **21**, 259 (1963).

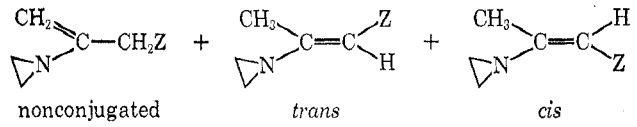
(9) R. C. Pink, R. Spratt, and C. J. M. Stirling, *J. Chem. Soc.*, 5714 (1965).

amines give only the *trans* adduct upon addition to acetylenic sulfones *via* initial *trans* addition giving the *cis* adduct which undergoes isomerization to the final product.[1] The ethylenimine adducts of the acetylenic sulfones and sulfoxides may be isomerized with potassium hydroxide in THF at room temperature giving the mixture shown in Table IX. Both the nonconjugated

TABLE IX

ISOMERIZATION OF NONCONJUGATED AND CONJUGATED ADDUCTS





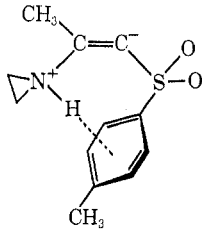
nonconjugated adduct 1 | *trans* 2 | *cis* 3

Z	Reaction time, hr	% yield[a]	% 1 in (1 + 2 + 3)	% 2 in (2 + 3)	% 3 in (2 + 3)
SOEt	48	69	12	88	15
SO_2Et	12	67	9	91	9
$SO_2C_6H_4CH_3$-*p*	30	80	7	95	5
$SO_2CH_2C_6H_5$	12	93	0	93	7
$SO_2CH_2CH_2C_6H_5$	12	91	6	87	13

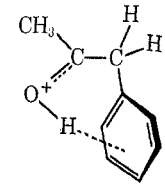
[a] The yields given were those obtained in the isomerization of the conjugated adducts. Similar results were obtained with the nonconjugated adducts.

and conjugated adducts give the same equilibrium mixture, with the *trans* conjugated adducts being the predominate isomer.

In comparing the ratios of *cis–trans* isomers obtained in the additions of ethylenimine to 1-*p*-tolylsulfonylpropyne and 1-ethylsulfonylpropyne, one finds quite a difference with the *p*-tolyl system giving more *cis* adduct in aprotic solvents while the ethyl system yields mostly *trans* product. The R′ group in $CH_3C{\equiv}CSO_2R'$ must therefore play a part in the determination of the overall stereochemistry. Models of the *cis* intermediate formed in the ethylenimine addition to 1-*p*-tolylsulfonylpropyne show the aromatic ring within π-hydrogen-bonding distance of the ammonium center, as shown.



This interaction may be similar to the participation depicted by Winstein and Levy in their study of protonated β-phenyl ketones. The greater population of the *syn* isomer, than predicted on the basis of steric effects, was accounted for on the basis of π-hydrogen bonding in the *syn* isomer.[10]



Models of the *cis* intermediate formed in the addition of the ethylenimine to 1-benzylsulfonylpropyne indicate that a similar neighboring-group effect is possible. If participation by the neighboring aromatic ring occurs, one would expect to find decreasing amounts of *cis* adduct as the aromatic ring is moved farther away from the sulfonyl grouping. As shown in Table X,

TABLE X

REACTION OF ETHYLENIMINE WITH $CH_3C{\equiv}CSO_2R'$ IN BENZENE

R′	Temp, °C	Reaction time, hr	Configuration, % cis	Configuration, % trans
$C_6H_4CH_3$-*p*	24–25	4	80	20
$CH_2C_6H_5$	28–29	4	72	28
$CH_2CH_2C_6H_5$	28–29	4	36	64
CH_2CH_3	25–26	4	16	84

such an effect is observed. The largest amount of *trans* adduct was obtained with 1-ethylsulfonylpropyne where stabilization of the *cis* intermediate as suggested is of course not possible. Neighboring-group stabilization of the initial dipolar intermediate may also be the basis for the fact that 1-ethylsulfinylpropyne gives greater amounts of *cis* adduct with ethylenimine than does 1-ethylsulfonylpropyne. This may be due to greater interaction of the sulfoxide oxygen *vs.* sulfonyl oxygens with the ammonium center.[11]

It was shown previously that the R group in the $RC{\equiv}CSO_2Et$ series affected the equilibrium mixtures obtained in the addition of *n*-propylamine.[1] As the steric bulk of the R group was increased, the amount of *cis* adduct increased owing to greater steric effects in the *trans* isomer. Such a phenomenon was observed in the additions of ethylenimine to 1-ethylsulfonylpropyne and 1-ethylsulfonyl-1-butyne in an aprotic solvent like benzene; however in ethanol this was not apparent as shown in Table XI. The trend observed in benzene

TABLE XI

REACTION OF ETHYLENIMINE WITH $RC{\equiv}CSO_2Et$

R	Solvent	Temp, °C	Reaction time, hr	Configuration, % cis	Configuration, % trans
CH_3	C_6H_6	24–25	4	16	84
	EtOH	25–26	4	62	38
CH_3CH_2	C_6H_6	25–26	4	37	63
	EtOH	25–26	4	62	38

may also be explained on the basis of steric interactions, the steric effect being observed in the *trans* intermediate giving more *cis* adduct *via* proton abstraction by the *cis* intermediate. Such an effect is not found in ethanol

(10) G. S. Levy and S. Winstein, *J. Amer. Chem. Soc.*, **90**, 3574(1968).

(11) (a) C. H. McMullen and C. J. M. Stirling, *J. Chem. Soc., B*, 1217 (1966); (b) H. Hogeveen, G. Maccagnani, and F. Montanari, *J. Chem. Soc., C*, 1585 (1966); (c) M. Cinquini, S. Colonna, and F. Montanari, *Tetrahedron Lett.*, 3181 (1966).

where ready proton abstraction from solvent (*trans* addition) washes out any steric effect by the R group.

In summary, it can be concluded that ethylenimine additions to acetylenic sulfones and sulfoxides involve the formation of two equilibrating and isomeric zwitterionic intermediates while addition to propiolic esters occurs with the formation of a single resonance-stabilized (linear) zwitterionic intermediate. Consistent with these hypotheses are the following facts: (a) the *cis–trans* ratio of adducts formed with *nonterminal* acetylenes is temperature dependent while the *cis–trans* ratio of adducts from methyl propiolate is unaffected by temperature; (b) a solvent effect was operative; (c) the R and R′ groups in $RC{\equiv}CSO_2R'$ affect the *cis–trans* ratio of products. Consistent with these facts is the elimination of a possible isomerization of the 1-propynyl sulfones and sulfoxides to the allene with subsequent addition of ethylenimine.

Work is continuing in this laboratory on further elucidating the factors which control the stereochemistry of amine additions to acetylenes.

Experimental Section[12]

Starting Materials.—Ethylenimine was generously supplied by The Dow Chemical Co. and was stored over caustic soda pellets.

General Procedure for the Preparation of 3-Propynyl Sulfides.—All of the 3-propynyl sulfides were prepared by adding a solution of 1 equiv of the corresponding sodium thiolate in methanol to 1 equiv of propargyl bromide in methanol. After stirring for 2 hr, the reaction mixture was dissolved in water and the aqueous mixture was extracted with methylene chloride. The methylene chloride layers were dried ($MgSO_4$) and concentrated, and distillation gave the 3-propynyl sulfides listed in Table XII.

TABLE XII

PREPARATION OF $HC{\equiv}CCH_2SR$

R	% yield	Bp (mm), °C	Ref
$C_6H_4CH_3$-*p*	77	84–85 (0.45)	*a*
$CH_2C_6H_5$	84	103–108 (7.0)	*b*
$CH_2CH_2C_6H_5$	82	84–87 (0.25)	
CH_2CH_3	65	72–75 (103)	*c*

[a] K. Sato and O. Mujamotto, *Nippon Kagaku Zasshi*, **77**, 1409 (1956). [b] Reference 9. [c] G. Pourcelot and P. Cadiot, *Bull. Soc. Chim. Fr.*, 3016 (1966).

General Procedure for the Preparation of 1-Propynyl Sulfides.—Three of the 1-propynyl sulfides were prepared by isomerization of the 3-propynyl sulfides with potassium hydroxide in THF.[2] After stirring, the potassium hydroxide was filtered off and the solvent was removed *in vacuo*. Distillation afforded the 1-propynyl sulfides given in Table XIII in good yield.

TABLE XIII

PREPARATION OF $CH_3C{\equiv}CSR$

R	% yield	Mp or bp (mm), °C	Ref
$C_6H_4CH_3$-*p*	79	26–28	*a*
$CH_2C_6H_5$	78	116–118 (6.0)	
$CH_2CH_2C_6H_5$	79	77–78 (0.17)	

[a] L. Maioli, G. Modena, and P. E. Todesco, *Boll. Sci. Fac. Chim. Ind. Bologna*, **18**, 66 (1960).

(12) All microanalytical analyses were carried out by Dr. C. S. Yeh and the staff of the Purdue Chemistry Microanalytical Laboratory. Elemental analyses were obtained only in representative cases. All nmr spectra were run on either a Varian A-60 or A-60a spectrometer operating at 60 Mc/sec using TMS as an internal standard. All melting points and boiling points are uncorrected. All infrared spectra were run on a Perkin-Elmer Model 137 B Infracord spectrophotometer. The nmr spectra of the adducts were taken on crude as well as on the purified products to preclude isomerization during purification steps.

1-Ethylthiopropyne.—This compound was prepared according to known procedures[13] by treating *cis*-1,2-bis(ethylthio)ethene with 2 equiv of sodium amide in liquid ammonia followed by addition of 2 equiv of methyl iodide. The colorless product had bp 122–128° (lit.[13] bp 134–144°) and was isolated in 56% yield.

1-Ethylthio-1-butyne.—Treatment of *cis*-1,2-bis(ethylthio)-ethene with 2 equiv of sodium amide in liquid ammonia followed by addition of 2 equiv of ethyl bromide afforded the desired product, bp 60–62° (26 mm) [lit.[1] bp 60–61° (25 mm)].

Preparation of Acetylenic Sulfones.—Oxidation of the acetylenic sulfides to the corresponding sulfones was generally effected in two ways. The first involved adding a solution of 2 equiv of *m*-chloroperbenzoic acid in $CHCl_3$ to 1 equiv of the sulfide in $CHCl_3$ at 0° and then allowing the mixture to stand for 1 day at room temperature. The reaction mixture was washed with a saturated solution of $NaHCO_3$ containing a small amount of Na_2SO_3. The $CHCl_3$ layers were dried ($MgSO_4$) and concentrated, and purification was effected by either recrystallization or by vacuum distillation. The second method used was oxidation of 1 equiv of sulfide with 4 equiv of 30% H_2O_2 in glacial acetic acid. The reaction mixture was gently refluxed for 1.5–2 hr after which time the mixture was added to ice-water. If the product was a solid, it precipitated out and was recrystallized. The liquid sulfones were purified by extracting the aqueous mixture with $CHCl_3$, drying the $CHCl_3$ layers ($MgSO_4$), concentration, and distillation.

3-Ethylsulfonylpropyne.—To 20 g (0.20 mol) of 3-ethylthiopropyne in 250 ml of glacial AcOH was added 83 ml (0.80 mol of peroxide) of 30% H_2O_2 dropwise. After gentle reflux, 500 ml of H_2O was added. The aqueous solution was extracted with $CHCl_3$. Work-up and distillation gave 14 g (53%) of product, bp 74° (0.20 mm) [lit.[14] 90–93° (0.001 mm)].

Anal. Calcd for $C_5H_8SO_2$: C, 45.42; H, 6.11; S, 24.26. Found: C, 45.18; H, 5.88; S, 24.19.

3-*p*-Tolylsulfonylpropyne.—To a solution of 30 g (0.19 mol) of 3-*p*-tolylthiopropyne in 250 ml of glacial AcOH was added slowly 77 ml (0.74 mol of peroxide) of 30% H_2O_2. After reflux, the mixture was poured into 1 l. of ice-water. Recrystallization (EtOH–isopropyl ether) gave 26 g (72%) of product, mp 103–105 [lit.[5] mp 99–100.5].

1-Ethylsulfonylpropyne.—Oxidation of 19.2 g (0.17 mol) of 1-ethylsulfinylpropyne in 100 ml of $CHCl_3$ at 0° with 30 g (0.17 mol) of 85% *m*-chloroperbenzoic acid dissolved in 500 ml of $CHCl_3$ yielded 18.6 g (84%) of product after distillation, bp 92–94° (1.35 mm) [lit.[1] bp 82–83° (0.4 mm)].

1-*p*-Tolylsulfonylpropyne.—To a solution of 27.6 g (0.17 mol) of 1-*p*-tolylthiopropyne in 200 ml of $CHCl_3$ cooled to 0° was added slowly 71 g (0.35 mol of peroxide) of 85% *m*-chloroperbenzoic acid dissolved in 800 ml of $CHCl_3$. After recrystallization (benzene–hexane) there was obtained 26.8 g (81%) of product, mp 98–99° (lit.[5] mp 98–99°).

1-Benzylsulfonylpropyne.—This acetylene was prepared by treating 9.3 g (0.057 mol) of 1-benzylthiopropyne with 24 ml (0.23 mol of peroxide) of 30% H_2O_2 in 200 ml of glacial AcOH. After reflux, work-up, and recrystallization (ethanol), 6.0 g (54%) of product was obtained, mp 75–76.5°.

Anal. Calcd for $C_{10}H_{10}SO_2$: C, 61.82; H, 5.20; S, 16.51. Found: C, 61.84; H, 5.19; S, 16.40.

1-(2-Phenylethylsulfonyl)propyne.—Oxidation of 11.6 g (0.066 mol) of 1-(2-phenylethylthio)propyne in 250 ml of glacial AcOH with 27 ml (0.26 mol of peroxide) of 30% H_2O_2 afforded 7.0 g (51%) of product after distillation, bp 145–147° (0.15 mm). Upon standing the product crystallized, mp 43–45°.

Anal. Calcd for $C_{11}H_{12}SO_2$: C, 63.42; H, 5.82; S, 15.40. Found: C, 63.53; H, 6.03; S, 15.26.

1-Ethylsulfonyl-1-butyne.—As previously prepared,[1] 1-ethylthio-1-butyne (1.8 g, 0.16 mol) in 100 ml of $CHCl_3$ at 0° was treated with 87% *m*-chloroperbenzoic acid (6.4 g, 0.032 mol of peroxide) in 100 ml of $CHCl_3$. Distillation gave 1.6 g (69%) of product, bp 78–80° (0.25 mm) [lit.[1] 87–88° (0.4 mm)].

Preparation of Acetylenic Sulfoxides.—The acetylenic sulfoxides were prepared by oxidation of 1 equiv of sulfide with either 1 equiv of sodium metaperiodate at 0° as previously shown[11a] or 1 equiv of *m*-chloroperbenzoic acid in $CHCl_3$ at 0°.

3-Ethylsulfinylpropyne.—Oxidation was effected by treating 15.7 g (0.157 mol) of 3-ethylthiopropyne in 500 ml of CH_3OH

(13) H. J. Boonstra and J. F. Arens, *Recl. Trav. Chim. Pays-Bas*, **79**, 866 (1960).

(14) G. Pourcelot and P. Cadiot, *Bull Soc. Chim. Fr.*, 3024 (1966).

at 0° with 33.6 g (0.157 mol) of sodium metaperiodate. After standing at 0° for 12 hr, the precipitated sodium iodate was filtered off and the filtrate was extracted with CH_2Cl_2. Drying ($MgSO_4$), concentration, and distillation gave 18 g (99%) of product, bp 80–82° (0.25 mm), $n^{26.5}D$ 1.513.

Anal. Calcd for C_5H_8SO: C, 51.69; H, 6.94; S, 27.60. Found: C, 51.87; H, 7.12; S, 27.53.

1-Ethylsulfinylpropyne.—This compound was prepared by treating 12.3 g (0.123 mol) of 1-ethylthiopropyne in 100 ml of $CHCl_3$ at 0° with 25 g (0.123 mol of peroxide) of 85% *m*-chloroperbenzoic acid in 300 ml of $CHCl_3$. The reaction mixture was allowed to stand 24 hr at 0°. The *m*-chlorobenzoic acid was filtered off and the filtrate was washed with a solution of $NaHCO_3$ containing Na_2SO_3. Drying the $CHCl_3$ layers ($MgSO_4$), concentration, and distillation gave 8.8 g (62%) of product, bp 58–61° (0.45 mm), $n^{20}D$ 1.5110.

Anal. Calcd for C_5H_8SO: C, 51.69; H, 6.94; S, 27.60. Found: C, 51.67; H, 7.13; S, 27.59.

Preparation of Allenic Sulfones and Sulfoxides.—The allenic sulfones and sulfoxides were prepared by isomerizing the 3-propynyl sulfones or sulfoxides with either triethylamine or activated alumina as previously published.[5,15]

Ethylsulfonylpropadiene.—This compound was prepared by stirring 4.9 g (0.037 mol) of 3-ethylsulfonylpropyne with 5.8 g (0.057 mol) of triethylamine in 100 ml of C_6H_6 for 1 hr. After concentration and distillation, there was obtained 4.1 g (84%) of product, bp 79–81° (0.15 mm), which consisted of 78% the allenic sulfone and 22% starting material. All attempts to remove the starting material with silver nitrate as in the preparation of ethylsulfinylpropadiene caused formation of 1-ethylsulfonylacetone as shown by nmr and ir.

***p*-Tolylsulfonylpropadiene.**—This compound was prepared by pouring 5.0 g (0.26 mol) of 3-*p*-tolylsulfonylpropyne dissolved in 15 ml of CH_2Cl_2 onto an activated alumina column according to known procedures.[5] Elution gave the allene which was recrystallized (EtOH), mp 89–90° (lit.[5] mp 85–87°).

Ethylsulfinylpropadiene.—This compound was synthesized by stirring 7.0 g (0.06 mol) of 3-ethylsulfinylpropyne with 20 g of activated alumina in 75 ml of CH_2Cl_2 for 4 hr. The alumina was removed by filtration and the solvent was removed *in vacuo*. The residue containing some starting material was poured into 150 ml of 5% $AgNO_3$–95% EtOH and to the milky solution was added 250 ml of H_2O. The clear aqueous mixture was extracted with CH_2Cl_2. The CH_2Cl_2 layers were dried ($MgSO_4$) and concentrated, and distillation gave 3.5 g (50%) of product, bp 68° (1.0 mm).

Anal. Calcd for C_5H_8SO: C, 61.69; H, 6.94; S, 27.60. Found: C, 61.81; H, 6.97; S, 27.20.

General Procedure for Ethylenimine Additions to 1-Propynyl-Sulfones and Sulfoxides.—Most of the reactions were run by dissolving 0.0043 mol of the acetylene in 20 ml of the appropriate solvent and placing the mixture in a previously flamed out 125-ml erlenmeyer flask. To the magnetically stirred mixture at the desired temperature was added 0.0043 mol of ethylenimine by means of a syringe. After stirring for the prescribed length of time, the solvent was removed *in vacuo* at room temperature. Purification was accomplished by recrystallization or distillation. The nmr data given for any crystalline product is that of the crude reaction mixture since recrystallization caused fractionation. Distillation of the liquid adducts did not change the *cis–trans* ratio. All of the reactions gave quantitative yields of aminovinylsulfones or sulfoxides as shown by nmr of the crude reaction mixtures.

1-Ethylsulfonyl-2-(ethylenimino)propene.—To 0.57 g (0.004 3 mol) of 1-ethylsulfonylpropyne in 20 ml of benzene was added 0.19 g (0.0043 mol) of ethylenimine. The reaction afforded 0.46 g (70%) of 16% *cis* and 84% *trans* adducts upon distillation, bp 118–120° (0.30 mm) [lit.[1] 115–118° (0.3 mm)].

1-*p*-Tolylsulfonyl-2-(ethylenimino)propene.—To 0.83 g (0.0043 mol) of 1-*p*-tolylsulfonylpropyne in 20 ml of benzene at 24–25° was added 0.19 g (0.0043 mol) of ethylenimine. There was obtained 0.90 g (88%) of product after recrystallization (benzene–hexane), mp 96–97°.

Anal. Calcd for $C_{12}H_{15}NSO_2$: C, 60.72; H, 6.38; N, 5.90; S, 13.51. Found: C, 60.76; H, 6.37; N, 5.94; S, 13.33.

1-Benzylsulfonyl-2-(ethylenimino)propene.—To 0.83 g (0.0043 mol) of 1-benzylsulfonylpropyne in 20 ml of benzene at 28–29° was added 0.19 g (0.0043 mol) of ethylenimine. The reaction gave 0.85 g (83%) of product after recrystallization (EtOH–hexane), mp 54–56°.

Anal. Calcd for $C_{12}H_{15}NSO_2$: C, 60.72; H, 6.38; N, 5.90; S, 13.51. Found: C, 60.75; H, 6.41; N, 5.88; S, 13.50.

1-(2-Phenylethylsulfonyl)-2-(ethylenimino)propene.—To 0.90 g (0.0043 mol) of 1-(2-phenylethylsulfonyl)propyne in 20 ml of benzene was added 0.19 g (0.0043 mol) of ethylenimine. There was obtained 0.81 g (75%) of product after recrystallization (EtOH–hexane), mp 62–64°.

1-Ethylsulfonyl-2-(ethylenimino)-1-butene.—To 0.80 g (0.0055 mol) of 1-ethylsulfonyl-1-butyne dissolved in 26 ml of ethanol was added 0.24 g (0.0055 mol) of ethylenimine. The reaction afforded 0.60 g (60%) of 62% *cis* and 38% *trans* adducts after distillation, bp 122° (0.20 mm).

1-Ethylsulfinyl-2-(ethylenimino)propene.—To 0.50 g (0.0043 mol) of 1-ethylsulfinylpropyne in 20 ml of benzene was added 0.19 g (0.0043 mol) of ethylenimine and there was formed at 26–27° 40% *cis* and 60% *trans* adducts. Distillation gave a 58% yield of pure product, bp 93–95° (0.20 mm).

Anal. Calcd for $C_7H_{13}NSO$: C, 52.79; H, 8.22; N, 8.80; S, 20.14. Found: C, 52.99; H, 8.04; N, 8.51; S, 20.16.

Preparation of the Nonconjugated Adducts.—The nonconjugated adducts were prepared by addition of ethylenimine to both the allenic sulfones and sulfoxides and the propargyl sulfones and sulfoxides. The larger quantities of nonconjugated adducts were prepared from the propargyl acetylenes and these preparations will be given. However the same adducts were obtained using the allenes or mixtures of allene and propargyl acetylene as shown in Table II.

3-Ethylsulfonyl-2-(ethylenimino)propene.—To 2.0 g (0.015 mol) of 3-ethylsulfonylpropyne in 80 ml of EtOH was added 0.64 g (0.015 mol) of ethylenimine. After stirring 4 hr, recrystallization (benzene–pentane) there was obtained 2.1 g (80%) of product, mp (sublimed) 64–65.5°.

Anal. Calcd for $C_7H_{13}NSO_2$: C, 47.96; H, 7.49; N, 7.99; S, 18.30. Found: C, 47.73; H, 7.54; N, 7.93; S, 18.02.

3-*p*-Tolylsulfonyl-2-(ethylenimino)propene.—To 2.0 g (0.010 mol) of 3-*p*-tolylsulfonylpropyne in 80 ml of ethanol was added 0.44 g (0.010 mol) of ethylenimine. After stirring 4 hr, the mixture given in Table II was obtained. Several recrystallizations (benzene–hexane) afforded 1.5 g (63%) pure nonconjugated adduct, mp 69.5–70.5°.

Anal. Calcd for $C_{12}H_{15}NSO_2$: C, 60.72; H, 6.38; N, 5.90; S, 13.51. Found: C, 60.92; H, 6.48; N, 5.78; S, 13.68.

3-Ethylsulfonyl-2-(ethylenimino)propene.—To 3.0 g (0.026 mol) of 3-ethylsulfinylpropyne in 80 ml of ethanol was added 1.11 g (0.026 mol) of ethylenimine. After stirring 2 days and distillation, 2.75 g (78%) of product was obtained, bp 87–91° (0.25 mm).

Anal. Calcd for $C_7H_{13}NSO$: C, 52.79; H, 8.22; N, 8.80; S, 20.14. Found: C, 52.76; H, 8.27; N, 8.78; S, 19.97.

Isomerization of Nonconjugated and Conjugated Adducts to the Thermodynamic Equilibrium Mixture.—As shown in Table IX, either the nonconjugated or conjugated ethylenimine adducts could be isomerized to the thermodynamic equilibrium mixture with KOH in THF at room temperature. The KOH was removed by filtration and the solvent was then removed *in vacuo*. An nmr was taken of the crude mixture before purification.

1-Ethylsulfinyl-2-(ethylenimino)propene.—To 0.58 g (0.0037 mol) of 87% *cis*- and 13% *trans*-1-ethylsulfinyl-2-(ethylenimino)-propene in 40 ml of THF was added 5.5 g (0.098 mol) of KOH. After stirring, filtration, concentration, and distillation, there was obtained 0.40 g (69%) of the mixture, bp 96–98° (0.20 mm) given in Table IX.

1-Ethylsulfonyl-2-(ethylenimino)propene.—To 1.2 g (0.069 mol) of a mixture of 16% *cis*- and 84% *trans*-1-ethylsulfonyl-2-(ethylenimino)propene in 50 ml of THF was added 6.2 g (0.11 mol) of KOH. After stirring, filtration, concentration, and distillation, the mixture, bp 110–112° (0.30 mm), given in Table IX was obtained.

1-*p*-Tolylsulfonyl-2-(ethylenimino)propene.—To 1.0 g (0.0042 mol) of a mixture of 79% *cis*- and 21% *trans*-1-*p*-tolylsulfonyl-2-(ethylenimino)-propene in 50 ml of THF was added 5 g (0.089 mol) of KOH. After stirring, filtration, and concentration, an nmr of the remaining white crystalline solid 0.80 g (80%) showed it to be the mixture given in Table IX.

1-Benzylsulfonyl-2-(ethylenimino)propene.—To 1.5 g (0.0063 mol) of a mixture of 72% *cis*- and 28% *trans*-1-benzylsulfonyl-2-(ethylenimino)propene in 50 ml of THF was added 6.1 g (0.11 mol) of KOH. After stirring, filtration, and concentration,

(15) C. J. M. Stirling, *J. Chem. Soc., Suppl. I*, 5856 (1964).

1.4 g (93%) of the remaining crystalline product was shown to be the mixture given in Table IX. Recrystallization (EtOH–hexane) gave 1.3 g (87%) of the product, mp 52–54°.

1-(2-Phenylethylsulfonyl)-2-(ethylenimino)propene.—To 1.1 g (0.0043 mol) of a mixture of 36% *cis*- and 64% *trans*-1-(2-phenylethylsulfonyl)-2-(ethylenimino)propene in 50 ml of THF was added 6.0 g (0.11 mol) of KOH. After stirring, filtration, and concentration, the mixture (1.0 g, 91%) given in Table IX was present. Recrystallization (EtOH–hexane) gave 0.80 g (73%) of product, mp 60–61°.

Infrared Data.[16]—The 3-propynyl sulfides exhibit the characteristic strong carbonh–ydrogen stretch at 3300 cm^{-1} and a very weak carbon–carbon triple bond stretch in the 2100–2200-cm^{-1} region. The corresponding 3-propynyl sulfones and sulfoxides show in addition to the acetylenes carbon–hydrogen stretch and the carbon–carbon triple bond stretch, the characteristic strong sulfone absorption in the 1300–1350- and 1120–1150-cm^{-1} regions and the strong sulfoxide absorption in the 1020–1060-cm^{-1} region, respectively. The 1-propynyl sulfides exhibit a weak carbon–carbon triple bond stretch at 2180 cm^{-1}. The corresponding sulfones and sulfoxides, however, show a very strong band at 2180–2200 cm^{-1}. The ethylsulfonylpropadiene and ethylsulfinylpropadiene exhibit a strong carbon–carbon double-bond stretch in the 1940–1980-cm^{-1} region which appears as a singlet. As previously published[5] the *p*-tolylsulfonylpropadiene shows a strong doublet at 1960 and 1920 cm^{-1}. The conjugated ethylenimine adducts exhibit strong olefinic absorption in the 1560–1640-cm^{-1} region in addition to the characteristic sulfone and sulfoxide bands which are shifted slightly lower. The nonconjugated ethylenimine adducts exhibit similar absorptions as the conjugated adducts with the olefinic band shifted ~50 cm^{-1} higher in the nonconjugated adduct from that in the conjugated.

(16) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Wiley, New York, N. Y., 1962.

Registry No.—**1**, Z = SOEt, 25557-97-5; **1**, Z = SO_2Et, 25557-98-6; **1**, Z = $SO_2C_6H_4CH_3$-*p*, 25557-99-7; **2**, Z = SOEt, 25558-40-1; **2**, Z = SO_2Et, 13894-33-2; **2**, Z = $SO_2C_6H_4CH_3$-*p*, 25558-42-3; **2**, Z = $SO_2CH_2C_6H_5$, 25558-43-4; **2**, Z = $SO_2CH_2CH_2C_6H_5$, 25558-44-5; **3**, Z = SOEt, 25558-45-6; **3**, Z = SO_2Et, 13894-50-3; **3**, Z = $SO_2C_6H_4CH_3$-*p*, 25558-47-8; **3**, Z = $SO_2CH_2C_6H_5$, 25558-48-9; **3**, Z = $SO_2CH_2CH_2C_6H_5$, 25558-49-0; $HC{\equiv}CCH_2SR$, R = $CH_2CH_2C_6H_5$, 25558-00-3; $CH_3C{\equiv}CSR$, R = $CH_2C_6H_5$, 22582-35-0; $CH_3C{\equiv}CSR$, R = $CH_2CH_2C_6H_5$, 25558-02-5; 1-benzylsulfonylpropyne. 25558-03-6; 1-(2-phenylethylsulfonyl)propyne, 25558-04-7; 3-ethylsulfinylpropyne, 25558-05-8; 1-ethylsulfinylpropyne, 25558-06-9; ethylsulfinylpropadiene, 25558-07-0; *cis*-1-ethylsulfonyl-2-(ethylenimino)-1-butene, 25558-50-3; *trans*-1-ethylsulfonyl-2-(ethylenimino)-1-butene, 25558-51-4.

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Reductive Dimerization of Difunctional Aryl Imines on Photolysis

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Irradiations of aryl imines which have a nitrile, amide, double bond, or hydroxyl group suitably positioned for interaction with the imine give the *meso*- and *dl*-1,2-diamines resulting from reductive dimerization. Nonconjugated diimines give polymeric products. In the case of 2-cyanoethylamine-N-benzylidene, the mechanism involves initial formation of α-hydroxy radicals by transfer of a hydrogen atom from the alcoholic solvent to the benzaldehyde sensitizer, sequentially followed by production of α-amino radicals by hydrogen transfer from the α-hydroxy radical to the imine and dimerization of the α-amino radicals. One anil and three imidates were found to be unreactive under the specified photolysis conditions.

Recent studies of the photochemistry of imines suggest that many of the reported reactions actually do not involve a photoexcited state of the imine. Aryl imines have been shown to undergo reduction[1,2] and reductive dimerization[3] on photolysis *via* an α-amino radical formed by hydrogen atom transfer to the imine from an α-hydroxy radical initially formed by abstraction of a hydrogen atom from the solvent by the sensitizer. Padwa, Bergmark, and Pashayan have noted the potential generality of this type of reaction for imines in the presence of added or adventitious sensitizers.[3] However, intramolecular reactions not usually explicable in terms of an α-amino radical are observed in some imine photolyses.[4,5]

We have investigated the photochemistry of some acyclic imines which have a second functional group suitably situated for intramolecular reaction with the imine. Although the photochemistry of analogous olefins and ketones suggests that intramolecular reaction might be expected,[6] only reductive dimerization involving conversion of the imine to a substituted 1,2-diamine is observed.

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(5) Exceptions to intramolecularity include photochemical cycloadditions [F. P. Woerner, H. Reimlinger, and D. R. Arnold, *Angew. Chem., Int. Ed. Engl.*, **7**, 130 (1968); L. A. Singer and P. D. Bartlett, *Tetrahedron Lett.*, 1887 (1964), and subsequent work; S. Searles, Jr., and R. A. Clasen, *ibid.*, 1627 (1965); J. C. Sheehan and I. Lengyel, *J. Org. Chem.*, **28**, 3252 (1963)] and possibly reactions which involved the direct formation of radicals [R. W. Binkley, *ibid.*, **34**, 931 (1969); J. H. Boyer and P. A. J. Frints, *Tetrahedron Lett.*, 3211 (1968)].
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