

Phosphonium salts and ylides in diarylethylenes and diarylacetylenes syntheses

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Possibilities of phosphonium salts and ylides use to synthesize organic luminophors have been discussed. Diarylethylenes are obtained from triphenylphosphonium salts of benzyl type and aromatic aldehydes by Wittig reaction, realized in various ways: in anhydrous alcohol with use of alcoholates or in two-phase system. Salts that contain electron-accepting groups interact with active aldehydes in the presence of triethylamine. Diarylacetylenes are obtained by thermolysis of acylated ylides. Methods have been developed to obtain such ylides by acylation of unstable arylidene phosphoranes with aryl chlorides in a two-phase system. Esters of arylpropenic (cinnamic) acids are obtained from cholesteryl-containing phosphonium salts. Many of them possess character of luminescent liquid crystals. Some of phosphonium salts as such are organic luminophors.

Показана возможность применения фосфониевых солей и илидов для синтеза органических люминофоров. Диарилэтилены получают из трифенилфосфониевых солей бензильного типа и ароматических альдегидов по реакции Виттига, проводимой разными вариантами: в абсолютном спирте с использованием алкоголятов либо в двухфазной системе. Соли, содержащие в бензильном радикале электроноакцепторные группы, реагируют с активными альдегидами в присутствии триэтиламина. Диарилацетилены получены термоллизом ацилированных илидов. Разработана методика синтеза таких илидов ацилированием нестабильных арилиденфосфоранов арилхлоридами в двухфазной системе. Из холестерилсодержащей фосфониевой соли получены эфиры арилпропеновых (коричных) кислот. Многие из них обладают свойствами люминесцентных жидких кристаллов. Некоторые из фосфониевых солей сами являются органическими люминофорами.

Diarylethylenes and diarylacetylenes consist an important and large enough class of organic luminophors [1, 2]. A series of methods is known to obtain diarylethylenes containing polycyclic rings and complex heterocyclic systems [3]. Here, we shall restrict ourselves to several typical examples described in works published recently and not included in the review [3].

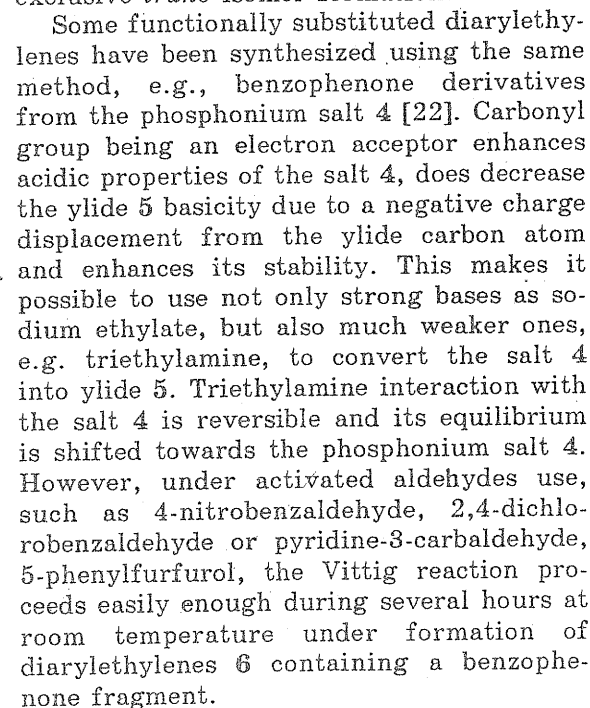
By the reaction of aryl dibromoethanes with biphenyl and terphenyl halide derivatives in the presence of titanium chloride, diarylethylenes were obtained containing bromine and iodine atoms which are fluorescence quenchers [4]. Substituted benzyl bromides give *trans*-stilbenes under the ac-

tion of lithium diisopropylamide [5]. By 5-arylfurfurols condensation with malonic acid, 3-arylpropenic acids have been obtained, arylation of those by aryl diazonium salts results also in diarylethylenes formation [6].

Known reactions of methylarenes with aniles of aromatic aldehydes [7] or the condensation with aldehydes as such [8] have been used to obtain heterocyclic bis-styryl derivatives. Diarylethylenes containing complex heterocyclic systems are effective luminophors [1, 9-14]. Some of those are obtained [10, 14] using the PO-activated olefination method, therewith, *trans*-isomers are formed.

crystallization, sometimes in the presence of iodine traces. The mixture can be transformed into *trans* isomer by boiling in xylene, toluene or other high-boiling solvent containing iodine traces.

Some regularities are observed as to amount ratio of formed geometric isomers depending on the aromatic radical nature both in phosphonium salts and aldehydes. Stronger steric hindrances in aryl radicals result in an increased amount of the *trans* isomer. So, 1- and 2-naphtic aldehydes give approximately equal amounts of *cis* and *trans* isomers in the Wittig reaction. In cases of 9-phenanthrenecarbaldehyde and 1-pyrenecarbaldehyde, the *trans* isomer is the main constituent of the reaction products mixture, while highly sterically hindered 9-anthryl group in aldehyde molecule as well as in phosphonium salt one favours almost exclusive *trans* isomer formation.



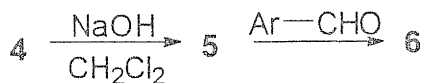
We have used Wittig reaction to obtain diarylethylenes 3 containing condensed naphthalene, phenanthrene and pyrene groups from corresponding phosphonium salts and aldehydes [21]. The syntheses were performed in absolute ethanol using sodium ethylate as the base. Therewith, diarylethylenes fall out into precipitate; sometimes, a slight solution dilution with water is required to that end.

$$\begin{array}{c}
 \text{Ph}_3\text{P}^+-\text{CH}_2-\text{C}_6\text{H}_4-\text{CO}-\text{Ph}[\text{Br}]^- \xrightleftharpoons[\text{HBr}]{\text{Et}_3\text{N}} \text{Ph}_3\text{P}=\text{CH}-\text{C}_6\text{H}_4-\text{CO}-\text{Ph} \quad \text{5} \\
 \text{4}
 \end{array}$$

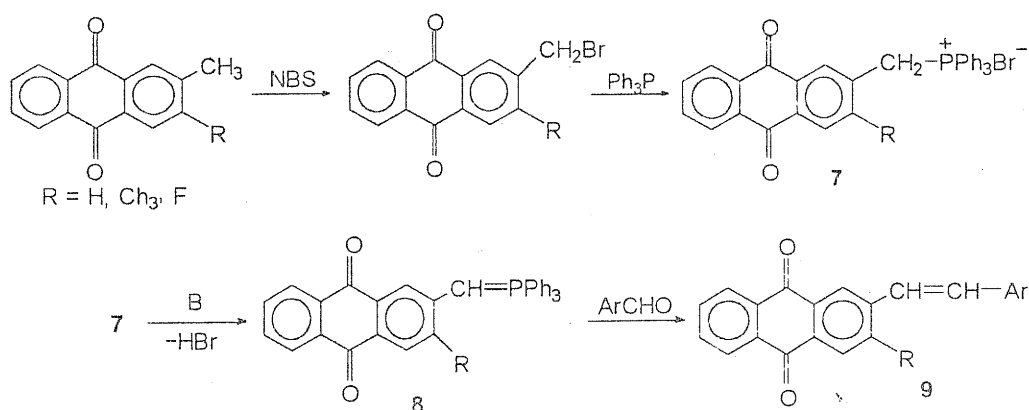
$$\text{Ph}_3-\text{CH}_2-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{Ph} \xrightarrow{\text{ArCHO}} \text{Ar}-\text{CH}=\text{CH}-\text{C}_6\text{H}_4-\text{CO}-\text{C}_6\text{H}_5 \quad \text{6}$$

$$\text{Ar} = 2,4\text{-Cl}_2\text{C}_6\text{H}_3, \quad 4\text{-O}_2\text{NC}_6\text{H}_4, \quad \text{pyridine-4-yl}, \quad \text{furan-2-yl}$$

The reaction with these and other aldehydes, including those reacting only slowly in the presence of triethylamine, can be performed using an interphase catalysis in the presence of an aqueous alkali.

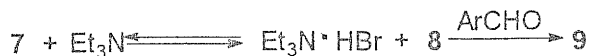


Diarylethylenes **9** containing an anthraquinone group were synthesized from phosphonium salts **7** through intermediate arylidenephosphoranes **8**. Initial methylanthraquinones were brominated using N-bromosuccinimide. Bromomethylanthraquinones do react easily with triphenylphosphine forming colorless salts **7**. The latter, when subjected to a base action, become converted into anthraquinonemethylenetriphenylphosphoranes **8** having emerald-green color. Ylides **8** may exist for several hours in solutions provided the latter do not contain substantial water amounts. However, they are too unstable for their isolation and storage under ordinary conditions. In a basic medium (a homogeneous alcoholic-aqueous solution), those become hydrolyzed after several minutes.

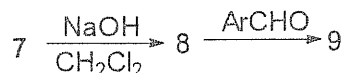


Phosphoranes **8** react easily in ordinary conditions with aromatic aldehydes forming styrylanthraquinones **9** [23]. The synthesis was performed using two methods: either with triethylamine as a base, or in two-phase system with an alkali (it is possible to proceed also in the absolute alcohol with alcoholates). Phosphonium salts **7** do react reversibly with triethylamine, since the latter is an insufficiently strong base, forming ylides **8**. Although the equilibrium is shifted to the left and the ylide **8** concentration in solution is low, the use of rather active aldehydes, as nitrobenzaldehydes, dichlorosalicylic, alpha-haptoic, pyridine-3-

carbaldehyde, 5-bromo- and 5-phenylfurfural, results in that the Wittig reaction proceeds fast enough (from one hour to several ones at 20°C) with diarylethylenes **9** formation.



Less active aldehydes do react more slowly under such conditions. Much faster (usually in several minutes) is the reaction in two-phase system CH₂Cl₂-50-percent NaOH.

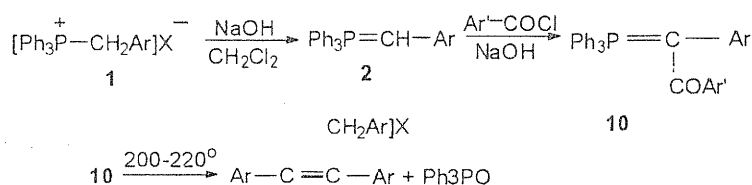


Styrylanthraquinones are obtained in the form of a *cis* and *trans* isomers mixture, the former are prevailing appreciably. *Trans* isomers having a lower solubility can be isolated as pure compounds using multiple crystallization. The mixture can be also separated on an alumina column or isomerized into the *trans* product in the presence of iodine traces.

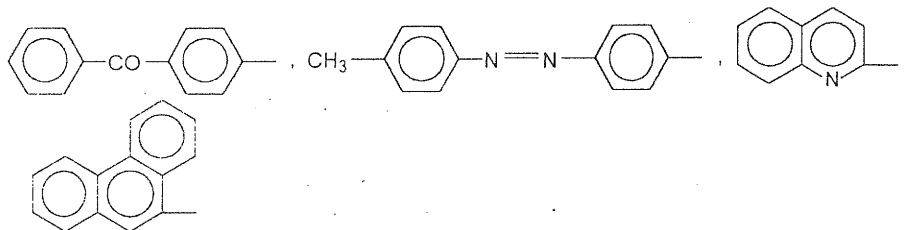
Phosphonium salts and ylides can be used as intermediates to synthesize another luminophors group similar to diarylethylenes, namely, diarylacetylenes. One of possible ways to obtain the latter is the thermolysis of corresponding acylated ylides [24]. Using that method, a series of diarylacetylenes was obtained containing anthracene, phenanthrene, pyrene and chryzene groups. Initial acylated phosphoranes required to that end were obtained from phosphonium salts **1** by conversion of the latter into arylidenephosphoranes **2** using phenyllithium in absolute xylene and under nitrogen atmosphere with subsequent addition of

a carboxylic acid chloride. This is an usual procedure to acylate instable ylides.

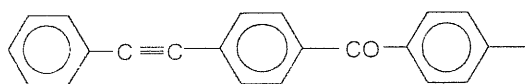
To simplify the synthesis, a procedure was developed [25] to acylate instable arylidenephosphoranes **2** using the inter-phase catalysis in a two-phase system (CH_2Cl_2 -50-percent NaOH). The initial salt **1** of benzyl type was dissolved in methylene chloride, the concentrated alkali solution was added and salt itself is the phase transfer catalyst. It extracts OH^- ions from the aqueous solution and, under their action, converts itself into ylide **2** that reacts further with the aroyl chloride giving the acylated ylide **10**.



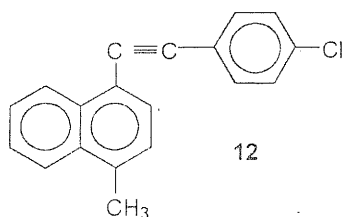
Ar = Ph, RC_6H_4 , 2,4- $\text{Cl}_2\text{C}_6\text{H}_3$, 1- C_{10}H_7 , 2- C_{10}H_7 , Biph.



Acylated ylides **10** are crystalline and, in contrast to **2**, stable substances which can be isolated and stored in ordinary conditions. Their yields, as calculated on initial salts **1** (chloroanhydride must be used in excess), are about 50 to 70 %, but can attain 85 % in the case of anthraquinone derivatives (see below). Some of those were subjected to thermolysis (therewith, the intramolecular Wittig reaction proceeds). As a result, diarylacetylenes were obtained, for example, **11** and **12**, with high stage yields (80-90% on the ylide **10**).

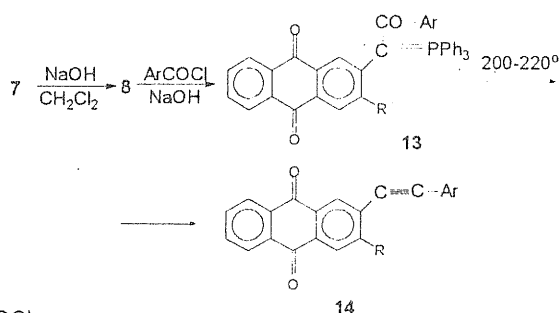


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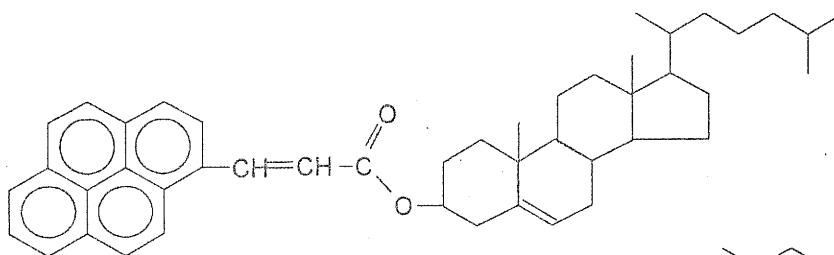
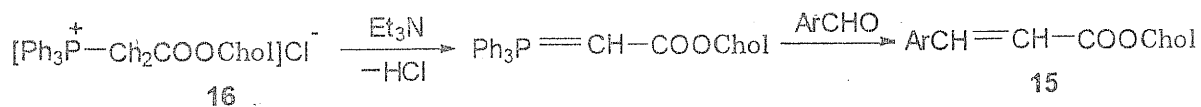
Anthraquinonylphosphoranes **8** are acylated in similar conditions [23, 26]. Stable ylides **13** were obtained containing anthraquinone groups. When thermolyzed (200-220°C), those give aryethynylantraquinones **14**.



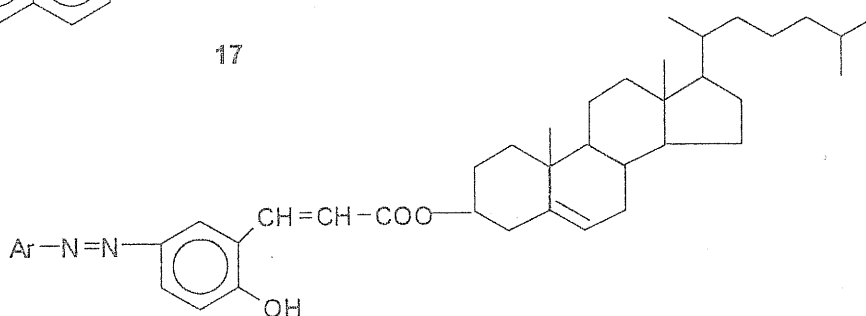
Still another compounds group which may be of a practical interest and can be synthesized through phosphorylides are cholesteryl esters of 3-arylpropenic acids **15**. Some compounds of that series are already in use as liquid crystals forming high-temperature and thermodynamically stable mesophases [27] and are now in production on industrial scale. Such esters were usually synthesized by acylation of cholesterol using suitable unsaturated acids at a high temperature or, what is better, their anhydrides or chloroanhydrides. However, substituted cinnamic acids are not always stable under those conditions. Moreover, their assortment is limited, their derivatives being still less available.

A method is developed to obtain esters **15** using the Wittig reaction from the phosphonium salt **16** containing cholesterol and aromatic aldehydes. The reaction is performed under surprisingly mild conditions and in a simple way. It is sufficient to dissolve the salt **16** and the aldehyde in ethanol and to add triethylamine; a few minutes later, the product **15** starts to crystallize

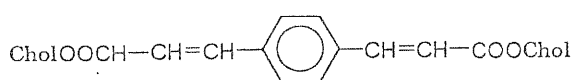
(in the scheme below, Chol = cholesterol group).



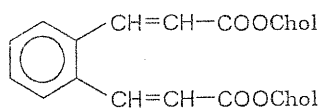
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18



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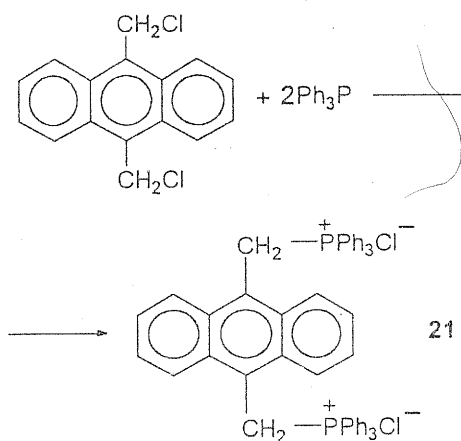
20

Besides of being liquid crystals, some esters 15 possess luminescent properties (i.e. are luminescent liquid crystals). Most of those are colorless in ordinary conditions; anthracene (Ar = 9-anthryl) and pyrene (17) derivatives are colored yellow, compounds 18 containing an azo group are red.

Luminescent liquid crystals 19 and 20 were obtained from terephthalic and phthalic aldehydes, respectively, and the salt 16.

Some phosphonium salts and stable phosphorylides as such are organic luminophors. In first turn, compounds containing polycyclic naphthalene, anthracene, pyrene and other similar groups are to be mentioned in this connection. For example, bis-phosphonium anthracene salt 21, which is easy to obtain by 9,10-di(chloromethyl)anthra-

cene heating with triphenylphosphine in dimethylformamide [28]:



21

It is of importance that the salt 21 is soluble not only in polar organic solvents, but also in water. That property distincts it from many other anthracene derivatives which are luminescent to one extent or another but are not water-soluble, so their application range is limited.

References

1. B.M.Krasovitskii, B.M.Bolotin, Organic Luminescent Materials, VCH Publ., Weinheim, Germany (1988).

2. B.M.Krasovitskii, *Zh.Vsesoyuzn. Khim. Obsch.*, 29, 667 (1984).
3. K.B.Becker, *Synthesis (BRD)*, 341 (1983).
4. E.A.Andreeshev, L.I.Karegishvili, K.K.A.Kovyrzina et al., *Zh.Org. Khim.*, 23, 2423 (1987).
5. R.S.Mali, P.G.Jagta, *Synth. Commun.*, 21, 841 (1991).
6. N.D.Obushak, N.I.Ganuschak, A.I.Lesyuk et al., *Zh. Org. Khim.*, 26, 873 (1990).
7. A.E.Siegrist, H.R.Meyer, P.Gassmann, S.Moss, *Helv. chim. acta*, 63, 1311 (1980).
8. E.M.Vernigor, M.V.Kuz'menko, S.A.Lebedev, *Khim. Geterocikl. Soed.*, No.6, 820 (1987).
9. B.M.Krasovitskii, L.Sh.Afanasiadi, A.I.Bykh et al., USSR Author's Sert. 2521988.
10. B.M.Krasovitskii, N.P.Egorova, L.Sh.Afanasiadi et al., *Khim. Geterocikl. Soed.*, No.5, 617 (1982).
11. N.M.Naik, K.R.Desai, *J.Indian Chem. Soc.*, 67, 84 (1990).
12. B.M.Krasovitskii, V.I.Grigor'eva, *Khim. Geterocikl. Soed.*, No.9, 1127 (1968).
13. L.Sh.Afanasiadi, L.D.Patsenker, S.A.Verezubova et al., *Khim. Geterocikl. Soed.*, No.9, 1267 (1986).
14. B.M.Krasovitskii, S.V.Tsukerman, L.Sh.Afanasiadi et al., *Khim. Geterocikl. Soed.*, No.12, 1616 (1977).
15. G.D.efahl, D.Lorenz, G.Schnitt, *J. Prakt. Chem.*, 23, 143 (1964).
16. K.Friedrich, H.G.Henning, *Chem. Ber.*, 92, 2944 (1959).
17. L.V.Shubina, L.Ya.Malkes, *Zh.Org. Khim.*, 1, 1040 (1965).
18. K.Jamamoto, T.Ikeda, T.Kitsuki et al., *J. Chem. Soc. Perkin I*, 271 (1990).
19. R.Schenk, H.Georgius, K.Meerholz et al., *J. Am. Chem. Soc.*, 113, 2634 (1991).
20. O.N.Bubel, V.S.Bezborodov, V.S.Rachkevich, *Zh.Org. Khim.*, 18, 1240 (1982).
21. V.N.Listvan, G.V.Gonchar, E.S.Rudenko et al., *Zh.Org. Khim.*, 17, 1711 (1981).
22. V.N.Listvan, S.V.Kovalenko, *Zh. Obsch. Khim.*, 50, 1523 (1980).
23. V.N.Listvan, A.P.Stasyuk, *Zh. Obsch. Khim.*, 55, 576 (1985).
24. S.Akiyama, K.Nakasuji, M.Nakagawa, *Bull. Chem. Soc. Jap.*, 44, 2231 (1971).
25. V.N.Listvan, A.P.Stasyuk, L.N.Kurgan, *Zh. Obsch. Khim.*, 57, 1534 (1987).
26. V.N.Listvan, A.P.Stasyuk, M.Ya.Kornilov et al., *Zh. Obsch. Khim.*, 60, 804 (1990).
27. L.A.Kutulya, R.M.Cherkashina, V.P.Tischenko et al., *Zh. Obsch. Khim.*, 53, 1655 (1983).
28. V.N.Listvan, *Zh. Obsch. Khim.*, 55, 2629 (1985).

Фосфонієві солі та іїди в синтезі діарилетиленів і діарилацетиленів

В.М.Листван

Показано можливість використання фосфонієвих солей та іїдів для синтезу органічних люмінофорів. Діарилетилені отримують з трифенілфосфонієвих солей бензильного типу і ароматичних альдегідів за реакцією Вітіга, яка здійснюється різними варіантами: в абсолютному спирті з використанням алкоголятів або в двофазній системі. Солі, що містять у бензильному радикалі електроноакцепторні групи, взаємодіють з активними альдегідами у присутності триетиламіну. Діарилацетилені добути термолізом ацильованих ілідів. Розроблено методику синтезу таких ілідів ацилюванням нестабільних ариліденфосфоранів ароїлхлоридами у двофазній системі. З холестеринвмісної фосфонієвої солі добуто ефіри арилпропенових (коричних) кислот. Багато з них мають властивості люмінесцентних рідких кристалів. Деякі з фосфонієвих солей самі по собі є органічними люмінофорами.