p-Methoxyphenyl ester of succinic acid, m.p. 117–118°. *Anal.* Calcd. for $C_{11}H_{12}O_5$: C, 58.98; H, 5.36. Found: C, 59.10; H, 5.52.

In view of the extreme tendency of the maleic ester to lose *p*-methoxyphenol, the sample was dried at room temperature and 2 mm. over phosphorus pentoxide for 12 hours. The ester released *p*-methoxyphenol quantitatively upon solvolysis.

The *p*-bromophenyl esters of the *gem*-dimethylsuccinic and glutaric acids were obtained as oils which did not crystallize on long standing. The esters of α,α- and β,β-dimethylglutaric acids were identified through their conversion to the known acid anilides, m.p. 128–130°[51] and 146–147°,[52] respectively. The monoesters of α,α-dimethylsuccinic acid and β-phenylglutaric acid were converted to their anilides in the usual manner.

Monoanilide of α,α-dimethylsuccinic acid, m.p. 185–186°. *Anal.* Calcd. for $C_{12}H_{15}O_3N$: C, 65.15; H, 6.58; N, 6.34. Found: C, 65.38; H, 6.85; N, 6.59.

Monoanilide of β-phenylglutaric acid, m.p. 168°. *Anal.* Calcd. for $C_{17}H_{17}O_3N$: C, 72.07; H, 5.99; N, 4.95. Found: C, 72.20; H, 6.15; N, 5.10.

The sodium salt of the *p*-methoxyphenyl ester of 3,6-endoxo-Δ^4-tetrahydrophthalic acid was so unstable that it could not be recrystallized or converted to its free acid. Data establishing the nature of this ester are given in the results section.

Kinetics Methods. (A).—The rates of solvolysis of the mono-*p*-bromophenyl esters as well as the mono-*p*-methoxyphenyl succinate esters were followed by mixing the reactants in quartz cuvettes placed in a thermostated spectrophotometer and observing the optical density change at the appropriate wave length.[53]

(B).—The solvolysis of the mono-*p*-methoxyphenyl esters of maleic acid and *exo*-3,6-endoxo-Δ^4-tetrahydrophthalic acid were followed by a procedure previously described for the solvolysis of *n*-propyl-γ-(4-imidazolyl)-thiol butyrate.[15]

(C).—The titrimetric procedure employed for determination of the solvolysis constants of the anhydrides has been described previously.[14–16]

Acknowledgments.—We should like to thank Professors J. M. Sturtevant, E. White, R. F. Brown and H. Morawetz for their comments. This research was supported by grants from The National Institutes of Health, The National Science Foundation and The Upjohn Company.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY, EVANSTON, ILL.]

The Mechanism of the Thermal Decomposition Reaction of Azines

BY HOWARD E. ZIMMERMAN[1] AND S. SOMASEKHARA

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The thermal decomposition of benzalazines with loss of nitrogen to afford stilbenes has been shown to proceed by an ionic chain mechanism, in which an aryldiazomethane molecule is the chain transfer species. The decomposition of unsymmetrical azines as well as of a mixture of two symmetrical azines leads to non-statistical mixtures of all three possible stilbenes under reaction conditions where neither the reactant azines nor the product stilbenes equilibrate. The minimum reaction temperature is dramatically lowered by 150° on introduction of a phenyldiazomethane catalyst.

The first report of the pyrolytic reaction of benzalazines to afford stilbenes was in 1889 by Curtius and Jay,[2] who described the conversion of benzalazine itself to stilbene.

$$C_6H_5CH{=}\ddot{N}{-}\ddot{N}{=}CHC_6H_5 \longrightarrow C_6H_5CH{=}CHC_6H_5 + :N{\equiv}N:$$

Subsequently, further examples were provided by Meisenheimer,[3] Pascal[4] and most recently by Howard and Hilbert.[5] Surprisingly little interest was exhibited in the mechanism of the reaction, perhaps because of its superficial simplicity.

Nevertheless, the literature afforded several pieces of mechanistically pertinent information. Firstly, there was the kinetic study of Williams and Lawrence[6] in which the reaction was described as first order. Secondly, Pascal[4] had reported the pyrolysis of 4-methylbenzalazine to afford only 4-methylstilbene and no stilbene or 4,4′-dimethylstilbene, a result suggestive of an intramolecular process. Finally, of interest were du Pont patents[7] which noted that benzalazines could be used as initiators for polymerizing ethylene as well as for alkylating toluene with ethylene at high temperature; this suggested the formation of unstable organic fragments from benzalazines and seemed inconsistent with the conclusion of intramolecularity.

It was with this as background and with the goal of elucidating the reaction mechanism of the benzalazine pyrolysis reaction that the present investigation began.

Preliminary to designing of experiments to determine the reaction mechanism, the gross features of the reaction, as reported by the earlier investigators, were checked. It was confirmed that the evolution of nitrogen from benzalazine, anisalazine and from 4,4′-dimethylbenzalazine proceeded at an appreciable rate only above 295°. Also, the products were found to correspond to those reported by the earlier workers. Thus (*cf.* Table I), from benzalazine stilbene was isolated as the major product together with benzonitrile and a small quantity of 2,4,5-triphenylimidazole. Similarly, from anisalazine and from 4,4′-dimethylbenzalazine the corresponding stilbenes and nitriles were obtained.

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[1] Chemistry Department, University of Wisconsin, Madison 6, Wis.

[2] T. Curtius and R. Jay, *J. prakt. Chem.*, [2] **39**, 45 (1889).

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[4] P. Pascal and L. Normand, *Bull. soc. chim. France*, [4] **9**, 1029, 1059 (19)); **11**, 21 (1912).

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[6] G. W. Williams and A. S. C. Lawrence, *Proc. Roy. Soc.* (*London*), **156A**, 444 (1936).

[7] U. S. Patent 2,439,528 to du Pont; *C. A.*, **42**, 6583 (1948); Brit. Patent 605,848 to du Pont; *C. A.*, **43**, 670 (1949); Brit. Patent 621,179 to du Pont; *C. A.*, **43**, 6657 (1949).

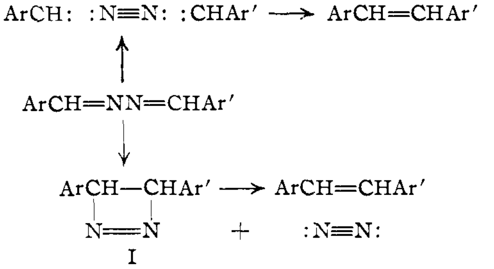
TABLE I

RESULTS OF PYROLYSIS OF SYMMETRICAL AZINES

Azine pyrolyzed[a]	N_2 evolved[b]	Corr. stilbene isolated[b]	Corr. nitrile isolated[b]
Benzalazine[c]	0.83	0.61	0.20
Anisalazine	.88	.35	.33
4,4'-Dimethylbenzalazine	.80	.38	.26

[a] Pyrolyses run at 300°. [b] Mmole/mmole azine employed. [c] Also isolated was 0.05 mmole of triphenylimidazole.

Most interesting from the viewpoint of reaction mechanism was the report of Pascal (*vide supra*) that pyrolysis of the unsymmetrical azine 4-methylbenzalazine afforded only 4-methylstilbene. Hence the question of the intramolecularity reaction was chosen for consideration next. It was clear that the reaction intramolecularity, if actually the case, could be rationalized either on the basis of a picture (*cf.* eq. 1) in which nitrogen is lost with simultaneous generation of two aryl carbene fragments which rapidly combine, or instead on the basis (*cf.* eq. 2) of a preliminary valence tautomerization to afford the four-membered ring intermediate I, followed by loss of nitrogen.



$$\mathrm{ArCH\colon\ \colon N{\equiv}N\colon\ \colon CHAr'} \longrightarrow \mathrm{ArCH{=}CHAr'} \qquad (1)$$

$$\uparrow$$

$$\mathrm{ArCH{=}NN{=}CHAr'}$$

$$\downarrow$$

$$\underset{\mathrm{I}}{\underset{\mathrm{N{=}N}}{\mathrm{ArCH{-}CHAr'}}} \longrightarrow \mathrm{ArCH{=}CHAr'} + \mathrm{\colon N{\equiv}N\colon} \qquad (2)$$

Repetition of the work of Pascal, however, did not support the picture of intramolecularity. 4-Methylbenzalazine on pyrolysis afforded a mixture of stilbenes which at one stage of purification did melt close to the reported melting point of 4-methylstilbene but which exhibited no constant melting point behavior on crystallization. This mixture of stilbenes was not readily separated either by crystallization or by chromatography, and it was felt that the pyrolysis of 4-methoxybenzalazine would provide a more suitable test of the reaction's intramolecularity, the corresponding stilbene products being known to be chromatographically separable.

The required 4-methoxybenzalazine was most easily obtained by chromatographing the mixture of azines obtained from treatment of an equimolar mixture of benzaldehyde and anisaldehyde with hydrazine. Pyrolysis of 4-methoxybenzalazine at 300° was found to afford not only 4-methoxystilbene but also both stilbene and 4,4'-dimethoxystilbene. These results are summarized in Table II (*cf.* runs 1 and 2). Furthermore, evidence was obtained that the formation of stilbene and of 4,4'-dimethoxystilbene was not due to disproportionation of the 4-methoxybenzalazine reactant into benzalazine and anisalazine prior to loss of nitrogen. Thus (*cf.* run 3, Table II) not only was 4-methoxybenzalazine quantitatively recovered when heated to 200° for a typical reaction time, precluding any facile equilibration of azines, but more convincingly, as indicated in run 2 of Table II, 4-methoxybenzalazine was the only azine isolable after running the pyrolysis partially to completion. Similarly, the less likely possibility of product disproportionation was excluded (runs 4 and 7) by the stability of 4-methoxystilbene at 300° and by the absence of 4-methoxystilbene among the products of pyrolysis of benzalazine in excess 4,4'-dimethoxystilbene.

TABLE II

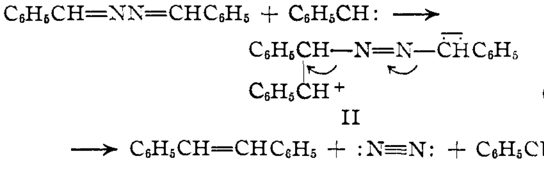
SUMMARY OF PYROLYSES OF UNSYMMETRICAL AZINES AND OF MIXTURES OF SYMMETRICAL AZINES INCLUDING CONTROL RUNS

Run	Reactants	Products isolated[a]
1[b]	4-Methoxybenzalazine	N_2 0.82, stilbene 0.05, 4-methoxystilbene 0.27, 4,4'-dimethoxystilbene 0.05, benzonitrile 0.06, anisonitrile 0.04
2[c,d]	4-Methoxybenzalazine	N_2 0.27, stilbene 0.08, 4-methoxystilbene 0.11, 4,4'-dimethoxystilbene 0.08, 4-methoxybenzalazine 0.70[e]
3[f]	4-Methoxybenzalazine	4-Methoxybenzalazine 1.00
4[c]	4-Methoxystilbene	4-Methoxystilbene 1.00
5[c]	1:1 mixt. of benzalazine and anisalazine	N_2 0.81, stilbene 0.33, 4-methoxystilbene 0.07, 4,4'-dimethoxystilbene 0.24, triphenylimidazole 0.05
6[d,g]	1:1 mixt. of benzalazine and anisalazine	N_2 0.45, stilbene 0.28, anisonitrile ~0.10, benzalazine ~0.10, anisalazine 0.61
7[c]	Benzalazine in excess 4,4-dimethoxystilbene	N_2 0.88, stilbene 0.52, 4,4'-dimethoxystilbene 0.98, triphenylimidazole 0.08[e]

[a] Mmole/mmole reactant (for runs using mixture of two symmetrical azine reactants, N_2 based on total of azine reactants), yields of nitriles and symmetrical stilbenes based on corresponding azine alone, yields of unsymmetrical stilbenes based on benzalazine alone. [b] Run at 295°. [c] Run at 300°. [d] Pyrol. terminated after partial reaction. [e] No attempt to isolate nitrile products. [f] Run at 200° for 40 min. [g] Run at 290°.

Thus it appeared certain that the reaction was intermolecular rather than intramolecular as suggested by Pascal. Further evidence on this point was obtained by pyrolyzing a 1:1 mixture of benzalazine and anisalazine (run 5, Table II). Not only were stilbene and 4,4'-dimethoxystilbene formed, but also there was obtained an appreciable although smaller quantity of 4'-methoxystilbene.

The intramolecular reaction mechanisms considered above having been ruled out, and with the du Pont patents in mind, the following carbene chain mechanism was entertained as a possibility



$$\mathrm{C_6H_5CH{=}NN{=}CHC_6H_5 + C_6H_5CH\colon} \longrightarrow \underset{\mathrm{II}}{\underset{\mathrm{C_6H_5CH^+}}{\mathrm{C_6H_5CH}}\mathrm{{-}N{=}N{-}\overset{-}{C}HC_6H_5}} \qquad (3)$$

$$\longrightarrow \mathrm{C_6H_5CH{=}CHC_6H_5 + \colon N{\equiv}N\colon + C_6H_5CH\colon}$$

Initially, there was indeed some strong support for this mechanism. It had been noted in the early experiments that although the majority of pyrolyses consistently proceeded only at temperatures approaching 300°, nevertheless, occasionally a run would proceed at a rapid rate at a considerably lower temperature. It was clear that the reaction was susceptible to catalysis by some impurity. The reaction was not catalyzed by copper, however, but it was found to be catalyzed by hydrazine, by sodium hydroxide and by tribenzylamine. The reaction proceeded nicely at 225° when 2.5% of hydrazine or 5% of sodium hydroxide was added. Similarly, when the reaction was run in the presence of excess tribenzyl amine, the pyrolysis proceeded smoothly at 250°. Most dramatic was the finding that the reaction was so efficiently catalyzed by phenyldiazomethane that it could be carried out at 150°, corresponding to a lowering of the required temperature by approximately 145°. While the significance of the hydrazine, tribenzylamine and hydroxide catalysis was uncertain, the phenyldiazomethane catalysis seemed to support the carbene chain mechanism (*vide supra*).

Further support for a chain process was found in runs in which a limited amount of phenyldiazomethane catalyst had been added; here it was observed (*cf.* runs in Table III) that the total nitrogen evolution and stilbene product formation corresponded to more than could be accounted for on the basis of decomposition of phenyldiazomethane alone. These runs suggested a chain length between five and ten.

The nature of the products of the phenyldiazomethane-catalyzed runs was the same as for the high temperature uncatalyzed runs, and hence it was felt that these runs differed only in availability of a reaction intermediate and not in mechanism.

TABLE III

AZINE PYROLYSES CATALYZED BY PHENYLDIAZOMETHANE

Run	Reactants[a]	Products isolated[a]
1[b]	Benzalazine, phenyldiazomethane 0.02	N_2 0.12, stilbene 0.06, benzalazine 0.94[c]
2[d]	Benzalazine, phenyldiazomethane 0.02	N_2 0.15, stilbene 0.08, benzalazine 0.81[c]
3[e]	4-Methoxybenzalazine, phenyldiazomethane 0.09	N_2 0.40, stilbene 0.09, 4-methoxystilbene 0.27, 4,4′-dimethoxystilbene 0.043, triphenylimidazole 0.03[c]
4[f]	Anisalazine, benzalazine 0.35, phenyldiazomethane 0.07	N_2 0.79, stilbene 0.021, 4-methoxystilbene 0.026, 4,4′-dimethoxystilbene 0.21, anisonitrile 0.076

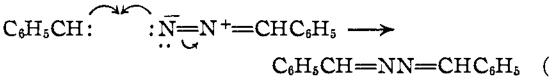
[a] Mmole/mmole of major azine reactant. [b] Run at 155°. [c] No attempt made to isolate nitrile products. [d] Run at 180°. [e] Run at 145°. [f] Run at 150°.

While it was clear that a chain reaction was operating, nevertheless there were at least two features of the reaction not consonant with an interpretation involving carbene intermediates. In the first place, the distribution of stilbenes isolated from experiments utilizing mixtures of azines and unsymmetrical azines deviated in each case from statistical with 4-methoxystilbene being favored in runs beginning with 4-methoxybenzalazine and the two symmetrical stilbenes being favored in runs beginning with a mixture of two symmetrical azines. Furthermore, in run 6 of Table II, where the pyrolysis of a 1:1 mixture of benzalazine and anisalazine was carried only 45% of the way to completion, it was found that benzalazine had preferentially reacted leaving mainly unreacted anisalazine.

On the basis of a carbene chain reaction one would expect, to the extent that any selectivity were found, a preferential decomposition of anisalazine, since the more electron rich anisalazine molecule should be more susceptible to attack by a carbene.[8]

The second inconsistent aspect of a carbene chain interpretation was lack of inhibition of the reaction and trapping of carbene intermediates when the decomposition was run either in 4,4′-dimethoxystilbene or in 2-ethoxynaphthalene, both solvents being susceptible to radical and electrophilic attack. Finally, it was found that pyrolysis of benzalazine through which oxygen was passed led to the normal products of pyrolysis, stilbene and benzonitrile, in average yield; additionally, there was isolated 3% of benzaldehyde. The benzaldehyde seemed most likely to arise from a reaction of molecular oxygen with phenylcarbene[9]; the formation, however, of only 3% seemed to suggest that phenylcarbene was a reaction artifact rather than an intermediate leading to stilbene formation.

In a further attempt to ascertain the reality of carbene intermediates, a mixture of benzalazine and phenyldiazomethane was irradiated. It was felt that, since the irradiation of diazo compounds is a means of generating divalent carbon species,[10] this would establish the behavior of phenylcarbene in the presence of benzalazine and indicate whether or not this was the reaction occurring thermally.[10] Experimentally, either in benzene or in dioxane solution, irradiation of a mixture of phenyldiazomethane and benzalazine afforded mainly benzalazine with only traces of stilbene, while at 80° without light stilbene was formed, although in smaller yield than at the higher pyrolytic temperatures. Thus it seems that phenylcarbene generated from phenyldiazomethane in the presence of benzalazine does not give the products characteristic of the azine pyrolysis reaction but rather attacks phenyldiazomethane affording benzalazine.



$$C_6H_5CH\colon \quad \colon\bar{\underset{\cdot\cdot}{N}}{=}N^+{=}CHC_6H_5 \longrightarrow C_6H_5CH{=}NN{=}CHC_6H_5 \qquad (4)$$

As a consequence of these several considerations we may dismiss the carbene chain reaction mechanism as incorrect.

There is, however, a reaction mechanism which accords with all of the experimental data, namely: (a) the absence of carbenes except as reaction

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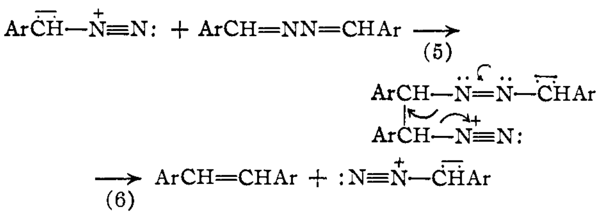
(8) The electrophilic character of simple carbenes is well known (*cf.* P. S. Skell and R. M. Etter, *Chemistry & Industry*, 624 (1958)). On the other hand, evidence has been presented (R. M. Etter, H. S. Skovronek and P. S. Skell, THIS JOURNAL, **81**, 1008 (1959)) that diphenylmethylene is basically diradical in nature. Should the species C_6H_5CH: similarly be diradical in character, it nevertheless would still be predicted to attack preferentially anisalazine, since the intermediate thus formed would be stabilized by interaction of the methoxyl group unshared electrons.

(9) *Cf.* W. Fielding and H. O. Pritchard, *J. Chem. Phys.*, **62**, 278 (1960), for evidence of capture of divalent carbon species by oxygen. In this case either pyrolysis or photolysis of diphenyldiazomethane in the presence of oxygen afforded benzophenone.

(10) This test suffers from the objection that the divalent benzal species generated photochemically may not be electronically the same as that formed in a thermal process.

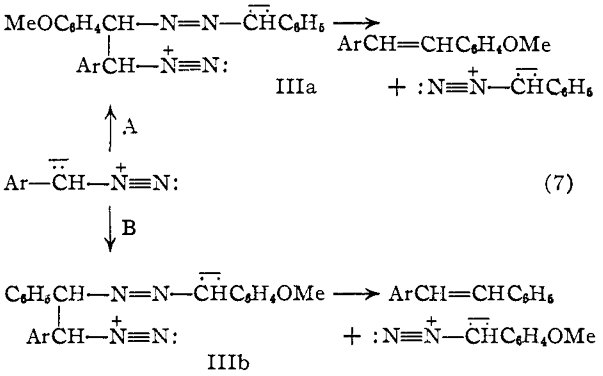
artifacts despite the phenyldiazomethane catalysis; (b) the reaction intermolecularity; (c) the associated non-statistical product distribution and related preferential reaction of benzalazine in a benzalazine–anisalazine mixture; and lastly, (d) the first-order kinetics reported by Williams and Lawrence.[6] This is an ionic chain reaction involving an aryldiazomethane molecule rather than a carbene as the chain carrying species[11]; the two propagation steps are



$$\mathrm{Ar\overset{-}{C}H{-}\overset{+}{N}{\equiv}N{:}} + \mathrm{ArCH{=}NN{=}CHAr} \xrightarrow{(5)} \begin{matrix}\mathrm{ArCH{-}\ddot{N}{=}\ddot{N}{-}\overset{-}{C}HAr}\\ |\\ \mathrm{ArCH{-}\overset{+}{N}{\equiv}N{:}}\end{matrix} \xrightarrow{(6)} \mathrm{ArCH{=}CHAr} + \mathrm{{:}N{\equiv}\overset{+}{N}{-}\overset{-}{C}HAr}$$

How this mechanism rationalizes the reaction intermolecularity and the non-statistical product distribution is readily understood by considering, in turn, the cases of pyrolysis of 4-methoxybenzalazine and of the mixture of benzalazine and anisalazine.

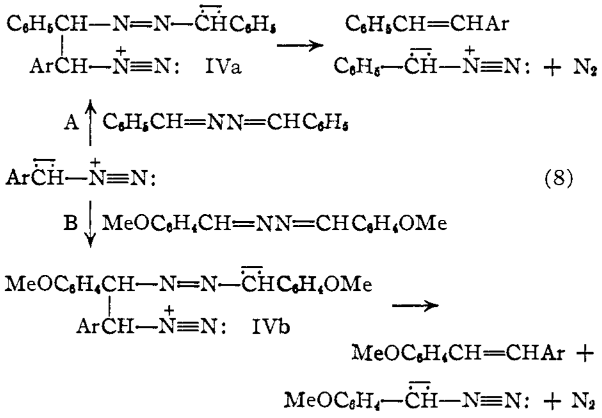
In the pyrolysis of 4-methoxybenzalazine, the chain-propagating steps will follow either path A or B



$$\begin{matrix}\begin{matrix}\mathrm{MeOC_6H_4CH{-}N{=}N{-}\overset{-}{C}HC_6H_5}\\ |\\ \mathrm{ArCH{-}\overset{+}{N}{\equiv}N{:}}\end{matrix}\ \text{IIIa} \longrightarrow \mathrm{ArCH{=}CHC_6H_4OMe} + \mathrm{{:}N{\equiv}\overset{+}{N}{-}\overset{-}{C}HC_6H_5}\\ \uparrow \text{A}\\ \mathrm{Ar{-}\overset{-}{C}H{-}\overset{+}{N}{\equiv}N{:}} \qquad (7)\\ \downarrow \text{B}\\ \begin{matrix}\mathrm{C_6H_5CH{-}N{=}N{-}\overset{-}{C}HC_6H_4OMe}\\ |\\ \mathrm{ArCH{-}\overset{+}{N}{\equiv}N{:}}\end{matrix}\ \text{IIIb} \longrightarrow \mathrm{ArCH{=}CHC_6H_5} + \mathrm{{:}N{\equiv}\overset{+}{N}{-}\overset{-}{C}HC_6H_4OMe}\end{matrix}$$

It seems probable that path A is preferred. In IIIb, the presence of two electron-donating groups, the methoxyl group and the negatively charged moiety, *para* to each other must lead to diminution of electron delocalization from each of these into the aromatic ring. Thus IIIb, and the transition state leading to IIIb, will have less electron delocalization and be of higher energy than IIIa and its corresponding transition state. As a result of path A being preferred, phenyldiazomethane is the preferred chain-carrying species and hence in eq. 7 it may be identified with $\mathrm{ArCHN_2}$, Ar– may be seen to be $\mathrm{C_6H_5}$–, and the product of path A is hence 4-methoxystilbene. To the extent that the selectivity is incomplete, phenyldiazomethane may follow path B with formation of stilbene and generation of an anisyldiazomethane molecule which due to the preference of path A is most likely to lead to 4,4′-dimethoxystilbene. Thus, on the basis of this reaction scheme, one would anticipate mainly 4-methoxystilbene plus smaller and nearly equal quantities of stilbene and 4,4′-dimethoxystilbene. This agrees with the facts (*cf.* Table I, runs 1 and 2).[12]

To be considered next is the pyrolysis of a mixture of benzalazine and anisalazine.



$$\begin{matrix}\begin{matrix}\mathrm{C_6H_5CH{-}N{=}N{-}\overset{-}{C}HC_6H_5}\\ |\\ \mathrm{ArCH{-}\overset{+}{N}{\equiv}N{:}}\end{matrix}\ \text{IVa} \longrightarrow \mathrm{C_6H_5CH{=}CHAr} + \mathrm{C_6H_5{-}\overset{-}{C}H{-}\overset{+}{N}{\equiv}N{:}} + \mathrm{N_2}\\ \text{A}\uparrow \mathrm{C_6H_5CH{=}NN{=}CHC_6H_5}\\ \mathrm{Ar\overset{-}{C}H{-}\overset{+}{N}{\equiv}N{:}} \qquad (8)\\ \text{B}\downarrow \mathrm{MeOC_6H_4CH{=}NN{=}CHC_6H_4OMe}\\ \begin{matrix}\mathrm{MeOC_6H_4CH{-}N{=}N{-}\overset{-}{C}HC_6H_4OMe}\\ |\\ \mathrm{ArCH{-}\overset{+}{N}{\equiv}N{:}}\end{matrix}\ \text{IVb} \longrightarrow \mathrm{MeOC_6H_4CH{=}CHAr} + \mathrm{MeOC_6H_4{-}\overset{-}{C}H{-}N{\equiv}N{:}} + \mathrm{N_2}\end{matrix}$$

The reaction of a chain-carrying aryldiazomethane molecule, $\mathrm{ArCHN_2}$ in eq. 8, with benzalazine (path A) would be expected to be faster than with anisalazine (path B) since electron delocalization from the methoxyl oxygen to the azine nitrogen system would be lost if path B were followed. Since path A is kinetically favored, the preferred chain-carrying species is phenyldiazomethane which now may be identified with $\mathrm{ArCHN_2}$ of eq. 8 with the consequence that the product of the kinetically preferred path (A) is stilbene. As the last of the benzalazine is almost consumed, the higher concentration of anisalazine forces intervention of path B with generation of 4-methoxystilbene. Finally, after all the benzalazine has reacted, anisalazine is forced to react with formation of dimethoxystilbene. This picture is supported by runs 5 and 6 of Table II.

Finally, the first-order kinetics observed for the benzalazine pyrolysis requires comment. In the reaction scheme

A	$\xrightarrow[k_1]{}$	D + C	chain initiation
A + D	$\xrightarrow[k_p]{}$	D + S + $\mathrm{N_2}$	chain propagation
D + X	$\xrightarrow[k_t]{}$	Y	chain termination

where A represents azine reactant, D represents diazo compound intermediate, S represents stilbene product, and where X and Y represent unknown species in the termination process, the assumption is made that there is no buildup of the phenyldiazomethane–azine adduct III. It is apparent that the over-all rate of disappearance of

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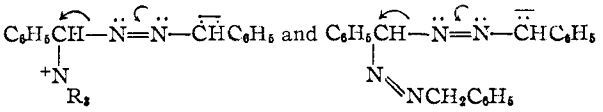
[11] Since phenyldiazomethane is actually the chain-carrying intermediate, the rate enhancement noted on addition of external phenyldiazomethane is expected. The hydrazine and the sodium hydroxide catalysis probably result from formation of benzalhydrazone. Catalysis by benzalhydrazone as well as by tribenzylamine seem attributable to the breakdown of the products of nucleophilic addition of these to benzalazine, yielding phenyldiazomethane.



$$\begin{matrix}\mathrm{C_6H_5CH{-}\ddot{N}{=}\ddot{N}{-}\overset{-}{C}HC_6H_5}\\ |\\ \mathrm{{}^{+}NR_3}\end{matrix} \text{ and } \begin{matrix}\mathrm{C_6H_5CH{-}\ddot{N}{=}\ddot{N}{-}\overset{-}{C}HC_6H_5}\\ |\\ \mathrm{N{\searrow}NCH_2C_6H_5}\end{matrix}$$

[12] It is interesting to note that the product distribution prediction depends on one of paths A and B being preferred; if path B were preferred, the same results as above would be predicted.

azine reactant is given by

$$-\,d(A)/dt = k_p(A)(D) + k_i(A) + k_t(D)(X)$$

and that hence the kinetics will be first order if the concentration (D) of the phenyldiazomethane intermediate is constant and X is equatable to A. The over-all rate of formation of phenyldiazomethane is given by

$$d(D)/dt = k_i(A) - k_t(D)(X)$$

Since the concentration of phenyldiazomethane present at 300° must be small, the steady state approximation may be applied, giving

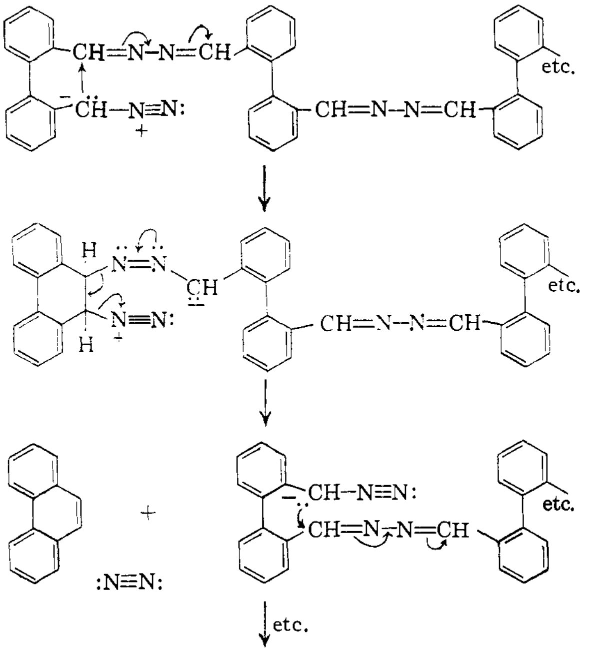
$$k_i(A) = k_t(D)(X) \text{ or } (D) = k_i(A)/k_t(X)$$

It may be seen that the concentration of phenyldiazomethane will be constant if the unknown species X is again taken as benzalazine (*i.e.*, A).[13]

In connection with the above kinetic scheme, it is pertinent that simple homolytic fission of benzalazine in the initiation step would also yield phenylcarbene, which is therefore most likely species C. Phenylcarbene molecules thus formed would account for the ability of benzalazine to polymerize ethylene noted in the du Pont patents as well as for the isolation of benzaldehyde in low yield from the pyrolysis in the presence of oxygen.[14,15]

Evidence having been presented supporting an ionic chain mechanism in which phenyldiazomethane is the chain-propagating species, it is of interest to consider some most interesting results reported by Bacon and Lindsay[16] and also by Hall, Ladbury, Lesslie and Turner[17] in which there was described a strikingly facile formation of phenanthrenes both from 2,2′-diacylbiphenyls and hydrazine as well as from the derived polymeric azines but not from the cyclic azines. Thus,[16] for example, the azine polymer resulting on low temperature reaction of biphenyl-2,2′-dicarboxaldehyde with hydrazine afforded phenanthrene on refluxing either in ethanol or acetic acid; under the same conditions phenanthrene could be obtained directly from the dialdehyde and hydrazine.[16] Similarly, 2,2′-diacetylbiphenyl and hydrazine afforded 9,10-dimethylphenanthrene; the cyclic azine by-product from this reaction was not readily convertible to 9,10-dimethylphenthrene. Only on heating with hydrazine was it slowly converted to 9,10-dimethylphenanthrene.[16]

An interesting mechanistic possibility suggested by the results of the present investigation is that the azine polymer is digested unit by unit, each being converted to the phenanthrene product in a process involving an intramolecular nucleophilic addition of a diazoalkyl end group to the nearest azine linkage[18]



Experimental Section[19]

Preparation of Benzalazine.—To 6.0 g. (0.10 mole) of hydrazine hydrate (85%) was added 21.0 g. (0.20 mole) of benzaldehyde with cooling and stirring. Within 10 minutes the reaction mixture set into a solid yellow cake; this was crushed with 100 ml. of cold water and filtered. The yield of crude benzalazine melting at 87–90° was 19.2 g. (92%). This was crystallized from ethanol to afford yellow needles melting at 92.0° (reported[2] 93°).

Preparation of Anisalazine.—To 6.0 g. (0.10 mole) of hydrazine hydrate (85%) was added 27.0 g. (0.20 mole) of anisaldehyde with cooling and stirring. The azine that was formed instantaneously was triturated with 100 ml. of cold water and filtered. The yield of slightly impure anisalazine melting at 161–165° was 27 g. (100%). This was crystallized from benzene–ethanol affording needles melting at 167.0–168.° (reported[20] 168.0°).

Preparation of 4-Methoxybenzalazine.—A mixture of 10.6 g. (0.10 mole) of benzaldehyde and 13.6 g. (0.10 mole) of anisaldehyde was added to 6.0 g. (0.10 mole) of 85% hydrazine hydrate cooled in ice; a yellow solid formed almost instantaneously. This was filtered and weighed 24 g. The solid was dissolved in 100 ml. of hot benzene; on cooling, the solution afforded 4 g. of anisalazine. The

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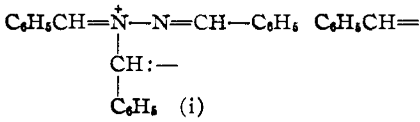
[13] That the steady state approximation is justified may be seen from the following expression which is rigorously true:

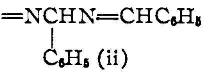
$$D = \frac{k_1}{k_t} - \frac{k_1}{k_t}e^{(k_tA - k_tA_o - k_pD - k_tD)(k_p + k_t)/(k_1k_p + 2k_ik_t)}$$

As the reaction proceeds, the term $(k_tA - k_tA_o)$ quickly becomes negative and dominates the exponential because the azine concentrations involved are large compared to diazo concentrations. Hence the second term drops out and D approaches (k_1/k_t).

[14] The yield of benzaldehyde may not correspond to the actual extent of phenylcarbene formation due to experimental difficulties in providing oxygen to the liquid phase reaction.

[15] It is uncertain whether benzonitrile and triphenylimidazole derive from reactions of the phenylcarbene formed in the initiation process, from the termination step itself or from independent reactions. One reasonable possibility is the formation of (i) by attack of phenyl-


$C_6H_5CH{=}\overset{+}{N}(CH{:}^{-}C_6H_5){-}N{=}CH{-}C_6H_5$ (i)


$C_6H_5CH{=}NCH(C_6H_5)N{=}CHC_6H_5$ (ii)

carbene on benzalazine. This could rearrange to dihydrobenzamide (ii) which is known to give (*cf.* ref. 5) triphenylimidazole, or instead it could β-eliminate to give the observed benzonitrile as one product.

[16] R. G. R. Bacon and W. S. Lindsay, *J. Chem Soc.*, 1375, 1382, (1958); ***Chemistry and Industry***, 1479 (1956).

[17] D. M. Hall, J. E. Ladbury, M. S. Lesslie and E. E. Turner, *J. Chem. Soc.*, 3475 (1956).

[18] The operation of such a mechanism, involving acid-sensitive diazoalkyl groups, under acidic conditions is not an objection, since the rate of intramolecular, electrophilic attack of an azine linkage on a given diazoalkyl carbon atom, which might itself be acid catalyzed, could easily be faster than the direct electrophilic attack by the proton donor itself.

[19] All melting points were taken on a Fisher–Johns block whose thermometer had been checked with compounds of known melting point.

[20] G. Knöpfer, *Monatsh.*, **30**, 32 (1909).

filtrate was concentrated and the residue of 20 g. was chromatographed on a 3 × 36 inch silica gel column slurry packed with 55:45 benzene–chloroform. After elution of the column with 1.2 liters the eluent began to contain benzalazine and the following 2.2 liters afforded 5.7 g. of benzalazine. Following this in 3.2 liters of eluent was 6.2 g. of 4-methoxybenzalazine melting at 80–82°. The subsequent 1.4 liters gave 7 g. of material which was mainly anisalazine contaminated with small amounts of 4-methoxybenzalazine. Two crystallizations of 4-methoxybenzalazine from benzene–hexane raised its melting point to 82.0–83.0°. The infrared spectrum of 4-methoxybenzalazine contained peaks at 6.27 and 6.32 mμ which are absent in both benzalazine and anisalazine.

Attempted direct synthesis of 4-methoxybenzalazine from anisaldehyde and benzalhydrazone gave a mixture of all three possible azines.

Anal. Calcd. for $C_{15}H_{14}N_2O$: C, 75.63; H, 5.88; N, 11.77. Found: C, 74.97; H, 5.95; N, 12.16.

Preparation of 4,4′-Dimethylbenzalazine.—To 1.50 g. (0.025 mole) of 85% hydrazine hydrate cooled in ice was added over 10 min. 6.0 g. (0.50 mole) of *p*-tolualdehyde. The yellow solid that formed was washed with 20 ml. of ice-water affording 5.8 g. of solid melting at 150–153°. Crystallization from ethanol afforded with little loss to the filtrate pure 4,4′-dimethylbenzalazine melting at 157° (reported[21] 154–155°).

Preparation of 4-Methylbenzalazine.—On being mixed, 0.35 g. of *p*-tolualdehyde and 0.36 g. of benzylhydrazine afforded a crystalline mass, the reaction requiring 30 min. Two crystallizations from ether–hexane gave 0.245 g. of colorless *p*-methylbenzalbenzylhydrazine, m.p. 57.5–58.5°. This was dissolved in 10 ml. of absolute ethanol and treated with 2.0 g. of yellow mercuric oxide; the mixture was stirred at room temperature for 6 hr. Filtration gave a pale yellow solution which was concentrated *in vacuo* leaving an oily residue. This was treated with 5 ml. of ether; 5 mg. of colorless solid was filtered and melted at 240–245°. The mother liquor was concentrated to about 1 ml. and this on standing afforded 0.21 g. of a yellow crystalline solid melting at 110–112° (reported[22] 112°).

Pyrolysis of Benzalazine.—Three grams (0.0144 mole) of benzalazine was placed in a flask equipped with a water-cooled condenser and an internal glass covered thermocouple; to the top of the condenser was connected a gas buret. The flask was heated in a metal-bath to an interna temperature of 300 ± 5°. The evolution of nitrogen, which began as the temperature of the reactants approached 300°, ceased after 40 min.; a total of 266 cc. (83%) (corrected to room temperature) had been collected. The infrared spectrum of the crude reaction product revealed the presence of a nitrile. The volatile fraction was removed by distillation at 0.3 mm. using a 100° water-bath and a Dry Ice-cooled receiver; the distillate weighed 0.30 g. and possessed an infrared spectrum identical to that of authentic benzonitrile.

The residue was chromatographed on a 3.8 × 75 cm. silica gel column slurry packed with 10% ether in hexane. From the first 800 ml. of 10% ether-in-hexane eluent 2.3 g. of a pale yellow solid, m.p. 60–72°, was obtained. It was dissolved in benzene, treated with activated charcoal and the filtrate concentrated. Crystallization of the concentrate from benzene–hexane afforded 1.61 g. (0.0088 mole) of colorless solid, m.p. 118–120°. A small portion was crystallized further to m.p. 123–124°. The infrared spectrum was that of stilbene (reported[23] 124°). The column was then eluted with 1 l. of chloroform affording 0.30 g. of brownish, gummy solid; this was triturated with 10 ml. of ether to yield 0.15 g. (0.00050 mole) of colorless solid melting at 260–263° One crystallization from pyridine–water raised the m.p. to 274–276° (reported[5] m.p. for lophine 275°).

Pyrolysis of Anisalazine.—Six grams (0.022 mole) of anisalazine was heated as described in the above experiment to 300 ± 5°. The nitrogen evolution became perceptible as the temperature reached 300° and ceased at the end of 45 min. by which time 440 ml. (88%, 0.02 mole) of gas had been collected. The infrared spectrum of the crude reaction product showed typical cyano absorption. The crude product was placed in a molecular still and heated to 130° at 0.02 mm. for 6 hr. There was collected on the cold finger 0.98 g. (0.0075 mole) of a very pale yellow solid melting at 47–50°; its identity with anisonitrile was established by comparison of its infrared spectrum with that of an authentic sample. The residue in the molecular still was subjected to heating to 200° at 0.01 mm. for 12 hr.; from this there was obtained 2.1 g. of sublimate, m.p. 187–192°. Crystallization from benzene–alcohol afforded 1.9 g. (0.008 mole) of colorless needles, m.p. 210–212°, proving on infrared comparison to be 4,4′-dimethoxystilbene (reported[24] m.p. 212°).

Pyrolysis of 4-Methoxybenzalazine.—A 6.00-g. (0.025 mole) sample of 4-methoxybenzalazine was heated in the apparatus described above. The evolution of nitrogen began as the temperature reached 295°, and the temperature was maintained at 295 ± 5° for 40 min. at the end of which time the gas evolution had ceased. A total of 479 cc. (corrected to room temperature, 82%) had been evolved. The crude reaction product was then transferred to a 20-ml. flask fitted with a 22-cm. Vigreux column, itself connected to a Dry Ice-cooled receiver. The flask was heated to 100° at 0.001 mm. for 6 hr. when 0.314 g. (0.003 mole) of benzonitrile had been collected in the receiver and 0.269 g. (0.002 mole) of anisonitrile had solidified in the Vigreux column. The latter was washed out with ether and obtained by concentration; its identity was established by infrared and mixed melting point comparison. The benzonitrile was identified by infrared comparison with a authentic sample.

The non-volatile residue was chromatographed on a 2.5 × 103 cm. silica gel column slurry packed with 1:3 benzene–hexane. Fractions 1 through 3, each 200 ml., were eluted with 35:65 benzene–hexane; fractions 4 through 10 with 1:1 benzene–hexane; fractions 11 through 13 with 3:1 benzene–hexane; fractions 14 through 18 with 7:1 benzene–hexane; 19 through 21 with 9:1 benzene–chloroform, and 22 through 24 with 7:3 benzene–chloroform; finally 3.5 l. of chloroform was passed through the column. Fractions 2–6 afforded 0.197 g. (0.0011 mole) of stilbene melting at 118–120°; fractions 13–17 gave 1.475 g. (0.0069 mole) of 4-methoxystilbene melting at 132–134° (reported[25] 136°). Fractions 27–30 yielded 0.310 g. (0.0013 mole) of 4,4′-dimethoxystilbene melting at 208–211°, while the chloroform elutes gave 3.0 g. of tarry material.

The tarry fraction was chromatographed on a 2.5 × 103 cm. alumina column slurry packed with benzene, and 250-ml. fractions were collected. Fractions 1–7 were eluted with benzene, 8–11 with 1:4 chloroform–benzene, 12–16 with 1:3 chloroform–benzene, 17–21 with 2:3 chloroform–benzene, 22–23 with 1:1 chloroform–benzene and 24–32 with chloroform. Fraction 4 afforded 1.34 g. of a brown viscous liquid; fractions 5–21 gave 0.13 g. (0.00043 mole) of lophine melting at 269–272°. Fraction 23 yielded 0.13 g. of a colorless solid melting at 198–203°, and the chloroform fractions gave a brown viscous oil weighing 0.18 g. Fraction 4 was dissolved in benzene and run through a 2.5 × 63 cm. column of activated charcoal; elution with 300 ml. of benzene gave material which would not crystallize. Fraction 23 was crystallized from ether–hexane to a constant m.p. of 218–220°; this material weighed 0.078 g. This material was tentatively assigned the structure of bis-1,2-(4-methoxyphenyl)-3-phenylcyclopropane.

Anal. Calcd. for $C_{23}H_{22}O_2$: C, 83.64; H, 6.66. Found: C, 83.69; H, 6.20.

The chloroform-eluted oil afforded small quantities of two pale yellow solids which were not characterized.

In a repetition of the above experiment, in which 2.00 g. (0.0084 mole) of 4-methoxybenzalazine was used, there were obtained: 160 ml. (0.0067 mole, 85%) of nitrogen, 0.098 g. (0.00097 mole) of benzonitrile, 0.074 g. (0.0004 mole) of anisonitrile, 0.10 g. (0.0005 mole) of stilbene, 0.46 g. (0.002 mole) of 4-methoxystilbene, 0.09 g. (0.00037 mole) of 4,4′-dimethoxystilbene and 1.0 g. (50%) of dark-brown tarry material which in this case was not further studied.

Pyrolysis of 4,4′-Dimethylbenzalazine.—One gram (0.0042 mole) of 4,4′-dimethylbenzalazine was heated in the pyrolysis apparatus described above to 300 ± 5°. The evolution of nitrogen, which began as the temperature of the

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(21) V. Hanzlik and A. L. Bianchi, *Ber.*, **32**, 1286 (1889).

(22) T. Curtius and H. Franzen, *Ber.*, **35**, 3238 (1902).

(23) A. Michaelis and H. Lange, *ibid.*, **8**, 1314 (1875).

(24) H. Wiechell, *Ann.*, **279**, 341 (1894).

(25) A. Oglialoro, *Gazz. chim. ital.*, **9**, 533 (1879); *Chem. Zentr.*, **51**, 230 (1880).

reactant reached 300°, ceased after 40 min. by which time 76 ml. (corrected to room temperature, 80%) of nitrogen had been collected. The reaction mixture was connected by a 75° adapter to a Dry Ice-cooled receiver with a vacuum line connection; at a bath temperature of 100° and at 0.3 mm. there was collected 0.134 g. (0.0011 mole) of 4-methylbenzonitrile, this being identified by its infrared spectrum. The non-volatile residue was subjected to sublimation at 150° and 0.2 mm. pressure; the sublimate thus obtained weighed 0.34 g. (0.0016 mole) and melted at 179–182° (reported[26] m.p. for 4,4′-dimethylstilbene is 179–180°).

Pyrolysis of 4-Methylbenzalazine.—One gram (0.0045 mole) of 4-methylbenzalazine was heated in the usual pyrolysis apparatus to 300 ± 5°. The evolution of nitrogen began as the temperature reached 300° and ceased at the end of 45 min. by which time 76 ml. (corrected to room temperature; 80%) of nitrogen had been collected. Distillation of the crude reaction product at a bath temperature of 100° and pressure of 0.3 mm. using a Dry Ice-cooled receiver gave 0.117 g. of distillate which was seen by its infrared spectrum to be a mixture of benzonitrile and *p*-tolunitrile. The non-volatile residue was chromatographed on a 2.5 × 125 cm. silica gel column slurry packed with 1:9 benzene in hexane. The column was then eluted with the same solvent. The first 1.8 l. contained no material. Fraction 1 (the next 200 ml.) contained 97.7 mg., m.p. 98–102°; fraction 2 (100 ml.), 95.8 mg., m.p. 114–117°; fraction 3 (100 ml.), 69.8 mg., m.p. 117–120°; fraction 4 (100 ml.), 34.7 mg., m.p. 110–114°; fraction 5 (100 ml.), 7.4 mg., m.p. 108–112°. Elution with increasing amounts of benzene and then chloroform yielded no further characterizable material. Combination of fractions 1 through 5 gave material melting at 116–118°, close to the reported[27] 117°, despite the obvious heterogeneity. Repeated crystallization from benzene–hexane resulted in a gradual rise in m.p. until 8 mg. of pure 4,4′-dimethylstilbene, m.p. 181–182°, was obtained.

Pyrolysis of a Mixture of Benzalazine and Anisalazine for a Limited Time.—A mixture of 1.046 g. (0.0050 mole) of benzalazine and 1.344 g. (0.0050 mole) of anisalazine was heated to 290 ± 5° in the usual pyrolysis apparatus. At the end of 10 min. 130 ml. (corrected to room temperature, 45%) of nitrogen had been collected and the pyrolysis was stopped. The product was chromatographed on a 2.8 × 76 cm. column of silica gel slurry packed with 1:3 benzene–hexane; 200-ml. fractions were collected as follows: 1–5 with 1:3 benzene–hexane, 6–8 with 1:1 benzene–hexane, 9–11 with benzene, 12–18 with 1:9 chloroform–benzene, 19–23 with 1:4 chloroform–benzene, 24–27 with 3:7 chloroform–benzene, 28–29 with 1:1 chloroform–benzene, 30–31 with 7:3 chloroform–benzene, and 32–45 with chloroform. Fractions 4–6 afforded 0.2528 g. (0.0014 mole) of stilbene melting at 119–121° identified by infrared; fractions 26–31 gave 0.1393 g. (0.0010 mole) of a mixture of anisonitrile and benzalazine, the infrared spectrum of which showed it to consist approximately of 50% of each component. Fractions 40–45 gave 1.0760 g. of impure anisalazine; this was washed with 10 ml. of 1:1 ether–hexane leaving 0.8116 g. (0.00303 mole) of anisalazine, m.p. 158–160°, whose infrared spectrum was that of pure compound.

Pyrolysis of a Mixture of Benzalazine and Anisalazine.—A mixture of 1.0 g. (0.0048 mole) of benzalazine and 1.0 g. (0.0037 mole) of anisalazine was heated in the usual pyrolysis apparatus. The evolution of nitrogen began as the temperature reached 300° and ceased after 45 min. of heating to 300 ± 5°; a total of 146 ml. (corrected to room temperature, 80%) of nitrogen was collected. The infrared spectrum of the crude pyrolysis product showed nitriles to be present; however, no attempt was made to isolate them. The crude product was chromatographed on a 2.5 × 113 cm. silica gel column slurry packed with 1:4 benzene–hexane; 250-ml. fractions were collected by eluting: with 1.75 liters of 1:4 benzene–hexane, 2.25 liters of 1:1 benzene–hexane, 500 ml. of 3:2 benzene–hexane, 500 ml. of 4:1 benzene–hexane, 500 ml. of benzene, 500 ml. of 1:4 chloroform–benzene, 1 liter of 2:3 chloroform–benzene, 500 ml. of 3:2 chloroform–benzene and 3.5 liters of chloroform. Fractions 3–6 afforded 0.296 g. (0.0016 mole) of stilbene, m.p. 116–118°; fractions 12–16 gave 0.0796 g. (0.00037 mole) of 4-methoxystilbene, m.p. 136–137°. Fractions 24–29 yielded 0.215 g. (0.00088 mole) of 4,4′-dimethoxystilbene melting at 210–212°, while the chloroform elutes gave 0.90 g. of a dark viscous material, which was not further investigated.

Stability of 4-Methoxybenzalazine at 200°.—A 1.0-g. sample of 4-methoxybenzalazine (0.0042 mole) was heated in the pyrolysis apparatus described above. The temperature was maintained at 200° for 40 min. with no perceptible evolution of nitrogen. The melting point and infrared spectrum of the recovered material was that of unchanged 4-methoxybenzalazine.

Stability of 4-Methoxystilbene at 300°.—A 0.50-g. (0.0023 mole) sample of 4-methoxystilbene was heated to 300° for 30 min. in the pyrolysis apparatus. The resolidified melt proved to be unchanged 4-methoxystilbene.

Stability of 4-Methoxybenzalazine under Pyrolysis Conditions: Identification of the Unreacted Azine Fraction.—A 2.0-g. (0.0084 mole) sample of 4-methoxybenzalazine was heated in the pyrolysis apparatus to 300°; the reaction was run only until 53 ml. (0.0023 mole) of nitrogen had been collected and was then cooled. An infrared spectrum indicated the crude product to contain nitriles, but no attempt was made to isolate these. The product was chromatographed on a 2.5 × 113 cm. silica gel column slurry packed with 1:3 benzene–hexane and 200-ml. fractions were collected: fractions 1–7 with 1:3 benzene–hexane, 8 and 9 with 3:7 benzene–hexane, 10–13 with 1:1 benzene–hexane, 14–17 with 3:2 benzene–hexane, 18 and 19 with 4:1 benzene–hexane, 20 and 21 with benzene, 22 and 23 with 9:1 benzene–chloroform, 24–28 with 7:3 benzene–chloroform, 29–39 with 1:1 benzene– chloroform, 40–44 with 1:3 benzene–chloroform, 45–50 with chloroform. Fractions 4 and 5 afforded 0.055 g. (0.00028 mole) of stilbene, m.p. 116–118°. Fractions 16 and 17 yielded 0.178 g. (0.00079 mole) of 4-methoxystilbene, m.p. 134–135°. Fractions 24–27 gave 0.066 g. (0.00028 mole) of 4,4′-dimethoxystilbene, m.p. 210–212°. Fractions 32–50 contained 1.4 g. (0.0058 mole) of 4-methoxybenzalazine melting at 80–82°. Each of the products was further identified by infrared comparison with authentic samples.

Pyrolysis of Benzalazine in 4,4′-Dimethoxystilbene.—A mixture of 0.40 g. (0.0019 mole) of benzalazine and 1.2 g. (0.005 mole) of 4,4′-dimethoxystilbene was heated in the pyrolysis apparatus to 300 ± 5° at which temperature an evolution of nitrogen became apparent. This temperature was maintained for 35 min., when the gas evolution had ceased and 38 ml. (corrected to room temperature, 88%) of gas had been collected. No attempt was made to isolate benzonitrile. The crude reaction product was chromatographed on a 2.5 × 113 cm. silica gel column slurry packed with 1:3 benzene–hexane; 250-ml. fractions were collected. Fractions 1–6 were obtained by elution with 1:3 benzene–hexane, fractions 7 and 8 with 1:1 benzene–hexane, 9,10 with benzene, 11–16 with 1:4 chloroform–benzene, 17 and 18 with 2:3 chloroform–benzene, and 25–34 with chloroform. Fractions 2–4 afforded 0.182 g. (0.00099 mole) of stilbene, m.p. 112–115°. Fractions 14–28 yielded 1.15 g. (0.0048 mole) of 4,4′-dimethoxystilbene, m.p. 209–212°, and fractions 33 and 34 gave 0.046 g. (0.00015 mole) of lophine, m.p. 271–274°. Each of these products was further identified by its infrared spectrum.

Pyrolysis of Benzalazine in 4-Methoxybenzonitrile.—A mixture of 0.52 g. (0.0025 mole) of benzalazine and 0.33 g. (0.0025 mole) of 4-methoxybenzonitrile was heated in the pyrolysis apparatus to 265° for 55 min. at the end of which time 27 ml. (0.00096 mole) of nitrogen had been collected. The reaction flask was then fitted with a 22-cm. Vigreux column attached to a Dry Ice-cooled receiver. The pot was then heated to 100° at 0.001 mm. for 4 hr. affording 8 mg. of distillate having the odor of benzonitrile and 0.325 g. (0.0025 mole) of *p*-methoxybenzonitrile which sublimed into the column. The non-volatile residue was chromatographed on a 4.3 × 75 cm. silica gel column slurry packed with 1:3 benzene–hexane and 250-ml. fractions were collected. Fractions 1–3 were obtained by elution with with 1:3 benzene–hexane, 4–6 with 1:1 benzene–hexane, 7–9 with 3:1 benzene–hexane, 10 and 11 with benzene, 12 and 13 with 1:4 chloroform–benzene, 14–17 with 1:1 chloroform–benzene, and 18–33 with chloroform. Fractions 2–4 afforded 0.192 g. (0.001 mole) of stilbene melting at 118–120°. Fractions 27–32 were combined to yield a brown tacky solid weighing 0.25 g. This was extracted with 50 ml. of hot hexane and the extracts were treated with activated charcoal,

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[26] W. Wislicenus and H. Wren, *Ber.*, **38**, 506 (1905).

[27] W. Mann, *ibid.*, **14**, 1646 (1881).

filtered and concentrated to yield 0.105 g. (0.0005 mole) of benzalazine, m.p. 90–92°. The residue from the hexane extraction was washed with 5 ml. of ether, leaving as an ether-insoluble residue 0.021 g. (0.00007 mole) of lophine, m.p. 270–273°. The chromatographic fractions which would elute mono- and dimethoxystilbenes were void of material.

Pyrolysis of Benzalazine in the Presence of Hydrazine.—A mixture of 1.0 g. (0.0048 mole) of benzalazine and 0.025 g. (0.00078 mole) of 85% hydrazine hydrate was heated in the pyrolysis apparatus to 235° at which temperature the evolution of nitrogen began; this temperature was maintained for 90 min. when the evolution of gas ceased, a total of 83 ml. (corrected to room temperature 80%) had been collected. The crude product was chromatographed on a 30 × 44 cm. column of silica gal slurry packed in 35:65 benzene–hexane, elution being with the same solvent. The first 600 ml. contained 0.365 g. (0.002 mole) of stilbene, m.p. 115–118°.

Pyrolysis of Benzalazine in the Presence of Sodium Hydroxide.—A mixture of 1.0 g. (0.0048 mole) of benzalazine and 0.05 g. (0.00125 mole) of sodium hydroxide was heated in the pyrolysis apparatus to 230° at which temperature nitrogen evolution became perceptible; this ceased at the end of 100 min. at this temperature when 82 ml. (corrected to room temperature, 80%) had been collected. Chromatography as in the preceding experiment afforded in the first 600 ml. of eluent 0.32 g. (0.0018 mole) of stilbene, m.p. 117–120°.

Pyrolysis of Benzalazine in the Presence of Tribenzylamine.—A mixture of 1.0 g. (0.0048 mole) of benzalazine and 5.0 g. (0.0174 mole) of tribenzylamine was heated in the usual pyrolysis apparatus to 250° at which temperature the evolution of nitrogen became appreciable. Heating at this temperature was continued for 90 min. when the gas evolution ceased and when a total of 100 ml. (corrected to room temperature 0.0045 mole) of gas had been collected. The product was chromatographed on a 3 × 80 cm. silica gel column slurry packed with 5:95 benzene–hexane and 200-ml. fractions were collected. Fractions 1–4 were eluted with 5:95 benzene–hexane, 5–11 with 1:9 benzene–hexane, 12–14 with 1:4 benzene–hexane, 15–18 with 3:7 benzene–hexane, 19–24 with 1:1 benzene–hexane, 25 and 26 with 7:3 benzene–hexane, 27 and 28 with benzene, 29–30 with 1:3 chloroform–benzene, 31–34 with 1:1 chloroform–benzene, 35 and 36 with 3:1 chloroform–benzene, and 37–60 with chloroform. Fractions 5–9 afforded 0.47 g. (0.0026 mole) of stilbene, m.p. 117–120°. Fractions 19–26 gave 5.0 g. (100%) of tribenzylamine, m.p. 90–92°. Fractions 55–59 yielded 0.22 g. (0.00073 mole) of lophine, m.p. 270–273°.

The Reactiviy of 4-Methoxybenzalazine under Miscellaneous Conditions.—There was no gas evolution when 4-methoxybenzalazine was heated under each of the following conditions: refluxing in decalin at 193° for 30 min., refluxing in decalin at 193° in the presence of 0.20 g. of copper powder for 30 min., refluxing in diphenyl ether at 259° for 30 min., refluxing in diphenyl ether in the presence of 0.20 g. of copper powder for 30 min.

Pyrolysis of Benzalazine in 2-Ethoxynaphthalene.—A mixture of 1.0 g. (0.0048 mole) of benzalazine and 5.0 g. of 2-ethoxynaphthalene was heated in the pyrolysis apparatus to 282° for 2.5 hr. giving 85 ml. (corrected to room temperature, 0.0018 mole) of gas. The reaction product was chromatographed on a 3.8 × 100 cm. silica gel column slurry packed with 1:3 benzene–hexane, and 250-ml. fractions were collected. Fractions 1–6 were eluted with 1:3 benzene–hexane, 7 and 8 with 3:7 benzene–hexane, 9 and 10 with 1:1 benzene–hexane, 11 and 12 with benzene, 13 and 14 with 1:9 chloroform–benzene, 15 and 16 with 3:7 chloroform–benzene, 17 and 18 with 3:2 chloroform–benzene, 19–32 with chloroform. Fractions 2 and 3 afforded 0.52 g. (0.0028 mole) of stilbene, m.p. 115–117°; fractions 5–10 gave 5.0 g. of 2-ethoxynaphthalene, m.p. 35–36°. Fractions 32 and 33 contained 0.050 g. 1(0.00016 mole) of lophine, m.p. 271–274°.

The Reactivity of Benzalazine at 212°.—A 1.0-g. sample of benzalazine in 5.0 g. of *p*-methoxyanisole was heated to 210° for 1 hr. with no evolution of gas.

Pyrolysis of a Mixture of Benzalazine with Phenyldiazomethane.—A mixture of 1.18 g. (0.0057) of benzalazine and 0.020 g. (0.00017 mole) of phenyldiazomethane was heated in the usual pyrolysis apparatus to 180° for 80 min. at the end of which time the gas evolution ceased and 24 ml. (corrected to room temperature, 0.0011 mole) had been collected. The product was chromatographed on a 3.8 × 87 cm. silica gel column slurry packed with 1:3 benzene–hexane with collection of 250-ml. fractions. Fractions 1–4 were eluted with 1:3 benzene–hexane, 5 and 6 with 2:3 benzene–hexane, 7–9 with 3:2 benzene–hexane, 10 and 11 with 4:1 benzene–hexane, 12 and 13 with benzene, 14–16 with 1:9 chloroform–benzene, 17 and 18 with 3:7 chloroform–benzene, 19 and 20 with 3:2 chloroform–benzene, 21 and 22 with 4:1 chloroform–benzene, 23 and 24 with 9:1 chloroform-benzene, and 25–36 with chloroform. Fractions 3 and 4 afforded 0.085 g. (0.00047 mole) of stilbene, m.p. 116–118°, and fractions 25–36 gave 0.962 g. (0.00462 mole) of benzalazine, m.p. 90–92°.

In a second run 1.00 g. (0.0048 mole) of benzalazine and 0.012 g. (0.0001mole) of pure phenyldiazomethane (checked with benzoic acid in a nitrometer) were heated together to 155° at which temperature the evolution of nitrogen became appreciable. At the end of 80 min. at this temperature 12 ml. of gas (corrected to room temperature, 0.00054 mole) had been collected and its evolution had ceased. The crude product was chromatographed on a 3.8 × 87 cm. silica gel column slurry packed with 1:3 benzene–hexane; 250-ml. fractions were collected: 1–4 with 1:3 benzene–hexane, 5 and 6 with 1:1 benzene–hexane, 7 and 8 with benzene, 9 and 10 with 1:9 chloroform–benzene, 11 and 12 with 1:1 benzene–chloroform, and 13–32 with chloroform. Fractions 3–6 gave 0.052 g. (0.00028 mole) of stilbene, m.p. 115–118°. Fractions 17–30 yielded 0.943 g. (0.0045 mole) of benzalazine, m.p. 90–92°.

Decomposition of Phenyldiazomethane in Benzene.—A solution of 0.28 g. (0.0022 mole) of phenyldiazomethane in 5.0 ml. of benzene was refluxed for 15 hr. at the end of which time the red color of the phenyldiazomethane had completely disappeared. The residue left after concentration *in vacuo* was chromatographed on a 2.5 × 100 cm. silica gel column slurry packed with 1:3 benzene–hexane; 250-ml. fractions were collected: 1–4 with 1:3 benzene–hexane, 5 with 3:2 benzene–hexane, 6 and 7 with benzene, 8 with 1:9 chloroform–benzene, 9 with 3:7 chloroform–benzene, 10 and 11 with 3:2 chloroform–benzene, and 12–17 with chloroform. Fraction 2 afforded 0.024 g. (0.00013 mole) of stilbene, m.p. 117–119°. Fractions 6 and 7 gave 0.032 g. of a product, melting at 305–308° (rapid temp. rise). Fractions 11–16 contained 0.16 g. (0.00077 mole) of benzalazine, m.p. 89–91°. The high melting solid from fractions 6 and 7 was crystallized from benzene–hexane to a constant m.p. of 298–299°.

Anal. Calcd. for C_7H_6: C, 93.29; H, 6.71. Found: C, 93.67; H, 6.59.

Pyrolysis of a Mixture of Anisalazine, Benzalazine and Phenyldiazomethane.—A 1.00-g. (0.0037 mole) sample of anisalazine was heated with 0.30 g. (0.00026 mole) of phenyldiazomethane and 0.27 g. of benzalazine. At the end of 180 min. at 150° the nitrogen evolution ceased and a total of 67 ml. (0.0029 mole, corrected to room temperature) had been collected. The product was chromatographed on a 3.8 × 87 cm. silica gel column slurry packed with 1:3 benzene–hexane; 250-ml. fractions were eluted: 1–6 with 1:3 benzene–hexane, 7–10 with 2:3 benzene–hexane, 11–13 with 3:2 benzene–hexane, 14–17 with 3:1 benzene–hexane, 18–21 with benzene, 22–25 with 1:19 chloroform–benzene, 26–30 with 1:3 chloroform–benzene, 31–33 with 1:1 chloroform–benzene, 34–37 with 3:2 chloroform–benzene, 38–41 with 3:1 chloroform–benzene, 42–48 with chloroform.

Fractions 2 and 3 gave 0.0139 g. (0.000077 mole) of stilbene, m.p. 117–120°. Fractions 11–14 gave 0.021 g. (0.000095 mole) of 4-methoxystilbene, m.p. 130–132°, identified also by mixed m.p. Fractions 25–29 contained 0.185 g. (0.00076 mole) of 4,4′-dimethoxystilbene, m.p. 206–210°. Fractions 34–37 afforded 0.0368 g. (0.00028 mole) of only slightly impure anisonitrile, m.p. 40–43°, identified also by its infrared spectrum. Fractions 48–56 contained 0.85 g. of a deep brown liquid which did not afford pure fractions on alumina chromatography.

Pyrolysis of 4-Methoxybenzalazine with Added Phenyldiazomethane.—A 1.00-g. (0.0042 mole) sample of 4-methoxybenzalazine was heated with 0,10 g. (0.00085 mole) of phenyldiazomethane in the usual pyrolysis apparatus. The evolution of nitrogen became noticeable at 145° and ceased after heating had been continued for 45 min. at this temperature. The total volume collected at room temperature was 68 ml. (0.0030 mole). The product was chromatographed on a 3.8 × 87 cm. silica gel column slurry packed with 1:3 benzene–hexane, and 250-ml. fractions were collected: fractions 1–4 with 1:3 benzene–hexane, 5 and 6 with 2:3 benzene–hexane, 7–10 with 3:2 benzene–hexane, 11 and 12 with 3:1 benzene–hexane, 13 and 14 with benzene, 15 and 16 with 1:19 chloroform–benzene, 17–20 with 1:3 chloroform–benzene, 21 and 22 with 1:1 chloroform–benzene, 23 and 24 with 4:1 chloroform–benzene, and 25–31 with chloroform.

Fractions 3–5 gave 0.0712 g. (0.00039 mole) of stilbene, m.p. 119–121°; fractions 9–12 afforded 0.251 g. (0.0012 mole) of 4-methoxystilbene, m.p. 131–133°. Fractions 17–20 yielded 0.0436 g. (0.0001 mole) of 4,4'-dimethoxystilbene, m.p. 209–210°; fractions 25–30 contained 0.061 g. (0.00045 mole) of nearly pure anisonitrile, m.p. 42–44°. Fractions 31–34 afforded 0.51 g. of a tarry material. This was chromatographed on a 2.5 × 50 cm. alumina column (Merck 71707) slurry packed with benzene; 100-ml. fractions were collected: fractions 1–5 with benzene, 6–8 with 1:4 chloroform–benzene, 9–11 with 2:3 chloroform–benzene, 12 and 13 with 7:3 chloroform–benzene and 14 and 15 with chloroform. Fractions 12 and 13 afforded 0.027 g. (0.000085 mole) of lophine, m.p. 262–266°, and fraction 15 gave a very small quantity (less than 10 mg.) of bis-1,2-(4-methoxyphenyl)-3-phenylcyclopropane, m.p. 215–218°.

Ultraviolet Irradiation of Phenyldiazomethane and Benzalazine in Benzene Solution.—A mixture of 2.011 g. (0.0095 mole) of benzalazine and 0.0731 g. (0.00062 mole) of phenyldiazomethane was dissolved in 15.0 ml. of benzene in a 50-ml. Pyrex flask fitted with a condenser and provided with a side thermocouple well. The solution was magnetically stirred and irradiated with a 125 watt Hanovia mercury vapor lamp for 1 hr. maintaining the temperature of the reactants at 17° with external cooling. The reaction mixture was then concentrated *in vacuo* and the residue chromatographed on a 2.5 × 31 cm. silica gel column slurry packed with 3:7 benzene–hexane; 250-ml. fractions were collected: 1–3 with 3:7 benzene–hexane, 4 with benzene, 5–8 with chloroform. Fraction 5–8 afforded 2.081 g. (0.010 mole) of benzalazine melting at 89–90°

Thermal Reaction of Phenyldiazomethane and Benzalazine in Benzene Solution.—A solution of 2.037 g. (0.0098 mole) of benzalazine and 0.0761 g. (0.000645 mole) of phenyldiazomethane in 15.0 ml. of benzene was refluxed for 1 hr. The mixture was concentrated under vacuum and the residue chromatographed on a 2.5 × 31 cm. silica gel column slurry packed with 3:7 benzene–hexane; 250-ml. fractions were collected: 1–3 with 3:7 benzene–hexane, 4 with benzene, 5–8 with chloroform. Fractions 2 and 3 afforded 0.0086 g. (0.0000477 mole) of stilbene; and fractions 5–8 yielded 2.1025 g. (0.010 mole) of benzalazine, m.p. 89–90°.

Pyrolysis of Benzalazine in the Presence of Oxygen.—A 2.019-g. (0.0097 mole) sample of benzalazine was placed in a 3 neck flask fitted with a capillary inlet for oxygen reaching to the flask bottom, a thermocouple well and a Dry Ice trap. The system was flushed with oxygen for 15 min. and the flask was then heated to 300° with oxygen passing through the capillary inlet. Part of the benzalazine sublimed. At the end of 10 min. the combined product was taken up in ether and concentrated under vacuum. The residue was subjected to heating to 120° at 0.2 mm. for 2 hr. with a Dry Ice-cooled receiver in order to remove volatile reaction products; the receiver contained 0.2665 g. of volatile material. One-fifth of this material was used for an infrared spectrum; this showed hydroxyl, carbonyl and cyano bands and indicated a mixture of ethanol, benzonitrile and benzaldehyde. The remainder of the volatile fraction was treated with 5.0 ml. of an aqueous solution containing 1.0 g. of semicarbazide hydrochloride and 1.0 g. of sodium acetate; 1.0 ml. of ethanol was then added and the mixture was heated on a steam-bath for 2 min. and cooled. On standing, the solution afforded 0.0420 g. of crystalline semicarbazone melting at 215–217° (benzaldehyde semicarbazone melts at 222°). The filtrate from the semicarbazone was made alkaline to litmus with 10% sodium hydroxide and ether extracted. The extract was dried over sodium sulfate and concentrated *in vacuo*. The residue weighed 0.0251 g. and proved to be benzonitrile by infrared comparison with an authentic sample. The yields, corrected for the material used for infrared analysis, were 0.00030 mole of benzaldehyde and 0.0003 mole of benzonitrile.

The non-volatile fraction was chromatographed on a 1.9 × 64 cm. silica gel column slurry packed with 1:3 benzene–hexane; 250 ml. fractions were collected: 1–3 with 1:3 benzene–hexane, 4–5 with benzene, 6–8 with 1:4 chloroform–benzene, 9–10 with 1:1 chloroform–benzene, 11–16 with chloroform. Fractions 1–2 afforded 0.2221 g. (0.00123 mole) of stilbene, m.p. 115–117°, identified by infrared comparison. Fractions 6–10 gave 1.4690 g. (0.00706 mole) of benzalazine, m.p. 85–87°, infrared agreeing with an authentic sample; fraction 16 consisted of 0.2066 g. of a dark brown viscous liquid which on trituration with 5 ml. of ether gave 0.0412 g. of 2,4,5-triphenylimidazole, m.p 270–272°.

To determine whether benzalazine reacts with oxygen at a temperature below that of its ordinary decomposition, a 1.048-g. (0.0050 mole) sample of benzalazine was heated to 235° in the above apparatus for 20 min. with bubbling of oxygen as before. The reaction product obtained proved to be unchanged benzalazine. The infrared spectrum was identical to that of benzalazine and showed no carbonyl or nitrile bands.

Irradiation of a Mixture of Benzalazine and Phenyldiazomethane in Dioxane.—A solution of 1.1008 g. (0.00528 mole) of benzalazine and 2.8784 g. (0.0244 mole) of phenyldiazomethane in 700 ml. of aldehyde- and acetal-free 90% aqueous dioxane was placed in a 700-ml. irradiation cell fitted with quartz windows and provided with stirrer, ketyl-purified nitrogen inlet, glass thermocouple well and cooling coils through which cold water was passed. The cell was irradiated with a 1000 watt AH6 G.E. lamp in a parabolic reflector; a Corning 9–53 glass filter cutting off radiation below 250 mmμ was used. The irradiation was begun after flushing with nitrogen for 15 min. and continued at 28° for 2 hr. Concentration of the dioxane solution afforded 2.9466 g. of a yellow, viscous oil. This was chromatographed on a 3.8 × 65 cm. silica gel column slurry packed in 1:3 benzene–hexane; 250 ml. fractions were collected: 1–4 with 1:3 benzene–hexane, 5–6 with 1:1 benzene-hexane, 7–8 with benzene, 9–10 with 1:4 chloroform–benzene, and 11–30 with chloroform. Fraction 3 afforded 0.0158 g. (0.000087 mole) of slightly impure stilbene, m.p. 110–115°. Fractions 9–16 gave 0.1329 g. of an uncharacterized yellow oil. Fractions 20–30 yielded 2.796 g. (0.0134 mole) of benzalazine, m.p. 88–90° identified by its infrared spectrum.

Irradiation of Benzalazine Alone in Dioxane.—The above experiment was repeated with 2.100 g. (0.010 mole) of benzalazine in 700 ml. of aldehyde- and acetal-free 90% aqueous dioxane. Again the 9–53 glass filter was used. The photolysis was for 2 hr. at 28°. Concentration gave 2.098 g. of benzalazine, m.p. 88–90°.

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