Chemistry

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Structural formula II

Figure 1: Structural formula II

Abstract

Full Text

Chemistry

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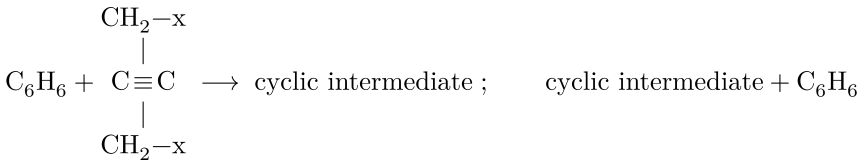
ON THE ALKYLATION OF BENZENE AND ITS HOMOLOGS WITH ACETIC ACID ESTERS OF γ-ACETYLENIC GLYCOLS

For a number of years we have been studying the alkylation of benzene both with butynediol and with its various homologs (1−6). For the first time, a series of polycyclic aromatic hydrocarbons was synthesized by this method; however, owing to inaccuracies in the determination of molecular weights (which were determined by the cryoscopic method in benzene) and for other reasons, we assigned to them an incorrect structure. In paper (7) we corrected the inaccuracy that had been made, recognizing the first of the hydrocarbons synthesized by us as 2-phenylnaphthalene (I). There we also gave a tentative scheme for the formation of 2-phenylnaphthalene. We sent a copy of our article to Prof. Hancock (Reed College, Portland, Oregon, USA), who is also studying the alkylation of aromatic hydrocarbons with butynediols and with whom we were in correspondence. In his reply, sent to us in July 1957, Prof. Hancock acknowledged that our new views on the structure of this hydrocarbon were correct. He merely proposed a different scheme for its formation, according to which 2,3-diphenylbutadiene-1,3 is first formed; under the action of HCl it is isomerized into 3-methyl-3-phenylhydrindene, which then, as a result of dehydrogenation and ring expansion under the action of Lewis acids, is converted into 2-phenylnaphthalene. He also drew our attention to the fact that the second of the hydrocarbons synthesized by us—the product of alkylation of benzene with the diacetate of tetramethylbutynediol, m.p. 83–84°, which was first obtained by one of us in 1952 (8,9)—is 5,5,10,10-tetramethyl-4b,5,9b,10-tetrahydroindeno(2,1-a)indene II (10).

II

The formation, upon alkylation of benzene with 2-butyne-1,4-diol diacetate, of 2-phenylnaphthalene together with acetyltetralin was also recently confirmed by Meyer (11). At present our scheme for the formation of hydrocarbon (I), as well as Hancock' s scheme, seems problematic. More probable to us is the formation of this hydrocarbon according to the scheme:



$$C_6H_6 + \begin{array}{c} CH_2{-}x \\ | \\ C{\equiv}C \\ | \\ CH_2{-}x \end{array} \longrightarrow \text{cyclic intermediate} \; ; \qquad \text{cyclic intermediate} + C_6H_6$$

[[chemical structural formula]] $\xrightarrow{-2H}$ [[chemical structural formula]]

As for the structure of the above-mentioned hydrocarbon with m.p. 83–84°, on the basis of the determination of molecular weights (already according to Rast), comparison of the corresponding properties, preparation of the bromide with m.p. 312–313°, and studies of its spectral character, we came to the conclusion that, as Henkok indeed believes, it should be assigned structure (II), and its homologues a structure analogous to that of the homologues of hydrocarbon (II) (^{9}).

In the present work we studied condensation reactions in the presence of anhydrous $AlCl_3$: 1) the diacetate of 2,5-dimethylhept-3-yne-2,5-diol with toluene, 2) the monoacetate of di-(1-oxy)-cyclohexylacetylene with toluene, and 3) the diacetate of tetramethylbutynediol with toluene and *p*-xylene.

I. The 2,5-dimethylhept-3-yne-2,5-diol synthesized by us, in agreement with the literature data, had m.p. 43-45° (^{12}). Acetylation of this diol with acetic anhydride under the conditions described earlier gave the diacetate with b.p. 97-100°/2-3 mm; d_4^{20} 0.9065; n_D^{20} 1.4531 (yield 60% of theory). 2.22 ml of 0.5 N alcoholic KOH solution was consumed, $C_{13}H_{20}O_4$. Calculated 2.26 ml. A qualitative test for an acetylenic triple bond gave a positive reaction.

To a mixture, cooled with ice water, of 60 g of benzene (0.769 mol) and 12.4 g of anhydrous $AlCl_3$ (0.094 mol), 10 g of the diacetate was added dropwise over 40 minutes. The temperature was maintained within 5-10°. The flask was gradually heated on a water bath. At about 40-45° a noticeable evolution of HCl began, which continued for a short time and resumed as the temperature was raised. After this the reaction was carried out at 70-80° for approximately another 2 hours. Work-up of the complex in the usual manner gave 11.57 g of condensate, from repeated fractionation of which a fraction of 3.58 g was isolated, b.p. 80-85°/1-2 mm, d_4^{20} 0.9964, n_D^{20} 1.4775. An identical product was also obtained by the direct interaction of free $AlCl_3$ with the diacetate in dearomatized ligroin, when the reactants were taken in equimolecular ratios and the reaction was carried out for about 2 hours by heating the mixture to 75-80°. The fraction with b.p. 80-85°/1-2 mm corresponds to 3-chloro-4-acetoxy-2,5-dimethylheptadiene-2,4.

Found, %: Cl 16.28; 16.61; M 212.06; 217.65
$C_{11}H_{17}O_2Cl$. Calculated, %: Cl 16.4; M 216.5.

0.7 g of the substance, dissolved in 60 ml of glacial acetic acid, was oxidized with 3.5 g of CrO_3 over 4 hours. It was diluted with distilled water and part of the liquid was distilled off. The first portions of the distillate were treated with a solution of 2,4-dinitrophenylhydrazine. Fractional crystallization of the precipitate gave a product with m.p. 125-127°, which showed no depression with the 2,4-dinitrophenylhydrazone of acetone with m.p. 125-126° ([13]), and a substance with m.p. 115-116°, which likewise gave no depression with the 2,4-dinitrophenylhydrazone of ethyl methyl ketone ([13]). The main part of the solution was extracted with ether (30 cm^3 × 5), the solvent was distilled off, and the residue was sublimed at 130-140° for 3 hours. The sublimate obtained in this way, recrystallized from ethyl alcohol, had m.p. 99-101° and, in a mixed sample with a pure specimen of oxalic acid, showed no depression of the melting point.

The fraction (2.76 g) with b.p. 170-172°/1-2 mm, d_4^{20} 1.0440; n_D^{20} 1.5825, corresponds to the hydrocarbon $C_{21}H_{24}$ (III) (yield 24% of theory). From the products of its oxidation with CrO_3 in glacial acetic acid under the above-described conditions, acetone, ethyl methyl ketone, and benzoic acid were isolated and identified. It exhibits the same properties as the other hydrocarbons obtained—

···by this route. By brief oxidation of (III) (see Table 1) with CrO_3 in glacial acetic acid for 30-40 min, a neutral crystalline substance was isolated, m.p. 144-145°.

Found, %: C 81.55; 81.50; H 7.18; 7.27; M 318.4; 324.3
$C_{21}H_{22}O_2$. Calculated, %: C 82.35; H 7.18.

By bromination of the fraction b.p. 170-172°/1-2 mm in CCl_4 in the cold, a bromide was obtained, m.p. 248-249°.

Found, %: Br 37.17
$C_{21}H_{22}Br_2$. Calculated, %: Br 36.86.

II. By condensation of the monoacetate of di-(1-hydroxy)cyclohexylacetylene with toluene under analogous conditions, a hydrocarbon of composition $C_{28}H_{34}$ (IV) was obtained (Table 1). It crystallized immediately after removal of the solvent from the condensate. The product, recrystallized twice (mixture of alcohol with benzene 2 : 1), has m.p. 250-251° and is characterized by the same properties as the hydrocarbons described earlier (yield 10-12% of theory).

Table 1

Hydrocarbon	Formula	Analysis	found, %	calculated, %	λ_{max}, mμ	lg ε_{max}
Hydrocarbon (III) $C_{21}H_{24}$, b.p. 170–172°/1–2 mm	[[structural formula as shown in the source table]]	C	91.2; 91.03	91.30	260	3.49
Hydrocarbon (III) $C_{21}H_{24}$, b.p. 170–172°/1–2 mm	[[structural formula as shown in the source table]]	H	8.60; 8.65	8.69	266	3.52
Hydrocarbon (III) $C_{21}H_{24}$, b.p. 170–172°/1–2 mm	[[structural formula as shown in the source table]]	M	273; 276	276	273	3.51
Hydrocarbon (III) $C_{21}H_{24}$, b.p. 170–172°/1–2 mm	[[structural formula as shown in the source table]]	MR	−88.29	−87.5		
Hydrocarbon (IV) $C_{28}H_{34}$, m.p. 250–251°	[[structural formula as shown in the source table]]	C	90.87; 90.94	90.81	(265)	(3.21)

Hydrocarbon	Formula	Analysis	found, %	calculated, %	λ_{max}, mμ	lg ε_{max}
Hydrocarbon (IV) $C_{28}H_{34}$, m.p. 250–251°	[[structural formula as shown in the source table]]	H	9.37; 9.38	9.18	271	3.42
Hydrocarbon (IV) $C_{28}H_{34}$, m.p. 250–251°	[[structural formula as shown in the source table]]	*M*	373.8; 363.6		278	3.52
Hydrocarbon (V) $C_{22}H_{26}$, b.p. 138–140°/1 mm	[[structural formula as shown in the source table]]	C	90.47; 90.61	91.03	258	3.40
Hydrocarbon (V) $C_{22}H_{26}$, b.p. 138–140°/1 mm	[[structural formula as shown in the source table]]	H	9.22; 9.14	8.96	272	3.49
Hydrocarbon (V) $C_{22}H_{26}$, b.p. 138–140°/1 mm	[[structural formula as shown in the source table]]	*M*	280; 285	290	278	3.51

Hydrocarbon	Formula	Analysis	found, %	calculated, %	$\lambda_{\max}$, mμ	lg $\varepsilon_{\max}$
Hydrocarbon (V) $C_{22}H_{26}$, b.p. 138–140°/1 mm	[[structural formula as shown in the source table]]	MR	−93.11	−92.19		
Hydrocarbon (VI) $C_{24}H_{30}$, m.p. 136–137°	[[structural formula as shown in the source table]]	C	90.27; 90.56	90.56		
Hydrocarbon (VI) $C_{24}H_{30}$, m.p. 136–137°	[[structural formula as shown in the source table]]	H	9.52; 9.68	9.43	267	2.71
Hydrocarbon (VI) $C_{24}H_{30}$, m.p. 136–137°	[[structural formula as shown in the source table]]	M	316	318		

III. Condensation of the diacetate of tetramethylbutynediol with toluene. Quantities of the reacting substances: diacetate 30 g (0.131 mol), anhydrous $AlCl_3$ 36 g (0.270 mol), toluene 88 g (0.956 mol). Duration of the condensation, 8 h. Maximum temperature at the end of the reaction, 97–100°. By repeated fractionation of the condensate, along with other substances that have not yet been investigated, a not entirely pure product was isolated, b.p. 138–140° (1 mm), d_4^{20} 1.0099; n_D^{20} 1.5670, approximating in composition $C_{22}H_{26}$ (V) (yield 20% of theory). In its chemical behavior it likewise shows similarity to the above-mentioned hydrocarbons. On standing it is noticeably oxidized, acquiring a yellow color.

IV. Condensation of tetramethylbutynediol diacetate with *p*-xylene. For the reaction, *p*-xylene twice distilled over metallic sodium was taken, b.p. 134°/730 mm; n_D^{20} 1.4950, freezing point +13° ([14]). The reaction was carried out under the conditions described above, with gradual heating of the flask (after addition of the diacetate) to 100° over 1 hour. From 20 g of the diacetate, 19.78 g of condensate was obtained; by distillation of it, three broad fractions were separated. The highest-boiling fraction, b.p. 170–190°/2–3 mm, in an amount of 4.1 g, upon addition of a small amount of acetone crystallized almost completely. The product, recrystallized several times from ethanol, has m.p. 136–137° and corresponds closely to a hydrocarbon of composition $C_{24}H_{30}$ (VI). The UV spectra and the proposed structures of the synthesized hydrocarbons are given in Table 1.

The spectrum of hydrocarbon (VI) has the same character as those of (II), (III), (IV), and (V), but in the region of 260 mμ the bands characteristic of a fine structure are absent. The intensity of the band is reduced in comparison with the intensity for hydrocarbons (III), (IV), and (V). Such a change in the absorption spectrum upon introduction of additional methyl groups may perhaps be connected with deformation of certain valence angles of the molecule. The presence in hydrocarbons (III) and (V) of absorption bands in the region of 295 mμ should apparently be explained by the presence of a minor impurity.

For (III), and also for the product of its dehydrogenation—the hydrocarbon with m.p. 216° ([6,9])—IR absorption spectra were obtained. (IKS-11 spectrometer, with a NaCl prism, in CCl_4 and CS_2 solutions.) The following bands were found (in cm^{-1}): (III)–725 (medium), 762 (very strong), 790 (weak), 809 (medium), 820 (weak), 867 (medium), 895 (medium), 916 (weak), 942 (strong), 977 (weak), 1012 (very strong), 1026 (strong), 1080 (medium), 1112 (medium), 1132 (weak), 1155 (strong), 1188 (medium), 1228 (strong), 1257 (weak), 1284 (strong), 1321 (medium), 1363 (strong), 1375 (very strong), 1423 (weak), 1446 (very strong), 1474 (very strong), 1580 (weak). For the hydrocarbon with m.p. 216–217°: 710 (medium), 753 (very strong), 762 (weak), 786 (weak), 857 (strong), 928 (medium), 986 (strong), 1010 (strong), 1072 (strong), 1110 (medium), 1144 (medium), 1168 (weak), 1214 (strong), 1248 (strong), 1298 (medium), 1330 (weak), 1360 (strong), 1368 (strong), 1458 (very strong), 1605 (strong). The general character of the IR spectrum of (III) is similar to that found earlier for (II); in particular, bands in the regions 730–760 cm^{-1}, 950–1050 cm^{-1}, and 1480–1580 cm^{-1} are characteristic of them. In addition, two bands are observed in them at 1363–1375 cm^{-1}, corresponding to the gem-substituted CH_3 group. It is interesting to note that on passing to the hydrocarbon with m.p. 216–217°, the frequencies of the gem-substituted carbon atom are retained, but new lines appear, usually associated with a monosubstituted aromatic ring: 710, 1010, 1072, 1605 cm^{-1}. At the same time, in the spectrum of the hydrocarbon with m.p. 216–217°, the intensity of the band at 753 cm^{-1}, encountered in (III) and other 1,2-disubstituted benzenes, is observed.

The ultraviolet absorption spectra were recorded by T. N. Shkurina, and the infrared spectra by Yu. P. Egorov.

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Note: Figure translations are in progress. See original paper for figures.