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.

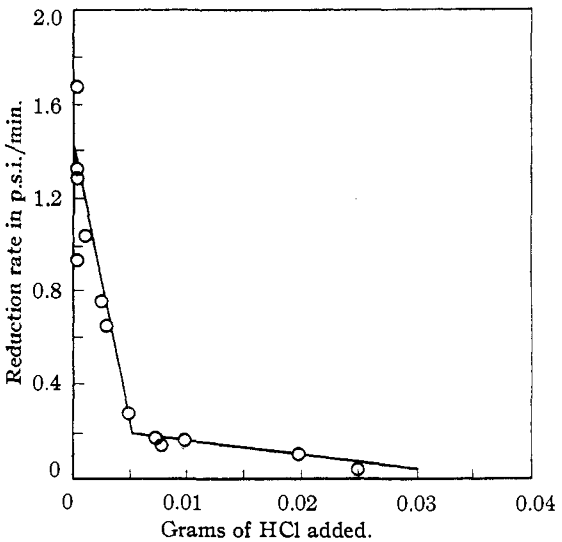

Fig. 1.—Poisoning of 0.34 g. of W-4 type Raney nickel by HCl.

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.*, **6**, 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.

TABLE I

RELATIVE POISONING EFFECT OF THE HALOGENS: Cl, Br AND I

Radical	Reduction rate, p.s.i./minute Cl	Br	I
n-Amyl	1.3, 1.6	0.65	0.10
s-Amyl (mixture)	0.75	..	..
t-Amyl	.85	..	..
n-Butyl	.60	.75	.15
s-Butyl	.35	.45	..
n-Propyl	.10	.10	.05
Ethyl	..	.50	.20
Phenyl	.58	.52	.13
2-Chloroethyl	.52	.50	..

It can be seen that in general the relative poisoning effect increases in the order Cl < Br < I. There is usually only a small difference between the chloride and the corresponding bromide. The iodides are far more poisonous than either the chlorides or the bromides.

Variation of Poisoning Effect with Chain Length.—A study was made of the normal straight chain alkyl halides to determine the effect of varying the chain length. Figure 2 shows the relationship between carbon chain length and poisoning effect. The reason for the shape of these curves is not clear at the present time. Two of the factors which should be involved in determining the shapes of the curves are the steric effects and the ease of ionization.

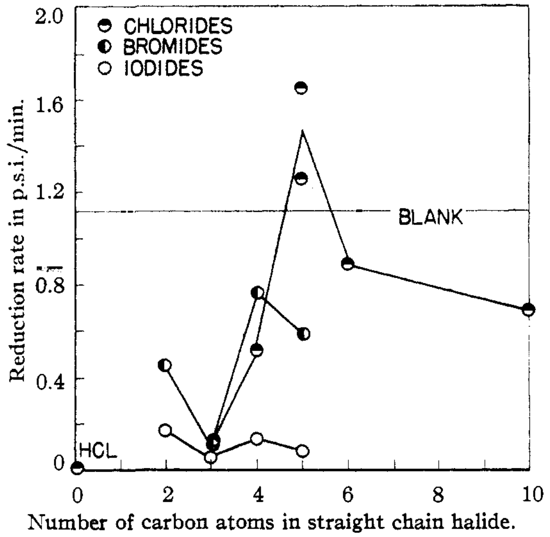


Fig. 2.—Relationship between chain length of normal aliphatic halides and poisoning effect of Raney nickel.

Position of the Halogen.—This effect was investigated with *n*-, *s*- and *t*-amyl chloride as well as with *n*-, *s*- and *t*-butyl chloride and *n*- and *s*-butyl bromide. The values for these runs are given in Table I. The decreased poisoning effect of tertiary halogens may be due to steric interference with the adsorption of the halogen atom.

Poisoning by Aromatic Halides.—No intensive study was made of this effect. However, a few miscellaneous runs are listed in Table II.

The *m*-aminoaryl chlorides are quite poisonous and so is iodobenzene. The others are moderately toxic.

TABLE II

POISONING BY AROMATIC HALIDES

Compound	Reduction rate, p.s.i./min.
Chlorobenzene	0.58
Bromobenzene	.52
Iodobenzene	.13
m-Chloroaniline	.20
6-Chloro-2-aminotoluene	.30
m-Chlorotoluene	.80

Poisoning by Polychlorides.—All compounds tested which had more than one chlorine on the same carbon atom were very poisonous to Raney nickel. The compounds tested are listed in Table III with the reduction rates obtained in their presence. Chloroacetic acid is listed for purposes of comparison.

TABLE III

POISONING BY POLYCHLORIDES

Compound	Rate p.s.i.min.	Compound	Rate, p.s.i./min.
Carbon tetrachloride	Nil	Chloroacetic acid	0.36
Chloral hydrate	Nil	Dichloroacetic acid	.02
Chloroform	0.05	Trichloroacetic acid	.04
Trichloroethanol	.10	Blank about	1.30

Miscellaneous Halogens.—A number of other halides were tested and are listed in Table IV.

TABLE IV

MISCELLANEOUS HALIDES

Compound	Rate, p.s.i./min.
Acetyl chloride	0.03
Allyl chloride	Nil
Benzyl chloride	0.05
β,β'-Dichlorodiethyl ether	.58

Chlorex, $(ClCH_2CH_2)_2O$, gives a value which is just about normal for a compound with two typically aliphatic chlorines. Acetyl chloride, allyl chloride and benzyl chloride each contain very active chlorines and this is apparent in their poisoning effects.

Discussion

Beeck[11] has shown that the 110 plane in face-centered cubic nickel is the most active catalytically for the reduction of ethylene. Taylor[12] has shown by a modification of the gas adsorption technique that at least some catalysts have more than one type of active surface. The study of the poisoning of Raney nickel by hydrogen chloride in the present work indicates that Raney nickel has at least two types of active surface. In order to draw this conclusion it is necessary to assume that the hydrogen chloride is preferentially attracted to the more active surfaces first. Using this postulate the steep part of the curve represents the preferential poisoning of the more active type of surface.

It has been shown that most halides have some poisoning effects on Raney nickel but at room temperature it is not difficult to do reductions in the presence of most chlorides and bromides. All iodides tested were very poisonous. With the exception of the polyhalides and propyl halides most of

(11) Beeck, *Bull. of Am. Physical Soc.*, **13**, No. 7, paper 57.

(12) Taylor and Liang, THIS JOURNAL, **69**, 1306 (1947).

the poisoning effects observed could be predicted reasonably well from a knowledge of the reactivity of these compounds in ordinary organic reactions.

Acknowledgment.—The authors are indebted to The Harshaw Chemical Company for financial support in the form of a fellowship.

Summary

A study of the poisoning of Raney nickel by hydrogen chloride and organic halides has indicated that there are at least two distinct types of active surface present on this catalyst. It has also been found that most of the poisoning effects observed could be predicted on the basis of the known reactivities of these halides. The notable exceptions to this rule are the apparent promoter effect of amyl chloride and the high toxicity of the propyl halides and compounds containing more than one halogen on the same carbon atom. Chlorides and bromides are in general moderately toxic whereas iodides are always highly toxic.

COLUMBUS, OHIO RECEIVED FEBRUARY 16, 1950

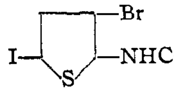
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Reactions of Aceto-2-thiophenamide

BY CHARLES D. HURD AND JAMES MOFFAT

It was shown[1] recently that 2-acetamido-5-bromothiophene was remarkable in that the bromine atom was replaceable during nitration or diazo coupling operations. The present work extends this study.

Since 3-bromo-5-iodo-2-acetamidothiophene (I) readily lost its iodine atom during substitution reactions, one might have predicted the same for the 4-bromo-5-iodo analog (II). This did not occur, however, but instead a conventional substitution reaction occurred on nitration with acetyl nitrate, giving rise to III. Synthesis of II was achieved by mercuration of 2-acetamido-4-bromothiophene, followed by cleavage with iodine.



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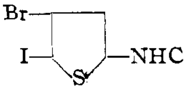

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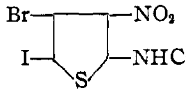

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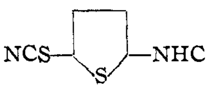
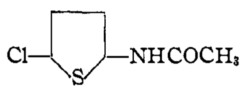


(IV)

Thiocyanation of aceto-2-thiophenamide gives rise to the 5-thiocyano derivative (IV). This is not surprising but it is interesting to point out that acetanilide[2] fails to react under comparable conditions. A similar difference in reactivities of aceto-2-thiophenamide and acetanilide was observed[1] with diazo coupling. The former reacted smoothly to yield an azo dye. On the other hand, acetanilide does not couple.

Chlorination experiments were performed also. Direct chlorination of aceto-2-thiophenamide in either chloroform or glacial acetic acid was unsatisfactory and no chloro derivatives were isolable. A 25% yield of ammonium chloride was isolated from the experiment using acetic acid.

N-Chloroacetamide proved to be an efficient chlorinating agent. The reaction could be controlled so that either the monochloro (V) or the dichloro (VI) derivatives could be prepared. The dichloro compound (VI) did not couple with sodium *p*-nitrobenzenediazoate but the monochloro compound (V) did. Coupling was at position 3, forming VII. This is the first example of a direct coupling of a diazo compound in a beta position of the thiophene nucleus. Of interest also is the fact that chlorine is not ejected in this process. This result is not entirely unexpected since it has been shown that 2,5-dibromothiophene,[3] 2,5-diiodothiophene,[3] 2,3,4,5-tetrabromothiophene[4] and 2,4,5-tribromo-3-methylthiophene[5] all react in the Friedel–Crafts reaction to form 2-acetyl derivatives with the ejection of halogen, whereas 2,5-dichlorothiophene reacts[6] to give 2,5-dichloro-3-acetylthiophene.



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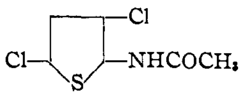

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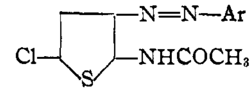

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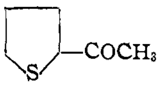

(VIII)

The synthesis of aceto-2-thiophenamide from nitrothiophene leaves much to be desired; hence alternative syntheses from methyl 2-thienyl ketone were investigated, namely, the Beckmann rearrangement of the ketoxime and the Schmidt reaction using hydrazoic and sulfuric acids. The Beckmann reaction has been reported previously,[7] but the yields of amide were very poor. Several methods for carrying out this rearrangement were tested in the present study but none was satisfactory.

The Schmidt reaction did give rise to aceto-2-thiophenamide, but apparently as an eutectic with the isomeric 2-thenomethylamide, $C_4H_3S{-}CO{-}NHCH_3$. The latter compound was prepared for purposes of characterization by reaction of methylamine and 2-thenoyl chloride. Only two other

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[1] Hurd and Priestley, THIS JOURNAL, **69**, 859, 1174 (1947).

[2] Brewster and Dains, *ibid.*, **58**, 1364 (1936).

[3] Gattermann and Römer, *Ber.*, **19**, 689 (1886).

[4] Steinkopf, Jacob and Penz, *Ann.*, **512**, 162 (1934).

[5] Steinkopf and Jacob, *ibid.*, **515**, 276 (1935).

[6] Steinkopf and Köhler, *ibid.*, **532**, 265 (1937).

[7] (a) Rimini, *Chem. Ztg.*, **23**, 266 (1899); (b) Steinkopf, *Ann.*, **403**, 17 (1914).