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 sample was withdrawn and the reaction stopped by the addition of 1 ml.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 sample was withdrawn at the same time and was analyzed for bromide ion.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 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 phenylacetylide. 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.

---

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

(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.

BOULDER, COLORADO

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

Cyclic Dienes. VII. Quinone Adducts of Substituted 1,2-Dimethylenecyclohexanes[1]

BY WILLIAM J. BAILEY,[2] JOSEPH ROSENBERG[3] AND LEWIS J. YOUNG[4]

RECEIVED DECEMBER 28, 1953

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 paper[5] 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 tetraethyltetrathiodiketal 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 John[6],

---

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

(2) Department of Chemistry, University of Maryland, College Park, Md.

(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).

does not appear to be well suited for the synthesis of substituted pentacenes. However, the synthesis of pentacene derivatives from the substituted octadecahydropentacenediones, such as VII, VIII, XII, XIII and XIV, appeared to be an elegant and general procedure, provided these Diels–Alder adducts were readily accessible. Since a general method for the synthesis of substituted cyclic dienes, such as V and VI, had been developed, the synthesis of various quinone adducts of these cyclic dienes was undertaken.

When 4,5-dimethyl-1,2-dimethylenecyclohexane (VI) was treated with a half-molar quantity of benzoquinone in dioxane, an 89% yield of 2,3,9,10-tetramethyl-$\Delta^{4a(14a),7a(11a)}$-octadecahydropentacene-6,13-dione (VIII) was obtained. When the 4-methyl-1,2-dimethylenecyclohexane (V) was treated with benzoquinone under the same conditions, only one (VII) of the two possible isomers was obtained in a 79% yield. The exact position of the methyl groups in the adduct was not determined, but it is very probable that the most symmetrical isomer, the 2,9-dimethylpentacene derivative VII, was obtained.

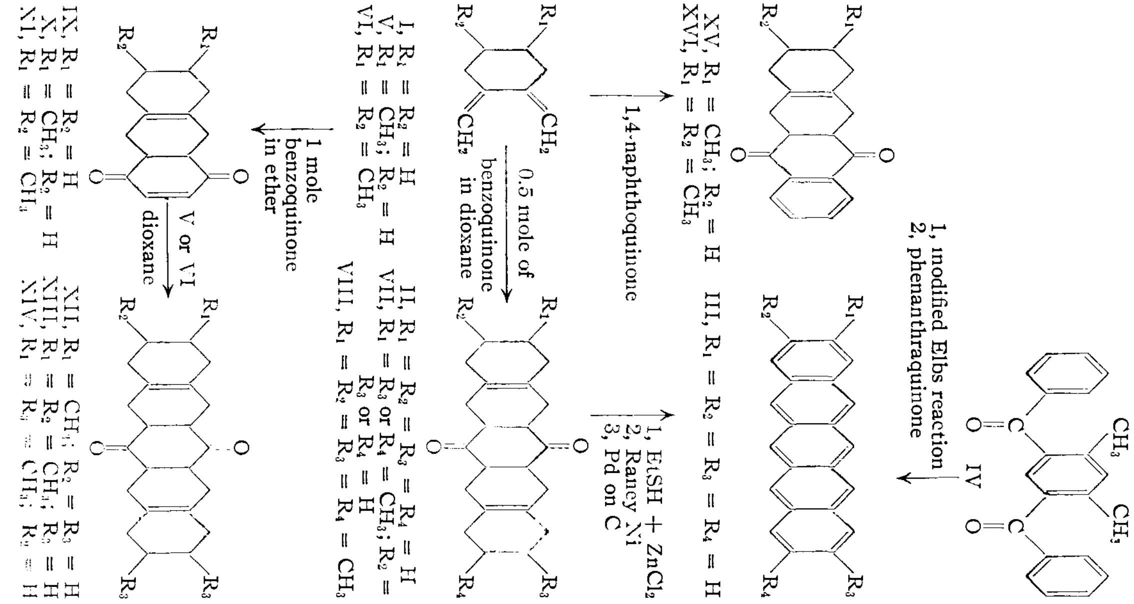

TABLE I

Compound	Yield Grams	Yield %	M.p., °C.	Diene	Amount Grams	Amount Mole	Dienophile	Amount Grams	Amount Mole	Solvent	Reflux, hours		Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
$\Delta^{2,8a(10a)}$-Decahydroanthracene-1,4-dione (IX)	20.3	94	141–142	1,2-Dimethylenecyclohexane (I)	10.8	0.10	Benzoquinone	10.8	0.10	Ether	8	$C_{14}H_{16}O_2$	77.77	78.02	7.41	7.31
6-Methyl-$\Delta^{2,8a(10a)}$-decahydroanthracene-1,4-dione (X)	11.1	96	143–144	4-Methyl-1,2-dimethylenecyclohexane (V)	6.1	.05	Benzoquinone	5.4	.05	Ether	1	$C_{15}H_{18}O_2$	78.22	78.20	7.87	7.91
6,7-Dimethyl-$\Delta^{2,8a(10a)}$-decahydroanthracene-1,4-dione (XI)	11.9	98	148–149	4,5-Dimethyl-1,2-dimethylenecyclohexane (VI)	6.8	.05	Benzoquinone	5.4	.05	Ether	2	$C_{16}H_{20}O_2$	78.69	78.92	8.19	8.26
2,3,9,10-Tetramethyl-$\Delta^{4a(14a),7a(11a)}$-octadecahydropentacene-6,13-dione (VIII)	15.9	89	229.5–230	4,5-Dimethyl-1,2-dimethylenecyclohexane (VI)	13.6	.10	Benzoquinone	5.4	.05	Dioxane	2	$C_{26}H_{36}O_2$	82.10	81.91	9.54	9.74
2,9-Dimethyl-$\Delta^{4a(14a),7a(11a)}$-octadecahydropentacene-6,13-dione (VII)	7.0	79	225–227	4-Methyl-1,2-dimethylenecyclohexane (V)	6.1	.05	Benzoquinone	2.7	.025	Dioxane	4	$C_{24}H_{32}O_2$	81.77	81.70	9.13	8.90
2,3-Dimethyl-$\Delta^{4a(14a),7a(11a)}$-octadecahydropentacene-6,13-dione (XIII)	5.2	92	188–189	4,5-Dimethyl-1,2-dimethylenecyclohexane (VI)	2.2	.16	$\Delta^{2,8a(10a)}$-Decahydroanthracene-1,4-dione (IX)	3.4	.16	Dioxane	3	$C_{24}H_{32}O_2$	81.77	81.50	9.13	9.25
2-Methyl-$\Delta^{4a(14a),7a(11a)}$-octadecahydropentacene-6,13-dione (XII)	2.0	84	196–197	4-Methyl-1,2-dimethylenecyclohexane (V)	0.85	.007	$\Delta^{2,8a(10a)}$-Decahydroanthracene-1,4-dione (IX)	1.5	.007	Dioxane	48	$C_{23}H_{30}O_2$	81.66	81.84	8.39	8.61
2,3,9-Trimethyl-$\Delta^{4a(14a),7a(11a)}$-octadecahydropentacene-6,13-dione (XIV)	5.4	83	230–231	4-Methyl-1,2-dimethylenecyclohexane (V)	1.8	.015	6,7-Dimethyl-$\Delta^{2,8a(10a)}$-decahydroanthracene-1,4-dione (XI)	4.7	.015	Dioxane	3	$C_{25}H_{34}O_2$	81.92	81.99	9.34	9.40
2-Methyl-1,2,3,4,5,5a,6,11,11a,12-decahydronaphthacene-6,11-dione (XV)	4.8	88	147–148	4-Methyl-1,2-dimethylenecyclohexane (V)	2.4	.02	1,4-Naphthoquinone	3.1	.02	Ether	8	$C_{19}H_{20}O_2$	81.43	81.18	7.14	6.92
2,3-Dimethyl-1,2,3,4,5,5a,6,11,11a,12-decahydronaphthacene-6,11-dione (XVI)	10.3	93	153.5–154	4,5-Dimethyl-1,2-dimethylenecyclohexane (VI)	5.2	.038	1,4-Naphthoquinone	6.0	.038	Ether	4	$C_{20}H_{22}O_2$	81.59	81.90	7.54	7.79

In order to prepare the possible unsymmetrical adducts, XII, XIII and XIV, a stepwise addition of the dienes to benzoquinone was attempted. When equimolar quantities of 1,2-dimethylenecyclohexane (I) and benzoquinone were refluxed in dioxane or benzene, a mixture of products was obtained. It was found, however, that the monoadduct, $\Delta^{2,8a(10a)}$-decahydroanthracene-1,4-dione (IX), was almost insoluble in boiling ether. Thus, when the reaction was carried out in ether, the monoadduct IX precipitated out as it was formed. The concentration of IX in solution was therefore very low, minimizing the formation of the diadduct II and producing a 94% yield of IX. In a similar manner, equimolar quantities of 4-methyl-1,2-dimethylenecyclohexane (V) and benzoquinone in ether produced a 96% yield of 6-methyl-$\Delta^{2,8a(10a)}$-decahydroanthracene-1,4-dione (X), and equimolar quantities of 4,5-dimethyl-1,2-dimethylenecyclohexane (VI) and benzoquinone in ether produced a 98% yield of 6,7-dimethyl-$\Delta^{2,8a(10a)}$-decahydroanthracene (XI).

If these monoadducts were treated with the appropriate diene, using dioxane as the solvent, a second molecule of diene added to the remaining activated double bond to produce the corresponding unsymmetrical diadducts. Thus, the monoadduct IX plus 4-methyl-1,2-dimethylenecyclohexane (V) produced an 84% yield of 2-methyl-$\Delta^{4a(14a),7a(11a)}$-octadecahydropentacene-6,13-dione (XII), and IX plus 4,5-dimethyl-1,2-dimethylenecyclohexane (VI) produced a 93% yield of 2,3-dimethyl-$\Delta^{4a(14a),7a(11a)}$-octadecahydropentacene-6,13-dione (XIII). In a similar reaction, the monoadduct XI plus the diene V produced an 83% yield of 2,3,9-trimethyl-$\Delta^{4a(14a),7a(11a)}$-octadecahydropentacene-6,13-dione (XIV). Thus, a very general method has been developed for the synthesis of both symmetrical and unsymmetrical pentacyclic quinone adducts that can be used as starting materials for the synthesis of substituted pentacenes.

Just as the octadecahydropentacenedione (II) was converted to pentacene (III), it was reasoned that tetracyclic derivatives, such as XV and XVI, could be converted to substituted napthacenes. These tetracyclic derivatives were available through a Diels–Alder reaction of a cyclic diene and 1,4-naphthoquinone. Thus, a solution of 1,4-naphthoquinone plus 4-methyl-1,2-dimethylenecyclohexane (V) in ether produced an 88% yield of 2-methyl-1,2,3,4,5,5a,6,11,11a,12-decahydronaphthacene-6,11-dione (XV). Similarly, 1,4-naphthoquinone plus 4,5-dimethyl-1,2-dimethylenecyclohexane (VI) produced a 93% yield of 2,3-dimethyl-1,2,3,4,5,5a,6,11,11a,12-decahydronaphthacene-6,11-dione (XVI). A general method for the synthesis of unsymmetrical naphthacene derivatives is now possible.

Experimental[7]

In a typical Diels–Alder reaction, 0.10 mole of the diene and 0.10 mole of the quinone were dissolved in 100 ml. of ether. After the reaction mixture had been heated under reflux for several hours, it was cooled and the precipitate was filtered off. In several experiments the solvent was evaporated to yield an additional quantity of adduct. In all runs except one, the crude adduct was recrystallized from ethanol to produce a white crystalline solid. Only 2,3,9-trimethyl-$\Delta^{4a(14a),7a(11a)}$-octahydropentacene-6,13-dione (XIV) was recrystallized from benzene.

---

[7] All melting points are corrected. The authors are indebted to Vivian Kapacinski, Robert Keen and James French for the analyses.

COLLEGE PARK, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NORTH CAROLINA]

Kinetics of Reactions of 2,4-Dinitrochlorobenzene with Some Familiar Nucleophilic Reagents[1]

BY J. F. BUNNETT AND GEORGE T. DAVIS

RECEIVED JANUARY 22, 1954

Rates of reactions of 2,4-dinitrochlorobenzene with five nucleophilic reagents in 60% dioxane have been measured or estimated. The following order of nucleophilic reactivity is established: thiophenoxide ion $\gg$ piperidine > methoxide ion > phenoxide ion $\gg$ hydroxide ion. Recognition of the low nucleophilic reactivity of the hydroxide ion allows rational explanation of several hitherto puzzling phenomena, including the Schotten–Baumann reaction.

In 1951, Bunnett and Zahler[2] commented on the paucity of information concerning the comparative activity of nucleophilic reagents in effecting aromatic substitution. The aim of the present research was to gather such information.

Our work was commenced with study of the reaction of hydroxide ion with 2,4-dinitrochlorobenzene. Except for some fragmentary reports,[3,4] no kinetic studies on the reactions of hydroxide ion with activated aryl halides have been published. The reason for this rather surprising gap in knowledge is evidently that alcohols have been the favorite solvents in which to measure the rates of aromatic nucleophilic substitution reactions, and solutions of hydroxide ion in alcohols act upon activated aryl halides to form principally ethers. To avoid this complication, we chose 60% dioxane:40% water (by volume) as the solvent for our studies; use of this solvent allows not only study of reactions with hydroxide ion, but also comparison of the reactivity of hydroxide ion with that of other nucleophilic reagents in the same solvent.

In Table I experiments are summarized which show the reaction of hydroxide ion with 2,4-dinitrochlorobenzene (equation 1) to be strictly second order, first order in hydroxide ion and first order in the aryl chloride. This result is of interest because

---

[1] Presented to the Southern Regional Conclave, American Chemical Society, New Orleans, La., December, 1953.

[2] J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 340 (1951).

[3] J. Miller, *Chemistry and Industry*, 40 (1953).

[4] (a) B. A. Bolto and J. Miller, *ibid.*, 640 (1953); (b) W. C. Spitzer and G. W. Wheland, THIS JOURNAL, **62**, 2995 (1940).