

along with our results at 24.4°, are given in Table VII.

TABLE VII

RATES AND EQUILIBRIA FOR THE ANILINE-2,4-DINITROCHLOROBENZENE REACTION IN ABSOLUTE ETHANOL

Temp., °C.	k_2 , l. mole ⁻¹ hr. ⁻¹	K , l. mole ⁻¹
24.4	0.29	0.45
35.0	.46	.19
45.0	.77	.10

From the slope of a plot of $\ln K$ vs. $1/T$, we can estimate ΔH° for the equilibrium between the complex and aniline and 2,4-dinitrochlorobenzene. Using the expressions $\Delta F^\circ = -RT \ln K$ and $\Delta H^\circ =$

TABLE VIII

ENTROPY, FREE ENERGY AND HEAT CONTENT OF THE ANILINE-2,4-DINITROCHLOROBENZENE MOLECULAR COMPLEX EQUILIBRIUM

Temp., °C.	ΔH° , kcal. mole ⁻¹	ΔF° , cal. mole ⁻¹	ΔS° , cal. mole ⁻¹
24.4	-13.1	+472	-45.8
35.0	-13.1	+1020	-46.0
45.0	-13.1	+1460	-45.9

$\Delta F^\circ - T\Delta S^\circ$, we can estimate ΔF° , ΔH° and ΔS° for this equilibrium. The results are presented in Table VIII.¹³

The data of Table VI permit us to draw some conclusions as to the effect of solvent on the extent of complexing between aniline and 2,4-dinitrochlorobenzene. Complexing is most extensive in the most polar solvent, ethanol, and is either absent or occurs to only a slight extent in the least polar solvent, ethyl acetate. In a mixture of these two solvents, the equilibrium constant has the expected intermediate value. The observed effect is that predicted by both Weiss^{4a} and Mulliken^{4d} for complexing of the charge-transfer type and lends support to their theories.

Acknowledgment.—It is a pleasure to acknowledge helpful and stimulating discussion with Prof. C. Gardner Swain of the Massachusetts Institute of Technology and with Drs. Fielding Brown and George J. Kahan of these laboratories.

(13) It is also possible to plot both $\ln k_2$ and $\ln k_1$ vs. $1/T$ and then to calculate the heat, entropy and free energy of activation for both k_1 and k_2 .

NORTH ADAMS, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

Mechanisms of Elimination Reactions. XI. Alkaline Dehydrobromination of Isomers of β -Bromostyrene and of *p*-Nitro- β -bromostyrene^{1,2}

BY STANLEY J. CRISTOL AND WILLIAM P. NORRIS

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Reaction-rate constants and quantities of activation for the dehydrobromination of the *cis* and *trans* isomers of β -bromostyrene and of *p*-nitro- β -bromostyrene with sodium hydroxide in isopropyl alcohol have been measured. The effect of the *p*-nitro substituent was found to be significantly greater in elimination of *cis* elements of hydrogen bromide than elimination of *trans* groups. The data are discussed in terms of a concerted process for *trans* elimination and a multiple-stage, carbanion-intermediate process for *cis* elimination.

It has been previously proposed²⁻⁴ that at least two mechanisms exist for base-promoted dehydrohalogenation of alkyl halides (and in general, for bimolecular elimination reactions). One of these has been described as a concerted process in which the removal of the proton by base is believed to be synchronous with the formation of the multiple bond and loss of halide ion. The second process has been termed "multiple-stage" and is presumed to involve a rate-determining removal of a proton by base yielding a carbanion, which then loses a halide ion to give the olefinic product. Elimination of *trans* groups has been assumed to use the concerted process, whereas *cis* elimination has been assumed to involve the multiple-stage process. Isotopic evidence that a carbanion intermediate is involved in elimination from β -benzene hexachloride has been described recently.²

A consequence of this dual mechanistic scheme

(1) This paper was presented in part before the Division of Organic Chemistry at the Spring 1953 meeting of the American Chemical Society in Los Angeles, California.

(2) Previous paper in series: S. J. Cristol and D. D. Fix, *THIS JOURNAL*, **75**, 2647 (1953).

(3) (a) S. J. Cristol, *ibid.*, **69**, 338 (1947); (b) S. J. Cristol, N. L. Hause and J. S. Meek, *ibid.*, **73**, 674 (1951); (c) S. J. Cristol and A. Begoon, *ibid.*, **74**, 5025 (1952).

(4) S. I. Miller and R. M. Noyes, *ibid.*, **74**, 629 (1952).

(see below for extended discussion) is that the appropriate placing of electron-attracting or electron-withdrawing groups on the β -carbon atoms should have a greater effect upon the multiple-stage process, where the carbanion is being formed, than on the concerted process, where much of the negative charge is being dispersed to the departing halogen rather than to the β -carbon atom. Accordingly data on elimination from the *cis* and *trans* isomers of β -bromostyrene and *p*-nitro- β -bromostyrene should be a test of this theory.

Product Study.—As ethanol was found to be an unsuitable solvent for the alkaline dehydrobromination of *trans-p*-nitro- β -bromostyrene, due to the formation of the ethyl acetal of *p*-nitrobenzaldehyde rather than the *p*-nitrophenylacetylene desired,⁵ the first problem was to find a solvent in which one could prove that elimination occurred. As sodium *t*-butoxide in *t*-butyl alcohol ordinarily is sluggish in addition to multiple bonds,⁶ this was first studied. It was found that *trans-p*-nitro- β -bromostyrene (the slower eliminating isomer) gave an 88% yield of *p*-nitrophenylacetylene upon

(5) S. J. Cristol, A. Begoon, W. P. Norris and P. S. Ramey, unpublished work.

(6) F. Beyerstadt and S. M. McElvain, *THIS JOURNAL*, **58**, 529 (1936); **59**, 2266 (1937).

treatment with this reagent. The reaction of the *cis* isomer was too fast to measure conveniently, however, in this solvent at room temperature, and *t*-butyl alcohol cannot be used as a solvent at low temperatures because of its melting point of about 25°.

Sodium hydroxide in isopropyl alcohol was next tried as a reagent. The reactions were found to go at convenient rates. *trans*- β -Bromostyrene gave 80% of the theoretical phenylacetylene (isolated as the mercuric derivative). *trans*-*p*-Nitrophenyl- β -bromostyrene gave considerably less than the theoretical amount of *p*-nitrophenylacetylene when treated with this reagent, but the fact that elimination was the initial step in the reaction could fortunately be demonstrated. The dehydrobromination of 232 mg. of this material was allowed to proceed to 54% completion, and the products were separated by chromatographic analysis. Ninety-eight per cent. (of theoretical) of the unreacted *p*-nitro- β -bromostyrene was isolated, along with 20% (of theoretical) of *p*-nitrophenylacetylene and 39% (calculated as diisopropyl acetal of *p*-nitrobenzaldehyde) of non-crystalline material. The nature of this oil was not investigated. As noted above, in ethanol the corresponding ethyl acetal is produced.⁵ A major share of the approximately 40% discrepancy in recovery can probably be attributed to loss of the fairly volatile *p*-nitrophenylacetylene under the conditions of the product isolation. A control experiment was then run to determine to what extent *p*-nitrophenylacetylene reacted with sodium hydroxide and isopropyl alcohol when exposed for the same length of time as in the dehydrobromination. Accordingly, 80 mg. of *p*-nitrophenylacetylene (the amount which would theoretically be formed in the dehydrobromination above) was exposed to the same concentration of alkali in isopropyl alcohol for the time calculated by integration to give the same exposure. Thirty per cent. of the original *p*-nitrophenylacetylene was recovered and a 30% yield (based upon the isopropyl acetal) of an oil was obtained also. The similarity in recovery in the two experiments indicates that the major initial reaction product is *p*-nitrophenylacetylene and that this solvent is satisfactory for elimination studies. *cis*-*p*-Nitro- β -bromostyrene gave excellent yields of *p*-nitrophenylacetylene with sodium hydroxide in 95% ethanol at room temperature,⁵ and it is safe to assume that this would also be true in isopropyl alcohol. *cis*- β -Bromostyrene was converted to the expected elimination product, phenylacetylene.

Measurement of Reaction Rates.—The rates were determined in isopropyl alcohol which was dried over calcium oxide before use, and the extent of reaction was determined by Volhard titrations for halide ion, substantially as described previously.³ A refrigerated thermostatted bath was used for temperatures below 20° and temperature control was $\pm 0.03^\circ$. A thermostatted water-bath was used between 20 and 45° and temperature control was $\pm 0.02^\circ$. Above 45° a thermostatted oil-bath was used and temperature control varied from ± 0.03 to $\pm 0.05^\circ$, with poorer control at the higher temperatures. *cis*- β -Bromostyrene

and *cis*- and *trans*-*p*-nitro- β -bromostyrene were run in volumetric flasks; *trans*- β -bromostyrene was run in sealed Pyrex test-tubes. The calculation of rate constants was done as described previously.³ Corrections of rate constant for expansion or contraction of solvent⁷ were made when appropriate. The rate data are given in Table I.

TABLE I
SECOND-ORDER RATE CONSTANTS FOR THE DEHYDROBROMINATION OF VARIOUS *cis*- AND *trans*- β -BROMOSTYRENES WITH SODIUM HYDROXIDE IN ISOPROPYL ALCOHOL

Compound	Temp., °C.	Halide, M	NaOH, M	10 ⁴ k, l./mole/ sec.	
<i>cis</i> - <i>p</i> -Nitro- β - bromostyrene	2.02	0.003433	0.01311	607	
		.003449	.007678	625	
		.003454	.007678	632	
			Av.	621	
	10.36	.003489	.007664	1730	
		.003503	.007664	1730	
			Av.	1730	
	22.15	.003499	.007565	5250	
		.003438	.007565	5230	
			Av.	5240	
	<i>trans</i> - <i>p</i> -Nitro- β - bromostyrene	43.04	.009987	.1262	2.48
			.01004	.1922	2.45
			Av.	2.46	
50.12		.01005	.2011	4.54	
		.01004	.2011	4.62	
			Av.	4.58	
61.40		.009899	.1849	15.3	
		.01089	.1849	15.2	
		.01000	.09645	16.8	
			Av.	15.8	
<i>cis</i> - β -Bromo- styrene		22.15	.01196	.1048	2.85
			.01111	.1048	2.83
			Av.	2.84	
	32.37	.01184	.1036	9.29	
		.01212	.1036	9.15	
			Av.	9.22	
	43.04	.01055	.06703	31.8	
		.01127	.06698	31.4	
		.009571	.1151	28.4	
			Av.	30.5	
	<i>trans</i> - β -Bromo- styrene	97.57	.01098	.3449	0.230
			.01000	.3449	.226
.01067			.1724	.240	
.01024			.1724	.247	
			Av.	.236	
107.42		.01018	.3796	.667	
		.01024	.3796	.660	
		.01025	.1898	.758	
		.01007	.1898	.764	
			Av.	.712	
118.27		.01045	.3755	2.14	
		.009747	.3755	2.08	
	.01015	.1878	2.51		
	.01033	.1878	2.55		
	.01041	.1879 ^a	2.55		
	.009339	.1879 ^a	2.66		
		Av.	2.42		

^a These solutions also contained sodium perchlorate, 0.1876 M.

(7) N. A. Lange, "Handbook of Chemistry," Sixth Ed., Handbook Publishers, Inc., Sandusky, Ohio, 1946, p. 1590.

Plots of rate data for the compounds studied gave good straight lines to at least 50% reaction and the rates were often followed to above 75% reaction. The constants for *cis-p*-nitro- β -bromostyrene began to drift down slightly at 75% reaction but this was not observed with the other compounds. A decrease in base concentration consistently produced a slight increase in second-order rate constant for the whole series of compounds. The differences appeared to be greater at higher temperatures. The possibility that this was due to an unusual salt effect was tested at 118° with *trans*- β -bromostyrene. Addition of sodium perchlorate to the more dilute base solution to increase the ionic strength to that of the more concentrated solution did not affect the rate constant. No evidence is at hand to explain these small effects, but they are not considered serious enough to invalidate the results for the purposes of the discussion which follows.

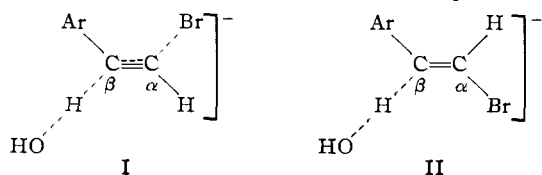
Discussion of Results.—Activation energies and entropies were calculated in the usual fashion³ from the data in Table I, and these data and rate constants read off the activation energy curves at 43° are summarized in Table II. It will be noted that, as usual,^{3,4} the *cis*- β -bromostyrenes (H,Br *trans*) react significantly more rapidly than the corresponding *trans* isomers, but that the ratios in rate constants are significantly different, being 210,000 for the unsubstituted series and 16,000 for the *p*-nitro compounds. It is of interest to compare the relative effects of a *p*-nitro substituent in *trans* elimination and in *cis* elimination. Such a substituent compared with hydrogen in the *cis* series (*trans* elimination) increases the rate of elimination by a factor of about 1200 and lowers the energy of activation by 4 kcal./mole. On the other hand, in *cis* elimination (*trans* compounds), the effect is much more marked, the rate constant ratio being approximately 18,000 and the activation energy difference being 10.5 kcal./mole.

TABLE II
RATE CONSTANTS AND QUANTITIES OF ACTIVATION AT 43°
FOR THE DEHYDROBROMINATION WITH SODIUM HYDROXIDE
IN ISOPROPYL ALCOHOL OF VARIOUS β -BROMOSTYRENES

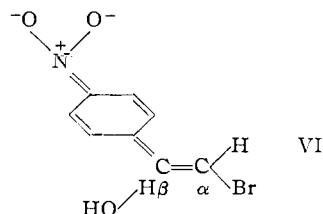
β -Bromo- styrene	k_1 , l./mole/ sec.	$\frac{k_{cis}}{k_{trans}}$	$E_{act.}$, kcal./ mole	ΔS^\ddagger , cal./ mole/ deg.
<i>cis-p</i> -Nitro	3.71×10^{10}	1.6×10^4	17.1	- 4.0
<i>trans-p</i> -Nitro	2.36×10^{-4}		21.3	-10.0
<i>cis</i>	3.00×10^{-3}	21×10^4	21.1	- 5.6
<i>trans</i>	1.4×10^{-8a}		31.8	+ 4.0

^a These rate constants were obtained by extrapolation.

The smaller differences in rate constant and activation energies for *trans* elimination can be interpreted in terms of the two mechanisms proposed for elimination. The transition states for the concerted process and for the carbanion-intermediate process may be indicated by I and II, respectively.³

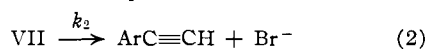
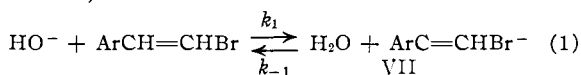


In the transition state for carbanion formation (II) a much larger negative charge is being developed upon the carbon atom β to the halogen than in the transition state for the concerted process (I).³ It would be expected that an electron-withdrawing group such as a nitro group would aid either process by decreasing the magnitude of this negative charge. In addition to the various resonance structures which can be formulated for the carbanion transition state for *trans*- β -bromostyrene and which would also apply to *trans-p*-nitro- β -bromostyrene, an additional structure VI can be drawn for the *p*-nitro system. This structure would also contribute to the transition state for the concerted process, but would be of much less importance because



of the lesser magnitude of the negative charge on C_β . Hence the dual mechanism theory would predict that a *p*-nitro group on the aryl ring would stabilize II more than I. The results then are in accord with predictions and illustrate the greater sensitivity of the carbanion-intermediate process to the electrical effects of substituents on C_β .

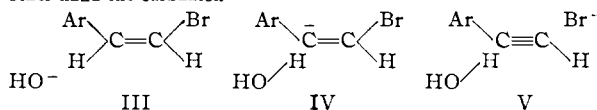
The alternative explanation that both *cis* and *trans* elimination in these systems involve a carbanion, *viz.*



may be considered briefly.

As the carbanion intermediate VII is mesomeric and thus would be common to both *cis* and *trans* elimination, it is not possible for k_2 to be rate determining for both members of an isomeric set. It is possible for k_1 to be the rate-controlling constant for the less reactive (*trans*) isomers and k_2 to be rate controlling for the more reactive isomers. This does not seem sound for, as noted above, the *p*-nitro compounds are much more reactive than the unsubstituted compounds in both *cis* and *trans* elimination, and one would not anticipate that $p\text{-O}_2\text{NC}_6\text{H}_4\text{C}=\text{CHBr}]^-$ would decompose to *p*-nitrophenylacetylene and bromide ion 1200 times more rapidly than the much less stable unsubstituted ion to the analogous substances. Further, one might expect to find the more reactive isomer rearranging to the less reactive one, if step (1) were reversible

(8) It may be useful to assume that the concerted transition state I is derived from contributions from resonance structures III, IV and V, plus whatever structures are permissibly derived from these. On the other hand the carbanion



process transition state II is derived only from structures analogous to III and IV.

and non-stereospecific; this has not been observed. The hydrogen-deuterium exchange predicted by the carbanion mechanism has not been investigated.

It has been observed that the entropy of activation for *cis* elimination is often higher than that for *trans* elimination,³ although there are at least three exceptions to this rule.^{4,9} This more favorable activation entropy term for *cis* elimination is observed with *trans*- β -bromostyrene ($\Delta S^\ddagger = 4.0$ e.u.) and *cis*- β -bromostyrene ($\Delta S^\ddagger = -5.6$ e.u.). However, an opposite entropy effect is observed with *p*-nitro- β -bromostyrenes where the *trans* isomer (*cis* elimination) has $\Delta S^\ddagger = -10$ e.u. as compared with the *cis* isomer value for ΔS^\ddagger of -4 e.u. These facts may be rationalized in terms of solvation effects on the transition-state ion and the reacting molecules.¹⁰ In the transition state for carbanion formation II in *cis* elimination the negative charge is spread over a three-membered system with most of the charge concentrated on the β -carbon and on the oxygen. The β -carbon has groups around it which may sterically hinder solvation^{8b,11} to such an extent that formation of the transition-state ion is attended with the usual desolvation of the oxygen but with only a little solvation of the β -carbon, resulting in a net liberation of solvent molecules and producing a positive entropy effect. In the case of the concerted mechanism the transition-state ion I has the negative charge spread over a five-membered system but the charge is probably concentrated on the oxygen and bromine where solvation would not be sterically hindered. Thus the number of molecules of solvent involved in solvation need not change appreciably during transition-state ion formation. The *trans*-*p*-nitro- β -bromostyrene case is a special one in which the negative charge in the transition state for carbanion formation may reside chiefly on the *para* nitro group where there is little steric hindrance to solvation. This would result in a lesser entropy of activation than for carbanion formation from *trans*- β -bromostyrene.

Acknowledgments.—The authors wish to acknowledge support of this work by a contract with the Office of Naval Research and by the American Cyanamid Company for a research fellowship for one of us (W.P.N.). The analyses were carried out by the Galbraith Laboratories.

Experimental

Standard Solutions.—Sodium hydroxide containing less than 0.01% halide was dissolved in isopropyl alcohol which had been dried over and distilled from calcium oxide; the solution was allowed to sit undisturbed for at least three days to let the sodium carbonate settle before it was standardized by titration with standard hydrochloric acid using phenolphthalein indicator. Enough water was always added to the base sample in the titration flask to reduce the isopropyl alcohol concentration to 20 or 25% at the endpoint. The concentration of sodium hydroxide in the

standard isopropyl alcohol solutions was usually between 0.2 and 0.4 *N*. A saturated solution of sodium hydroxide in isopropyl alcohol at room temperature is about 0.46 *N*. The standard base solution was kept in a constant temperature bath at 22°.

Solutions of 0.03 *N* silver nitrate and 0.02 *N* potassium thiocyanate were prepared from the reagent-grade chemicals and standardized by the Volhard procedure.

cis-*p*-Nitro- β -bromostyrene, m.p. 48–49°, was prepared by treatment of *trans*-*p*-nitrocinnamic acid dibromide with sodium acetate in absolute ethanol, substantially as described by Reich and Chang¹² and Dann, Howard and Davies.¹³ Considerable improvement in the ease of purification of the product was effected by selective adsorption on and desorption from activated alumina.

cis- β -Bromostyrene, m.p. -7 to -6° , was prepared by treatment of *trans*-cinnamic acid dibromide with sodium bicarbonate in dry acetone.¹⁴ The compound had n_D^{20} 1.6007 and n_D^{25} 1.5983. Grovenstein and Lee¹⁵ report n_D^{25} 1.5980.

1,1-Dibromo-2-(*p*-nitrophenyl)-ethane.—This compound was prepared by a procedure adapted from those outlined for similar reactions.^{16,17} Seventy grams (0.50 mole) of recrystallized *p*-nitroaniline was dissolved in a hot solution of 135 ml. of 48% hydrogen bromide and 50 ml. of water. The solution was stirred rapidly and cooled to 0° in an ice-salt mixture. Fifty grams of ice was added followed by a solution of 35 g. (0.50 mole) of sodium nitrite in 60 ml. of water. The addition of the sodium nitrite solution required one-half hour. The temperature was kept between -4 and $+4^\circ$. Stirring was continued for an additional 20 minutes after addition of the sodium nitrite solution. The diazotized *p*-nitroaniline solution was then added, over a period of 45 minutes, to an acetone solution to which had been added 40 g. (0.50 mole) of sodium acetate in 50 ml. of water, 22 g. (0.10 mole) of cupric bromide in 50 ml. of water and 52 ml. (0.75 mole) of vinyl bromide. The reaction mixture was maintained at -3 to $+5^\circ$. The solution was then allowed to warm to room temperature and was stirred for an additional 2 hours, then was warmed to 45°. After being cooled to room temperature, the solution was extracted with 500 ml. of ether. The ether extract was washed 4 times with 500-ml. portions of water. The ether was evaporated and 130 g. of crude, dark-colored product was obtained. This product was dissolved in carbon tetrachloride and passed over an alumina column containing about 100 g. of Fisher activated alumina (80–200 mesh). Most of the dark colored material was removed in this way. One hundred and twenty grams (77%) of crude product, m.p. 50–60°, was obtained. After several recrystallizations from cyclohexane, the compound melted at 79–79.5°.

Anal. Calcd. for $C_8H_7Br_2NO_2$: C, 31.09; H, 2.28. Found: C, 31.22; H, 2.19.

trans-*p*-Nitro- β -bromostyrene.—One hundred and fifteen grams of crude 1,1-dibromo-2-(*p*-nitrophenyl)-ethane, m.p. 50–60°, was dissolved in 250 ml. of 95% ethanol and treated with 20 g. of sodium hydroxide in 100 ml. of ethanol. The sodium hydroxide solution was added slowly with stirring and cooling of the reaction vessel. *trans*-*p*-Nitro- β -bromostyrene began to crystallize from solution soon after the initial addition of sodium hydroxide solution. After completion of the addition of the sodium hydroxide solution the reaction mixture was cooled and filtered. The crystals on the filter were washed with water several times and dried. A yield of 43 g. (50% based upon crude starting material) of *trans*-*p*-nitro- β -bromostyrene, m.p. 156–157°, was obtained. A mixed m.p. with an authentic sample prepared by irradiation of the *cis* isomer¹² was not depressed.

trans- β -Bromostyrene, m.p. 6–7°, was obtained by partial freezing of the redistilled, b.p. 65–75° (4 mm.) commercial (Eastman Kodak Co.) mixture, m.p. -1 to 4° , followed by recrystallization at -40° from methanol. The compound had n_D^{20} 1.6100 and n_D^{25} 1.6076. Grovenstein and Lee¹⁵ report n_D^{25} 1.6071.

(9) F. Stermitz, Master's thesis, University of Colorado, 1951.

(10) See: ref. 4; S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes" McGraw-Hill Book Co., New York, N. Y., 1941, p. 417; A. F. Chadwick and E. Pacsu, *THIS JOURNAL*, **65**, 392 (1943); J. Gripenberg, E. D. Hughes and C. K. Ingold, *Nature*, **161**, 480 (1948); J. F. Lane and H. W. Heine, *THIS JOURNAL*, **73**, 1348 (1951); R. G. Pearson, *J. Chem. Phys.*, **20**, 1478 (1952); J. K. Kochi and G. S. Hammond, *THIS JOURNAL*, **75**, 3445 (1953); H. W. Heine, E. Becker and J. F. Lane, *ibid.*, **75**, 4514 (1953).

(11) A. von Egidy, Master's thesis, University of Colorado, 1949.

(12) S. Reich and N. Y. Chang, *Helv. Chim. Acta*, **3**, 235 (1920).

(13) A. T. Dann, A. Howard and W. Davies, *J. Chem. Soc.*, 805 (1928).

(14) S. J. Cristol and W. P. Norris, *THIS JOURNAL*, **75**, 2645 (1953).

(15) E. Grovenstein, Jr., and D. E. Lee, *ibid.*, **75**, 2639 (1953).

(16) H. Meerwein, E. Büchner and K. van Emster, *J. prakt. Chem.*, **152**, 237 (1939).

(17) E. Müller, *Angew. Chem.*, **61**, 179 (1949).

Treatment of *trans*-*p*-Nitro- β -bromostyrene with Sodium *t*-Butoxide in *t*-Butyl Alcohol.—A solution of 2.00 g. (0.0088 mole) of *trans*-*p*-nitro- β -bromostyrene in 250 ml. of *t*-butyl alcohol was added to 50 ml. of *t*-butyl alcohol in which 200 mg. (0.0088 mole) of sodium had been dissolved. The reaction was kept at 43° for 24 hours. The solvent was removed under reduced pressure, water was added to dissolve the inorganic residues and 1.23 g. (95%) of organic material, m.p. 140–143°, was collected on a filter. Recrystallization of the material from ethanol gave 1.08 g. (83%) of almost pure *p*-nitrophenylacetylene, m.p. 147–148°. Müller^{18a} and Wieland^{18b} report this melting point as 149°, which m.p. we reproduced in another preparation.

Product Determination for the Treatment of *trans*-*p*-Nitro- β -bromostyrene with Sodium Hydroxide in Isopropyl Alcohol.—A solution of 580 mg. (2.54 mmoles) of *trans*-*p*-nitro- β -bromostyrene in isopropyl alcohol was added to 125 ml. of 0.256 *N* sodium hydroxide-isopropyl alcohol solution. The reaction solution was made up to 250 ml. at 43° with isopropyl alcohol. The reaction was kept at 43° for 6 hours. A 100-ml. sample was withdrawn and the reaction stopped by the addition of 1 ml. of acetic acid. A 10-ml. sample was withdrawn at the same time and was analyzed for bromide ion. The analysis showed that 54% of the *trans*-*p*-nitro- β -bromostyrene had reacted. The solvent was removed from the 100-ml. sample under reduced pressure, the residue extracted with hot petroleum ether (boiling range 60–70°) and the extract was poured onto an alumina column containing 50 g. of Fisher activated alumina (80–200 mesh). Sixteen milligrams (20% based upon reacted material) of *p*-nitrophenylacetylene, m.p. 147–148°, was eluted from the column with 2.1 l. of petroleum ether (boiling range 60–70°). The next 300 ml. of petroleum ether removed only traces of material. The next liter of petroleum ether removed 105 mg. (98% based upon unreacted material) of *trans*-*p*-nitro- β -bromostyrene, m.p. 153–155°. Carbon tetrachloride removed 46 mg. of an oil and chloroform removed another 10 mg. The oils were not identified.

Treatment of *p*-Nitrophenylacetylene with Sodium Hydroxide in Isopropyl Alcohol.—This was a control experiment to determine to what extent *p*-nitrophenylacetylene reacted with sodium hydroxide and isopropyl alcohol when exposed for the same amount of time as in the dehydrobromination of *trans*-*p*-nitro- β -bromostyrene (see previous experiment). Eighty milligrams of *p*-nitrophenylacetylene and 50 ml. of 0.256 *N* sodium hydroxide in isopropyl alcohol were placed in a 100-ml. volumetric flask and made up to volume at 43°. The reaction was kept at 43° for 4 hours and

(18) (a) C. L. Müller, *Ann.*, **212**, 122 (1882); (b) H. Wieland, *ibid.*, **328**, 233 (1903).

11 minutes. The reaction was stopped by adding 1 ml. of acetic acid. Solvent was removed under reduced pressure and the residue extracted with hot petroleum ether (boiling range 60–70°). The petroleum ether solution was poured onto an alumina column containing about 50 g. of activated alumina. Twenty-four milligrams (30%) of *p*-nitrophenylacetylene, m.p. 146–147°, was eluted from the column with 2.4 l. of petroleum ether. Carbon tetrachloride removed 33 mg. of an oil containing a little solid and chloroform removed another 10 mg. of oil.

Product Determination for the Reaction of *trans*- β -Bromostyrene with Sodium Hydroxide in Isopropyl Alcohol.—A solution of 137 mg. (0.747 mmole) of *trans*- β -bromostyrene in 70 ml. of isopropyl alcohol, 0.415 *N* in sodium hydroxide, was heated at 107° for 50 hours (89% reaction as determined by halide analysis) in sealed tubes. The sealed tubes were opened and emptied into a flask containing 1.0 g. (4.6 mmoles) of powdered mercuric oxide; then the mixture was placed on a mechanical shaker for 12 hours. The reaction mixture was filtered to remove the unreacted mercuric oxide and the residue was washed with hot acetone. Most of the solvent was then removed with an air jet. Water was added to the residue and bis-(phenylethynyl)-mercury precipitated and was filtered off and dried. There was 107 mg. (80%) of crude bis-(phenylethynyl)-mercury, m.p. 118–122°. Johnson and McEwen give m.p. 124.5–125° for this compound.¹⁹

Product Determination for the Reaction of *cis*- β -Bromostyrene with Sodium Hydroxide in Isopropyl Alcohol.²⁰—A solution of 411 mg. (2.3 mmoles) of *cis*- β -bromostyrene in 190 ml. of 0.4 *M* sodium hydroxide in isopropyl alcohol was heated at 49° for 2 hours. The solution was cooled and 200 ml. of water was added. The solution was extracted with low-boiling petroleum ether. The non-aqueous layer was washed with water and aliquots were then treated with methanolic ammoniacal silver nitrate to precipitate silver phenylacetylde. This material was filtered and washed, then dissolved in nitric acid and the silver titrated with standard potassium thiocyanate.²¹ In duplicate samples, 75 and 80% of the theoretical amount of phenylacetylene were produced. In our hands the procedure followed above gives 80–95% recovery starting with phenylacetylene. Volhard titration of the aqueous phase indicated that complete dehydrobromination had occurred.

(19) J. R. Johnson and W. L. McEwen, *THIS JOURNAL*, **48**, 469 (1926).

(20) This experiment was conducted by Mrs. Patricia S. Ramey.

(21) This procedure follows one used by the Dow Chemical Company, private communication.

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[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, WAYNE UNIVERSITY, AND UNIVERSITY OF MARYLAND]

Cyclic Dienes. VII. Quinone Adducts of Substituted 1,2-Dimethylenecyclohexanes¹

BY WILLIAM J. BAILEY,² JOSEPH ROSENBERG³ AND LEWIS J. YOUNG⁴

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As possible starting materials for the syntheses of pentacene and naphthacene derivatives, a series of ten symmetrical and unsymmetrical adducts of benzoquinone and naphthoquinone with 1,2-dimethylenecyclohexane, 4-methyl-1,2-dimethylenecyclohexane and 4,5-dimethyl-1,2-dimethylenecyclohexane were prepared.

In a previous paper⁵ in this series, 1,2-dimethylenecyclohexane (I) was converted to $\Delta^{4a(14a),7a(11a)}$ -octadecahydropentacene-6,13-dione (II) by a Diels-Alder reaction with benzoquinone. II was further converted to pentacene (III) in a 30% yield in a three-step synthesis consisting of formation of the

tetraethyltetraethiodiketal derivative and desulfurization with Raney nickel, followed by dehydrogenation with palladium. This synthesis was a marked improvement on the method of Clar and John,⁶ which involved a modified Elbs reaction on 4,6-dimethyl-1,3-dibenzoylbenzene (IV) to produce a dihydropentacene, which in turn was converted by dehydrogenation with phenanthraquinone to III in an unreported yield. Because of the many chances for isomerism, the method of Clar and John⁶,

(1) Previous paper in this series, *THIS JOURNAL*, **76**, 2251 (1954).

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(3) Office of Naval Research Fellow, Wayne University, 1950–1951.

(4) Office of Naval Research Fellow, Wayne University, 1949–1950; Atomic Energy Commission Fellow, Wayne University, 1950–1952.

(5) W. J. Bailey and M. Madoff, *THIS JOURNAL*, **75**, 5603 (1953).

(6) E. Clar and F. John, *Ber.*, **62**, 3027 (1929); **63**, 2967 (1930); **64**, 2194 (1931).