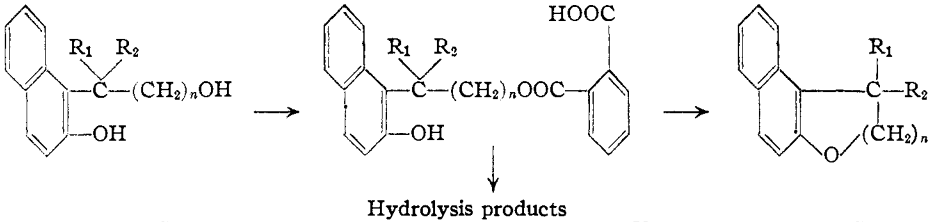
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

Intramolecular Displacement of Carboxylate Ion. II. The Effect of Some Variations in Structure of Phenol-alcohols

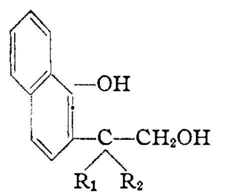
BY CYRUS O. GUSS

An earlier paper[1] described the behavior of the acid phthalate of 2-(2-hydroxy-1-naphthyl)-2-phenylethanol (I) in aqueous sodium hydroxide. It was shown that cyclization to the dihydrofuran (VIII) was a faster reaction in this medium than the usual ester hydrolysis. The effect of the phenyl group beta to the ester linkage on the cyclization reaction has now been studied. Results indicate that this group (R_2) in I plays an important role but is not indispensable for the success of the cyclization. This intramolecular alkylation appears to be relatively general and is especially favored when a five-membered ring is being formed from a phenol-alcohol.

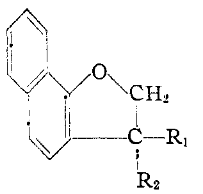


I, R_1 = H, R_2 = C_6H_5, n = 1
II, R_1 = R_2 = C_6H_5, n = 1
III, R_1 = R_2 = H, n = 1
IV, R_1 = R_2 = H, n = 2

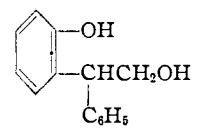
VIII, R_1 = H, R_2 = C_6H_5, n = 1
IX, R_1 = R_2 = C_6H_5, n = 1
X, R_1 = R_2 = H, n = 1
XI, R_1 = R_2 = H, n = 2



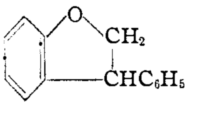
V, R_1 = H, R_2 = C_6H_5
VI, R_1 = R_2 = C_6H_5



XII, R_1 = H, R_2 = C_6H_5
XIII, R_1 = R_2 = C_6H_5



VII



XIV

Several phenol-alcohols (II to VII), having structural variations considered pertinent to the present study, were prepared. With previous procedures[1] as a pattern, the phenol-alcohols were converted into their acid phthalates and, in a sodium bicarbonate solution, treated with aqueous sodium hydroxide. Two different hydroxyl ion concentrations were used in order to obtain some comparison of the ability of the esters of the phenol-alcohols to cyclize. Complete data are recorded in Table I. The earlier results[1] are included for convenience.

It is apparent, from a comparison of the results obtained with the esters of I, II and III, and with the esters of V and VI, that the presence of a phenyl group on the carbon atom beta to the ester linkage favored cyclization over hydrolysis. When two phenyl groups were present, as in II and VI, the cyclization reaction in the stronger alkali was very rapid and quantitative at room temperature. An interesting reversal of the expected behavior was observed with VI in the weaker alkali, in which more hydrolysis than cyclization occurred. This diortho substituted phenol did not readily form a sodium salt in aqueous alkali, which is not uncommon for phenols so substituted,[2] and therein lies an explanation for the hydrolysis of its ester in the weaker alkali. With II this phenomenon was not observed.

In very dilute sodium hydroxide cyclization was the only observed reaction when there were no phenyl groups on the beta carbon as in III. This result would lead one to expect cyclization to occur quite generally whenever a furan ring is thus formed. Whenever a six-membered ring would result, as in IV → XI, the tendency to cyclize was relatively less pronounced, presumably because of

TABLE I

EFFECT OF STRUCTURE AND ALKALI CONCENTRATION ON THE DISPLACEMENT OF CARBOXYLATE ION FROM THE ACID PHTHALATES OF PHENOL-ALCOHOLS

Acid phthalate[a] of	NaOH Moles per liter	Yield, % Cyclized product	Hydrolysis[b] product
I	0.208	93.5	0
	3.124	67.1	24.6
II[c]	0.208	96.3	0
	3.124	99.3	0
III	0.208	88.2	0
	3.124	0	85.1
IV	0.208	21.7	74.3
V	0.208	87.4	0
	3.124	14.2	75.7
VI[c]	0.208	40	60
	3.124	99.3	0
VII	0.208	81.6	0
	3.124	(2.5)	84.1

[a] The concentration of the sodium salt of the acid phthalate in aqueous sodium bicarbonate was 0.0833 mole per liter, subject to a correction arising from incomplete extraction of the acid phthalate from an ether solution.[1] [b] The yield data are for the recovered phenol-alcohols. [c] The sodium salt of the acid phthalate was not completely soluble in the bicarbonate solution. See experimental details for the specific procedures used.

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[1] Guss and Jules, THIS JOURNAL, **72**, 3462 (1950).

[2] Stillson, Sawyer and Hunt, *ibid.*, **67**, 303 (1945); Coggeshall, *ibid.*, **69**, 1620 (1947); Coggeshall and Glessner, Jr., *ibid.*, **71**, 3150 (1949); Coggeshall and Glessner, Jr., *ibid.*, **72**, 2275 (1950).

the spatial factor. It would be expected, however, that if an ester of IV were made in which the carbonyl was adequately hindered, hydrolysis would be retarded sufficiently to allow the cyclization to become predominant or exclusive.[3] This latter expedient might also lead to a synthesis of monocyclic compounds if the intermolecular displacement reaction could be controlled. One could also avoid a hydrolytic medium or reduce the concentration of the ester in order to favor the displacement of carboxylate ion. It seems reasonable to believe that this cyclization reaction could be extended to sulfur and nitrogen analogs.

The rate of this intramolecular reaction ought to be dependent upon: (a) the nucleophilic character of the phenol alcohol; (b) the electrophilic character of the alpha carbon of the alkoxy portion, which would be affected, for example, by the strength of the acid from which the ester is derived[4]; and (c) spatial factors that affect the close approach to each other of the atoms involved in the formation of the new bond. One aspect of this spatial factor is exemplified by a comparison of III and IV.

An inspection of an atomic model of I indicated that there was some restriction to free rotation around the carbon–carbon bond between the naphthalene ring and the beta carbon of the alkoxy group. The phenyl group on the beta carbon could be rotated past the hydrogen on the 8-position of the naphthalene ring only with difficulty. Any hindrance to this rotation would tend to hold the alpha carbon nearer the phenolic anion than would otherwise be the case, and a promotion of cyclization should result. Two phenyl groups on the beta carbon atom, astraddle the 8-position, would hold the alpha carbon immediately adjacent to the anionic oxygen. However, since the acid strength of these phenols is unknown, one cannot readily assign a definite role to the phenyl group on the basis of the present data.

Experimental[5]

Preparation of 2-(2-Hydroxy-1-naphthyl)-2,2-diphenylethanol (II).—The procedure of Arventi[6] was used to prepare the lactone of α-(2-hydroxy-1-naphthyl)-diphenylacetic acid from benzilic acid and 2-naphthol at 150–155° in 63–66% yield. Recrystallization of the product from acetic acid gave white platelets, m.p. 191–192°. Arventi[6] and Geipert[7] reported a m.p. of 182–183° for this lactone.

Anal. Calcd. for $C_{24}H_{16}O_2$: C, 85.69; H, 4.80. Found: C, 85.74; H, 4.98.

The foregoing lactone (16.8 g., 0.05 mole) was reduced with lithium aluminum hydride (3.0 g., 0.08 mole) in ether (100 cc.), the lactone being added as a solid in small portions. After the addition of the lactone, the reaction mixture was allowed to stand 1 hour and then worked up to give 16.8 g. (98.7%) of crude II, which was not very soluble in ether. The pure II, recrystallized from ethanol as platelets, melted at 202–204°. The sodium salt of this phenol was rather insoluble in cold water.

Anal. Calcd. for $C_{24}H_{20}O_2$: C, 84.68; H, 5.92. Found: C, 84.99; H, 6.02.

Preparation of 2-(2-Hydroxy-1-naphthyl)-ethanol (III).—The preparation of 2-hydroxy-1-naphthaleneacetic acid was accomplished by heating 2-naphthol (57.6 g., 0.4 mole) and chloroacetic acid (47.3 g., 0.5 mole) under gentle reflux for 192 hours as suggested by a patented procedure.[8] The dark reaction mixture was dissolved in ether and extracted with sodium bicarbonate (40 g. in 400 cc. of water) to remove a small amount of 2-naphthoxyacetic acid. The ether solution was then extracted with sodium hydroxide (20 g. in 300 cc. of water), and the aqueous alkaline liquid treated with carbon dioxide to precipitate unreacted 2-naphthol (21.6 g.). The filtrate from the removal of the 2-naphthol was acidified to give, after filtering and washing, 8.75 g. (17.3% based on recovered 2-naphthol) of the desired acid, m.p. 137–145°. Recrystallization from ethanol–water gave leaves, m.p. 147–148° as reported by Stoermer.[9] There appeared to be some lactonization of this compound at its melting point. Di-2-naphthyl ether was also isolated in 35.5% yield in this preparation.

Reduction of 2-hydroxy-1-naphthaleneacetic acid (6.0 g., 0.03 mole) in ether (90 cc.) by lithium aluminum hydride (3.0 g., 0.08 mole) in ether (50 cc.) readily produced 4.8 g. (90%) of III, m.p. 114–120°. Recrystallization from hot water produced leaves, m.p. 122.5–123.5°.

Anal. Calcd. for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.84; H, 6.62.

Preparation of 3-(2-Hydroxy-1-naphthyl)-propanol (IV).—The lactone of 2-hydroxy-1-naphthalenepropionic acid was prepared by the procedure of Hardman[10] from 2-naphthol and acrylonitrile. This lactone (9.9 g., 0.05 mole, m.p. 72–73°) was added in small portions to lithium aluminum hydride (3.0 g., 0.08 mole) in ether (100 cc.). The reaction mixture was allowed to stand for 1 hour before working up to obtain 9.6 g. (95%) of IV, m.p. 95–132°. Large flat needles were formed on recrystallization from ethanol-water, m.p. 132.5–133.5°.

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.62; H, 6.83.

Preparation of 2-(1-Hydroxy-2-naphthyl)-2-phenylethanol (V).—Mandelic acid and 1-naphthol were used to obtain the lactone of α-(1-hydroxy-2-naphthyl)-phenylacetic acid by the procedure of Arventi.[6] The lactone (26.0 g., 0.1 mole, m.p. 127–129°) was reduced with lithium aluminum hydride (8.0 g., 0.21 mole) in ether (200 cc.). In the reduction the lactone was added in small portions, and the reaction mixture was allowed to stand for 2 days at room temperature. A quantitative yield of an amber oil was obtained when this preparation was completed in the usual manner. The oil was soluble in sodium hydroxide and insoluble in sodium bicarbonate; it did not crystallize, and when similar preparations were distilled, some alkali-insoluble material was present in the distillate. The analysis showed that this oil was impure, but it was used without further purification in subsequent experiments.

Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 80.02; H, 6.37.

Preparation of 2-(1-Hydroxy-2-naphthyl)-2,2-diphenylethanol (VI).—The lactone[6] (16.8 g., 0.05 mole) of α-(1-hydroxy-2-naphthyl)-diphenylacetic acid in dioxane (100 cc.) was added to lithium aluminum hydride (4.0 g., 0.105 mole) in dioxane (100 cc.). There was no apparent reaction until the solution was warmed and then a rapid reaction occurred near the boiling point. The mixture was refluxed for 1 hour, then decomposed with water and hydrochloric acid in the usual way. A quantitative yield of a tan solid, m.p. 176–179°, was easily recovered. Recrystallization was best effected by adding the crude product to boiling alcohol, followed by dilution with water prior to cooling. The faintly cream-colored crystals so obtained melted at 177–179° with some evidence of cyclization at the melting point. This phenol-alcohol was insoluble in 4% sodium hydroxide at room temperature but was soluble in the hot alkali.

Anal. Calcd. for $C_{24}H_{20}O_2$: C, 84.68; H, 5.92. Found: C, 84.72; H, 5.99.

Preparation of 2-(2-Hydroxyphenyl)-2-phenylethanol (VII).—The preparation of this compound was a part of another investigation which will be described in a forth-

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(3) Bunnett, Robison and Pennington, THIS JOURNAL, **72**, 2378 (1950).

(4) Hammett and Pfluger, *ibid.*, **55**, 4079 (1933).

(5) All melting points are uncorrected. Microanalyses are by Mr. Joseph Pirie of this Department and the Elek Micro Analytical Laboratories, Los Angeles 16, Cal.

(6) Arventi, *Ann. sci. univ. Jassy*, Pt. I, **23**, 344 (1937).

(7) Geipert, *Ber.*, **37**, 664 (1904).

(8) Wolfram, Schörnig and Hausdörfer, German Patent 562,391 (Feb. 2, 1929), *C. A.*, **27**, 734 (1933).

(9) Stoermer, *Ann.*, **313**, 91 (1900).

(10) Hardman, THIS JOURNAL, **70**, 2119 (1948).

coming publication.[11] The material used in the present work melted at 76–77°.

General Procedure.—The phenol-alcohols were converted into the acid phthalates by allowing a solution of the phenol-alcohol (0.01 mole), phthalic anhydride (0.02 mole), pyridine (3 cc.) and dioxane (15 cc.) to stand at room temperature for 48 hours or some convenient time in excess of this period. In some cases one-half of these quantities were used. The reaction mixture was then dissolved in ether (50 cc.), washed with dilute hydrochloric acid (5 cc. of concd. acid in 50 cc. of water), and then washed with water (50 cc.). The ester was extracted with 4% sodium bicarbonate (four 25-cc. portions) except when the esters of II and VI were involved. With the latter two compounds, since the sodium salts were insoluble in the bicarbonate solution to the extent that extraction was inconvenient, the ether was evaporated under vacuum, and 4% sodium bicarbonate (100 cc.) was added to the residue to form a slurry of the sodium salt of the ester.[12]

To the bicarbonate solution or slurry of the esters was added, in one portion, a solution of sodium hydroxide (1 g. or 15 g.) in water (20 cc.). From this point on certain differences in the procedure used merit a separate description of experimental details.

Formation of 1,1-Diphenyl-1,2-dihydronaphtho(2,1-b)-furan (IX).—After addition of the weaker solution of sodium hydroxide, the slurry was heated at reflux temperature for 1 hour. The solid was filtered from the cooled mixture and dried to give a 96.3% yield of IX, m.p. 168–174°. This product was crystallized from ethanol-water or from acetic acid as white plates, m.p. 172–174°.[13]

When the stronger solution of sodium hydroxide was added, there was an immediate transformation of the ester into the furan (IX) at room temperature. After 5 minutes the solid was filtered off, washed, and dried to obtain a 99.3% yield, m.p. 168–171°. Purifying recrystallizations gave a m.p. 172–174°. There was no precipitate formed when excess carbon dioxide was added to the filtrate from the separation of the furan in either instance.

The acid-catalyzed cyclization[1] gave a quantitative yield of the same furan (IX).

Anal.[14] Calcd. for $C_{24}H_{18}O$: C, 89.41; H, 5.63. Found: C, 89.64, 89.52; H, 5.91, 5.46.

Formation of 1,2-Dihydronaphtho(2,1-b)furan (X).—The clear solution from the addition of the weaker alkali to the bicarbonate solution of the ester of III was heated at the reflux temperature for 1 hour. A turbidity quickly developed as the boiling point was approached. Sodium hydroxide (10 g.) was added to the cooled mixture and the insoluble oil extracted with ether. Carbon dioxide did not cause any precipitation from the alkaline solution. The dried ether solution was evaporated under vacuum to leave an 88.2% yield of an oil (X) which, by simple distillation, boiled at 154° (10 mm.) and was obtained as a clear liquid, n^{20}_{D} 1.6432.

Anal. Calcd. for $C_{12}H_{10}O$: C, 84.68; H, 5.92. Found: C, 84.84; H, 6.06.

This furan (X) has been reported previously,[15] admittedly impure, as a viscous dark oil, b.p. 185° (10 mm.), n^{33}_{D} 1.482.

In the experiment in which the stronger solution of sodium hydroxide was employed, there was no evidence for the formation of any cyclized product. After the solution was refluxed for 1 hour, cooled and carbon dioxide added, an 85.1% yield of crude III, m.p. 119–122°, resulted.

Formation of Benzo(f)chroman (XI).—The bicarbonate solution of the ester, after addition of the weaker alkali solution, was refluxed for 1 hour. A turbidity quickly appeared as the solution was warmed to the boiling point. To the cooled mixture was added sodium hydroxide (10 g.) and the oil extracted with ether. The ether solution was washed with 10% sodium hydroxide, and this wash liquor was added to the first alkaline solution. Addition of carbon dioxide to the combined alkaline solutions brought about the precipitation of a 74.3% yield, m.p. 130–132°, of the phenol-alcohol (IV). Evaporation of the ether solution left a 21.7% yield, m.p. 37–40°, of benzo(f)chroman (XI). One recrystallization from ethanol–water gave needles, m.p. 41–42°, as reported in the literature.[15] In view of this result, the experiment with the stronger alkali was not run.

Acid-catalyzed cyclization[1] of IV gave a 96% crude yield of XI, m.p. 39–41°.

Formation of 3-Phenyl-2,3-dihydronaphtho(1,2-b)furan (XII).—The solution from the addition of the smaller amount of alkali to the bicarbonate solution of the ester was warmed to the boiling point. The insoluble material that separated was extracted with ether. After the ether solution was dried and evaporated under vacuum, a tan solid (XII) remained in 87.4% yield, m.p. 60–76°. Two recrystallizations, with Norite treatment, from ethanol–water gave white needles, m.p. 77–79°.

When the stronger alkali solution was used, an immediate reaction occurred and an oil separated. The darkened mixture was warmed, then cooled and extracted with ether. The dried ether solution was evaporated under vacuum to leave a 14.2% yield of a tan solid (XII) which, after recrystallization from ethanol–water as before, gave a m.p. 77–79°. Treatment of the alkaline solution from the ether extraction with carbon dioxide gave a 75.7% yield of V as an oil.

Acid-catalyzed cyclization[1] of V gave an 88.4% yield of XII, which was purified by distillation (b.p. 190° at 1 mm.) and subsequent recrystallization from ethanol–water, m.p. 78–79°.

Anal. Calcd. for $C_{18}H_{14}O$: C, 87.77; H, 5.73. Found: C, 88.04; H, 5.60.

Formation of 3,3-Diphenyl-2,3-dihydronaphtho(1,2-b)-furan (XIII).—After the addition of the weaker alkali solution, the slurry was refluxed for 1 hour. The tan solid (1.7 g. from 1.7 g. of VI) that was filtered off, washed and dried, melted at 150–165°. An additional hour of refluxing in an alkaline solution identical with that used before gave a solid (1.65 g.), m.p. 145–165°. One gram of this solid was added to 4% sodium hydroxide (50 cc.) and heated to boiling. The resulting mixture was filtered while hot to obtain 0.37 g. of cream-colored XIII, m.p. 131–136°. Two recrystallizations from ethanol–water gave needles, m.p. 140–142°. The filtrate from the separation of XIII was treated with carbon dioxide to give 0.58 g. of the phenol-alcohol (VI), m.p. 173–177°. Assuming, then, that the crude mixture was 40% XIII and 60% VI, and since the yield appeared to be quantitative, it was concluded that these values were reasonably valid as a representation of the behavior of the ester of VI in the weaker alkali.

When the stronger alkali solution was used, the slurry was warmed to 50–60° for a few minutes, then filtered, and the solid washed and dried to obtain a 99.3% yield of XIII, m.p. 135–139°. There was no precipitate when the filtrate was treated with carbon dioxide. The product (XIII), recrystallized three times, with Norite treatment, from ethanol-water, was obtained as white needles, m.p. 142–143°.

Anal. Calcd. for $C_{24}H_{18}O$: C, 89.41, H, 5.63. Found: C, 89.54; H, 5.57.

Formation of 3-Phenyl-2,3-dihydrobenzofuran (XIV).—After addition of the weaker alkali solution, the mixture was refluxed 1 hour, then cooled, and sodium hydroxide (10 g.) added. An oil was extracted with ether from which an 81.6% yield of a solid (XIV), m.p. 37–39°, was obtained. One recrystallization of this crude product from ethanol–water gave white needles, m.p. 38–39°, as reported by others[16] for XIV.

The stronger alkali solution was added and the mixture refluxed for 1 hour. When this mixture was cooled and extracted with ether, a 2.5% yield of an oil, presumed to be XIV, was obtained. Attempts to crystallize this oil were unsuccessful, so its identity is conjectural. An 84.1% yield of VII, m.p. 76–77°, after one recrystallization from

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(11) Guss, Williams and Jules, THIS JOURNAL, **73**, March (1951).

(12) This accounts for the high yields of cyclization product obtained from II and VI. When the other esters were extracted from an ether solution, there was some loss in yield of isolated product because of incomplete extraction.[1]

(13) This furan (IX) was considered by Buttenberg (*Ann.*, **279**, 333 (1894)) as a possible product from the reaction of 2-naphthol with diphenylacetaldehyde or with ethyl β,β-diphenylvinyl ether; the isomeric furan, 2,2-diphenyl-1,2-dihydronaphtho(2,1-b)furan was given as an alternative structure for the product. The compound obtained by Buttenberg as needles melted at 141–142° and was probably the isomer of IX named.

(14) The two analyses are for two different samples, one from the weaker alkali and the other from the run in the strong alkali.

(15) Rindfusz, Ginnings and Harnack, THIS JOURNAL, **42**, 157 (1920).

(16) Stoermer and Reuter, *Ber.*, **36**, 3979 (1903).

toluene, was obtained from the alkaline solution after the ether extraction.

Summary

Cyclization of the acid phthalates of several phenol-alcohols by intramolecular displacement of the carboxylate ion was studied. This method of cyclization was successfully carried out in aqueous alkali to form benzofurans and naphthofurans without concurrent hydrolysis; if a chroman was to be formed, hydrolysis was the predominant reaction in the one example studied.

When the hydroxyl ion concentration was varied, differences in the ease of cyclization of the esters were observed. The factors that one would expect to affect the rate of this cyclization reaction are discussed with reference to the present results.

LOS ANGELES 7, CAL. RECEIVED JULY 14, 1950

[CONTRIBUTION FROM THE PURDUE RESEARCH FOUNDATION AND THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Some Factors Influencing the Activity of Raney Nickel Catalyst. III. The Poisoning of Raney Nickel by Halogen Compounds[1]

BY JOHN N. PATTISON[2] WITH ED. F. DEGERING[3]

The poisoning of catalysts has been studied extensively, especially in connection with the active point theory of catalysis.[4] This work has led to some of the modern ideas of the nature of catalyst surfaces. The poisoning of Raney nickel by sulfur compounds has been studied by Maxted and Titt[5] but no studies of the poisoning of this catalyst by halides has been reported. A number of authors[6,7,8] have carried out reductions in the presence of organic halides, and Schwenk, Papa and Ginsberg[9] have used Raney nickel to remove halogens quantitatively from organic molecules. Adkins[10] states that refluxing with Raney nickel is the surest way to remove traces of halogens and sulfur from an organic material. This paper shows the effect of poisoning Raney nickel by hydrogen chloride and lists the relative poisoning effects of a number of organic halides.

Experimental

Poisoning by HCl

The work of Schwenk, *et al.*,[9] suggested that the poisoning by halides was due to free halogen ions and it was considered desirable to determine the relationship between catalytic activity and the amount of halogen ion present. Hydrogen chloride was taken as the reference poison and tests were conducted as follows: One hundred ml. of dioxane containing a known weight of anhydrous hydrogen chloride was added to the reactor bottle which contained 0.34 g. of W-4 type Raney nickel and 25 ml. of styrene. The reduction was carried out in a Parr model Adams Reductor. A plot of the pressure *versus* the time was made and the slope of this graph at the point of inflection was taken as the activity. These activities are plotted in Fig. 1 *versus* the amount of hydrogen chloride added.

There is a sharp break in the curve at about 0.006 g. of hydrogen chloride. This represents a 57:1 weight ratio or 36:1 mole ratio of nickel to hydrogen chloride. The presence of two straight line portions to the curve indicates that there are two distinct types of active surface present in Raney nickel and that one of these, although present in a relatively small proportion, accounts for about 85% of the activity.

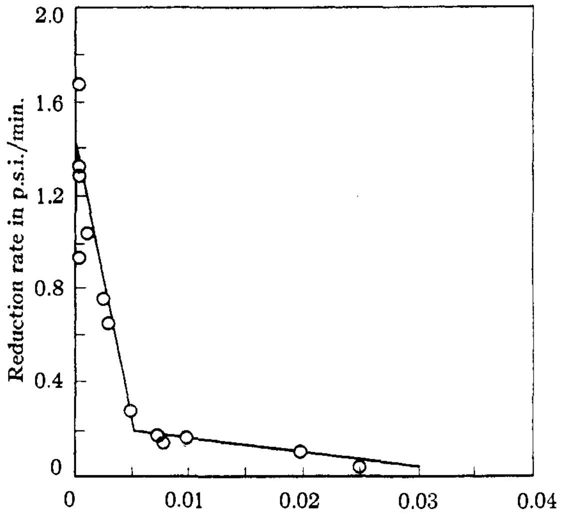

Fig. 1.—Poisoning of 0.34 g. of W-4 type Raney nickel by HCl.

Poisoning by Organic Halides

The materials used were all commercial products. Most of them were freshly distilled before use and then treated with Norite activated carbon. Experiments showed that Norite was quite effective in removing HCl from solutions of this type.

Activity Tests.—Twenty-five ml. of styrene was put into the pressure bottle along with one level spoonful of catalyst (about 0.4 g. Ni). The bottle was evacuated, then the system was pressurized to 57 p.s.i. and the reduction carried out in the usual fashion. The tests were started at room temperature and allowed to warm up as a result of the heat of hydrogenation. At the completion of the reduction, the sample was cooled to room temperature and another 25 ml. of styrene was added. Five ml. of the halide to be tested was then added and the mixture reduced as above. In each reduction a record of the pressure and time was kept and plotted. The slopes of these curves at their flex points (straight part) were compared to determine the amount of poisoning.

Results

Relative Poisoning Effects of Cl, Br and I.—Table I lists a number of comparisons of the effect of changing the halogen on a given radical.

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[1] From the Ph.D. Thesis of John N. Pattison, Purdue University, June, 1948.

[2] Battelle Memorial Institute, Columbus, Ohio.

[3] Miner Laboratories, Chicago, Illinois.

[4] H. S. Taylor, *J. Phys. Chem.*, **28**, 898 (1924).

[5] Maxted and Titt, *J. Soc. Chem. Ind.*, **57**, 197 (1938).

[6] Angelade, *Bull. soc. chim.*, **6**, 473 (1939).

[7] Paty, *Bull. soc. chim.*, **5**, 1276, 1600 (1939).

[8] Winans, THIS JOURNAL, **61**, 3564 (1939).

[9] Schwenk, Papa and Ginsberg, *Ind. Eng. Chem., Anal. Ed.*, **15**, 576 (1943).

[10] Adkins, "Reactions of Hydrogen," Wisconsin Press, Univ. of Wisconsin, Madison, Wisc., 1937, p. 28.