DIBEPIN-2: A NEW COLOR REAGENT FOR PRIMARY ALIPHATIC AMINES

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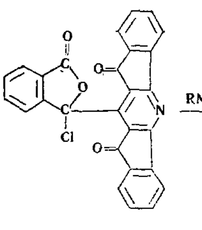
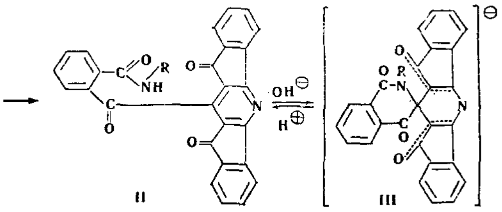
3-Chloro-3-[2', 3'(CO), 6', 5'(CO)dibenzoylene-4'-pyridyl]phthalide (Dibepin-2) is an analytical color reagent for primary aliphatic amines and arylalkylamines (with the exception of ethylenediamine and 1, 2-diaminopropane). The reaction is always negative with secondary and tertiary amines.

Some years ago, we discovered and investigated an analytical color reagent for primary amines (mainly alkylamines and arylalkylamines), Dibepin, i.e., 8-[2', 3'(CO), 6', 5'(CO)-dibenzoylene-4'-pyridyl]-1-naphthoyl chloride [1, 2]. Dibepin can be used for the detection [3, 4] and quantitative determination [5] of primary amines. A convenient method for the synthesis of Dibepin has been developed [6, 7] and the mechanism of the color reaction has been shown [8], from which it follows that: 1) the reaction can be positive only with primary amines; and 2) it is right to expect that a similar intramolecular reaction will take place in other cases with a suitable mutual arrangement of the reaction centers. In actual fact, the action of primary amines on 3-chloro-3-[2', 3'(CO), 6', 5'(CO)-dibenzoylene-4'-pyridyl]phthalide (I) [9] forms monosubstituted amides of o-[2, 3(CO), 6, 5(CO)-dibenzoylene-isonicotinoyl]benzoic acid (II) which, in alkaline solution, as a result of reversible intramolecular cyclization, form deep blue-violet solutions. We have studied the possibility of using I (for which we propose the name Dibepin-2) as an analytical reagent for primary amines.

Sensitivity of the Color Reaction

Amine	Time of heating, min	Limiting concentration, M	Limiting dilution in weight ratios
Ethanolamine	0.5	0.01	1 : 1640
	2	0.002	1 : 8200
	5	0.001	1 : 16400
n-Octadecylamine	0.5	0.005	1 : 740
	2	0.001	1 : 3700
	5	0.0005	1 : 7400
Tetramethylenediamine	0.5	0.002	1 : 5630
	2	0.001	1 : 11360
	5	0.0004	1 : 28600
Hexamethylenediamine	0.5	0.005	1 : 1800
	2	0.005	1 : 1800
	5	0.0025	1 : 3600





METHOD OF PERFORMING THE REACTION

In a test tube are placed a sample of the substance, Dibepin-2 (0.5 to 1 mg), and potassium carbonate (or dry sodium hydroxide in the case of amine salts), then it is filled with dioxane. The mixture is boiled for 30 seconds, and a few drops of a 5% aqueous solution of sodium hydroxide and ethanol are added. The appearance of a deep blue-violet coloration shows the presence of a primary amine. Primary alkylamines and arylalkylamines give a positive reaction in the majority of cases (ethyl-, n-propyl-, isopropyl-, n-butyl-, isoamyl-, n-hexyl, n-heptyl-, n-undecyl-, n-dodecyl-, n-octadecyl-, allyl-, cyclohexyl-, ethanol-, benzyl-, and β-phenylisopropylamines, and tetramethylene- and hexamethylenediamines).

An interesting exception is formed by diamines containing the two amino groups on neighboring carbon atoms; for example, ethylenediamine and 1, 2-diaminopropane, which do not give the positive reaction even on heating for 5 minutes. As was to be expected, the reaction is negative with secondary and tertiary amines (diethyl-, di-n-propyl-, di-n-butyl-, diethanol-, trimethyl-, triethyl-, and triethanolamines, hordenine, and ephedrine). The reaction is negative (with heating for 2 minutes) with almost all primary aromatic amines (m- and p-phenylenediamines, o- and m-toluidines, o- and p-aminophenols, p-anisidine, and p-bromoaniline). Only in individual cases (aniline, o-anisidine, p-phenetidine) does an indistinct violet tinge appear. Dibepin-2 acts extremely slowly with the more basic (more reactive) aliphatic amines (pK_B from 2.8 to 4.7). Consequently, the limiting concentration of amines varies according to the time of heating. It is obvious that with aromatic amines (pK_B greater than 8.0), the rate of the reaction is too slow. This agrees with the proposed cyclic structure I [9].

Thus, the color reaction of Dibepin-2, with a few exceptions, is specific for primary aliphatic amines and arylalkylamines. This is an advantage of the reagent, since there are few color reactions which permit the rapid distinction of a primary amino group, particularly in the aliphatic series. It may be assumed that Dibepin and Dibepin-2 are only the first representatives of a new group of analytical reagents with a peculiar mechanism of their action.

REFERENCES

1. G. Ya. Vanag and G. Ya. Dubur, ZhOKh, **30**, 1898, 1960.
2. G. Ya. Vanag and G. Ya. Dubur, Authors' Certificate 143030, 1961.
3. G. Ya. Dubur and G. Ya. Vanag, in collection: Organic Analysis; Proceedings of the Commission on Analytical Chemistry [in Russian], Izd-vo AN SSSR, Moscow, Vol. 13, p. 429, 1963.
4. G. Ya. Dubur and G. Ya. Vanag, Izv. AN Latv. SSR, ser. khim., 25, 1962.
5. L. Ya. Leitis, G. Ya. Dubur, M. V. Shimanskaya, and G. Ya. Vanag, Izv. AN Latv. SSR, ser. khim., 41, 1963.
6. G. Ya. Dubur, G. Ya. Vanag, and Ya. R. Uldrikis, in collection: Methods of Obtaining Chemical Reagents and Materials [in Russian], Moscow, no. 14, p. 30, 1966.
7. G. Ya. Dubur and Ya. R. Uldrikis, KhGS [Chemistry of Heterocyclic Compounds], collection 1, p. 322, 1967.
8. G. Ya. Dubur and G. Ya. Vanag, DAN, **134**, 1356, 1960.
9. G. Ya. Dubur and G. Ya. Vanag, Izv. AN Latv. SSR, ser. khim., 235, 1961.

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THE REACTION OF SELENIUM WITH PHENYLACETYLENE

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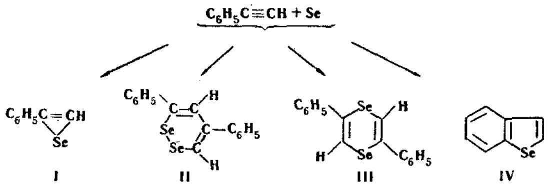
The reaction of selenium with phenylacetylene in the presence of sodium ethoxide in boiling dioxane has given 2,5-diphenyl-1,4-diselenacyclohexa-2,5-diene, whose molecules have the boat conformation.

Several variants have been proposed for the reaction of selenium with phenylacetylene in equimolar ratios, leading to the formation of different substances.

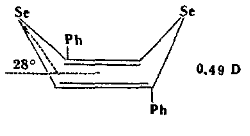


We have obtained a yellow crystalline substance with mp 136° C, the structure of which was to be established.

Structures I and IV cannot be accepted, since the molecular weight calculated for them (181.09) does not agree with that found experimentally, (366.5). Structure IV is also excluded because the benzoselenophene corresponding to it is a liquid with bp 150° C [1]. It remains only to make a choice between structures II and III, for which the calculated molecular weight (362.18) is in good agreement with the figure found experimentally. For this purpose, we used the dipole moment method.

The dipole moment calculated for the diselenide II is 1.81 D. A comparison of this value with the figure found experimentally of 0.45 D enables structure II to be excluded.

For the cyclic selenide III we calculated the dipole moments on the assumption of the chair conformation, 0.0 D and the boat conformation.



A comparison of these values with that found experimentally of 0.45 D shows that the product of the reaction of sulfur with phenylacetylene is 2,5-diphenyl-1,4-diselenacyclohexa-2,5-diene, the molecules of which have the boat conformation. We may note that the boat conformation has also been found for the corresponding sulfur analog, 2,5-diphenyl-1,4-dithiin