TRIAZOLINES-IV*

SOLVATION EFFECTS AND THE ROLE OF PROTIC-DIPOLAR APROTIC SOLVENTS IN 1,3-CYCLOADDITION REACTIONS¹

P. K. KADABA²

Department of Chemistry, Christian Brothers College, Memphis, Tennessee 38104

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Abstract—Though kinetic investigations of the bimolecular addition reaction of diazomethane to aromatic Schiff bases reveal that the reaction follows essentially a concerted process and is not generally dependent on solvent polarity, a sizeable increase in rate is generally noticed in the presence of protic solvents such as water and a considerable rate enhancement occurs in the case of certain anils but not others in dipolar aprotic solvents such as DMF. The results are discussed in terms of better solvation of the negatively charged transition state II, relative to the polar reactant molecules in the protic or dipolar aprotic solvent media. Solvation by dipolar aprotic solvents is greatest for the transition state resulting from the reaction of benzal *p*-nitroaniline with maximum charge dissipation and least for the one corresponding to benzalaniline with minimum charge distribution. Solvation by protic solvents follows a reverse order.

A concerted mechanism involving a charge imbalance in the transition state is characteristic of 1,3cycloaddition reactions in general; consequently, the solvation effects observed here, might well apply to other cycloaddition reactions. Investigation indicates that this is indeed the case. The many isolated reports on the catalytic effect of water, the alcohols and DMF on cycloaddition reactions can now be unified and explained as a direct consequence of solvation effects in these solvents. Solvation effects enhance the utility and versatility of cycloaddition reactions and can be used to advantage in performing many cycloadditions with synthetical applications. A number of examples are presented including the synthesis of 3,4-diphenyl pyrazoline for the first time by utilizing the catalytic effect of water on the cycloaddition of diazomethane to stilbene.

INTRODUCTION

KINETIC investigations^{3,4} in our laboratories on the addition of diazomethane to aromatic Schiff bases (anils) have revealed that the reaction occurs via an essentially concerted process, involving a transition state (II) in which charge is partially developed as indicated. Electron withdrawing substituents, especially on the N-Ph, thus



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enhanced the rate by stabilizing the negative charge on the nitrogen, and striking results were observed where resonance conjugation was possible.

In accordance with the criterion for a concerted process,⁵ the reaction showed no general dependence of rate on the dielectric constant of the solvent medium which is a measure of solvent polarity.⁴ However, in DMF, a considerable enhancement in rate resulted in the case of certain anils but not others. In addition, a sizeable increase in rate has been generally noticed in the presence of small amounts of water.⁴ Also, similar results have been reported for other cycloaddition reactions (Table 3), though without any explanation. In this paper, an attempt has been made to provide a consistent explanation for these apparently puzzling solvent effects, based on the concept of differences in "solvating power" of protic (e.g. water, the alcohols) vs dipolar aprotic (e.g. DMF, DMSO) solvents.^{6, 7}

RESULTS AND DISCUSSION

Chemical and kinetic data for the cycloaddition of diazomethane to Schiff bases (Table 1) reveal the following: (1) In the case of anils bearing a nitro group on the C- or N-Ph or a OMe or Cl on the C-Ph, upon transfer from dioxan to DMF, there is a rate enhancement, which is greatest for the N-Ph nitro compound. (2) The rate constant for these anils increases with increasing proportions of DMF in the solvent medium. (3) These same anils do not show any increase in rate with increasing dielectric constant of solvent medium. (4) Rate enhancement in changing from dioxan to DMF is greatest when N-Ph substituent Y is nitro and smallest when Y is hydrogen. A reverse order is observed in changing to the protic solvent water, the increase in product formation being greatest when Y is hydrogen and least when Y is nitro.

In Table 1, the absence of a general dependence of rate on the dielectric constant of the reaction solvent is consistent with the concerted mechanism proposed for the addition (Scheme A).⁴ Thus the rate increases in water and DMF do not seem to result from the high dielectric constant of the solvent medium; instead, the parallelism between acceleration in DMF and the degree of electron delocalization in the transition state, as well as the reversed nature of the effects in the two solvents, suggested the possibility, that specific solvation effects involving the transition state and the solvent molecules may be in operation. That the solvation effects may be specific is borne out by the increase in rate with increasing proportions of DMF (Table 1). Also chemical and kinetic data for other cycloaddition reactions (Table 3) support the validity of the conclusions derived.

Solvent-solute interaction mechanisms in protic and dipolar aprotic solvents are well understood as a result of extensive investigations by Parker on the rates of bimolecular substitution reactions.^{6,7} Many polar organic compounds, that are not strong hydrogen bond donors or acceptors, are solvated 2–50 times more in DMF than in a protic solvent. In the case of anions, small anions generally have a strong H-bonding interaction with protic solvents; as the anion becomes larger and its negative charge is dispersed, solvation through H-bonding decreases and polarizability interactions, based on the mutual polarizability of solvent and solute molecules, become stronger in dipolar aprotic solvents. For example, in the phenoxide ion, Hbonding interactions with protic solvents become weaker, as nitro groups are added to the aromatic system and the negative charge on the phenoxide oxygen is dispersed.⁸

In order to understand the influence of solvent on rate, solvation effects of both

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Solvent	Luelectric		Subst	ituent Y = F	land			Subst	ituent X = F	l and	
		Н = Х	NOz	σ	CH3	0CH3	Y = H	NO1	δ	CH3	осн
yciohexane	2.0	-	8-79						4:29		
kenzene	2.2	ļ	I		-	1	١		5.81	ļ	1
Dioxane	2-2	3-50	7-60	1-50	1	0-81	3-50	45-0	6-40	<u>4</u>	241
Chlorobenzene	5-7	ł	7-81	1-30		1	I	35-2	1	1	-
Acetone	20-7	2.63	8.70	•		1	2.63	-	3-25	1	ł
Dioxane 75 ml [*] + DMF 25ml +	*****	1	ŀ		-	1		87.6	1	1	
Dioxane Soml +	ŀ	ł	12.7	2-72	I	ł	1	185-2	ł	Ι	
Dioxane 25ml +	ł	1	ł		1	ł	ł	232-0	ļ	ļ	
DMF	37-6	2-0	24-52	6-05	1-90	1-59	2-0	320-9	16-2	1-54	\$
Ether + Dioxan [*] (Dry)	*****	0-6% of	product.					32·3% of	product		
Sther + Dioxan (Wet)	I	45-0% of	product.					57.5% of	product		

» Experimentation of diazomethane cannot be obtained in water, a diethyl ether-dioxan mixture has been used and the effect of water studied from the increases obtained in product formation when dried and undried solutions are used under identical conditions (Experimental).

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reactants and transition state must be taken into consideration.⁹ However, in the cycloaddition reaction systems, where the reactants are polar molecules and the transition state is a charged species, solvation of the latter appears to be more important in determining the extent of protic-dipolar aprotic solvent effect on rate. The importance of transition state solvation in an SN₂ reaction between polar molecules has also been pointed out recently.⁹⁴

In the cycloaddition of diazomethane to Schiff bases, the transition state II is the carrier of a partial negative charge bearing structural resemblance to the phenoxide ion. A nitro group on the N-ph ring would disperse the negative charge on the nitrogen through resonance conjugation; as such the anionic transition state II will be



most solvated in DMF and least in water.^{9b,*} Thus, in the extreme case of diazomethane-benzal-*p*-nitroaniline reaction, though the polar reactant molecules could be well solvated in DMF (and hence less reactive), this is more than compensated for by the better solvation of the charged transition state. The result is a sevenfold increase in rate. When the nitro group is on the C-Ph, there is a threefold increase in DMF. Since the resonance between the C-ph ring and the double bond is broken as the new sigma bonds are formed, the C-ph nitro group should disperse the negative charge but not to a large extent. In the reaction of diazomethane and benzalaniline, the negative charge in transition is more localized on the N-Ph nitrogen and the solvent effect is largely due to solvation through H-bonding in water. The greater reactivity of polar reactant molecules poorly solvated in water relative to DMF might also contribute to the acceleration in water, particularly in the case of the nitro compounds.

The threefold increase in DMF for the *p*-chloro and *p*-methoxy compounds presumably arises from mesomeric effects of the type,



which would lead to a certain degree of polarizability or electron delocalization in the transition state II. The existence of such mesomeric effects is also reflected in the unusually low rate for *p*-chlorobenzalaniline³ and the striking increases obtained for the ortho isomers^{1, 3, 10a} (Table 2); while mesomeric effects lower the ground state

* The colour change, from yellow to deep red, in the reaction mixture, when transferred from aqueous dioxan to DMF-dioxan mixture, is indicative of smaller transition energies in DMF for the charge transfer

process, $-\overset{\bullet}{N} - \overset{\bullet}{\bigvee} - \overset{\bullet}{NO_2} \leftrightarrow \overset{\bullet}{N} = \overset{\bullet}{\bigvee} \overset{\bullet}{\overset{\bullet}{\overset{\bullet}{O}}} ,$ similar to those reported for 4-nitrophenoxide,

and its sulphur and selenium analogues.

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energy in the *p*-compound, in the *ortho* case, steric inhibition of such effects raises the ground state energy, thus decreasing the activation energy.^{10a} The operation of steric effects is also indicated in the UV absorption spectra of the anils^{10b} and the failure to obtain rate increases comparable to those found in the *p*-compounds, in changing from dioxan to DMF (Table 2).^{10a}

		$k_2 \times 1$	0 ² l. mole ⁻	¹ hr ⁻¹	
c-Pnenyl - substituent		DMF		Dioxan	
x	P-	m-	0-	p -	0-
н	2.0			3.5	_
NO ₂	24-5	24-5	27-1	7-6	17-4
Cl	6.1	5-6	16-2	1.5	8∙7
OCH ₃	1.6		5.6	0-81	3.2

Table 2. Rate constants for the addition of diazomethane to p-, m- and o-substituted schiff bases at $24.9^{\circ 10a}$

General significance.

As may be anticipated for reactions involving no ions, the solvation effects observed in the cycloaddition of diazomethane to Schiff bases are small; however, they have great significance in synthesis and rate studies as the *rho* value itself for cycloaddition



FIG. 1 Hammett plot of $\log k_x/k_0$ against Taft σ° values for the addition reaction of diazomethane to N-phenyl-*p*-substituted anils in dioxane and DMF at 24.9°; k_x and k_0 are second order rate constants for the substituted and unsubstituted anils respectively. \bigcirc Indicates values in DMF, \triangle , values in dioxane.







cyanogen azide to olefins to give alkylidene cyanamides and/or N-cyanoaziridines, has been postulated to proceed via unstable triazoline intermediates.^{24e} Likewise, the formation of a phosphorylated amidate from the reaction of diethyl phosphorazidate and norbornylene, has been shown to involve a triazoline intermediate.²⁴⁶

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C Reaction re	Conventional solvent and reaction time	Yield % of pure product	Protic or Dipolar aprotic solvent and reaction time	Yield % of pure product	
H 1. XH₄C₅—C=N—C₅H₄Y + CH₂N₂→ D	Dry ether	No reaction in many cases or insignificant yield ²⁵⁶	Aqueous dioxan	Good to high ^{4, 1}	1
XH4C6-C-N-C6H4Y H2CNN	Dry ether + little methanol	Poor yield ¹⁸			
H 2. (p)CIH₄C₅—C=N—C₅H₃ D	Dry ether + little methanol,	1018	Aqueous dioxan, 168 hr	414	
$\begin{array}{ccc} + & & \downarrow & & 2^{2} \\ CH_{2}N_{2} & & & \downarrow & & D \\ \end{array}$	240 hr Dry ether, 168 hr	ī	Dry ether + DMF, 168 hr	36	
(p)CIH4C6-C			Aqueous dioxan + DMF, ^b 168 hr	59	
H2C			Aqueous dioxan + DMF, 144 hr	46	
3. $H_2C = CHC_6H_5 + C_6H_5N_3 \rightarrow H_2C_5 - C_6H_5$	Ethyl acetate,	11.96.18	Ethanol,	6	
N _{NN} N-C ₆ H ₅ E R	kenux, 4 nr Ethyl acetate, Reflux 6 hr	£	kenux o nr DMF, heat 6 hr	7	

TABLE 4. SYNTHETIC UTILITY OF SOLVATION EFFECTS IN CYCLOADDITION REACTIONS

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⁴ This is the crude yield, with no mention of m.p. The yield of recrystallized material is not recorded.

⁴ Under the relatively mild reaction conditions employed in protic or dipolar aprotic solvent, no 1,4-diphenyl-1,2,3-triazole or 1,5-diphenyl-1,2,3-triazole¹⁶ was obtained. reactions is not large. When studying substituent effects, the selection of an inert solvent medium becomes important. The poor fit to the Hammett line, generally characteristic of substituent groups capable of resonance interaction with the reaction center, becomes more greatly pronounced in dipolar aprotic solvent media (Fig. 1). The steric accelerating effect of C-Ph *ortho* substituent groups (NO₂, Cl and OMe) in the Schiff base becomes more apparent in the inert solvent dioxan, as these substituents cause a threefold increase in rate in DMF (Table 2).^{10a} when present in the *para* position.

A concerted mechanism involving a charge imbalance in the transition state is characteristic of 1,3-cycloaddition reactions in general.⁵ Consequently, the solvation effects observed here might well apply to other cycloadditions (Table 3). And this is indeed the case. In the reaction of diazomethane with substituted styrenes, the rate acceleration in DMF, exclusively for the nitrostyrene, must be due to better solvation of the transition state relative to the reactants in the dipolar aprotic solvent.¹¹ Apparently, the reaction involves a B-addition and the negative charge formed in transition on the C-Ph carbon is dispersed by the nitro substituent. The many isolated reports on the catalytic effect of water, the alcohols and DMF on cycloaddition reactions can now be unified and explained as a direct consequence of solvation effects in these solvents. The cycloaddition of diphenyldiazomethane to dimethyl fumarate, upon transfer from dioxan, is accelerated 3.2 times in glycol monomethyl ether and 4.6 times in ethanol.¹² Protic solvents also catalyze the addition reactions of diazoalkanes to carbonyl compounds.^{13,23} Ethyl chlorocrotonate requires the presence of a little water as a catalyst for the reaction with diazomethane.¹⁴ Piperonal in ether solution is practically inert to diazomethane if every trace of water and alcohol is removed.^{14a} The addition of inorganic azides to alkyl or aryl nitriles, is greatly facilitated in DMSO and dimethylformamide;¹⁵ unlike other cycloadditions, this is an anion-molecule reaction and the solvent effect here must be largely due to the greater reactivity of the azide ion poorly solvated relative to the transition state in the dipolar aprotic solvents.

The solvation effects in protic and dipolar aprotic solvents could be used to advantage in performing many cycloadditions with synthetical applications (Table 4). Reactions in conventional solvents such as benzene, diethyl ether, petroleum ether, toluene, ethyl acetate, etc., under dry conditions often give poor yields or fail altogether.⁴ By proper choice of solvent, a number of cycloadditions can be effected under mild reaction conditions to give good yields of products.

The catalytic effect of water on the cycloaddition of diazomethane to Schiff bases has led to a versatile method for the synthesis of the rarely encountered 1,5-diaryl-1,2,3-triazolines, which could not be obtained by other methods of synthesis, by carrying out the cycloaddition reaction in aqueous dioxan solutions.^{4,1} The mesomeric effect in *p*-chlorobenzalaniline leading to a low yield of triazoline even in wet dioxan, can be turned to advantage by carrying out the reaction in DMF. Phenyl azide, reported to react with ω -nitrostyrenes in toluene at elevated temperatures and pressures,¹⁶ undergoes reaction in DMF or propanol at relatively low temperatures and eliminates the need for pressure equipments. The catalytic effect of either solvent may be understood in terms of the proposed transition state¹⁷ with negative charge formed on the α -nitrogen. Styrene reacts with phenyl azide much more readily in ethanol than in ethyl acetate.¹⁸ The addition of diphenyldiazomethane to fumaric

alkanes and olefi

ester is several times faster in ethanol than in dry ether. Diazoalkanes and olefins react more readily in aqueous dioxan solutions. Styrene and diazomethane, known to react very slowly,¹⁹ have now yielded more than 70% of the pyrazoline adduct. Stilbene, which has failed to react with diazoacetic ester,²⁰ diazomethane²¹ and phenyldiazomethane,²² for the first time, has yielded a pyrazoline with diazomethane. The facile addition of diazomethane to styrenes and stilbenes makes possible the synthesis of a number of 3-aryl and 3,4-diaryl pyrazolines which are not readily available at present. The possibilities for the application of solvation energy to assist bimolecular cycloaddition reactions are many; while the examples given in Table 3 and 4 do not provide an exhaustive list of solvation effects in cycloaddition reactions, they serve to amply indicate how proper understanding and use of solvation effects could help enhance the versatility and synthetic utility of cycloaddition reactions in general.

EXPERIMENTAL*

Syntheses. All experiments on syntheses described below were carried out by a single individual under carefully controlled conditions to obtain semiquantitative results which could be duplicated in all cases with only $\pm 0.5\%$ deviation.

Cycloaddition of diazomethane to Schiff bases

1-Phenyl-5-p-chlorophenyl- Δ^2 1,2,3-triazoline (DMF as solvent)

Diazomethane (0.05 mole) was reacted with Schiff base (0.015 mole) according to procedures described earlier,^{4,1} but using DMF as the solvent in place of aqueous dioxan. DMF, however, could not be used directly in place of ether for the preparation of diazomethane from nitrosomethylurea, in the same manner undistilled ethereal solns are obtained,²⁶ since this involved use of 40% KOH, which led to extensive hydrolysis of DMF. The diazomethane was, therefore, prepared in dioxan (50 ml) and to the aqueous dioxan soln of diazomethane was added DMF (30 ml). The dry ether + DMF soln was obtained by preparing the diazomethane in alcohol free ether (50 ml), followed by drying over KOH pellets, and then adding dry DMF (30 ml).

The triazoline was precipitated by the addition of water to the reaction mixture and recrystallized from EtOH, to give product, m.p. 126–128°.

1,5-Diphenyl-1,2,3-triazoline

(A) Ether + dioxan (dry). Benzalaniline (2.71 g, 0.015 mole) was dissolved in 40 ml dried alcohol free ethereal diazomethane (2.1 g, 0.05 mole) and 40 ml dry dioxan and the mixture allowed to stand at R.T. for 192 hr. It was then diluted with water, and extracted with ether. The ether extract after drying and distillation, yielded 2.5 g crude product, m.p. 42–100°. Two crystallizations from EtOH-water gave ~ 20 mg product, m.p. 105–125°. Further fractionation of the mother liquor gave only material, m.p. 52–60°, and its mixture m.p. with benzalaniline was undepressed.

(B) Ether + dioxan (wet). The reaction was carried out under conditions exactly similar to those for reaction A above. Diazomethane was prepared in dioxan (40 ml) and ether (40 ml) was added to it. The crude product upon crystallization from EtOH yielded 1.5 g pure 1,5-diphenyl-1,2,3-triazoline, m.p. 129-130°.

1-p-Nitrophenyl-5-phenyl-1,2,3-triazoline

The reactions were performed in the same manner as described above for the 1,5-diphenyl triazoline. The reaction mixtures were allowed to stand 21 hr each, and the product was precipitated in both cases by diluting the reaction mixture with water. 3.0 g triazoline resulted under dry conditions, m.p. 115-140°. One crystallization from acetone yielded 1.3 g pure product, m.p. 146-149°.

* M.ps were determined in a Thiele's tube using mineral oil. All m.ps. are uncorrected. Microanalyses are by Dr. Kurt Eder, Laboratoire Microchimique, Ecole de Chimie, Geneve, Switzerland, and nitrogen analyses are by Dumas method.

Under wet conditions, 2.7 g triazoline, m.p. 139-143° with sintering at 115°, resulted. It crystallized from acetone to give 2.3 g pure compound, m.p. 146-149°.

Cycloaddition of Phenyl Azide to Styrenes

1,5-Diphenyl-1,2,3-triazoline

(A) Ethanol. A mixture of styrene (6.24 g, 0.06 mole) and phenyl azide (7.2 g, 0.06 mole)²⁷ in EtOH (30 ml) was refluxed for 6 hr. To the cooled mixture were added crushed ice and water, when a semisolid material separated out. This was stirred well with a small amount of pet. ether (25–30 ml) when the unreacted oily phenyl azide went into soln and the triazoline was obtained as a crystalline material, 1.4 g; m.p. 118–127° with sintering at 111°. One crystallization from EtOH yielded product, 0.8 g, m.p. 128–130°.

(B) Ethyl acetate. The reaction was repeated using EtOAc (30 ml) in place of EtOH. The solvent was removed under reduced press and a mixture of pet. ether-ether added to the residue, when the product separated out as a white crystalline material, yield 0.8 g, m.p. 120-126° with previous sintering at 111°. It was recrystallized from EtOH to give 0.4 g pure product, m.p. 128-130°.

(C) DMF. When the reaction was carried out using DMF (30 ml) b.p. 152-153°, in place of EtOH, the reaction mixture was heated on a steam bath. The product appeared sticky and when heated with EtOH, a gummy polymer like material insoluble in EtOH was left behind. The latter, however, was soluble in acetone and crystallized from acetone-pet. ether to give colorless crystals, ~10 mg, m.p. and mixture m.p. 124-128°, same as that of an authentic sample of 1,5-diphenyl-1,2,3-triazoline.

The EtOH soluble fraction yielded 1.65 g, material, which softened at 112° and melted at 118–124°. One crystallization from EtOH and one from acetone gave colorless crystals, 0.9 g, m.p. 128–130°.

1,5-Diphenyl-4-nitro-1,2,3-triazoline

(A) DMF. A mixture of ω -nitrostyrene (4.5 g, 0.03 mole) and phenyl azide (6.0 g, 0.05 mole) in DMF (20 ml) was heated on a steam bath for 9 hr. The mixture was then cooled, and treated with crushed ice. A dark coloured semisolid material separated out; this was ground with pet. ether-ether. The resulting tan solid, 1.5 g, m.p. 145-162°, was crystallized once from EtOH, once from acetone-EtOH mixture, and finally from acetone, when the 1,5-diphenyl-4-nitro-1,2,3-triazoline was obtained as a silvery white shining crystalline material, yield 0.9 gm m.p. 174-177°. (Reported m.p. 178°¹⁶).

(B) 1-Propanol. The reaction was repeated using 1-propanol (20 ml). 1-Propanol was preferred to EtOH, so that the same reaction temp as in (A) above could be attained. The cooled reaction mixture was diluted with cold water and refrigerated overnight, when pale yellow needles appeared, yield 10 g, m.p. 142-172°. Crystallization from acetone-pet. ether followed by recrystallization from acetone-EtOH yielded the pure triazoline, very pale yellowish white crystals, yield 0-7 g, m.p. 174-177°. Mixture m.p. with a sample obtained from reaction A using DMF as solvent, was undepressed.

Though the yield was better in DMF, the reaction mixture was much cleaner in 1-propanol and the triazoline separated out directly from the reaction mixture as a light coloured crystalline material.

Cycloaddition of Diazomethane to Styrenes

3-Phenyl-2-pyrazoline

(A) Dry ether. Styrene (1.5 g, 0.015 mole) was added to an ethereal soln of diazomethane (2.1 g, 0.05 mole) (prepared from nitrosomethylurea, in the same manner undistilled ethereal solns are obtained) dried over KOH pellets and the mixture allowed to stand at R.T. for 169 hr. At the end of this period, it was extracted with 150 ml cold dil HCl (3 parts conc acid and 20 parts water). The acid extract was shaken twice with ether to remove any acid insoluble organic matter. It was then cooled to 0° and treated with a conc soln of the calculated amount of sodium nitrite. Almost immediately a voluminous ppt was formed, yield 10 g, m.p. 148–152° with previous sintering at 140°. It was recrystallized from acetone-pet. ether and the pure N-nitroso-3-phenyl-2-pyrazoline was obtained as pale straw yellow needles, yield 0.7 g, m.p. 150–152°. Reported m.p. 150°.²⁸

(B) Aqueous dioxan. The reaction was repeated using an aqueous dioxan soln of diazomethane, prepared according to procedure described.⁴ The reaction mixture, after a period of 168 hr, was filtered and diluted with water. Ether (100 ml) was then added and the mixture extracted with cold dil HCl. The pyrazoline was isolated as the N-nitroso derivative, yield 1-9 g, m.p. 149–153°. It was recrystallized from acetone-pet. ether to give 1-6 g pure compound, m.p. 150–152°.

Cycloaddition of Diazomethane to Stilbene

3,4-Diphenyl-2-pyrazoline

(A) Dry ether. A mixture of trans-stilbene (2.7 g, 0.015 mole) and diazomethane (2.1 g, 0.05 mole) in dry alcohol free ether was allowed to stand for 171 hr. It was worked up in the same manner as the 3-phenyl pyrazoline. Only a very small amount of the N-nitroso derivative was obtained; it separated out as a thin layer on the surface of the reaction mixture and was estimated to be less than 5 mg.

(B) Aqueous dioxan. The reaction when carried out in aqueous dioxan, yielded the N-nitroso-3,4diphenyl-2-pyrazoline as a pale yellow crystalline material, yield 0.5 g, m.p. 158–162.5°. Recrystallization from acetone-pet. ether did not raise the m.p. (Found: C, 71.63; H, 5.24; N, 16.58. Calc. for $C_{15}H_{13}N_3O$: C, 71.71; H, 5.18; N, 16.73%).

Kinetics. The Schiff bases required for the kinetic studies were synthesized by known methods and purified by distillation under reduced press or by crystallization from appropriate solvents.⁴

Rate constants for the addition reaction of diazomethane to Schiff bases were determined by the pseudo first order technique described earlier.³ The solvents used for the kinetic runs were all of reagent grade quality. To study the effect of increasing amounts of DMF on reaction rate, the solutions were prepared in 100 ml volumetric flasks by dissolving the anils in a mixture of dioxan and DMF with the DMF accurately measured out in the specified amounts. The diazomethane solutions were prepared in dioxan, for use in these runs.

For rate determinations in solvents other than dioxan, the diazomethane was prepared in the solvent in question. In the case of solvents such as acetone and DMF, blank experiments were carried out and the results indicated that there was no reaction whatsoever between the solvent and diazomethane.

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