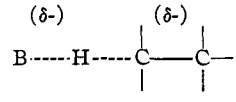
should be 7 to 14 kcal./mole lower than that required to produce the transition state



II

assuming, as mentioned above, no resonance stabilization of carbanion or olefin, and assuming further, that the solvation energies of both transition-state complexes would be approximately equal. The latter assumption seems valid since whatever apparent advantage transition state II might have in small charge dispersal[8] should be counteracted by difficulty of solvation due to steric hindrance at the carbanion carbon atom.[40]

The benzene hexachloride isomers are in accord with the above assumption that resonance effects are minimal, and the observation that the energy of activation for the β-isomer (*cis* elimination) is 9.6 to 12.5 kcal./mole higher than those for the other isomers (*trans* elimination) is in excellent agreement with the calculated estimates of 7–14 kcal./mole. Thus the major contribution to the superiority of the *trans* system over the *cis* system in elimination seems to be the existence of a concerted process for the *trans* system, with consequent lowering of activation energy, at least in cases where resonance effects are small.[41]

Dehydrochlorination of δ-Benzene Hexachloride.—To an ice-cold solution of 0.985 g. (0.0034 mole) of δ-benzene hexachloride in 15 ml. of 95% ethyl alcohol was added 6.98 ml. of 0.485 *N* NaOH solution over a period of 40 minutes. The reaction mixture was allowed to stand for 90 minutes in an ice-bath, after which time, the solution had become neutral. Seventy-five ml. of water was added, and the solution was placed in a refrigerator. After standing 24 hours, the reaction mixture was filtered and 480 mg. (0.0023 mole) of crystalline product was obtained, m.p. 55–62°. After recrystallizations from aqueous ethanol and drying over phosphorus pentoxide the material melted at 68–68.5° (cor.).

Anal.[42] Calcd. for $C_6H_5Cl_5$: C, 28.33; H, 1.98; Cl, 69.69. Found: C, 28.56; H, 2.14; Cl, 69.61.

This compound thus has an analysis corresponding to that of a pentachlorocyclohexene. We hope to continue work on its structure.

Materials Used.—The samples of the α-, β-, γ- and δ-isomers were those described previously.[1b] The ε-isomer[43] was kindly furnished by Mr. W. W. Allen of the Dow Chemical Company, and was recrystallized to constant m.p. 219–220° (cor.), and dried *in vacuo* before use.

Summary

A study has been made of the rates of dehydrochlorination with sodium hydroxide in 76.1% ethanol of four of the isomers of benzene hexachloride. The β-isomer, in which all vicinal pairs of hydrogen and chlorine atoms are *cis*, reacts at a rate 7000 to 24000 times slower, and with activation energies 9.6 to 12.5 kcal./mole greater, than the α-, γ- and ε-isomers, where *trans* elimination is possible.

The possibility that repulsive forces are the major contributors to this superiority of *trans* elimination over *cis* is considered and shown to be unlikely. The data seem best explained on the basis of two different mechanisms for elimination. One, *trans* elimination, involves a one-stage concerted process, in which the proton is removed, the double bond is formed, and halide ion is evolved in one step. The second, apparently observed in *cis* elimination, involves a multiple-stage process, in which only the proton is removed in the rate-determining step, yielding a carbanion intermediate. Approximate calculations of activation energy differences for these two processes are in agreement with observed differences.

(40) von Egidy, M.A. thesis, University of Colorado, 1949.

(41) A case where this is not true will be discussed in a later paper.

(42) Analysis by H. S. Clark, Urbana, Illinois.

(43) Kauer, DuVall and Alquist, *Ind. Eng. Chem.*, **39**, 1335 (1947).

BOULDER, COLORADO RECEIVED MAY 15, 1950

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

Dehydrobromination of α,β-Dibromohydrocinnamic Acid in Liquid Ammonia[1]

BY R. V. PAULSON[1] AND WARREN S. MACGREGOR

The dehydrobromination of sodium α,β-dibromohydrocinnamate with aqueous or alcoholic alkalies at room temperature or at the boiling point has been shown to yield mixtures of *cis*- and *trans*-α-bromocinnamic acids when two equivalent amounts of alkali were used and phenylpropiolic acid when three or more equivalents were used.[2] The two β-bromocinnamic acids generally have been obtained, not by dehydrobromination, but from the addition of hydrogen bromide to phenylpropiolic acid.[3] When the addition was conducted in aqueous, acetic acid, or alcoholic solution the principal products were the two β-bromocinnamic acids while in carbon disulfide or benzene solutions the main product was α-bromo-*trans*-cinnamic acid.[4] This change in the mode of addition was represented by Michael[5] as a solvent effect that was particularly evident because all four of the olefinic acids had approximately the same heats of formation.

The course of the dehydrobromination of α,β-dibromohydrocinnamic acid might be expected to show a similar response to solvent change if the activation energies of the reaction paths leading to the α- or β-bromocinnamic acids were not too different. Such an alteration was encountered when liquid ammonia rather than water or alcohol was used as the solvent for the dehydrobromination with sodium ethoxide. The reaction of ammonium α,β-dibromohydrocinnamate in liquid ammonia with sodium ethoxide was rapid and occurred in well-defined steps. The first equivalent of sodium ethoxide was consumed in reaction with the ammonium

(1) From the M.S. Thesis of R. V. Paulson, August, 1949.

(2) Sudborough and Thompson, *J. Chem. Soc.*, **83**, 666 (1903).

(3) Michael and Brown, *Ber.*, **19**, 1397 (1886).

(4) Sudborough and Thompson, *J. Chem. Soc.*, **83**, 1153 (1903).

(5) Michael, *J. Org. Chem.*, **4**, 128 (1939).

TABLE I

REACTIONS WITH ONE MOLE OF α,β-DIBROMOHYDROCINNAMIC ACID

Reagent	Moles	Products	Yield, %	Acid, m. p., °C. Found	Acid, m. p., °C. Reported	Amide, m. p., °C. Found	Amide, m. p., °C. Reported
$NaOC_2H_5$	6	PhC≡CCOOH	86	135–136	137[a]	97.5–98	99–100[b]
$NaOC_2H_5$	3	PhC≡CCOOH	63				
$NaOC_2H_5$	2	*cis*-PhCBr=CHCOOH	74	159–160	160[a]	115–116	115–116[c]
$NaOC_2H_5$	1	PhCHBrCHBrCOOH	82	198–199	197–199[j]		
$NaNH_2$	3	*trans*-PhCH=CHCOOH	82	132–133	133[a]	145–146	147[d]
$NaNH_2$	2	*trans*-PhCH=CBrCOOH	15	131–133	130–131[a]	119–120	117–118[e]
		cis-PhCBr=CHCOOH	27				
$NaNH_2$	1	PhCHBrCHBrCOOH	83				
NaC≡CH	8	*trans*-PhCH=CHCOOH	91				
$NaC{\equiv}CC_4H_9$	5	*trans*-PhCH=CHCOOH	72				
Na	5	$PhCH_2CH_2COOH$	73	47–48	48[f]	99–102	101[g]
Na	2	$PhCH_2CHNH_2COOH$	8	266–268	263–265[h]		
		$PhCHBrCH_2COOH$	5	134–135	137[i]		

[a] Sudborough and Roberts, *J. Chem. Soc.*, **87**, 1840 (1905). [b] Stockhauser and Gatterman, *Ber.*, **25**, 3537 (1892). [c] Auwers and Walters, *Ann.*, **492**, 283 (1932). [d] Posner, *Ber.*, **38**, 2320 (1905). [e] Stoermer and Kirchner, *ibid.*, **53B**, 1289 (1920). [f] Merz and Weith, *ibid.*, **10**, 758 (1877). [g] King and McMillan, THIS JOURNAL, **68**, 633 (1946). [h] Sasaki, *Ber.*, **54**, 163 (1921). The hydrochloride m.p. was 123–125°. [i] Fittig and Binder, *Ann.*, **195**, 132 (1879). The m.p. was depressed by mixing with phenylpropiolic acid, *trans*-cinnamic acid or α-bromo-*trans*-cinnamic acid. [j] Schmitt, *Ann.*, **127**, 320 (1864).

ion. The second equivalent removed the alpha bromine by dehydrobromination forming sodium β-bromo-*cis*-cinnamate, and the third equivalent removed the remaining bromine to form the expected sodium phenylpropiolate. The reactions offer convenient methods for preparing either of the latter two compounds in reasonable yield. Sodium hydroxide reacted in the same manner.

In the reaction with sodamide the first equivalent again reacted with the ammonium ion and the second equivalent was consumed in dehydrobromination. The dehydrobromination in this case was not selective but produced a mixture from which α-bromo-*trans*-cinnamic acid and β-bromo-*cis*-cinnamic acid were isolated. The reaction with three or more equivalents of sodamide produced sodium *trans*-cinnamate in good yield. The second bromine thus was removed by reduction and the overall reaction corresponded to a debromination. Debromination of α,β-dibromohydrocinnamic acid has been effected previously by heating with alcoholic dimethylaniline[2] or pyridine.[6,7] Although the usual reaction of sodamide in liquid ammonia with vicinal dibromides is to form the corresponding acetylenic compounds, other exceptions have been observed.[8]

The reactions with either sodium acetylide or the sodium derivative of 1-hexyne were similar to the sodamide reaction in that excesses of the basic reagent produced sodium *trans*-cinnamate. The reaction with sodium, as shown in Table I, produced hydrocinnamic acid when a sufficient quantity of sodium was used. Attempted reductions using only two equivalents of sodium were inefficient and produced mixtures from which small amounts of phenylalanine and β-bromohydrocinnamic acid were recovered.

Experimental

General Procedure.—The experiments giving the results summarized in Table I were run using 6.0 g. (0.019 mole) of α,β-dibromohydrocinnamic acid, m.p. 197–199°. The alkaline reagents were prepared immediately prior to use by the addition of water, ethanol, acetylene, etc., to a solution of the calculated amount of sodium dissolved in 300 cc. of anhydrous ammonia. Sodamide was prepared using a trace of ferric nitrate as a catalyst. The reaction vessel was a 500-cc. 3-neck flask fitted with a sealed stirrer, addition tube and a drying tube containing Drierite. In reactions using an excess, or amount of the alkaline reagent calculated for complete reaction, the dibromide was added over a period of 2 to 5 minutes to the freshly-prepared reagent solution or suspension. In the reactions with intermediate amounts of alkaline reagent the reagent solution or suspension was added from a dropping funnel to a solution of the ammonium salt of the acid in ammonia. Although the reactions were rapid, probably complete within 10 minutes, the mixtures were stirred from 1 to 3 hours. The ammonia was then evaporated by pouring the suspension into a 500-cc. Claisen flask which was attached to an aspirator and heated in a 30° water-bath. The residual salts were dissolved in water, filtered when necessary and the acids precipitated by acidifying with 50% sulfuric acid in the presence of ice. Decarboxylation occurred only in minor extent.

When a single main product resulted purification was effected by recrystallization: cinnamic, phenylpropiolic and β-bromo-*cis*-cinnamic acids from water and unreacted dibromide from glacial acetic acid. Hydrocinnamic acid was purified by distillation.

The mixture of acids (3.56 g.) obtained from the reaction with 2 equivalents of sodamide was leached with 12 cc. of ethanol leaving a residue of 1.5 g. of the original dibromide. After evaporating the ethanol the acids were taken up in dilute ammonium hydroxide and a 20% solution of barium chloride added to precipitate the barium salt of α-bromo-*trans*-cinnamic acid. Macerating the salt with dilute hydrochloric acid, making the solution basic and filtering gave a filtrate that deposited 0.66 g. of α-bromo-*trans*-cinnamic acid, m.p. 131–133°, when acidified. When the solution of soluble barium salts was acidified 1.2 g. of impure β-bromo-*cis*-cinnamic acid, m.p. 138–160°, was deposited. Recrystallization from water raised the m.p. to 159–160°.

When the mixture of acids (2.61 g.) resulting from the reaction of 2 equivalents of sodium was macerated with 8 cc. of ethanol at 50° and the mixture cooled to 5°, 0.34 g. of phenylalanine, m.p. 266–268° (dec.), was deposited. The ethanolic filtrate, heated to 50°, was diluted with 10 cc. of water which caused rapid crystallization of 1.7 g. of crude α,β-dibromohydrocinnamic acid, m.p. 180–195°. The solvent was then evaporated from the mother liquor and the residual acids recrystallized from ethanol to obtain 0.22 g. of β-bromohydrocinnamic acid, m.p. 134–135°.

Identification of the acids was facilitated because a large melting point depression occurred when any two were mixed. Confirmation was achieved by preparing the amides.

β-Bromo-*cis*-cinnamic Acid.—α,β-Dibromohydrocinnamic acid (72.0 g., 0.25 mole) was dissolved in 500 ml. of anhydrous ammonia contained in a 3-liter, 3-neck flask

(6) Pfeiffer, *Ber.*, **43**, 3041 (1910).
(7) Alberts and Bachman, THIS JOURNAL, **57**, 1284 (1935).
(8) Vaughn, Vogt and Niewland, *ibid.*, **56**, 2120 (1934).

fitted with stirrer, 2-liter dropping funnel and vent to the atmosphere. Ethanol (30 cc.) was added to 1200 ml. of anhydrous ammonia in the separatory funnel and 11.5 g. (0.50 mole) of sodium added in small pieces while the contents of the separatory funnel were stirred mechanically. The resulting sodium ethoxide suspension was added over a period of 10 minutes to the mixture in the main reaction flask. Both the sodium ethoxide suspension and the reaction mixture were stirred during the addition. The ammonia was then evaporated using an aspirator and a bath of running cold tap water. The residual salts were taken up in water, filtered to clarify, cooled with crushed ice and carefully acidified with sulfuric acid whereupon 43.6 g. (82%) of crude product, m.p. 143–149°, separated. Recrystallization from 140 cc. of 60% aqueous ethanol gave 24.5 g. (46%) of β-bromo-*cis*-cinnamic acid, m.p. 159–160°.

Acknowledgment.—We wish to thank Research Corporation for a grant in support of this work.

Summary

Dehydrobromination of α,β-dibromohydrocinnamic acid with two equivalents of sodium ethoxide or sodium hydroxide in liquid ammonia formed β-bromo-*cis*-cinnamic acid rather than the mixture of α-bromocinnamic acids which result from the use of aqueous or alcoholic alkalies. Excess of these alkaline reagents produced phenylpropiolic acid.

The reaction with an excess of sodamide or sodium acetylides formed cinnamic acid. The sodamide reaction apparently involved dehydrobromination to a mixture of α- and β-bromocinnamic acids followed by reductive cleavage of the remaining bromine.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Rearrangement and Reduction of Hindered 2-Hydroxy-3-alkyl-1,4-naphthoquinones

BY LOUIS F. FIESER AND ALFRED R. BADER[1]

When a solution of 2-hydroxy-3-cyclohexyl-1,4-naphthoquinone[2] (I) in 5% aqueous alkali is heated on the steam-bath with exclusion of air, the initially deep red solution becomes pure yellow in about 27 hours and acidification then precipitates a yellow, non-quinonoid isomer of I for which the structure of 2-cyclohexylindenone-3-carboxylic acid (III) has been tentatively suggested.[3] Further investigation has substantiated this assignment of structure. The yellow isomer has the ultraviolet absorption characteristics expected for III, it forms ester, amide and semicarbazone derivatives, and it is reduced by zinc dust and either acetic acid or alkali to a colorless dihydride of properties consistent with the indanone formula IX. Thus IX has an ultraviolet absorption spectrum similar to that of acetophenone and is reducible by the Clemmensen method to 2-cyclohexylindane-3-carboxylic acid. The indenone III also reacts with excess diazomethane to give a pyrazoline ester of the probable structure X.

Dr. Martin G. Ettlinger of this Laboratory observed in 1947 that 2-hydroxy-3-*t*-butyl-1,4-naphthoquinone (Ia) is rapidly converted by alkali into a similar yellow non-quinone and that a colorless intermediate is formed at about the same rate when the rearrangement is conducted in a buffer of *p*H 9.2. We isolated these products and found the properties in accordance with the indenone structure IIIa for the yellow compound and the 3-hydroxyindanone-3-carboxylic acid structure II for the intermediate. Colorless II, of acetophenone-like spectrum, is converted rapidly by alkali into IIIa. Cooke and Somers[4] have reported the independent isolation of the *t*-butyl compound IIIa and the isolation and synthesis of the corresponding isopropyl derivative[5]; these authors comment on the analogy, considered also by Dr. Ettlinger, to the rearrangement of dunnione to allodunnione.[6]

According to our observations isomerization of 2-hydroxy-3-*t*-butyl-1,4-naphthoquinone by 5% alkali at 90° is complete in 1 hour. 2-Hydroxy-3-cyclohexyl-1,4-naphthoquinone is isomerized by 5% alkali in some 27 to 30 hours, and a trace of the indanone IX was isolated from the reaction mixture. When the rearrangement was conducted in 2% alkali, no by-product was observed and pure III was isolated in 88% yield. When the compound I was heated in a buffer at *p*H 9.2, the sole product was the indenone III (91% yield). In this instance the hydroxyindanonecarboxylic acid is probably the initial product but undergoes dehydration at a rate exceeding the rate of formation. Whereas the dehydration is base catalyzed, the rate of rearrangement is independent of the concentration of hydroxide ion, provided this is sufficient to maintain the quinone largely in the form of the anion.

The mechanism suggested in the formulation is that the hydroxyquinone anion present in the red solution affords a hydrate that undergoes aldol cleavage and recondensation to II; the reaction can be regarded alternately as a benzilic acid rearrangement of the trione anion. The mechanism evidently is the same as that of the alkaline cleavage of 2- and 3-hydroxy-1,4-phenanthrenequinone observed by one of us.[7] In the case of the 2-hydroxy-3-alkyl-1,4-naphthoquinones, a possible explanation of the fact that a bulky alkyl group favors rearrangement is that hindrance in the planar anion is relieved by formation of the non-planar hydrate.

The intermediates in the Hooker oxidation[8] of 2-hydroxy-3-alkyl-1,4-naphthoquinones, obtained in high yield by the action of alkaline hydrogen peroxide, have been shown to be 2,3-dihydroxy-2-alkylindanone-3-carboxylic acids,[9] but

(1) Abbott Laboratories Fellow, 1948–1950.
(2) Fieser, THIS JOURNAL, **70**, 3165 (1948).
(3) Fieser, *ibid.*, **70**, 3237 (1948).
(4) Cooke and Somers, *Nature*, **165**, 314 (1950).
(5) See also Cooke, *ibid.*, **162**, 178 (1948); Shchukina, Kondrat'eva and Shemyakin, *J. Gen. Chem.*, **18**, 2121 (1948).
(6) Price and Robinson, *J. Chem. Soc.*, 1522 (1939).
(7) Fieser, THIS JOURNAL, **51**, 940, 1896 (1929).
(8) Hooker, *ibid.*, **58**, 1164, 1174, 1179 1(936).
(9) Fieser and Fieser, *ibid.*, **70**, 3215 (1948).