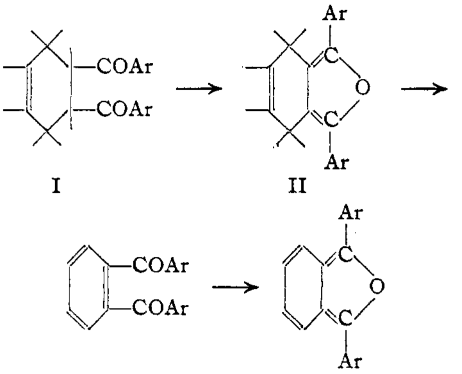
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Absorption and Fluorescence Spectra of Certain Dihydroisobenzofurans and Isobenzofurans

BY ROGER ADAMS AND MARVIN H. GOLD[1]

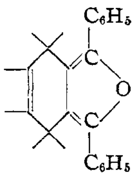
It has been shown recently that butadiene and 2,3-dimethylbutadiene may undergo essentially quantitative addition to various diaroylethylenes to produce diaroylcyclohexenes (I).[2] Syntheses from these adducts were developed, among which may be mentioned the corresponding dihydroisobenzofurans (II), *o*-diaroylbenzenes (III) and isobenzofurans (IV). In this communication are reported analogous reactions with the addition products of *trans*-dixenoylethylene with butadiene and 2,3-dimethylbutadiene.



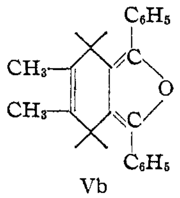
I II

III IV

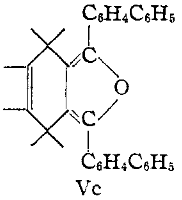
The dihydroisobenzofurans and the isobenzofurans are fluorescent substances. When the eight compounds (Va, b, c, d and VIa, b, c, d) were excited in the solid state with ultraviolet light, all but VIb and c exhibited visible fluorescence. The absorption and fluorescence spectra of the dihydroisobenzofurans (Va, b, c, d) and isobenzofurans (VIa, b, c, d) prepared from dibenzoyl- and dixenoylethylenes and butadiene and 2,3-dimethylbutadiene have been studied and compared in order to observe if possible the relationship of fluorescence to chemical constitution.



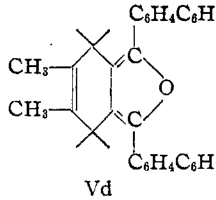
Va



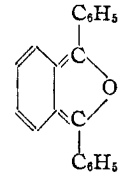
Vb



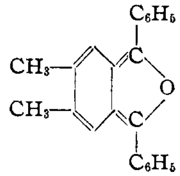
Vc



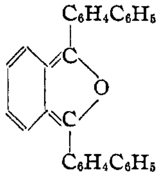
Vd



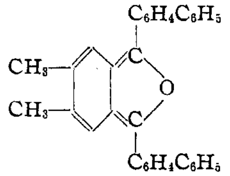
VIa



VIb



VIc



VId

The absorption spectra in ether solution of compounds Va, b, c, d between wave lengths of 2400–4900 Å. are shown in Fig. 1 and of compounds VIa, b, c, d are shown in Fig. 2. In each case there is a wide and intense absorption band in the near ultraviolet; it is in this region that energy is absorbed to produce fluorescence emission. It is obvious that the effect of the two methyl groups in such large molecules as Vb, d, VIb, d is of minor significance though they do influence both the intensity and position of the bands. The difference between the dihydroisobenzofurans (V) and the isobenzofurans (VI) is marked as might be expected due to the isolated double bond in the former and complete conjugation in the latter. In both types, the substitution of xenyl for phenyl groups has the effect of shifting the corresponding band maxima toward the visible by about 200–300 Å. Xenyl groups also tend to round out the curves, remove secondary peaks and fine structure, thereby giving a more diffuse spectrum.

The fluorescent spectra of the isobenzofurans (VI) exhibited strong continuous bands completely in the visible region. The fluorescence of the dihydroisobenzofurans (V) was shifted more to-

---

[1] An abstract of a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry.

[2] (a) Adams and Gold, THIS JOURNAL, **62**, 56 (1940); (b) Adams and Wearn, *ibid.*, **62**, 1233 (1940); (c) Adams and Geissman, *ibid.*, **61**, 2083 (1939).

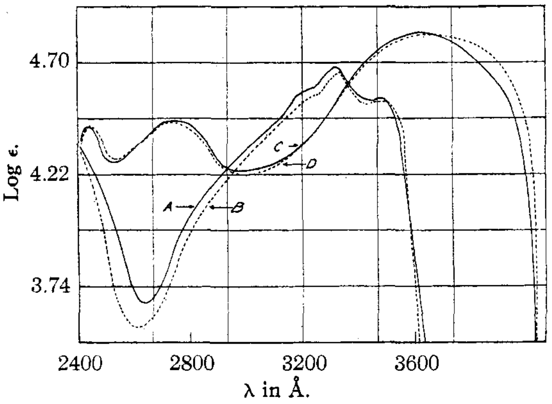


Fig. 1.—Absorption curves: A, 1,3-diphenyl-4,7-dihydroisobenzofuran (Va); B, 1,3-diphenyl-5,6-dimethyl-4,7-dihydroisobenzofuran (Vb); C, 1,3-dixenyl-4,7-dihydroisobenzofuran (Vc); D, 1,3-dixenyl-5,6-dimethyl-4,7-dihydroisobenzofuran (Vd).

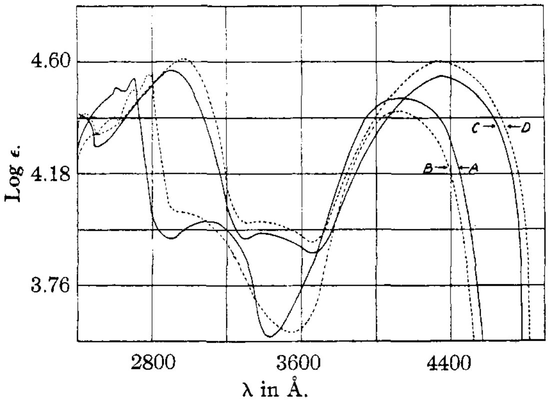


Fig. 2.—Absorption curves: A, 1,3-diphenylisobenzofuran (VIa); B, 1,3-diphenyl-5,6-dimethylisobenzofuran (VIb); C, 1,3-dixenylisobenzofuran (VIc); D, 1,3-dixenyl-5,6-dimethylisobenzofuran (VId).

ward the shorter end of the spectrum and showed a decided band structure (Figs. 3 and 4).

As in the case of absorption, the methyl groups have only a minor effect, that of varying the intensity of fluorescence and position of the bands. The substitution of xenyl for phenyl groups causes a shift in the wave length at which emission begins about 375 Å. toward the red but does not appreciably alter the character of the fluorescence curves.

The complete data for the absorption and fluorescence are summarized in Table I.

All known organic compounds which exhibit fluorescence have two factors in common; (1) they possess two or more resonating structures, (2) every fluorescent molecule is capable of producing transitory free radicals.[3] Waters believes that fluorescence is associated with the recombination of neutral free radicals, an idea which was used also by Mumm[4] in his explanation of the fluorescence of N-methylpyridones.

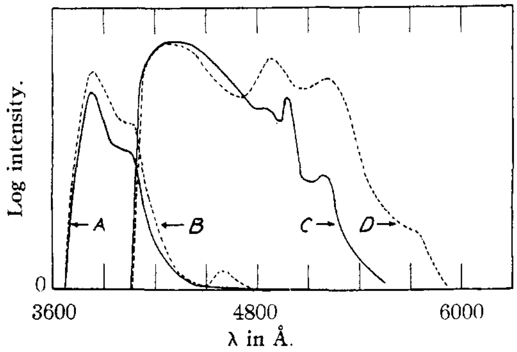


Fig. 3.—Fluorescence curves: A, 1,3-diphenyl-4,7-dihydroisobenzofuran (Va); B, 1,3-diphenyl-5,6-dimethyl-4,7-dihydroisobenzofuran (Vb); C, 1,3-dixenyl-4,7-dihydroisobenzofuran (Vc); D, 1,3-dixenyl-5,6-dimethyl-4,7-dihydroisobenzofuran (Vd).

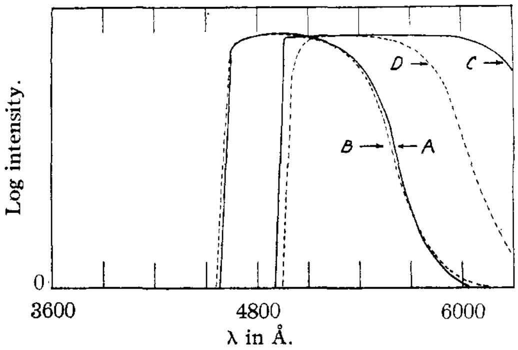


Fig. 4.—Fluorescence curves: A, 1,3-diphenylisobenzofuran (VIa); B, 1,3-diphenyl-5,6-dimethylisobenzofuran (VIb); C, 1,3-dixenylisobenzofuran (VIc); D, 1,3-dixenyl-5,6-dimethylisobenzofuran (VId).

Apparently the ability of a molecule to resonate between two or more equilibrium structures, exerts a certain amount of stabilization upon the excited energy states. This, combined with a complex structure, protects the molecule from loss of the energy through collision processes and it is reemitted preferably as radiant energy.

The energy necessary to produce free radicals depends upon the stability of the molecule. The isobenzofurans are much more easily oxidized than the corresponding dihydroisobenzofurans. It would be expected, therefore, that the energies involved in the transference of an electron to a higher energy level would be less in the isobenzofurans than in the dihydro derivatives. The

---

(3) Waters, *Nature*, **128**, 905 (1931).

(4) Mumm, *Ber.*, **72B**, 29 (1939).

TABLE I

OPTICAL DATA FOR ISOBENZOFURANS

Substituted isobenzofuran	Absorption		Fluorescence	
	Band maximum	Log extinction coefficient	Band maximum of benzene solution	Color in solid state
VIa	2610	4.5	4860	Yellow-green
	2700	4.5		
	3100	3.95		
	4150	4.45		
VIb	2490	4.3	4860	None
	2580	4.4		
	2690	4.5		
	2770	4.55		
	3100	3.95		
	4150	4.4		
VIc	2400	4.4	5250	None
	2920	4.6		
	3350	3.95		
	4360	4.55		
VId	2440	4.4	5250	Orange-yellow
	2960	4.6		
	3400	4.0		
	4350	4.6		
Va	2300	4.4	3840	Blue
	3320	4.7	4050	
	3480	4.55		
Vb	2300	4.4	3840	Blue-green
	3330	4.65	4080	
	3490	4.5	4590	
Vc	2440	4.4	4290	Yellow-green
	2720	4.45	4845	
	3620	4.8	4965	
			5160	
Vd	2450	4.4	4290	Yellow-green
	2710	4.45	4915	
	3670	4.8	5025	
			5250	

absorption and fluorescence spectra are shifted toward the visible for the isobenzofurans.

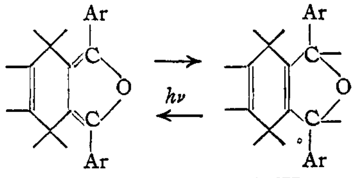
Studies of the hexaaryl ethanes[5] have shown that resonance plays an important part in the stabilization of free radicals. Thus, hexaphenylethane is only slightly dissociated in solution, whereas stepwise substitution of biphenyl for phenyl groups causes a corresponding increase in dissociation to form triarylmethyl radicals.

Certain chemical evidence for possible transitory existence of free radicals in isobenzofurans has been observed. Oxygen is absorbed readily from the air by solutions of isobenzofurans (just as triarylmethyls do) with production of *o*-diaroylbenzenes. The addition of an α,β-unsaturated carbonyl compound to a solution of an isobenzofuran produces a flash of bright red color which is then followed by the precipitation of the addition compound.[6] Certain of these white addition compounds, when melted, produce red liquids which become white solids again on cooling. In the case of the dihydroisobenzofurans, the reaction is so reversible that pure addition products cannot be isolated; in this case the intermediate bright color persists for several minutes.

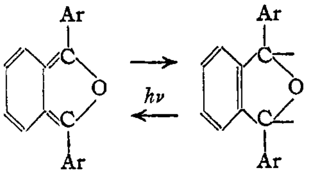
Reasoning by analogy to the triarylmethyls, more resonance forms will be present in the dixenyl than in the diphenylisobenzofurans and, consequently, in the former there will be a greater stabilization effect upon the transitory free-radical structures. This tends to decrease the dissociation energy and thereby shifts the position of the absorption and fluorescence spectra to longer wave lengths for the dixenyl as compared with the diphenyl derivative.

A similar reasoning applies to the dihydroisobenzofurans. The lack of complete conjugation, due to the isolated double bond in the nucleus, has the effect of decreasing the number of resonance forms, thereby accounting for the lesser stability of the free-radical phase. The molecules would then retain a correspondingly greater dissociation energy than its more highly conjugated analog. This is evidenced by a shift to shorter wave lengths for absorption and fluorescence spectra.

The result of such a mechanism would be the temporary formation of a mono- or di-free radical upon the absorption of energy. Upon return to the normal state the absorbed energy would be emitted as fluorescence. Thus, the changes in the dihydroisobenzofurans may be illustrated in structures VII and VIII and in the isobenzofurans by structures IX and X. This assumption of free radicals would also serve to explain the dimer of 1,3-diphenylisobenzofuran[7] obtained by ex-



VII VIII



IX X

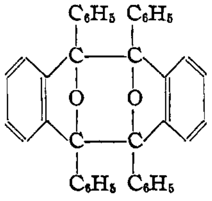
---

[5] Pauling and Wheland, *J. Chem. Phys.*, **1**, 362 (1933); Hückel, *Z. Physik*, **83**, 632 (1933).

[6] Unpublished results.

[7] Guyot and Catel, *Bull. soc. chim.*, [3] **35**, 1127 (1906).

posure of the isobenzofuran to sunlight in absence of air. An activated molecule could condense with one in a normal state to form the white dimer (XI).



XI

The transitory color in the addition of the isobenzofurans to α,β-unsaturated carbonyl groups is experimental evidence that this Diels–Alder reaction takes place through an intermediate free radical. From this may be inferred that possibly all Diels–Alder reactions proceed in a similar manner.

Experimental

A Bausch and Lomb medium quartz spectrograph and a Moll type recording densitometer were used for both absorption and fluorescence spectra. The ultraviolet absorption spectra were taken on 2.5×10^{-5} *M* solutions in ether, whereas the fluorescent spectra were taken on 1×10^{-4} *M* solutions in thiophene-free benzene.

The fluorescence was excited by means of a 250-watt General Electric mercury lamp, type H_2. Eastman B-II spectrographic plates were chosen for the fluorescence spectra because they offered the most uniform sensitivity over the major portion of the visible spectrum. Under these conditions the fluorescence efficiency was so high as to produce sufficient blackening on the photographic plate in ninety seconds. The slit-width in the fluorescence spectra determinations was 60 microns.

***trans*-Dixenoylethylene.**—This was prepared by a modification of the method of Oddy.[8] To 85 g. of biphenyl in 300 cc. of nitrobenzene was added 80 g. of aluminum chloride. The resulting hot, dark solution was cooled in an ice-bath, after which 38 g. of fumaryl chloride was added dropwise over a period of fifteen minutes. Stirring was allowed to continue for twenty minutes longer, the reaction mixture then poured onto ice and acidified with hydrochloric acid. A yellow solid separated which was removed by decantation, then filtration from the nitrobenzene and aqueous layers. It was purified by crystallization from chloroform: tiny yellow crystals, m. p. 247–248° (cor.); yield 90 g. (79%) (Oddy reported m. p. 247.5–248°).

4,5-Dixenoylcyclohexene.—A solution of 5 g. of butadiene in 200 cc. of cold benzene and 6 g. of *trans*-dixenoylethylene was heated at 100° for three hours in a pressure bomb with constant agitation. At the end of this period, the reaction mixture was evaporated to a small volume and the product allowed to crystallize. It was purified by crystallization from toluene: white crystals, m. p. 267–268° (cor.); yield 6 g. (87%).

Anal. Calcd. for $C_{32}H_{26}O_2$: C, 86.88; H, 5.89. Found: C, 86.72; H, 6.28.

1,3-Dixenyl-4,7-dihydroisobenzofuran.—A suspension of 6 g. of 4,5-dixenoylcyclohexene in 250 cc. of acetic anhydride was heated to boiling and a few drops of concentrated sulfuric acid was then added. Immediately solution took place with appearance of a greenish-yellow fluorescence. After ten minutes of refluxing the solution was cooled and the precipitated product filtered. It was purified by crystallization from benzene: tiny yellow crystals, m. p. 238–239° (cor.); yield 5.3 g. (93%).

Anal. Calcd. for $C_{32}H_{24}O$: C, 90.57; H, 5.66. Found: C, 90.28; H, 5.96.

***o*-Dixenoylbenzene.**—To a boiling suspension of 4 g. of 1,3-dixenyl-4,7-dihydroisobenzofuran in 225 cc. of acetic acid, 10 g. of sodium acetate and 5 cc. of water was added dropwise 1 cc. of bromine (2 moles) in 15 cc. of acetic acid. The furan dissolved and the bromine color faded. After refluxing for forty-five minutes, the hot solution was poured into 400–500 cc. of hot water and allowed to cool slowly. The product which separated was purified by dissolving in 50 cc. of benzene, treating with Norit, evaporating to 30 cc. and allowing to cool. A second crystallization from benzene–petroleum ether (b. p. 60–110°) gave small white prisms, m. p. 191–192° (cor.); yield 3.3 g. (81%).

Anal. Calcd. for $C_{32}H_{22}O_2$: C, 87.67; H, 5.06. Found: C, 87.94; H, 5.38.

1,3-Dixenylisobenzofuran.—A mixture of a hot solution of 1 g. of *o*-dixenoylbenzene in 30 cc. of benzene, 1 g. of potassium hydroxide, 25 cc. of 95% ethanol and 1 cc. of water was refluxed for two hours. To the brownish-yellow solution was added 1 g. of activated zinc dust and refluxing was continued until the solution was yellow (about ten minutes). The hot mixture was filtered immediately and 30 cc. of acetic acid and 10 cc. of water were added with stirring. Within one minute, the furan began to crystallize. The solution was cooled and the product purified by crystallization from benzene; golden-brown needles melted at 247–249° (cor.) to a red liquid which turned to a white solid on cooling; yield 0.7 g. (70%). From the original filtrate, a small amount of starting material could be recovered.

Anal. Calcd. for $C_{32}H_{22}O$: C, 91.00; H, 5.25. Found: C, 91.05; H, 5.46.

1,2-Dimethyl-4,5-dixenoylcyclohexene.—From 2,3-dimethylbutadiene and 4,5-dixenoylethylene, an 83% yield of product resulted. It was purified from benzene; white crystals, m. p. (sealed tube) 280–281° (cor.) with decomposition.

Anal. Calcd. for $C_{34}H_{30}O_2$: C, 86.77; H, 6.43. Found: C, 86.55; H, 6.76.

1,3-Dixenyl-5,6-dimethyl-4,7-dihydroisobenzofuran.—This was prepared in a manner similar to that used for the compound without the methyl groups; yield 99%. It was purified from toluene; yellow needles, m. p. 239–241° (cor.).

Anal. Calcd. for $C_{34}H_{28}O$: C, 90.26; H, 6.24. Found: C, 90.15; H, 6.38.

1,2-Dimethyl-4,5-dixenoylbenzene.—It was prepared similarly to the 1,2-dixenoylbenzene in 82% yield. It was

---

(8) Oddy, THIS JOURNAL, **45**, 2160 (1923).

crystallized from benzene; tiny white crystals, m. p. 218–219° (cor.).

Anal. Calcd. for $C_{34}H_{26}O_2$: C, 87.52; H, 5.62. Found: C, 87.41; H, 5.88.

1,3-Dixenyl-5,6-dimethylisobenzofuran.—It was prepared similarly to the 1,3-dixenylisobenzofuran in 78% yields; bright orange needles from toluene, m. p. 245–247° (cor.).

Anal. Calcd. for $C_{34}H_{26}O$: C, 90.67; H, 5.82. Found: C, 90.42; H, 6.01.

Summary

The preparation of certain dixenyldihydroisobenzofurans and isobenzofurans is described.

The absorption spectra and fluorescence spectra of various diphenyl and dixenyldihydroisobenzofurans and isobenzofurans were compared. The substitution of xenyl for phenyl groups in absorption spectra shifts the band maxima toward the visible by about 200–300 Å.; and in fluorescence spectra shifts the wave length at which emission begins about 375 Å. toward the red.

A discussion of fluorescence change in relation to the tendency of the molecules to give free radicals is given.

URBANA, ILLINOIS RECEIVED JUNE 3, 1940

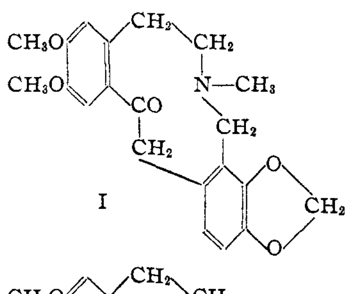
[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, NATIONAL RESEARCH LABORATORIES]

The Alkaloids of Fumariaceous Plants. XXIX. The Constitution of Cryptocavine[1]

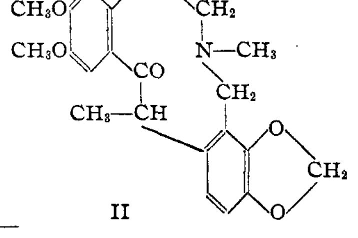
BY RICHARD H. F. MANSKE AND LÉO MARION

The alkaloid for which the name cryptocavine has been suggested has thus far been isolated from *Fumaria officinalis*,[2] *Dicentra chrysantha*,[3] *Corydalis ophiocarpa*[4] and *C. ochotensis*,[5] it being most abundant in the last named species.

Cryptocavine (m. p. 223°)[6] shows no optical activity in chloroform solution and yields analytical figures which agree equally well with $C_{21}H_{23}O_5N$ or with $C_{22}H_{25}O_5N$. It contains two methoxyl groups and a methylenedioxy group. Since cryptopine (I) $C_{21}H_{23}O_5N$, m. p. 221°, is not identical with cryptocavine, a mixture of the two alkaloids being liquid at 205°, the latter was at first considered by us to be $C_{22}H_{25}O_5N$. In view of the color reaction, which is that given by the protopine type of alkaloids, expression (II) seemed a reasonable one for cryptocavine. The alternative formula in which the positions of the methylenedioxy group and the two methoxyl groups are reversed has been shown to apply to corycavidine.[7]



I



II

Degradation of a substance having formula II by Perkin's method,[8] should yield 4,5-dimethoxy-2-β-dimethylaminoethylbenzaldehyde and 2-methyl-3-acetopiperone. The former degradative base was obtained by Perkin[8] from cryptopine which also yielded instead of a ketone an aldehyde, namely, 5,6-methylenedioxy-*o*-toluic aldehyde. Our degradation experiments followed Perkin's procedure in detail. In order to obtain reference compounds we carried out the degradation of cryptopine in parallel experiments and obtained in addition to small amounts of secondary derivatives the two main fragments mentioned above, namely, the amino-aldehyde and the toluic aldehyde. Furthermore and this could not have been anticipated, cryptocavine yielded the same two degradation products. It is to be pointed out that the two degradation fragments of cryptopine together contain the nitrogen atom and all of the carbon atoms of the alkaloid plus an extra N-carbon introduced by methylation. We have looked in vain for a

---

(1) Published as N. R. C. No. 917.

(2) Manske, *Can. J. Research*, **B16**, 438 (1938).

(3) Manske, *ibid.*, **B15**, 274 (1937).

(4) Manske, *ibid.*, **B17**, 51 (1939).

(5) Manske, *ibid.*, **B18**, 75 (1940).

(6) All melting points are corrected.

(7) Bruchhausen, *Arch. Pharm.*, **263**, 570 (1925).

(8) Perkin, *J. Chem. Soc.*, **109**, 815 (1916).