This compound could be distilled at atmospheric pressure without polymerization, b.p. 296–297° at 750 mm., but some slight decomposition due to oxidation occurred, and a slight odor of formaldehyde was noted in the product.

The densities, refractive indices, molar refractions, melting points and heats of vaporization of the siloxanes are listed in Table I. The latent heats of vaporization were obtained from the slopes of straight line plots of log p *vs.* T^{-1} using the boiling points of the siloxanes at various temperatures.

The cylic methylvinylsiloxanes had similar infrared absorption spectra, but with slight shifts in certain peaks with different compounds. The tetramer exhibited the following principal peaks: 3.28 μ (C–H); 3.33 μ (C–H); 3.39 μ (C–H); 6.25 μ (C=C); 7.11 μ (C–H); 7.95 μ (C–H); 9.32 μ (Si–O); 9.94 μ (C=C); 10.43 μ (C=C); 12.14 μ (Si–C); 13.02 μ; 13.36 μ; and 14.65 μ.

1,3-Divinyltetramethyldisiloxane.[7]—A mixture of 100 ml. of acetone, 10 ml. of 0.1 N hydrochloric acid and 20.9 g. of vinyldimethylethoxysilane[6] (b.p. 99°, $n^{20}\mathrm{D}$ 1.3982, d^{20}_4 0.7934) was refluxed for 4 hours. The acetone was then distilled and the oil was washed with water, dried over calcium chloride and distilled to give 13.0 g. (61%) of 1,3-divinyltetramethyldisiloxane, b.p. 139°. The properties of this siloxane are listed in Table I.

Addition of Bromine to Methylvinylsiloxanes.—The addition of bromine to the methylvinylsiloxanes in carbon tetrachloride or carbon disulfide solution was slow but quantitative. The addition reaction was found to be very rapid in acetic acid solution or in the absence of solvent.

(a) $[(CH_3)(CH_2{=}CH)SiO]_4$.—A solution of 1.00 g. of the tetramer in 10 ml. of acetic acid absorbed 1.90 g. of Br_2 corresponding to 103% of the theoretical amount. The solvent was removed under vacuum and residual octabromide remained as a liquid, $n^{20}\mathrm{D}$ 1.5621. A solution of bromine in CCl_4 (0.113 g. of Br_2 per g. of solution) was added over a period of 4 hours at −30 to −10° to a solution of 1.00 g. of $[(CH_3)(CH_2{=}CH)SiO]_4$ in 10 ml. of CCl_4 until 3 drops of bromine solution caused a yellowish-brown color lasting for 1 hour. A total of 16.0 g. of solution (1.81 g. Br_2) was used, equivalent to 98% of the theoretical amount. The solvent could be removed under vacuum, leaving the liquid octabromide as before.

(b) $[(CH_3)(CH_2{=}CH)SiO]_5$.—A solution of 1.05 g. of the pentamer in 10 ml. of acetic acid absorbed 1.94 g. of Br_2 corresponding to 100% of the theoretical amount. The decabromide separated during the reaction but did not interfere with the titration. The solvent was removed under vacuum to leave the liquid decabromide, $n^{20}\mathrm{D}$ 1.5663.

(c) $[(CH_3)(CH_2{=}CH)SiO]_6$.—One gram of the hexamer in 10 ml. of acetic acid absorbed 1.80 g. of Br_2 corresponding to 98% of the theoretical amount. The dodecabromide was quite insoluble in acetic acid. The last traces of acid were removed under vacuum to leave the liquid dodecabromide, $n^{20}\mathrm{D}$ 1.5680.

(d) $[(CH_3)_2(CH_2{=}CH)Si]_2O$.—One gram of $[(CH_3)_2(CH_2{=}CH)Si]_2O$ in 10 ml. of acetic acid absorbed 1.74 g. of bromine corresponding to 101% of the theoretical amount. The solvent was removed under vacuum to leave the liquid tetrabromide, $n^{20}\mathrm{D}$ 1.5322.

Reaction of Methyldibromoethylsiloxanes with Methanolic Potassium Hydroxide.—A solution of 14.3 g. (0.0145 mole) of $[(CH_3)(CH_2BrCHBr)SiO]_4$ in 250 ml. of methanol was placed in a 500-ml. 3-necked flask equipped with addition tube, stirrer and a water-cooled condenser, the top of which was connected to a trap immersed in a Dry Ice–acetone bath. The open end of the trap was protected with a by-pass stream of dry nitrogen. A solution of 25 g. of 85% potassium hydroxide (0.38 mole) in 80 ml. of methanol was added to the stirred and refluxing methanol solution over a period of one-half hour, during which time a precipitate of potassium bromide formed in the flask and vinyl bromide collected in the trap. The mixture was refluxed for an additional one-half hour, then most of the methanol was removed by distillation. The residue in the flask was dissolved in 150 ml. of water. Upon acidification of this solution with 6 N HCl, a precipitate of polymethyltrisiloxane (methyl-T gel) was formed. It was filtered and air-dried to a constant weight of 3.85 g., 99% of the theoretical amount.

The vinyl bromide was distilled in a low-temperature Podbielniak column, b.p. 0° at 400 mm.

Similarly, the other bromo derivatives $[(CH_3)(CH_2BrCHBr)SiO]_5$, $[(CH_3)(CH_2BrCHBr)SiO]_6$ and $[(CH_3)_2(CH_2BrCHBr)Si]_2O$ reacted with methanolic potassium hydroxide to produce vinyl bromide and the corresponding potassium silanolates.

Polymerization of Methylvinylsiloxanes.—A solution of 6 g. of $[(CH_3)(CH_2{=}CH)SiO]_5$ in 200 g. of octamethylcyclotetrasiloxane, $[(CH_3)_2SiO]_4$, was heated to 150° and 0.02 g. of solid cesium hydroxide was added with stirring. The catalyst dissolved, and within 10 minutes the mixture had become a very stiff, rubbery polymer (gum). This gum was soluble in toluene, but it could be cross-linked and rendered insoluble by treating it with 0.1% benzoyl peroxide at 120°.

Acknowledgment.—The authors wish to thank Mr. J. G. Keil for assistance, and Dr. J. R. Ladd for a generous supply of methylvinyldiethoxysilane and dimethylvinylethoxysilane.

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(7) This compound was first obtained by this method in this Laboratory by M. Cohen and J. R. Ladd.

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cis- and *trans-*2-Styrylquinolinium Compounds[1a]

BY LESTER HORWITZ

RECEIVED AUGUST 20, 1954

2-Styrylquinolines and their salts may exist as *cis* and *trans* isomers, although such isomers never have been reported. Räth and Lehmann[1b] have isolated *cis* and *trans*-2-*o*-nitrostilbazole, which they were able to separate by fractional crystallizations. During a study of the preparation of 1-methyl-2-(*m*-nitrostyryl)-6-ethoxyquinolinium methosulfate, photographically important as a desensitizing dye, it appeared that this compound could be prepared in *cis* and *trans* forms with different ultraviolet absorption spectra. The methods employed were extended to the preparation of other *cis* and *trans*-2-styrylquinolinium salts.[1c]

It seems possible to assign a *trans* configuration to the 2-styrylquinolinium compounds prepared by the piperidine-catalyzed condensation of quinaldinium salts with aromatic aldehydes (Table I) on the basis of ultraviolet spectra. The main peaks of these compounds generally appeared at longer wave length of 25 to 75 mμ than did the main peaks of their isomers, prepared by the quaternation of 2-styrylquinolines, obtained from the condensation of quinaldines with aromatic aldehydes in acetic anhydride (Table III). To these latter compounds a *cis* structure is assigned. In the case of the *cis* configuration, coplanarity of the entire molecule is expected to be inhibited which would prevent full chromophoric conjugation. Depending on the degree of steric hindrance, there will be either a displacement of the absorption peak to shorter wave lengths or a fall in the extinction coefficient (or both) displayed by the spectrum of the *cis* when compared to that of the *trans* form.[2a] A change occurring only in the intensity of absorption with steric inhibition of coplanarity has been suggested as resulting from a transition between a non-planar

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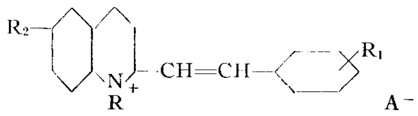
(1) (a) Presented before the Organic Division of the American Chemical Society at New York City, Sept., 1954; (b) C. Räth and E. Lehmann, *Ber.*, **58B**, 342 (1925). (c) The extension of these methods to the stilbazole series will be the subject of a future communication.

(2) (a) E. A. Braude, E. R. H. Jones, H. P. Koch, R. W. Richardson, F. Sondheimer and J. B. Toogood, *J. Chem. Soc.*, 1890 (1949); (b) E. A. Braude, F. Sondheimer and W. F. Forbes, *Nature*, **173**, 117 (1954).

TABLE I[a]

PIPERIDINE-CATALYZED CONDENSATION OF QUINALDINIUM SALTS WITH AROMATIC ALDEHYDES (METHOD A)

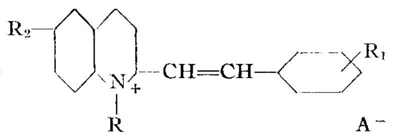


	R	R₁	R₂	A⁻	Yield, %	M.p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	λ, mμ[b]	ε
I	CH_3–	*p*-NO_2–	H	Methosulfate	91	283–285	$C_{19}H_{18}N_2O_6S$	56.68	57.24	4.51	4.65	6.96	7.29	302	17,500
														365	25,900
II	CH_3–	*m*-NO_2–	H	Methosulfate	99	203–204	$C_{19}H_{18}N_2O_6S$	56.68	56.60	4.51	4.64	6.96	7.14	362	47,000
III	CH_3–	3,4-Methylenedioxy–	H	Methosulfate	90	262–263	$C_{20}H_{19}NO_6S$	59.84	59.85	4.77	4.74	3.49	3.71	423	35,200
IV[c]	C_2H_5–	(*p*-$CH_3)_2N$–	H	Iodide	87	249–250								278[d]	10,600
														324	11,900
														524	151,000
V	CH_3–	*p*-NO_2–	C_2H_5O–	Methosulfate	79	278–279	$C_{21}H_{22}N_2O_7S$	56.48	56.70	4.97	5.10	6.28	6.15	310	29,000
														388	31,000
VI	CH_3–	*m*-NO_2–	C_2H_5O–	Methosulfate	93	268–269	$C_{21}H_{22}N_2O_7S$	56.48	56.45	4.97	5.03	6.28	6.27	302	44,000
														385	39,900
VII	CH_3–	3,4-Methylenedioxy–	C_2H_5O–	Methosulfate	73	249–250	$C_{22}H_{23}NO_7S$	59.30	58.91	5.20	4.90	3.14	3.28	356	25,600

[a] Solvent of recrystallization was methanol in all cases. [b] Based on 10^{-5} *M* in methanol [c] Reference 12, m.p. 249°. [d] Estimated from broad band.

TABLE III[a]

FROM 2-STYRYLQUINOLINES PREPARED WITH ACETIC ANHYDRIDE (TABLE II)

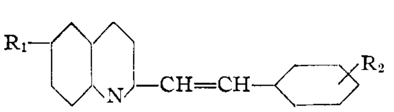


	R	R₁	R₂	A⁻	M.p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	λ, mμ[b]	ε
XV	CH_3–	*p*-NO_2–	H	Methosulfate	303–310	$C_{19}H_{18}N_2O_6S$					6.96	7.23	250	27,500
													342	23,000
XVI	CH_3–	*m*-NO_2–	H	Methosulfate	237–238	$C_{19}H_{18}N_2O_6S$	56.68	56.61	4.51	4.36	6.96	6.99	275	40,000
													318[c]	26,000
XVII	CH_3–	3,4-Methylenedioxy–	H	Methosulfate	261–262	$C_{20}H_{19}NO_6S$	59.84	59.59	4.77	4.68	3.49	3.59	348	21,000
XVIII	C_2H_5–	*p*-$(CH_3)_2N$–	H	Iodide	231–232	$C_{21}H_{23}IN_2$	58.61	58.50	5.39	5.46	6.51	6.43	266	25,100
													320	20,100
													524	141,000
XIX	CH_3–	*p*-NO_2–	C_2H_5O–	Methosulfate	249–250	$C_{21}H_{22}N_2O_7S$					6.28	6.31	262	22,900
													360	21,500
XX	CH_3–	*m*-NO_2–	C_2H_5O–	Methosulfate	252–253	$C_{21}H_{22}N_2O_7S$	56.48	56.64	4.97	5.00	6.28	6.21	285	31,200
													360	22,800
XXI	CH_3–	3,4-Methylenedioxy–	C_2H_5O–	Methosulfate	281–282	$C_{22}H_{23}NO_7S$	59.30	59.24	5.20	5.19	3.14	3.13	263	15,800
													307	15,200

[a] Quaternation by methyl sulfate was carried out in nitrobenzene on the steam-bath (see under method B). The ethiodide XVIII was obtained by heating the base (XI) with an excess of ethyl iodide in a bomb at steam-bath temperature for 12 hours. Only XVIII was isolated even when a huge excess of ethyl iodide was used, and it is presumed that XVIII corresponds to the more stable monoquaternary form with the ethiodide group quaternating the heterocyclic nitrogen. All were purified by recrystallization from methanol. [b] Based on 10^{-5} *M* in methanol. [c] Estimated from broad band.

TABLE II[a]

2-STYRYLQUINOLINES OBTAINED BY THE CONDENSATION OF QUINALDINES WITH AROMATIC ALDEHYDES IN ACETIC ANHYDRIDE (METHOD B)



	R_1	R_2	Yield, %	M.p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
VIII[b]	H	*p*-NO_2–	95	172–173							
IX[c]	H	*m*-NO_2–	97	157–158							
X[d]	H	3,4-Methylenedioxy–	94	156–157							
XI[e]	H	*p*-$(CH_3)_2N$–	87	185–186							
XII	C_2H_5O–	*p*-NO_2–	99	168–169	$C_{19}H_{16}N_2O_3$	71.25	71.25	5.04	5.16	8.75	8.68
XIII	C_2H_5O–	*m*-NO_2–	98	148–148.5	$C_{19}H_{16}N_2O_3$	71.25	71.32	5.04	5.06	8.75	9.00
XIV	C_2H_5O–	3,4-Methylenedioxy–	96	190–191	$C_{20}H_{17}NO_3$	75.20	75.20	5.37	5.51	4.39	4.57

[a] Solvent of recrystallization in all cases was methanol. [b] Reference 7 reported m.p. 171–172°. [c] Above reference, m.p. 157–158°; reference 13, m.p. 154–155°. [d] C. Renz and K. Loew, *Ber.*, **36**, 4330 (1903), m.p. 249°, by heating for five hours in bomb at 110°. [e] Reference 15, m.p. 184–185°.

ground state and a planar excited state.[2b] This may be the case with *cis*- and *trans*-1-ethyl-2-(*p*-dimethylaminostyryl)-quinolinium iodide (compounds XVIII and IV), and it is hoped to investigate this feature further.

The mechanism for the piperidine-catalyzed condensation of a quinaldinium salt with an aldehyde has been dealt with by Mills and co-workers[3a,b] and on an electronic basis appears analogous to the aldol condensation.[4] The last step can be visualized as an elimination reaction in which it is reasonable to expect the quinolyl and phenyl groups to assume *trans* positions in the final state.

Quaternation of the 2-styrylquinolines should not be expected to change any pre-existing geometric configuration. Structural specificity then should have arisen during the condensation of the quinaldines with aromatic aldehydes in acetic anhydride. Phenylquinaldylcarbinols have been shown to be formed by the interaction of quinaldines with aromatic aldehydes.[5,6] Walton, Tipson and Cretcher[7] have prepared *m*- and *p*-nitrophenylquinaldylcarbinols and their acetates, and they have converted these to *m*- and *p*-nitrostyrylquinolines in acetic anhydride. If one invokes an acetate decomposition as the final step in the formation of the styryl compounds, then a *cis* configuration is explainable. The formation of an olefin by the pyrolysis of a carboxylic ester appears to be a transformation related to the thermal decomposition of a xanthate, the Chugaev reaction. Evidence indicates that these decompositions occur as *cis* eliminations, for which cyclic six-membered transition states are envisaged.[8a,b] The decomposition of the quinaldylcarbinol acetate would be facilitated by resonance contributions from the phenyl and quinolyl groups to the cyclic transition state. For such resonance contribution, coplanarity between these groups and the cyclic structure is required. A *cis*-styryl compound then is obtained as a final product (Fig. 1).

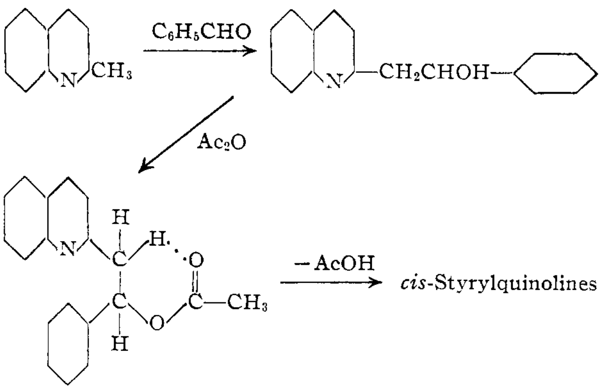


Fig. 1.—Probable steps for the formation of the *cis* compounds.

Several experimental findings are worthy of mention. In some cases the yield obtained from the piperidine-catalyzed condensation of the quinaldinium salt with the aromatic aldehyde (Table I and method A) depended on the rapidity with which a reflux temperature was reached. This is evident in the formation of 1-methyl-2-(*m*-nitrostyryl)-6-ethoxyquinolonium methosulfate (VI), whose preparation has been described previously.[9,10] It was found in this case that when the time required to achieve reflux temperature was prolonged the yield of isolable styryl product decreased; if too prolonged, no styryl product could be isolated. However, by bringing the condensation mixture to reflux temperature within a very short time excellent yields are obtained. Another example is found in the case of the formation of 1-ethyl-2-(*p*-dimethylaminostyryl)-quinolinium iodide (IV). Hamer[11] found that she could improve the yield for this compound from 23 to 76% by increasing the time of heating reported by König and Treichel[12] from one to 24 hours. In this case, too, by attaining a reflux temperature quickly an excellent yield (87%) was obtained in 40 minutes. All the yields obtained by this quick heating method were good.

All the 2-styrylquinolines listed in Table II were

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(3) (a) W. H. Mills and J. L. B. Smith, *J. Chem. Soc.*, **121**, 2724 (1922); (b) W. H. Mills and R. Raper, *ibid.*, **127**, 2466 (1925).

(4) R. C. Elderfield, "Heterocyclic Compounds," Vol. 4, John Wiley and Sons, Inc., New York, N. Y., 1952, p. 86.

(5) C. T. Bahner and E. S. Pace, THIS JOURNAL, **74**, 3932 (1952).

(6) F. Bell, *J. Chem. Soc.*, 348 (1953).

(7) A. F. Walton, R. S. Tipson and L. H. Cretcher, THIS JOURNAL, **67**, 1501 (1945).

(8) (a) E. R. Alexander and A. Mudrak, *ibid.*, **72**, 1810 (1950); **72**, 3194 (1950); **73**, 59 (1951); (b) G. L. O'Connor and H. R. Nace, *ibid.*, **75**, 2118 (1953).

(9) German Patent 296,402 (May 31, 1924) and 468,093 (Oct. 25, 1928).

(10) M. A. Atabekova, I. N. Gorbacheva and I. I. Levkoev, *Analinodrasochnays Prom.*, **4**, 609 (1934); *C. A.*, **29**, 25379 (1935).

(11) F. M. Hamer, *J. Chem. Soc.*, **127**, 211 (1925).

(12) W. König and O. Treichel, *J. prakt, Chem.*, **102**, 63 (1921).

prepared by condensation in acetic anhydride (method B). The general applicability of acetic anhydride for such condensations has been reported on by Kaslow and Stayner[13] and by Shaw and Wagstaff.[14] An inferior yield of 13% was reported by Tipson[15] for use of this method in preparing 2-(*p*-dimethylaminostyryl)-quinoline (XI). The 87% yield reported here can be attributed to the longer heating period employed.

Experimental

Piperidine-catalyzed Condensation of Quinaldinium Salts with Aromatic Aldehydes. Method A.—1-Methylquinaldinium methosulfate was purified by several recrystallizations from isopropyl alcohol, m.p. 151–152° (lit.[16] m.p. 223–224°).

Anal. Calcd. for $C_{12}H_{15}NO_4S$: C, 53.51; H, 5.62; N, 5.20. Found: C, 53.60; H, 5.81; N, 5.37.

After recrystallizations from isopropyl alcohol 1-methyl-6-ethoxyquinaldinium methosulfate melted 134–135° (lit.[10] m.p. 98°).

Anal. Calcd. for $C_{14}H_{19}NO_5S$: C, 53.64; H, 6.11; N, 4.47. Found: C, 53.50; H, 6.08; N, 4.38.

The preparation of all the 2-styrylquinolinium compounds shown in Table I was essentially the same as that described below for 1-methyl-2-(*m*-nitrostyryl)-6-ethoxyquinolinium methosulfate (VI).

A mixture of 18.8 g. (0.06 mole) of 1-methyl-6-ethoxyquinaldinium methosulfate, 9.1 g. (0.06 mole) of *m*-nitrobenzaldehyde and 1 ml. of piperidine in 100 ml. of isopropyl alcohol was brought to reflux temperature in two minutes. Refluxing then was continued for an additional 40 minutes. The reaction mixture was cooled and the product collected by filtration. After washing with ice-water and drying, there was obtained 25 g. of the styryl salt, which melted at 266–267°, yield 93%.

Condensation of Quinaldines with Aromatic Aldehydes in Acetic Anhydride. Method B.—All the 2-styrylquinolines shown in Table II were prepared essentially as described below for 2-(*m*-nitrostyryl)-6-ethoxyquinoline (XIII). This procedure is essentially analogous to that described by Kaslow and Stayner.[13]

A mixture of 18.7 g. (0.1 mole) of 6-ethoxyquinaldine, 15.1 g. (0.1 mole) of *m*-nitrobenzaldehyde and 8.0 g. (0.06 mole) of acetic anhydride was heated under reflux for six hours. The hot solution was poured into excess cold water. After standing overnight the product was collected by filtration. The crude material was dried, yield 31 g. (98%), m.p. 137–139°.

Quaternation was effected by heating 5 g. (0.016 mole) of the above base with 3.8 g. (0.03 mole) of methyl sulfate in 10 ml. of nitrobenzene on the steam-bath until a solution was obtained (about 5 minutes). After cooling, the product (XX) was collected by filtration, washed well with ether, and dried; yield 6.1 g. (89%), m.p. 252–253°, after recrystallizations from methanol.

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[13] C. E. Kaslow and R. O. Stayner, THIS JOURNAL, **67**, 1717 (1945).

[14] B. D. Shaw and E. A. Wagstaff, *J. Chem. Soc.*, 77 (1933).

[15] R. S. Tipson, THIS JOURNAL, **67**, 507 (1945).

[16] H. Rupe, H. Hagenbach and A. Collin, *Helv. Chim. Acta*, **18**, 1395 (1935).

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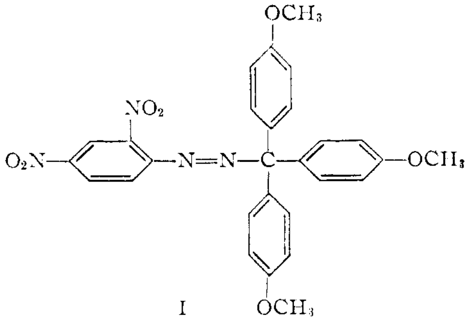
The Reductive Decomposition of an Azo Compound

BY J. E. LEFFLER AND L. M. BARBATO

RECEIVED SEPTEMBER 29, 1954

In connection with a study of the effects of solvent and structural changes on the free radical decomposition of organic compounds and on the shift to polar reaction mechanisms we have studied the azo compound 2,4-dinitrophenylazotris-(*p*-anisyl)-methane (I).



I

We found, however, that we were hampered in our original purpose by the tendency of the azo compound to be reduced to the corresponding hydrazo compound. With three nitro substituents the effect should be still more pronounced and we were in fact unable to prepare 2,4,6-trinitrophenyl-azo-tris-(*p*-anisyl)-methane by oxidation of the hydrazo compound.

In benzene at 75° the dinitro compound I is half reduced to the hydrazo compound and half decomposed to a complicated mixture of products suggestive of a radical reaction. In other radical decomposition reactions a frequent feature has been the displacement of hydrogen atoms from the solvent by attacking free radicals.[1] It is not generally believed that atomic hydrogen is set free in such reactions but only that a second radical accepts the hydrogen atom at some stage, perhaps by reaction with a radical–solvent complex. We suspect that in the decomposition of the azo compound I, molecules of the undecomposed azo compound play the role ordinarily played by a second free radical, accepting hydrogen from a solvent–radical complex and becoming reduced to the hydrazo compound. The first-order rate constant for the formation of radicals from the azo compound in benzene at 75° in the presence of α,α-diphenyl-β-picrylhydrazyl is about 10^{-4} sec.$^{-1}$ as determined by the fading of the diphenylpicrylhydrazyl color. Since α,α-diphenyl-β-picrylhydrazyl reacts, but not instantaneously, with 2,4-dinitrophenylhydrazo-tris-(*p*-anisyl)-methane, the rate constant is only an approximate one.

Experimental

2,4-Dinitrophenylhydrazotris-(*p*-anisyl)-methane.—To a boiling benzene solution of 1.3 g. of 2,4-dinitrophenylhydrazine is added 1 g. of trianisylmethyl chloride, the mixture boiled for one hour, filtered and the filtrate concentrated to dryness. The residue after washing with warm alcohol is crystallized several times from chloroform–alcohol; the product melts at 165–168°.

Anal.[3] Calcd. for $C_{28}H_{26}N_4O_7$: C, 63.38; H, 4.94. Found: C, 63.08, 62.82; H, 4.86, 4.73.

2,4-Dinitrophenylazotris-(*p*-anisyl)-methane.—The hydrazo compound in chloroform solution is shaken with excess lead dioxide and anhydrous sodium sulfate for one week at room temperature. Crystallization from chloroform–alcohol gives orange crystals, m.p. 132–133°. Unless the characteristic hydrazo absorption band at 3300 cm.$^{-1}$ is absent, the oxidation is repeated. The infrared spectrum of

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[1] D. I. Relyea and D. F. DeTar, THIS JOURNAL, **76**, 1202 (1954); D. F. DeTar and S. V. Sagmanli, *ibid.*, **72**, 965 (1950); C. E. Boozer and G. S. Hammond, *ibid.*, **76**, 3862 (1954); G. S. Hammond, J. T. Rudesill and F. J. Modic, *ibid.*, **73**, 3229 (1951).