

the solution it was cooled and extracted with ether. The ether extract was washed with water and dried over sodium sulfate. The ether was removed and the substance was crystallized from butyl ether. It melted at 149°.

Anal. Subs., 0.0927: CO₂, 0.2177; H₂O, 0.0506. Calcd. for C₂₁H₂₅O₃: C, 64.16; H, 6.09. Found: C, 64.05; H, 6.11.

Oxidation of Dehydrodihydroxy- β -Dihydrorotenonic Acid to Derric Acid.—One gram of acid was dissolved in 12 cc. of 5% sodium hydroxide solution. The solution was gently heated and 3 cc. of 30% hydrogen peroxide was gradually added. The solution was finally heated to boiling for a few minutes, then cooled and acidified with dilute sulfuric acid. The solution was extracted with ether, the ether extract was washed with water and dried over sodium sulfate. After removal of the ether the substance was crystallized from butyl ether. It melted at 167° and was found to be identical with derric acid.

Summary

Rotenonic acid in glacial acetic acid and sulfuric acid is isomerized to a substance which is insoluble in alkali and appears to be a saturated lactone. This compound has been named β -dihydrorotenone.

β -Dihydrorotenone gives the typical reactions of rotenone. It yields a dehydro compound which adds two moles of water to form an acid. It gives a diketone. With potassium hydroxide it yields an acid isomeric with dihydrotubaic acid.

A possible explanation is given of the fact that rotenone is readily reduced and isorotenone is not, and a relation between the two is indicated.

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[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

THE SPECTROCHEMISTRY OF FURAN AND ITS DERIVATIVES¹

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Absorption spectra and molecular refraction have proved to be of considerable value in attacking chemical problems from a physical standpoint. In the furan series no extensive study has been made of these optical properties, although a number of observations are reported in the literature. The present work was undertaken with the object of making a rather extensive study of furan derivatives with the idea of discovering any general relationships which might prove useful in elucidating the structure and behavior of furan and its derivatives.

Preliminary observations of absorption spectra showed that furan and its simpler derivatives do not exhibit selective absorption in the visible and ultraviolet regions (to 2200 Å.). It was hoped that there would be a difference in the absorption spectra of the isomeric alpha- and beta-sub-

¹ This article is an abstract of a thesis submitted to the Faculty of the Graduate School of Cornell University by Everett C. Hughes, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1930.

stituted furans that would be of value in distinguishing between them. Even in the case of the carboxylic acid derivatives, which do exhibit a characteristic absorption, there was not observed any regular or sufficient difference that would be of value in distinguishing between isomeric compounds. The only real difference lies in the molecular absorption coefficients (Fig. 2), which are consistently higher for the alpha-derivatives than for the beta-derivatives. These differences are directly related to the differences in optical dispersion; the latter, as will be shown below, prove to be of value as a criterion for distinguishing between the alpha- and beta-substituted derivatives.

Early investigations of the refractive index of compounds containing the furan ring have shown that the law of refraction equivalence is not strictly followed.² From theoretical considerations of molecular refraction as presented by Lorentz and discussed by later investigators³ it appears that no absolute agreement between the calculated and observed values can be expected.

It was found, however, that the furan derivatives under examination could be divided into two categories on the basis of the differences between the observed and calculated values. Furthermore, the exaltations of the dispersion of compounds of the furan series may furnish information bearing upon the fundamental question of the structure of the ring and the position of substituents.

In order to provide data for study, furan and twenty furan derivatives were prepared in a high state of purity, and their refractive indices and densities were determined. These data, together with a number of values taken from the literature, are shown in Table V. The calculations made from these observations are collected in Table I.

An examination of the results indicates that these furan derivatives can be divided into two categories: one in which the value *EMR* is negative, and another in which this value is positive.

In the first class are found furan and all of the derivatives (Table I, 1-13) in which the substituents do not contain a double bond on the atom immediately attached to the ring in the alpha-position.⁴ These compounds

² (a) Brühl, *Ann.*, **235**, 1 (1886); (b) Nasini and Carrara, *Gazz. chim. ital.*, **24**, I, 255 (1894); (c) Auwers, *Ber.*, **45**, 3077 (1912).

³ (a) Lorentz, "The Theory of Electrons," B. G. Teubner, Leipzig, 1909, p. 89; (b) Swietoslawski, *THIS JOURNAL*, **42**, 1945 (1920); (c) Fajans and Knorr, *Ber.*, **59**, 249 (1926).

⁴ Ethyl pyrotritarate (2,5-dimethyl-3-carbethoxyfuran) is an exception to this statement. If the above constitution is correct, there is present a cross-conjugated system, the effect of which is uncertain—due to the lack of a sufficient number of known examples for examination. The only other available example of cross-conjugation is 2-methyl-3-carbethoxyfuran, which is not an exception to the general statement given above.

TABLE I
 REFRACTOMETRIC DATA FOR DERIVATIVES OF FURAN

No.	Compound	MR _D obs.	EMR _D ^a	E _{Σβ-α} ^b	E _{Σγ-α}	EMR _∞	Constants of Sellmeier equation		
							M	λ ₀	C + 1
1	Furan	18.426	-0.761	-11.57	-6.11	-0.612	1.43407	1572	1.9762
2	2-Methylfuran	23.337	- .462	13.0	10.0	- .474	1.77000	742	2.00105
3	2,5-Dimethylfuran ^c	28.178	- .239	3.88	4.5	- .267	1.75185	334	2.03167
4	Furfuryl alcohol	24.874	- .450	0.0	1.0	- .410	1.74927	1478	2.15834
5	Furfuryl acetate	33.920	- .769	3.93	5.36	- .669	1.47193	1575	2.08682
6	Ethyl furylpropionate	43.474	- .451	...	5.50	- .008	0.80218	2791	2.09081
7	Furylbutanone	37.530	- .134	2.84	7.86	- .209	1.86697	202	2.10557
8	Furylpentanone	42.083	- .199	0.0	9.78	- .235	1.70486	912	2.10115
9	2-Chlorofuran	23.420	- .628	-3.77	1.24	- .517	1.63804	1553	2.07304
10	3-Chlorofuran	23.157	- .891	-9.62	-9.49	- .745	1.58428	1460	2.07993
11	2-Bromofuran	26.119	- .825	4.0	1.0	- .947	2.32088	796	2.17583
12	3-Bromofuran	25.868	-1.078	-13.5	-12.4	- .996	1.80747	1581	2.18264
13	2-Methyl-3-carbethoxyfuran	38.267	-1.04	-8.25	-12.08	- .757	1.1147	100	1.9725
14	Ethyl furoate	35.61	0.921	43.0	47.8	0.615	1.98841	1712	2.09814
15	Ethyl 5-chlorofuroate	40.94	1.384 ^d	54.2	60.9	1.051	2.03544	2006	2.16719
16	Ethyl 3-chlorofuroate	40.37	0.814	40.1	47.5	0.55	1.76727	1972	2.15016
17	Methyl furoate ^e	30.896	.825	42.0	44.5	.511	2.30746	1393	2.1343
18	Propyl furoate ^f	40.255	.948	38.9	41.0	.572	2.12725	1183	2.10839
19	Ethyl pyrotritarate ^g	44.618	.693	...	20.1	.529	1.7509	1196	2.10418
20	Furyl cyanide	24.40	.89	33.2	48.3	.667	1.94803	2130	2.12493
21	Furfural ^d	25.42	1.61	95	110	1.040	3.25164	2042	2.22256
22	Furylethylene	29.58	1.63	60.2	79.4	1.257	2.54077	2325	2.15765
23	Furylbutenone	42.72	5.523	340.6	421	2.868	4.37428	2967	2.32375
24	Furylpentenone	46.634	4.824	301	376	2.921	4.08374	2888	2.336
25	Ethyl furylacrylate	48.27	4.481	161.0	227.1	3.203	3.4039	2754	2.26431
26	Furfural pinacolone	56.57	5.524	201.8	268.5	3.55	3.30667	2983	2.27162

^a EMR_D = MR_D observed - MR_D calculated. The revised values of Eisenlohr were used for the atomic refractions [Landolt-Börnstein, "Physikalisch-chemische Tabellen," Julius Springer, Berlin, 5th Ed., Vol. II, 1923, p. 985]. The furan ring was considered to have two ethylenic double bonds and an ethereal oxygen atom.

^b E_{Σβ-α} is calculated from the specific refractions according to the empirical formula of Auwers (see below).

^c Nasini and Carrara, *Gazz. chim. ital.*, **24**, I, 271 (1894); ^d Brühl, *Ann.*, **235**, 1 (1886);

^e Auwers, *Ber.*, **44**, 3690 (1912); ^f Brühl, *J. prakt. Chem.*, [2] **50**, 142 (1894); ^g Gennari, *Gazz. chim. ital.*, **24**, I, 253 (1894).

might be termed normal furan derivatives. The differences in the group, for the D line, vary from -0.134 to -1.078 and the average difference is -0.479. It is of interest to point out in this connection that the tetrahydro derivatives of furan show much less difference in the values of EMR than do the furan derivatives; *e. g.*, five typical tetrahydrofuran derivatives showed differences from -0.31 to +0.03.⁵

In the second class are found all of the furan derivatives in which the side chain contains a double bond forming a conjugated system with the ring (Table I, 14-26). The differences in the group, for the D line, vary from +0.814 to +5.523. This result is not surprising in view of the many observations of optical exaltations caused by the presence of conjugated

⁵ Tetrahydrofuran, -0.13; 3-methyltetrahydrofuran, +0.03; tetrahydrofurfuryl alcohol, -0.16; tetrahydrofurfural, -0.31; tetrahydrofuroic acid, -0.11.

systems. Since all of these compounds exhibit absorption in the near ultraviolet region, the exaltations are probably caused by the proximity of this absorption band. It has previously been demonstrated that the refractive index increases rapidly as an absorption band is approached and apparently rises to infinity at the center of the band. The absorption spectra of a number of the furan derivatives used in this investigation are shown in Figs. 1 and 2.

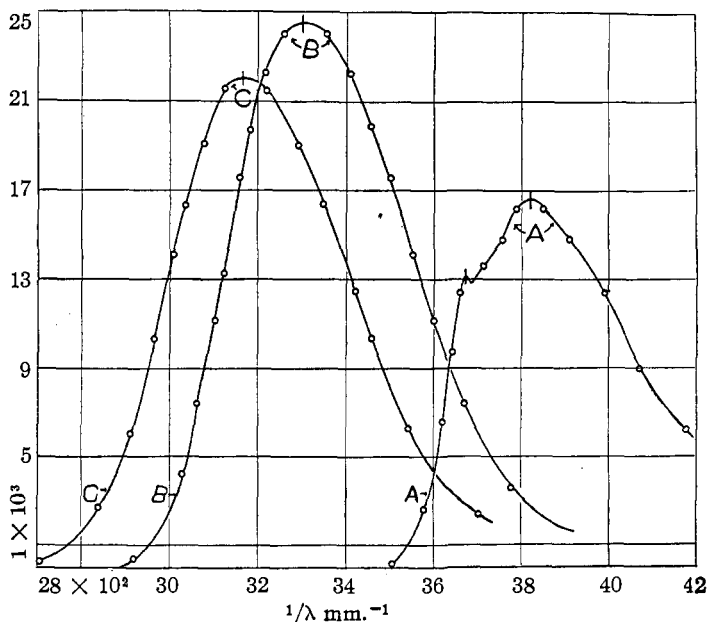


Fig. 1.—A, Furylethylene; B, ethyl furylacrylate; C, furylbutenone; solvent, ethyl alcohol.

In an effort to obviate the effect of the ultraviolet absorption bands it seemed of interest to make use of a proposal of Hunter.⁶ He suggested that if the Sellmeier equation for dispersion (1) be used to calculate a value for the refractive index at a wave length sufficiently removed from the major absorption bands to be uninfluenced by them, the observed and calculated values would agree better than at visible wave lengths. By the use of three simultaneous equations, the constants for the following form of the Sellmeier dispersion formula were calculated for a number of furan derivatives.

$$n^2 = \frac{M}{\lambda^2 - \lambda_0^2} + C + 1 \quad (1)$$

In this equation λ is the wave length of light used in the determination of n , λ_0 is the free vibrational period of the electron which is responsible

⁶ Hunter, *J. Chem. Soc.*, 123, 434, 1671 (1923).

for the refraction and also for the absorption of light, and M is an intensity factor. The value of λ_0 should represent an absorption band in the ultra-violet; that it does so has been verified experimentally for five of the com-

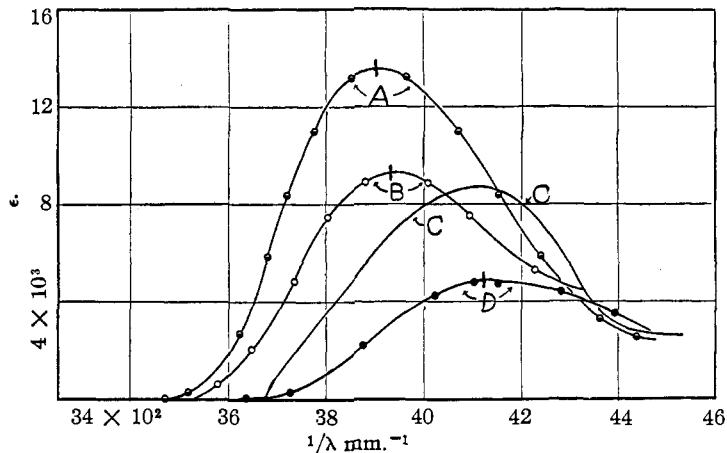


Fig. 2.—A, 5-Chlorofuroic acid; B, 3-chlorofuroic acid; C, 2-furoic acid; D, 2-methyl-3-furoic acid; solvent, ethyl alcohol.

pounds used (Table II). The calculated and observed values for the absorption bands were found to differ by only 250 Å., an effect which can be attributed to the influence of the solvent (alcohol).

TABLE II
ABSORPTION SPECTRA MAXIMA FOR FIVE DERIVATIVES OF FURAN

	Compound	Molecular extinction coefficient	Maxima in Å.	Sellmeier equation constant λ_0
1	Furylethylene	16600	2600	2325
2	Furylbutenone	22000	3100	2967
3	Furylpentenone	22800	3100	2888
4	Ethyl furylacrylate	24500	3000	2754
5	Furfural pinacolone	20500	3200	2983

In the above equation the first term will vanish if λ is taken to be infinite, and the square root of $(C + 1)$ will be the refractive index at infinite wave length. The exalting effect of the ultraviolet absorption band should therefore be at a minimum. The values obtained from these calculations at infinite wave length are shown in Table I. The results show that the differences are somewhat less than those at visible wave lengths but they are far too great to constitute any improvement in the situation.

The most satisfactory application of an empirical relation derived from refractive indices, to the study of structural problems has been made by

Auwers.⁷ He uses the following calculation of the percentage exaltation of dispersion (E)

$$E = \frac{(\Sigma_{\gamma} - \Sigma_{\alpha})_{\text{obs.}} - (\Sigma_{\gamma} - \Sigma_{\alpha})_{\text{calcd.}}}{(\Sigma_{\gamma} - \Sigma_{\alpha})_{\text{calcd.}}} \times 100\%$$

Σ = specific refraction $\times 100$

This method was tried in the furan series for four pairs of isomeric alpha- and beta-substituted compounds. The values of E , listed in Table I, show that there is a very large difference between the alpha- and beta-isomers, and that the value for the alpha compound is always larger than that of the beta-compound. A comparison of the densities, boiling points, refractive indices and other properties indicates that the exaltation of the dispersion is unique in showing a marked difference between the isomers.⁸ Although the differences in the percentage exaltation of the dispersion constitute a satisfactory means of distinguishing between the alpha- and beta-isomers, this method has the serious limitation of requiring that both isomers be available for comparison.

It was also observed that the constant M of the Sellmeir equation differs quite markedly in the alpha- and beta-derivatives of furan (see Table I). This constant is a value which, by deduction, represents the intensity of the vibration producing the absorption band and is directly related to the exaltations of the dispersion. In the compounds examined, the value of M was always higher for the alpha-isomer. This evidence of higher vibrational intensity in the alpha-isomers might be interpreted to mean that the alpha-derivative would be more reactive than the beta-derivative. With the present incomplete knowledge of the relative reactivity of substituents in the alpha- and beta-positions this interpretation cannot be confirmed from the chemical standpoint. This conclusion is in agreement with the observation that a halogen atom in the beta-position is less reactive than one in the alpha-position.

In its chemical behavior, in general, the furan ring occupies a position intermediate between the unsaturated aliphatics and the typically aromatic benzene ring. A comparison of the exaltations of the dispersion of corresponding benzene and furan derivatives (Table III) indicates a similarity in the compounds that have simple substituents (Cl, Br, CH₃). The effect of a substituent containing a double bond in the α,β -position of the side chain is much more marked in the furan series than in the benzene series. This result appears to parallel the unusual chemical behavior of furan derivatives with a double bond in the α,β -position of the side chain;

⁷ Auwers, *Ber.*, **43**, 806 (1910); *Ann.*, **408**, 212 (1915); **422**, 160 (1921).

⁸ The generalization made here is based on a comparison involving only a few pairs of alpha- and beta-isomers. It is our intention to synthesize a number of other beta-substituted furan derivatives in order to test the validity of this general statement.

these compounds readily undergo a scission of the ring, accompanied by an unusual rearrangement.⁹

TABLE III
PERCENTAGE EXALTATION OF DISPERSION IN BENZENE AND FURAN SERIES

Substituent	$E_{\Sigma\gamma} - \Sigma\alpha$							
	—H	—Cl	—Br	—CH ₃	—COOC ₂ H ₅	—CH=CH ₂	—CH=CH— COOC ₂ H ₅	—CH=O
Benzene series ^a	7	10	11	11	26	45	105	49
α -Furan series	-6	1.2 ^b	1.0 ^b	10	48	79	227 ^c	110 ^c

^a The data for the benzene series are those of Auwers [*Ber.*, 45, 2769 (1915); *Ann.*, 408, 212 (1915)]. ^b Values for the β -substituted furan derivatives are Cl, -3.77; Br, -12.4. ^c The values for the furan series are much higher than those of a simple ethylenic series. In the series, CH₃CH=CH—, the values are —CH=O, 55; —CH=CH—COOC₂H₅, 128 [Auwers and Eisenlohr, *J. prakt. Chem.*, [2] 84, 34, 108 (1911)]. The effect of ring closure on spectrochemical properties has been studied by Auwers [*Ann.*, 415, 98 (1918); 422, 133 (1921)].

It is of interest to note that the model of benzene suggested by Dupont¹⁰ and by Latimer and Porter,¹¹ can be applied also to furan and other five-membered heterocyclic rings of aromatic character, such as thiophene,

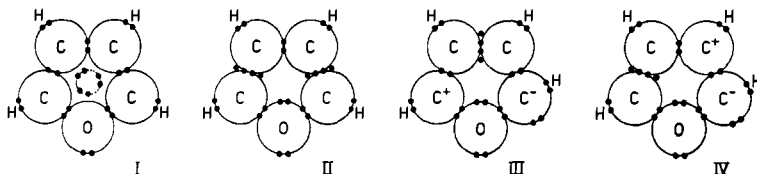


Fig. 3.—Electronic formulas for furan: I, centric formula; II, ethylenic formula; III, active form for 1,4-addition; IV, active form for 1,2-addition.

pyrrole and glyoxaline. The essential feature of this model is a "centric" system of six electrons, which in the benzene ring may be considered to be formed by a contribution of one electron from each carbon atom of the ring. In the case of furan the "centric" system is also one of six electrons, four of which may be considered to be contributed from the four carbon atoms and *two* from the oxygen atom (Fig. 3, I). The system in furan may then be represented by equilibria of the following types of electronic arrangements.

Active forms of furan may be postulated to explain either 1,2- or 1,4-addition (Fig. 3, III and IV) by use of the general conceptions of Carothers concerning the double bond.¹² A consideration of 1,4-addition to the furan ring will be presented in a later publication dealing with the mechanism of rearrangements in the furan series.¹³

⁹ Pummerer and Gump, *Ber.*, 56, 999 (1923).

¹⁰ Dupont, *Bull. soc. chim.*, [4] 41, 1334 (1927).

¹¹ Latimer and Porter, *THIS JOURNAL*, 52, 206 (1930).

¹² Carothers, *ibid.*, 46, 2226 (1924).

¹³ Reichstein, *Ber.*, 63, 750 (1930); Runde, Scott, and Johnson, *THIS JOURNAL*, 52, 1284 (1930). See also, Pummerer and Gump, *Ber.*, 56, 999 (1923).

Experimental

The furan derivatives used in this investigation were prepared with only minor deviations from methods which previously have been described in the literature. The final purifications were always carried out with consideration only of purity of the product, and not of yield. In Table IV are given the physical constants and references to the methods of preparation.

TABLE IV
PHYSICAL CONSTANTS OF COMPOUNDS

No.	Compound	Reference	Boiling point, °C.
1	Furan	<i>a</i>	31 ₇₄₅
2	2-Methylfuran	<i>b</i>	63.1 ₇₄₉
3	Furfuryl alcohol	<i>c</i>	80 ₁₉
4	Furfuryl acetate	<i>d</i>	67 ₈ ; 180 ₇₄₂
5	Ethyl furylpropionate	<i>e</i>	101-102 ₂₂
6	1-Furylbutane-3-one	<i>f</i>	95 ₁₈
7	1-Furylpentane-3-one	<i>g</i>	88.5 ₁₀
8	2-Chlorofuran	<i>h</i>	77.5 ₇₅₀
9	3-Chlorofuran	<i>h</i>	79 ₇₄₂
10	2-Bromofuran	<i>h</i>	102.2 ₇₅₀
11	3-Bromofuran	<i>h</i>	102.5 ₇₄₃
12	2-Methyl-3-carbethoxyfuran	<i>i</i>	49.5 ₁₀ ; 57 ₁₇
13	Ethyl furoate	<i>j</i>	128 ₉₅ ; m. p. 34
14	Ethyl 5-chlorofuroate	<i>k</i>	88 ₈
15	Ethyl 3-chlorofuroate	<i>k</i>	217 ₇₅ ; m. p. 21.7
16	Furyl cyanide	<i>l</i>	146 ₇₃₈
17	Furylethylene	<i>m</i>	94 ₇₄₂
18	1-Furyl-1-butene-3-one	<i>n</i>	116 ₁₀ ; m. p. 39.7
19	1-Furyl-1-pentene-3-one	<i>g</i>	128 ₁₅
20	Ethyl furylacrylate	<i>o</i>	118-119 ₁₀
21	Furfural pinacolone	<i>g</i>	120 ₈

^a "Organic Syntheses," John Wiley and Sons, Inc., New York, 1927, Vol. VII, p. 40.

^b Wolff, *Ann.*, 394, 101 (1912). ^c Wienhaus, *Ber.*, 53, 1657 (1920). ^d Zanetti, *THIS JOURNAL*, 47, 535 (1925). ^e Windaus and Dalmer, *Ber.*, 53, 2304 (1920). ^f Harries and Kaiser, *ibid.*, 32, 1320 (1899). ^g Kasiwagi, *Bull. Chem. Soc. Japan*, 1, 90 (1926); *Chemical Abstracts*, 20, 3004 (1926). ^h Shepard, Winslow and Johnson, *THIS JOURNAL*, 52, 2083 (1930). ⁱ Benary, *Ber.*, 44, 493 (1911). ^j Gennari, *Gazz. chim. ital.*, 24, I, 250 (1894). ^k Hill and Jackson, *Am. Chem. J.*, 12, 30, 36 (1890). ^l From the dehydration of furfuraldoxime, cf. Runde, Scott and Johnson, *THIS JOURNAL*, 52, 128 (1930). ^m Moureu, Dufraisse and Johnson, *Ann. chim.*, [10] 7, 14 (1927). ⁿ "Organic Syntheses," Vol. VII, p. 42. ^o From the silver salt and ethyl iodide, cf. Gibson and Kahnweiler, *Am. Chem. J.*, 12, 315 (1890).

The method employed in the examination of the absorption spectra was that described by Orndorff, Gibbs and McNulty,¹⁴ using a Hilger spectrograph in conjunction with a Hilger sector photometer. The light source was a high tension spark between brass electrodes under water.

The refractive indices were measured at five wave lengths and three dif-

¹⁴ Orndorff, Gibbs and McNulty, *THIS JOURNAL*, 47, 2767 (1925).

ferent temperatures, using a water-jacketed Pulfrich refractometer. The densities were determined in carefully standardized pycnometers of two and five cc. capacity. In Table V the numerical results are summarized and tabulated. In addition to these values, certain previously recorded values from the literature were used in making the calculations given in Table I.

TABLE V
REFRACTIVE INDICES FOR FURAN AND DERIVATIVES

No.	Compound	$t, ^\circ\text{C.}$	d_t^t	$\frac{dn}{dt} \times 10^6$	$\lambda 6438$	$\lambda 5893$	$\lambda 5790$	$\lambda 5461$	$\lambda 4359$
1	Furan	20	0.9366	62	1.4188	1.4214	1.4221	1.4243	1.4363
2	2-Methylfuran	20	.9132	56	1.4298	1.4335	1.4337	1.4358	1.4481
3	Furfuryl alcohol	20	1.1285	41	1.4820	1.4848	1.4854	1.4879	1.5010
4	Furfuryl acetate	25	1.1131	42	1.4576	1.4603	1.4609	1.4631	1.4751
5	Ethyl furyl-propionate	25	1.0527	52	1.4534	1.4569	1.4576	1.4585	1.4705
6	Furylbutanone	25	1.0258	42	1.4653	1.4697	1.4703	1.4725	1.4847
7	Furylpentanone	25	1.0029	44	1.4628	1.4670	1.4675	1.4697	1.4816
8	2-Chlorofuran	20	1.1922	52	1.4543	1.4571	1.4580	1.4604	1.4737
9	3-Chlorofuran	20	1.2098	54	1.4561	1.4589	1.4596	1.4619	1.4744
10	2-Bromofuran	20	1.6500	55	1.4927	1.4981	1.4988	1.5018	1.5173
11	3-Bromofuran	20	1.6605	50	1.4930	1.4962	1.4970	1.4996	1.5140
12	2-Methyl-3-carbethoxyfuran	25	1.0102	43	1.4140	1.4159	1.4163	1.4177	1.4252
13	Ethyl furoate	40	1.0974	48	1.4662	1.4699	1.4706	1.4738	1.4906
14	Ethyl 5-chlorofuroate	25	1.2418	44	1.4905	1.4944	1.4954	1.4987	1.5176
15	Ethyl 3-chlorofuroate	35	1.2408	42	1.4823	1.4857	1.4864	1.4894	1.5057
16	Furyl cyanide	20	1.0822	50	1.4757	1.4798	1.4808	1.4839	1.5032
17	Furylethylene	25	0.9316	60	1.4927	1.4981	1.4991	1.5039	1.5312
18	Furylbutenone	45	1.0572	54	1.5635	1.5788	1.5813	1.5909	1.6588
19	Furylpentenone	25	1.0685	50	1.5651	1.5787	1.5912	1.5901	1.6496
20	Ethyl furylacrylate	25	1.0891	50	1.5347	1.5459	1.5479	1.5548	1.6008
21	Furfural pinacolone	25	1.0022	49	1.5373	1.5495	1.5513	1.5588	1.6124

Summary

1. The densities and refractive indices (in the visible region of the spectrum) have been measured for furan and twenty furan derivatives. The absorption spectra of eight furan derivatives are reported.

2. From the molecular refractions and the exaltations of the dispersion, calculated from these data, certain generalizations have been made concerning the effects of various types of substituents in the furan ring.

3. It has been shown that isomeric alpha- and beta-substituted furan derivatives may be distinguished from each other by spectrochemical means. The exaltations of the dispersion for the alpha-isomers are invariably higher than for the beta-isomers.

4. It has been shown for five furan derivatives that the wave lengths

of the absorption maxima (in the near ultraviolet) calculated from the Sellmeier dispersion formula are in agreement with the wave lengths of the absorption maxima actually observed.

5. Electronic formulas for the furan ring have been proposed and discussed briefly from the standpoint of interpretation of reactions of furan derivatives.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, COLLEGE OF LIBERAL ARTS,
NORTHWESTERN UNIVERSITY]

SOME ARSONIC ACIDS OF FLUORENE AND ITS DERIVATIVES

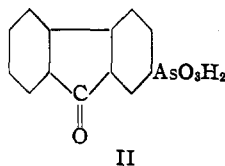
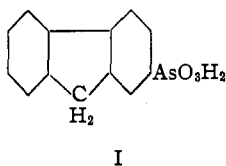
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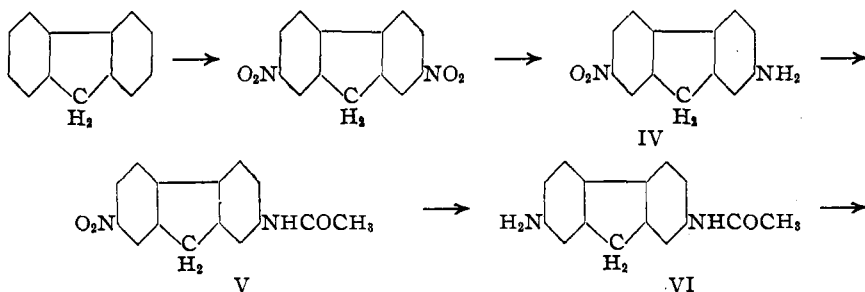
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In an attempt to find arsenicals which might be of value from the standpoint of chemotherapy, it seemed desirable to make a study of arsonic acids of fluorene and of some of its derivatives.²

Bart's³ method of preparing arylarsonic acids was adapted to the preparation of 2-arsonofluorene (I), 2-arsonofluorenone (II) and 2-acetamino-



7-arsonofluorene (III). In the preparation of (III) the steps taken are indicated graphically below; the yield of (III) from (VI) was extremely low.



¹ This article is an abstract of Part II of a thesis submitted to the Graduate School of Northwestern University by F. E. Cislak in partial fulfilment of the requirements for the degree of Doctor of Philosophy. The work was made possible by a grant from Parke, Davis and Company.

² Some of the compounds described in this article are being tested pharmacologically at the University of Wisconsin under the direction of Dr. A. L. Tatum, but no data are available at this time.

³ Bart, *Ann.*, **429**, 55 (1922).