synthetic polyvinyl alcohol catalyst, and catalytic dehydration of the butenol to isoprene on activated alumina. An over-all yield of 77 g. (65%) of isoprene per 100 g. of acetone has been obtained and yields up to 90 g. should be practicable.

PRINCETON, NEW JERSEY RECEIVED AUGUST 8, 1941

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Some Kinetic Considerations of the Thermal Decomposition of Benzenediazonium Chloride in Various Solvents*

BY CHAS. E. WARING AND JOHN R. ABRAMS

The thermal decomposition of benzenediazonium chloride in a number of different alcohols and acids has been studied by Pray,[1] who found a substantially constant rate in all the alcohols and a slightly different but also substantially constant rate in acids, the rate in water being closely the same as that for acids. The purpose of the present investigation has been to extend the work of Pray and others to cover several amyl alcohols in order to ascertain whether the rate is affected by branched chains or by the increased viscosity of the solvent. It has also been our purpose to analyze these reactions in terms of the more recent theories of the kinetics of reactions in solution.

Experimental

(a) **Material.**—Since traces of water would influence the rate of decomposition of benzenediazonium chloride, precaution was taken to ensure the dryness of all materials employed. All solvents were tested for moisture just before using. All starting materials were of the highest purity obtainable commercially.

(1) Isoamyl, active amyl, *t*-amyl, pentanol-2 and ethyl alcohols were dried by refluxing for four to five hours over fresh lime and then distilled. Purity was established by boiling point determinations.

(2) Benzenediazonium chloride was prepared by the method of Hantzsch and Jochem.[2] Only that material which was white and in a fine crystalline condition (not in clumps) was used to make a run. It was found that the salt could be stored under anhydrous ether in an ice-box for several weeks without deterioration.

(b) **Apparatus.**—The reaction vessel, partially submerged in a thermostat regulated to within 0.01°, was a large Pyrex test-tube with a capillary side arm connected to a 100-ml. water-jacketed nitrometer graduated in tenths of a ml. This was provided with a glass stirrer rotating in a mercury seal in a rubber stopper. All glass to rubber joints were sealed with Picein cement.

(c) **Procedure.**—In making a run, essentially the same procedure as that of Pray was followed. Throughout each run the temperature of the nitrometer and the barometric pressure were recorded regularly. Volume readings, which were accurate to ±0.02 ml. below 50° and to about 0.05 ml. at 50°, were corrected to S. T. P.

TABLE I

DECOMPOSITION OF BENZENEDIAZONIUM CHLORIDE IN ISOAMYL ALCOHOL, t = 20.0°

Time, min.	Vol., ml.	$\log (V_\infty - V_t)$	$k \times 10^3$, min.$^{-1}$
0	0	1.8441	
10	1.66	1.8337	2.40
20	3.27	1.8233	2.39
30	4.94	1.8122	2.54
40	6.59	1.8011	2.58
50	8.21	1.7898	2.59
60	9.79	1.7785	2.60
70	11.37	1.7670	2.65
80	12.87	1.7557	2.62
90	14.33	1.7444	2.60
100	15.76	1.7326	2.72
120	18.49	1.7105	2.53
140	21.08	1.6881	2.59
160	23.57	1.6653	2.62
180	25.88	1.6431	2.56
200	28.17	1.6198	2.67
220	30.32	1.5968	2.65
240	32.32	1.5743	2.60
260	34.24	1.5515	2.63
280	36.10	1.5282	2.68
300	37.76	1.5062	2.56
320	39.41	1.4833	2.64
340	40.94	1.4609	2.58
360	42.44	1.4378	2.66
380	43.74	1.4148	2.64
410	45.88	1.3795	2.71
∞	69.84		
			Av. = 2.60 ± 0.05

ISOAMYL ALCOHOL

Temp., °C.	$k_{av.} \times 10^3$, min.$^{-1}$	No. runs	$r \times 10^3$
20.0	2.61	3	±0.0144
30.0	11.6	4	.143
40.0	47.5	6	.342
50.0	192	5	2.33

ACTIVE AMYL ALCOHOL

Temp., °C.	$k_{av.} \times 10^3$, min.$^{-1}$	Duplicate
30.0	11.9	11.9
35.0	24.8	24.5
40.0	50.4	51.4

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* Presented at the Detroit Meeting of the American Chemical Society.

[1] Pray, *J. Phys. Chem.*, **30**, 1417 and 1477 (1926).

[2] Hantzsch and Jochem, *Ber.*, **34**, 337 (1901).

Rates of Reaction.—The decomposition rate was found to be first order in all solvents investigated. In order to obtain the best average value, the rate constants were determined by the method of Guggenheim.[3] From the logarithm of the volume difference *vs.* time plot, the average k was calculated by the method of least squares. The time interval between each series of volume readings was in all cases several times that of the half-life period.

The data for a typical run (no. 4) are presented in Table I. Included also in this table are the rates at various temperatures in isoamyl and in active amyl alcohols.

In *t*-amyl alcohol and pentanol-2 benzenediazonium chloride was so insoluble that rate measurements were made in ethyl alcohol solutions of these solvents. Table II shows the variation of rate with solvent composition.

TABLE II

RATE OF DECOMPOSITION OF BENZENEDIAZONIUM CHLORIDE IN *t*-AMYL– AND PENTANOL-2–ETHYL ALCOHOL MIXTURES AT 40°

Mole % EtOH	$k \times 10^2$ min.$^{-1}$	Duplicate
	t-Amyl	
80	5.52	5.52
60	5.52	5.54
40	5.75	5.75
	Pentanol-2	
60	5.82	
40	5.90	
20	5.78	

$k_{\text{EtOH}} = 5.02 \times 10^{-2}$ min.$^{-1}$

Although the above rates are somewhat different from those determined for ethyl, isoamyl and active amyl alcohols, it is seen that concentration changes apparently do not affect the rate to any great extent.

Catalytic Effects.—In agreement with Pray's results, it was found that salts did not catalyze the decomposition.

A 33.3% increase in the benzenediazonium chloride concentration failed to affect the rate. The presence of reaction products also produced no change.

The rate was unaffected by the use of reaction vessels of different sizes. The addition of glass beads produced no change and finely powdered Pyrex glass increased the rate but slightly. It is concluded, therefore, that to ordinary changes in surface, the decomposition is predominantly homogeneous.

Reaction Products.—The gas evolved from the decomposition of benzenediazonium chloride was qualitatively identified as nitrogen. Tests for oxygen, hydrogen chloride and ammonia were negative.

In order to determine the number of moles of alcohol used up per mole of salt decomposed, weighed quantities of benzenediazonium chloride and isoamyl alcohol were placed in a thermostat at 50°. When decomposition was complete, the remaining alcohol was carefully separated from the solution by distillation through an efficient column and its loss in weight determined. The result showed that one mole of alcohol was used up per mole of diazonium salt decomposed within a 5% error.

These results, though rather qualitative, suggest the reaction to be bimolecular in mechanism. That the rate of nitrogen evolved shows it to be of the first order is to be expected because of the large excess of solvent.

Theoretically, the final volume of nitrogen evolved should be a direct measure of the original concentration of benzenediazonium chloride. Actually, the observed volume was found to be from 2–5% less than that calculated from the weight of starting material. This difference may be explained by the fact that some of the diazo compound is converted to a colored substance containing nitrogen, as evidenced by the solution turning from light amber at the start to a port wine color at the end of the reaction. The presence of small amounts of water might lead to the formation of phenols. However, no traces of water nor phenols were detected. The colored substance, therefore, is not the result of a coupling between the salt and phenol. It is assumed, then, that the predominant products of decomposition are: nitrogen, hydrogen chloride, phenyl isoamyl ether and valeric aldehyde.

Activation Energy.—From the values of k obtained for isoamyl and active amyl alcohols at different temperatures, the energy of activation, E_a, was determined in the usual manner. The values were 26,620 cal./mole and 27,260 cal./mole, respectively.

Discussion

To explain the fact that the rate of decomposition of benzenediazonium chloride was the same in all solvents of the same type, Pray attempted to correlate k with various physical properties of the solvent. Dielectric constant, viscosity, surface tension, etc., were tried but without success.

TABLE III

Compounds	k in sec.$^{-1}$ $\times 10^4$	E_a	F^a	log $A = PZ^b$	Dipole moments $\times 10^{18}$ E. S. U.
		Alcohols			
Methyl	2.07	27,388	5	15.936	1.68
Ethyl	2.05	27,526	6	16.062	1.70
n-Propyl	1.98	24,964	4	14.177	1.66
i-Propyl	2.63	24,575	7	14.020	1.70
n-Butyl	1.92	25,240	5	14.403	1.65
i-Butyl	2.07	24,546	5	13.916	1.70
i-Amyl	1.93	26,620	7	15.366	1.70
Active amyl	1.98	27,260	9	15.847	?
		Acids			
Formic	0.712	30,861	7	17.973	1.51
Acetic	.717	26,179	3	14.606	1.73
Propionic	.725	26,593	2	14.910	1.74
Butyric	.878	30,820	8	18.024	0.9
Water	.961	23,360	2	12.720	1.85

[a] The F values of column 4 are calculated from the equation $k = Ze^{-E/RT}(E/RT)F/F!$, where F, according to Moelwyn-Hughes; (*cf.* Moelwyn-Hughes, "The Kinetics of Reactions in Solution," Oxford, Clarendon Press, 1933, p. 162) represents the number of internal degrees of freedom of the molecule minus one. [b] Log PZ is obtained from the Arrhenius equation, $k = Ae^{-E/RT}$, where $A = PZ$ = probability factor times the collision number.

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[3] Guggenheim, *Phil. Mag.*, [7] **2**, 538 (1926).

In Table III are listed a number of alcohols and acids for which sufficient data were available to enable the calculation of activation energies and a number of other factors which might be correlated to advantage.

It has been suggested that the variation of the F value from solvent to solvent may indicate in a quasi-quantitative manner the extent to which the solvent enters into partnership with the reactant for the purposes of decomposition. In a few cases, some correlation has been found; *i. e.*, a regular variation in F with change in solvent composition. In the present case, the F terms vary from 4 to 9 in alcohols, but there appears to be no definite correlation between solvents of this type. With the acids, there are marked differences for which there is no adequate explanation. However, from the position of these two acids in Fig. 1, it is interesting to note that formic and butyric acids have about the same values.

The conclusion from this particular treatment is that no sensible correlation exists between F terms and E_a, PZ, solvent types, etc. About all one is able to infer safely is that all solvents are apparently involved to quite some extent with the reactant.

Hinshelwood[4,5,6] has pointed out that quite frequently a correlation exists between log PZ and E when reactions are carried out in various solvents. Since this correlation is found to exist in unimolecular reactions, it may presumably be connected with a bond-breaking process. Thus, if the activation energy is changed by the variation of solvent molecules, the change is due either to one single factor, or to the simultaneous cooperation of a number of factors. It is only in the latter case that a correlation is to be expected, *i. e.*, log PZ and E changing in a parallel manner. In solvents of different polarity, the activation energy is often found to vary from solvent to solvent.[6] Here the change may be attributed to a single factor. Table III, column 6, shows that the polarities of the solvents in this case are essentially identical. Fairclough and Hinshelwood[7] have shown that a log PZ-E correlation is to be expected under these conditions. Here several factors may operate within the PZ term to keep it changing in parallel with changes in E.

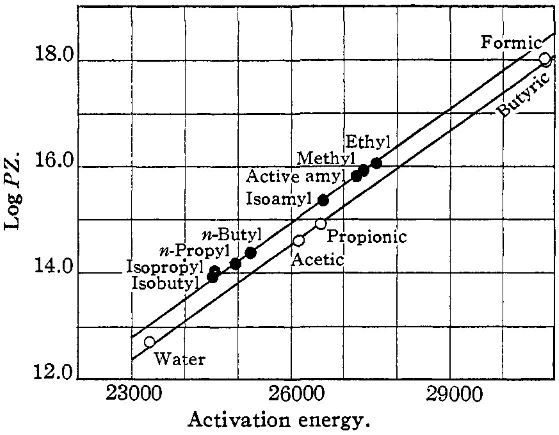

Fig. 1.—Slope = 7.20×10^{-4}: ○, acid; ●, alcohol.

Examination of Fig. 1 reveals that an unusually good straight line results when log PZ is plotted against E for the decomposition of benzenediazonium chloride in various solvents. The solvents divide themselves into two distinct classes, water, more or less logically, falling on the acid curve. The slopes of the two lines are identical, namely, $7.20 \times 10^{-4} = 1/2.3\ RT$. This means that when E changes, PZ also changes so as to keep the reaction rate constant.

It is possible to offer only a general explanation for the striking phenomena exhibited by Fig. 1. From Table III, column 3, it may be seen that the difference between the lowest and highest activation energy for alcohols is 3000 cal./mole—a divergence well outside the limit of experimental error. If the rupture of a bond were the only requirement for reaction, then the activation energies would be expected to be the same in all solvents of the same polarity. Evans and Polanyi[8] have shown that bond strengths are not the only factors determining activation energies: energy may be required to bring up the attacking reagent to the reactive center against a repulsive force.

In the present reaction, we may assume that the energy required for the activation or stretching of the reactive bond remains the same, while the repulsive energy differs from solvent to solvent by virtue of structure or substituents. Once this repulsion is overcome, reaction would tend to take place at the same rate in solvents of the same type, providing the dipole moments are of the same order of magnitude. Such a state of affairs would explain why the rate constants were the same in alcohols or in acids. It does not ex-

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[4] Hinshelwood, *J. Chem. Soc.*, 538 (1937).

[5] Hinshelwood, *Trans. Farad. Soc.*, **34**, I, 138 (1938).

[6] Hinshelwood, *J. Chem. Soc.*, 1378 (1939).

[7] Fairclough and Hinshelwood, *ibid.*, 1573 (1937); also, *cf.* (6).

[8] Evans and Polanyi, *Trans. Farad. Soc.*, **34**, 11 (1938).

plain, however, why the rates in alcohols and acids differ when there is no appreciable difference in their polarity.

This anomaly may be explained in terms of the possible repulsive forces acting in these different solvents. The active group of an alcohol or an acid involved in the diazo decomposition is the hydrogen on the OH. This is evidenced by the fact that the predominant reaction products in pure alcohols and acids are phenyl ethers and phenyl esters, respectively. Now, although the dipole moments of alcohols and acids are practically identical, dipole moments are merely the resultants of the summation of the vector forces within the molecules. Hence, the bond strength of the hydrogen on the OH group may be different in each solvent and thus lead to different repulsive energies. In other words, a different amount of work necessary to bring up the attacking solvent molecules would be expected.

The reaction products further indicate that the predominant bond-breaking process occurs at the hydrocarbon–nitrogen bond. Since the polarity of the solvents is the same, the amount of activation energy utilized for this process should be identical. However, the energy necessary to bring up an alcohol or acid against the repulsive force will be greater or less in the different solvents depending, perhaps, upon the magnitude of the electrostatic forces about the OH group. It is not difficult to imagine that these forces would be, in general, different for alcohols and for acids. Consequently, the fact that different rates are obtained in the two types of solvents does not appear surprising nor unreasonable.

The above hypothesis may be stated in a somewhat more general fashion. There may be, in cases where the solvent plays a role in the reaction, a necessity for a favorable disposition of a number of solvent molecules, achieved by chance, around the reactant in order to lower the activation energy sufficiently to permit reaction. This favorable arrangement may depend upon some fixed set of geometrical conditions. These conditions may have to be such as to permit the attacking molecule to approach sufficiently close for reaction to take place. Or, they may be such that once exact geometrical arrangement is attained, the forces involved between the surrounding solvent molecules and the reactant may cause electronic disturbances which lead to the decomposition of the latter.[8a] In either case, this is analogous to inferring that solvated complexes are formed. This view is supported by the fact that benzenediazonium chloride does not react (at least not appreciably) in solvents in which it is not readily soluble.

Pray pointed out that any proposed mechanism for the decomposition of benzenediazonium chloride must explain the fact that "although the diazo compound is an electrolyte, the addition of an acid or a common ion has no effect on the rate of reaction." This indicates that he considered the decomposition mechanism to be ionic in character. Waters,[9] however, has given good experimental evidence that diazo compounds decompose by a radical mechanism

$$\mathrm{PhN_2Cl} \longrightarrow \mathrm{Ph} + \mathrm{N_2} + \mathrm{Cl}$$

It has also been pointed out that the formation of an aldehyde in the reaction[10]

$$\mathrm{PhN_2Cl} + \mathrm{RCH_2OH} \longrightarrow \mathrm{PhH} + \mathrm{RCHO} + \mathrm{PhOR} + \mathrm{HCl} + \mathrm{N_2}$$

is difficult to explain on the basis of an ionic mechanism. Further, the activation energy for the benzenediazonium chloride decomposition appears to be about 10,000 cal./mole too high for a simple ionic type reaction.

From a consideration of all the above arguments, it is possible to propose a general mechanism that is in accordance with the known facts

$$\mathrm{PhN_2Cl} + \mathrm{ROH} \longrightarrow \mathrm{PhN_2Cl\cdot(ROH)_x} \quad \text{(solution)} \quad (1)$$

$$\mathrm{PhN_2Cl(ROH)_x} \rightleftharpoons [\mathrm{PhN_2Cl(ROH)_x}]^* \longrightarrow \mathrm{Ph} + \mathrm{Cl} + \mathrm{ROH} + \mathrm{N_2} \quad (2)$$

$$\mathrm{Ph} + \mathrm{Cl} + \mathrm{ROH} \longrightarrow \mathrm{PhOR}\text{[11]} + \mathrm{PhH} + \mathrm{RCHO} + \mathrm{HCl} \quad \text{(fast)} \quad (3)$$

Step (1) represents the formation of the solvated complex. The activation process of (2) may occur due to the electron rearrangement in the reactant caused by the correct disposition of solvent molecules around it; or, by a collision resulting in a propitious penetration of the protecting solvent sheath. If the activated complex, $[\mathrm{PhN_2Cl\cdot(ROH)_x}]^*$, suffers no deactivating collision, phenyl and chlorine radicals and nitrogen molecules are produced. This transformation may be

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[8a] It should be pointed out that in reactions where large amounts of energy are available for activation, the geometry of the situation obviously ceases to have much significance and no correlation between log *PZ* and *E* is to be expected. The change in rate, then, will simply be due to changes in *E*. Under these conditions, a correlation between log *k* and *E* is often observed.

[9] Waters, *J. Chem. Soc.*, 2007 and 2014 (1937); 1077 (1938).

[10] Hantzsch, *Ber.*, **63**, 1786 (1930).

[11] The relative amounts of phenyl ether, benzene and aldehyde formed are dependent upon the alcohol.

regarded as the rate-determining step. The free phenyl and chlorine radicals produced in (2) react rapidly in (3) with the alcohol or acid. This step is necessarily fast due to the large excess of solvent. Reactions (2) and (3) may be considered as analogous to a gas phase decomposition in which the free radicals initially produced in the primary, or rate-determining, step react subsequently in a bimolecular process.

The above mechanism, as previously mentioned, lays claim to no great specificity. It is only qualitative and by no means quantitative. However, it does explain why neither acids nor common ions affect the rate constant; and it also suggests that different repulsive energies would be involved depending upon the degree of solvation of the different solvents or the chance of a favorable arrangement of the solvent molecules about the reactant.

One final point should be discussed in connection with this reaction. When log *PZ* is plotted against *E* one might reasonably expect, in a homologous series, some sort of orderly arrangement among the solvents, *e. g.*, methyl, ethyl, propyl, etc. Figure 1 shows that this is not the case. There appears to be no correlation in regard to structure as to how the solvents align themselves along the curve. This lack of uniformity, which further emphasizes the complex role played by the solvent in reaction kinetics, may be somewhat clarified by the following analysis.

In Fig. 2 the activation energy is plotted against the number of carbon atoms. The curves are instructive. None of the ordinary properties of alcohols or acids show an extreme value (*i. e.*, a maximum or minimum) as a function of the number of carbon atoms. However, all properties are either monotone increasing or decreasing functions of the carbon atom number. It is obvious that the sum of an increasing and a decreasing function can give a curve with a minimum. Some decreasing functions are hydrogen bond energy per unit volume, dielectric constant, etc. Of the increasing functions, viscosity would probably be the most important one in the present case. It is quite possible that some such sets of functions are operative in this reaction.

We have attempted in the present paper to point out some of the interesting aspects of the decomposition of benzenediazonium chloride in various alcohols and acids. Research is now in progress in this Laboratory to determine the effects produced in the *k*, *PZ*, and *E* values when substituted benzenediazonium compounds are allowed to react in different solvents.

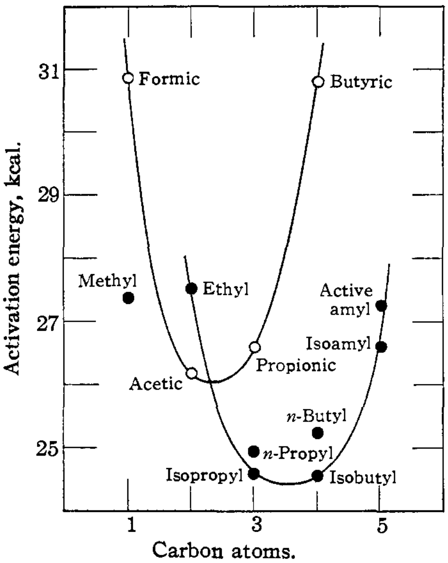


Fig. 2.—Variation of activation energy with the number of carbon atoms in the solvent molecules: ○, acids; ●, alcohols.

Summary

The rate of decomposition of benzenediazonium chloride has been investigated in isoamyl, active amyl, *t*-amyl alcohols and pentanol-2. The rates are found to be essentially the same. The activation energies differ, however, indicating that some function is varying in a manner that keeps the rates constant.

A plot of log *PZ vs*. *E* for the decomposition in various alcohols and acids give a straight line correlation; the data for alcohols give one curve, the acids, a line parallel to it.

On the basis of this correlation, the relative importance of bond strengths and repulsive energies involved in this decomposition is discussed.

Explanations have been advanced to account for the facts: that the rate of decomposition is the same in all solvents of the same type, and that the addition of acids and common ions does not affect the rate.

A mechanism for the diazo decomposition has been proposed. This mechanism involves the solvation of the diazonium compound as an initial step and the subsequent formation of free phenyl and chloride radicals which then react with the solvent molecules.

A curve is given showing the variation of the activation energy with the number of carbon atoms in the solvents. The theoretical implications of the minimum found are discussed.

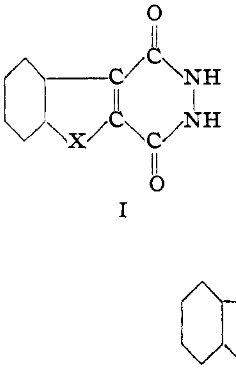
BROOKLYN, N. Y. RECEIVED MARCH 15, 1941

[CONTRIBUTION NO. 251 FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

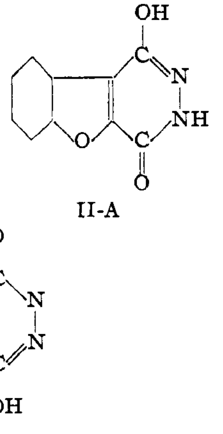
The Synthesis of the Cyclohydrazides of Coumarone-, Thionaphthene- and Indole-2,3-dicarboxylic Acids

BY ERNEST H. HUNTRESS AND WILLIAM M. HEARON[1,2]

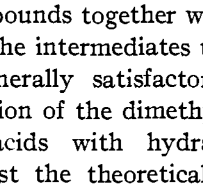
In the course of another investigation to be reported later it became necessary to prepare the cyclohydrazides of certain α,β-dicarboxylic acids of the coumarone (I, X = O), thionaphthene (I, X = S), and indole (I, X = NH) series, none of which have previously been reported. The present paper describes the syntheses and properties of all three compounds together with certain new information on the intermediates used.



I



II-A



II-B

The most generally satisfactory method involved the reaction of the dimethyl esters of the corresponding acids with hydrazine hydrate. This gave almost the theoretical yields of the coumarone (94%) and thionaphthene (90%) derivatives and a very satisfactory result (76%) with the indole analog. The coumarone and thionaphthene derivatives were also prepared from the acids themselves and the latter was also prepared from the corresponding anhydride but the yields by these methods were never as high as from the esters.

These three analogously constituted cyclohydrazides are all colorless, high-melting solids sparingly soluble in most solvents. They all act as mono-enols, however, and can be titrated as such with dilute aqueous alkali. They all form monoacetates and give colorations with ferric chloride but do not reduce ammoniacal silver nitrate solution. In the case of the cyclohydrazide of coumarone-2,3-dicarboxylic acid, both the enol and keto forms were isolated but only one desmotrope was observed for the corresponding cyclohydrazides of the other two series.

The synthesis of these cyclohydrazides thus required the preparation of the respective 2,3-dicarboxylic acids and/or their dimethyl esters.

At the time this work was carried out, coumarone-2,3-dicarboxylic acid had been reported only once,[3] but by two rather similar methods both starting from isatin. The first passed through the following sequence (yields in parentheses): isatin → (30%) coumarandione-2,3 → (39.6%) *o*-oxalophenoxyacetic acid → (100% ?) dimethyl *o*-oxalophenoxyacetate → (32.5%) coumarone-2,3-dicarboxylic acid. Assuming quantitative methylation at the third stage (for which no data were reported), the over-all yield was $30 \times 39.6 \times 100 \times 32.5 = 3.9\%$. The second method was: isatin → (30%) coumarandione-2,3 → (39.6%) *o*-oxalophenoxyacetic acid → (16.3%) coumarone-2,3-dicarboxylic acid. For this method the over-all yield was therefore $30 \times 39.6 \times 16.3 = 2.0\%$. It thus appears definite that Reichstein's conversion of isatin to coumarone-2,3-dicarboxylic acid gave an over-all yield of only 2–4%.

By the methods detailed in the experimental part, Reichstein's method has been so greatly improved that the over-all yield is about seven times as great, *i. e.*, 30.5%. This improvement is attributable to two principal factors. First, the conversion of isatin to coumarandione-2,3 has been developed to give yields of 50%. Second, the transformation of this dione to coumarone-

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(1) This paper is contributed from part of a dissertation submitted in June, 1940, by W. M. Hearon to the Faculty of the Massachusetts Institute of Technology in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) Present address: Eastman Kodak Company, Rochester, New York.

(3) Titoff, Müller and Reichstein, *Helv. Chim. Acta*, **20**, 883–892 (1937).