# POLYENES

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## 1, 3, 5-HEXATRIENES

B. M. Mikhailov and G. S. Ter-Sarkisyan

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The simple method which we have described for the preparation of 5-phenyl-2,4-pentadienal [1] from cinnamaldehyde diethyl acetal and ethyl vinyl ether has made wide application of this aldehyde, which was previously not readily accessible, in the synthesis of various compounds. In particular, from this compound one may prepare various unsymmetrical 1, 6-disubstituted 1, 3, 5-hexatrienes, which have as yet received little study and are of interest for the study of the relation between the structure and the fluorescence properties of these compounds.

In the present paper we give the synthesis of the following compounds: 1,6-diphenyl-, 1-(1-naphthyl)-6phenyl-, 1-(9-phenanthryl)-6-phenyl-, 1-(4-biphenylyl)-6-phenyl-, 1-phenyl-6-(2-pyridyl)-, and 1-phenyl-6-(2-quinolyl)-1,3,5-hexatrienes. These hexatrienes were prepared by the action on 5-phenyl-2,4-pentadienal of either organometallic compounds or the corresponding arylacetic acids by Kuhn's method [2]. Thus, the important 1,6-diphenyl-1,3,5-hexatriene (I) may be prepared by the action on 5-phenyl-2,4-pentadienal of benzylmagnesium chloride, benzylsodium, or phenylacetic acid. The most convenient preparative method for this hydrocarbon is reaction between the aldehyde and phenylacetic acid.

In the same way, from 5-phenyl-2,4-pentadienal and 1-naphthalene-acetic acid we obtained 1-(1-naphthyl)-6-phenyl-1,3,5-hexatriene (II), which showed bright fluorescence, both in solutions and in the crystalline state, and thus differs from 1,6-diphenyl-1,3,5-hexatriene, which does not fluoresce in the crystalline state:

By the action of 5-pheny1-2,4-pentadienal on (9-phenanthryl)methyl-magnesium chloride we synthesized 1-(9-phenanthryl)-6-pheny1-1,3,5-hexatriene (III) in the form of strongly fluorescent colorless crystals:

<sup>\*</sup>For Communication 10 see Izvest. Akad. Nauk SSSR, Otel. Khim. Nauk 372 (1960). [C. B. translation].



As shown previously [3], the quantum yield of the fluorescence of 1-phenyl-6-p-tolyl-1,3,5-hexatriene in benzene and heptane is higher than for the corresponding solutions of 1,6-diphenyl-1,3,5-hexatriene. It was of interest to determine the effect produced on the brightness of the fluorescence of the introduction of phenyl, instead of methyl, into the p-position of one of the phenyls of 1,6-diphenyl-1,3,5-hexatriene. With this object we synthesized 1-(4-biphenylyl)-6-phenyl-1,3,5-hexatriene. On reaction between 5-phenyl-2,4-pentadienal and p-phenylbenzylmagnesium chloride we obtained 1-(4-biphenylyl)-6-phenyl-3,5-hexatriene (V), which on boiling with glacial acetic acid was converted into 1-(4-biphenylyl)-6-phenyl-1,3,5-hexatriene (V), which was strongly fluorescent in benzene solution:



To determine the effect of the presence of nitrogen-containing heterocycles on the fluorescence of hexatrienes we synthesized hexatrienes containing heterocyclic substituents. Thus, by the action of (2-pyridyl)methyllithium on 5-phenyl-2,4-pentadienal we obtained 1-phenyl-6-(2-pyridyl)-1,3,5-hexatriene (VI), and by the reaction of the same aldehyde with (2-quinolyl)methyllithium we succeeded in isolating 6-phenyl-1-(2quinolyl)-3,5-hexadien-2-ol (VII), which when boiled with a mixture of acetic acid and hydrochloric acids was converted into 1-phenyl-6-(2-quinolyl)-1,3,5-hexatriene (VIII):

$$\mathbf{C}_{\mathbf{6}}\mathbf{H}_{\mathbf{5}}\mathbf{C}\mathbf{H} = \mathbf{C}\mathbf{H} - \mathbf{C}\mathbf{H} = \mathbf{C}\mathbf{H}$$

The fluorescence of (VI) and (VIII) was weaker than that of the aryl derivatives of 1,3,5-hexatriene.

The results of the investigation of the optical properties of the products will be reported later.

### EXPERIMENTAL

1,6-Diphenyl-1,3,5-hexatriene (I). 1. A solution of 13 g (0.082 mole) of 5-phenyl-2,4-pentadienal [1] in 60 ml of dry ether was added over a period of one hour to a solution of a Grignard reagent prepared from 13.9 g (0.11 mole) of benzyl chloride, 2.88 g (0.12 g-atom) of magnesium, and 100 ml of dry ether. A precipitate formed during the addition of the aldehyde, but in the subsequent two hours at room temperature this went completely into solution. The reaction mixture was decomposed with 25% ammonium chloride solution, and the ether layer was washed with water and dried. After removal of ether we obtained an orange-red viscous oil, which was heated for 90 minutes with 400 ml of ethanol and 38 ml of 40% hydrobromic acid. From the cooled solution we filtered 12.1 g of 1,6-diphenyl-1,3,5-hexatriene, m.p. 153-176°. After chromatography on alumina,1,6-diphenyl-1,3,5-hexatriene formed pale-yellow crystals, m.p. 199-201° (yield 5 g, i.e., 26.5%). The literature [2] gives m.p. 200°. 2. A solution of 11.53 g (0.073 mole) of 5-phenyl-2,4-hexadienal in 25 ml of toluene was added over a period of 25 minutes to a solution of benzylsodium prepared from 11.2 g (0.1 mole) of chlorobenzene, 4.6 g (0.2 g-atom) of sodium, and 35 ml of toluene. After the usual treatment and distillation of toluene we obtained 17.3 g of a viscous oil, which was heated with alcohol and HBr as described for the preceding experiment. After chromatography on alumina we isolated 5.35 g (31.5%) of 1,6-diphenyl-1,3,5-hexatriene, m.p. 199-200.5°.

3. A mixture of 4.74 g (0.03 mole) of 5-phenyl-2,4-pentadienal, 4.08 g (0.03 mole) of phenylacetic acid, 3.5 g litharge, and 4 ml of acetic anhydride was boiled in a stream of nitrogen for 4.5 hours. When cooled to room temperature, the reaction mixture crystallized, and the precipitate was filtered off and washed, twice with alcohol and once with a mixture of equal parts of ethanol and acetone. We obtained 2.1 g of 1,6-diphenyl-1,3,5hexatriene, m.p. 198-200°. We isolated a further 0.3 g of the hydrocarbon from the mother liquor. Yield 2.4 g (34.5%). On dilution of the mother liquor with water, lead phenylacetate separated, and this, after several crystallizations from acetone and then from dioxane, was a crystalline substance, m.p. 198-199°. Found: C 40.50; 40.32; H 3.00; 3.08; ash 46.54; 46.31%. C  $_{16}H_{14}O_4Pb$ . Calculated: C 40.25; H 2.96; ash 46.75%.

1-(1-Naphthyl)-6-phenyl-1,3,5-hexatriene (II). A mixture of 4.1 g (0.026 mole) of 5-phenyl-2,4-pentadienal, 4.9 g (0.026 mole) of 1-naphthaleneacetic acid, 3 g of litharge, and 4 ml of acetic anhydride was refluxed for five hours. When cool, the mixture crystallized to form a thick slurry, which was diluted with 5 ml of ethanol. The precipitate was filtered off and washed with a mixture of equal amounts of benzene and ethanol. We obtained 1.5 g (20.4%) of 1-(1-naphthyl)-6-phenyl-1,3,5-hexatriene, m.p. 150-154°. After chromatography on alumina the hydrocarbon was obtained in the form of bright-yellow crystals, m.p. 159-160°. Found: C 93.40; 93.36; H 6.58; 6.51%. C<sub>22</sub>H<sub>18</sub>. Calculated: C 93.57; H 6.43.

<u>1-(9-Phenanthryl)-6-phenyl-1,3,5-hexatriene (III)</u>. A solution of 2.28 g (0.01 mole) of 9-(chloromethyl)phenanthrene in 40 ml of a mixture of equal amounts of dry ether and benzene together with a few drops of ethyl bromide was added to 0.3 g of magnesium, and the whole was boiled for one hour in a water bath. A solution of 1.58 g (0.01 mole) of 5-phenyl-2,4-pentadienal in 10 ml of dry ether was added to the cooled Grignard reagent. The mixture was boiled for 30 minutes, kept at room temperature for two hours, and decomposed with ammonium chloride solution. The undissolved precipitate of di-9-phenanthryl-ethane was filtered off, washed with alcohol, and dried; m.p.  $249-251^{\circ}$ ; yield 1.1 g (57.5%). The literature [4] gives m.p.  $251-253^{\circ}$ .

The benzene-ether solution was washed with water and dried over potassium carbonate. After removal of solvent we obtained 1.74 g of pale-yellow oil, which was boiled with 50 ml of ethanol and 0.5 ml of HBr for 3.5 hours. From the cooled solution we filtered 0.29 g of 1-(9-phenanthryl)-6-phenyl-1.3,5-hexatriene, m.p. 239-245°, and on evaporation of the mother liquor we obtained a further 0.35 g of the hydrocarbon, which melted at 240-246° after crystallization from toluene. Yield 0.56 g (39.5%). After chromatography on alumina and recrystallization from toluene. 1-(9-phenanthryl)-6-phenyl-1.3,5-hexatriene formed colorless crystals having a blue fluorescence, m.p. 253-253.5°. Found: C 94.12; 93.77; H 5.96; 6.00%. C<sub>25</sub>H<sub>20</sub>. Calculated: C 93.94; H 6.06%.

<u>1-(4-Biphenylyl)-6-phenyl-3,5-hexadien-2-ol (IV)</u>. A solution of 2 g (0.0126 mole) of 5-phenyl-2,4pentadienal in 10 ml of dry ether was added over a period of 20 minutes to a Grignard reagent prepared from 2.6 g (0.0128 mole) of p-phenylbenzyl chloride, 0.4 g of magnesium, and 10 ml of dry ether. The mixture was kept at room temperature for 30 minutes and then decomposed with ammonium chloride. The ether was distilled off, and the oily residue crystallized out. We obtained 1.9 g (46.5%) of 1-(4-biphenylyl)-6-phenyl-3,5hexadien-2-ol, m.p. 125-145°, which, after two crystallizations from ethanol and then from ethyl acetate, had m.p. 133-136°. Found: C 88.67; 88.51; H 6.51; 6.56%. C<sub>24</sub>H<sub>22</sub>O. Calculated: C 88.30; H 6.80%.

<u>1-(4-Biphenylyl)-6-phenyl-1,3,5-hexatriene (V).</u> A solution of 0.5 g of 1-(4-biphenylyl)-6-phenyl-3,5-hexadien-2-ol in 10 ml of glacial acetic acid was boiled for 15 minutes. When the solution was cool we filtered off 0.46 g (almost quantitative yield) of a yellow precipitate of 1-(4-biphenylyl)-6-phenyl-1,3,5-hexa-triene, which melted at 228-229° after crystallization from xylene. Found: C 93.10; 93.10; H 6.60; 6.73%.  $C_{24}H_{20}$ . Calculated: C 93.46; H 6.54%.

<u>1-Phenyl-6-(2-pyridyl)-1,3,5-hexatriene (VI)</u>. A solution of 6.8 g (0.072 mole) of 2-picoline in 15 ml of dry ether was added to a solution of phenyllithium prepared from 11 g (0.07 mole) of bromobenzene, 1.1 g of lithium, and 70 ml of dry ether. After one hour a solution of 9.48 g (0.06 mole) of 5-phenyl-2,4-pentadienal in 15 ml of ether was added over a period of 45 minutes to the cooled solution of (2-pyridyl)methyllithium, and

the mixture was then stirred further for two hours. The precipitate formed was filtered off (20.2 g) and was gradually added with stirring to 200 ml of 4% hydrochloric acid. The acid solution was neutralized with sodium carbonate, and the oil that separated was boiled for one hour with a mixture of 60 ml of acetic and 10 ml of hydrochloric acids. After being cooled, the solution was poured into water and neutralized with ammonia. The precipitate was filtered off and washed with a mixture of equal amounts of ethanol and acetone. We obtained 4.5 g of 1-phenyl-6-(2-pyridyl)-1,3,5-hexatriene, m.p. 140-156°, which, after several crystallizations from alcohol, melted at 175-180°; yield 2.13 g (15.2%). After chromatography on alumina 1-phenyl-6-(2-pyridyl)-1,3,5-hexatriene formed slightly yellowish crystals, m.p. 178,5-180°. Found: C 87.56; 87.66; H 6.51; 6.60; N 6.29; 6.00%. C<sub>17</sub>H<sub>15</sub>N. Calculated: C 87.51; H 6.48; N 6.01%.

<u>6-Phenyl-1-(2-quinolyl)-3,5-hexadien-2-ol(VII)</u>. A solution of 4.74 g (0.03 mole) of 5-phenyl-2,4pentadienal in 15 ml of ether was added over a period of 45 minutes to an ethereal solution of (2-quinolyl)methyllithium prepared from 4.29 g (0.03 mole) of quinaldine and an equimolecular amount of phenyllithium. The mixture was stirred at room temperature for one hour and decomposed with water. We filtered off 1.9 g (20%) of the precipitated 6-phenyl-1-(2-quinolyl)-3,5-hexadien-2-ol; after several crystallizations from ethanol this formed yellow crystals, m.p. 145-146°. Found: C 83.66; 83.50; H 6.55; 6.24; N 5.06; 5.13%.  $C_{21}H_{19}NO$ . Calculated: C 83.69; H 6.36; N 4.65%.

<u>1-Phenyl-6-(2-quinolyl)-1,3,5-hexatriene (VIII)</u>. A solution of 0.6 g of 6-phenyl-1-(2-quinolyl)-3,5-hexadien-2-ol in 3 ml of glacial acetic acid and 0.5 ml of concentrated hydrochloric acid was boiled for one hour, after which it was poured into cold water and neutralized. We obtained 0.48 g (almost quantitative yield) of 1-phenyl-6-(2-quinolyl)-1,3,5-hexatriene, m.p. 148-157°. After chromatography on alumina and crystallization from benzene,1-phenyl-6-(2-quinolyl)-1,3,5-hexatriene formed bright-yellow needles, m.p. 161-162°, which fluoresced in ultraviolet radiation. Found: C 88.72; 88.88; H 6.07; 6.08; N 5.14; 5.13%.  $C_{21}H_{17}N$ . Calculated: C 89.01; H 6.05; N 4.94%.

#### SUMMARY

1. Some new unsymmetrical 1,6-disubstituted 1,3,5-hexatrienes containing aromatic and heterocyclic substituents were synthesized.

2. Convenient methods were found for the preparation of 1,6-diphenyl-1,3,5-hexatriene from 5-phenyl-2,4-hexadienal.

### LITERATURE CITED

- 1. B. M. Mikhailov and G. S. Ter-Sarkisyan, Zhur. Obshch. Khim. 29, 2560 (1959).\*
- 2. R. Kuhn and A. Winterstein, Helv. Chim. Acta 11, 87 (1928).
- A. N. Nikitina, M. D. Galanin, G. S. Ter-Sarkisyan, and B. M. Mikhailov, Optika i Spektroskopiya 6, 3, 354 (1959).
- 4. D. S. Tarbell, and V. P. Wystrach, J. Am. Chem. Soc. 65, 2149 (1943).

\*Original Russian pagination. See C. B. translation.