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Abstract

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Formation of a 1,2,3-Oxadiazine Ring in the Reaction of 1,1′-Diacetylferrocene with Aryldiazonium Compounds

Diazo compounds of the aromatic series, as is known (1, 2, 3), arylate ferrocene with the formation of mono-, di-, and polyarylferrocenes. 1,1′-Diacetylferrocene reacts with diazo compounds in an entirely different way, as we showed earlier (4): the ferrocene nucleus is destroyed and compounds not containing iron are formed. In their carbon, hydrogen, and nitrogen content these compounds correspond to arylazoacetocyclopentadienes, but their structure had not been established.

In the present work we have carried out the synthesis of these compounds (I, II) by another route, studied their properties, and proposed for them the structure of substituted 1,2,3-oxadiazines. We found that when aryldiazonium salts act on the acetate of the enolic form of acetylcyclopentadiene (III), recently described by Riemschneider and Krüger (5), intensely colored substances are obtained that are identical with those formed from 1,1′-diacetylferrocene:

$$\mathrm{Fe(C_5H_4COCH_3)_2} \xrightarrow{\mathrm{ArN_2X}} [\mathrm{CH_3COC_5H_4N_2Ar}] \xleftarrow{\mathrm{ArN_2X}} \text{acetate of the enolic form of acetylcyclopentadiene (III)}$$

$$\begin{aligned} &(\mathrm{I}) \quad \mathrm{Ar} = \mathrm{C_6H_5}- \\ &(\mathrm{II}) \quad \mathrm{Ar} = p\text{-}\mathrm{NO_2C_6H_4}- \end{aligned}$$

On the basis of the method of preparation and of the elemental composition of compounds I and II, it was possible to propose for them one of the following structures:

cyclopentadiene structure bearing $COCH_3$ and N=N−Ar   cyclopentadiene structure bearing $COCH_3$ and N

However, study of the properties of these substances showed that they are not arylazoacetocyclopentadienes. Compounds I and II are quite stable; they give no derivatives either through the ketone (4) or through the hydroxyl group; qualitative reactions for enols are negative. In the IR spectra of I and II there are no bands corresponding to C=O, C—OH, and N—H groups. The presence of an intense band at 1563–1590 cm^{-1} indicates the presence of a system of conjugated bonds C=C—C=N. The dipole moment* of I in benzene is $1.70\,D$, which excludes the possibility of polar structures, for example of the ylide type. I forms a complex with cadmium chloride, similarly to isoxazoles.

* For the measurement of the dipole moment we express our gratitude to Ya. K. Syrkin and E. A. Shott-Lvova.

In catalytic hydrogenation over Pt, I absorbs 2 moles of hydrogen and is converted into 5-methyl-3,4-cyclopentano-1-phenylpyrazole (IV)

$$\text{I} \xrightarrow{H_2/Pt} \text{(IV)}$$

Hydrogenation of II is accompanied by reduction of the NO_2 group, giving 5-methyl-3,4-cyclopentano-1-(*p*-aminophenyl)pyrazole (V). The formation of substituted pyrazoles (IV and V) upon hydrogenation of I and II indicates that, in the reaction of 1,1′-diacetylferrocene with aryldiazonium, the five-membered carbon ring is preserved and the reaction proceeds at the α-position with respect to the acetyl group.

The structure of pyrazole IV was proved by counter-synthesis from acetylcyclopentane (VI) and phenylhydrazine

$$\text{(VI)} \xrightarrow{C_6H_5NHNH_2} \text{(IV)} + \text{(VII)}$$

In the reaction of VI with phenylhydrazine, a mixture of the isomeric pyrazoles IV and VII is formed in 95% yield of theory; we separated this mixture chromatographically. The amount of the isomer identical with the substance formed upon hydrogenation of compound I is only 2.5% in this mixture. This can only be 5-methyl-3,4-cyclopentano-1-phenylpyrazole (IV), since the phenyl group in the pyrazole formed upon hydrogenation of I must be in position 1, because the starting compound I is obtained by the action of phenyldiazonium.

Upon nitration of 5-methyl-3,4-cyclopentano-1-phenylpyrazole (IV), 5-methyl-3,4-(*p*-nitrophenyl)pyrazole (VIII) was obtained; its catalytic reduction gave the corresponding *p*-aminophenylpyrazole (V), identical with that obtained upon hydrogenation of II.

$$\text{(IV)} \xrightarrow{HNO_3} \text{(VIII)} \xrightarrow{H_2/Pt} \text{(V)}$$

The facts set forth provide grounds for assuming the presence of a 1,2,3-oxadiazine ring in compounds I and II and for considering that the substances studied have the structure of substituted 1,2,3-oxadiazines:

A or B or C

The formation of pyrazoles upon hydrogenation is an argument (although not decisive, since isomerization is possible) in favor of structures A and B.

Experimental Part

Reaction of the acetate of the enolic form of acetylcyclopentadiene$^{(5)}$ **(III) with phenyldiazonium chloride.** To a solution of phenyldiazonium chloride, prepared from 6.1 moles of aniline, an alcoholic ···

solution of 13.3 g (0.088 mole) of III, then stirring was continued for 5 h, after which the alcohol was distilled off in vacuo. The residue was extracted repeatedly with benzene. The benzene solution was diluted with petroleum ether, chromatographed on Al_2O_3 deactivated in air for 2 h, and then on Al_2O_3 deactivated in air for 1 h. Elution was carried out with a mixture of benzene and petroleum ether (1 : 4). 6.0 g (32% of theoretical) of substance I was obtained in the form of beautiful bright-red crystals. M.p. 72–73° (from petroleum ether).

Found, %: C 73.33; 73.58; H 5.92; 5.80; N 13.08; 12.86
$C_{13}H_{12}N_2O$. Calculated, %: C 73.56; H 5.69; N 13.20

IR spectrum (in Vaseline oil and perfluorohydrocarbon, NaCl prism): 1563, 1488, 1422, 1375, 1352, 1279, 1252, 1190, 1163, 1074, 1060, 1028, 935, 853, 764, 754, 674 cm^{-1}.

UV spectrum (in $CHCl_3$): λ_max 262, 422, 477 (log ϵ 4.41; 4.15; 4.21).

A mixed sample with the substance formed in the reaction of 1,1′-diacetylferrocene with benzenediazonium chloride [4] melted without depression. Both substances are identical according to their IR spectra and by paper chromatography (in the ethanol-formamide system (1 : 1) on Leningrad chromatographic paper impregnated with a 30% solution of formamide in methanol and dried in air (5 min.); $R_f = 0.67$).

Reaction of III with p-nitrobenzenediazonium chloride. To an alcoholic solution of 0.5 g (0.003 mole) of III, with stirring, there was gradually added a solution of p-nitrobenzenediazonium chloride, prepared from 0.003 mole of p-nitroaniline. After one hour the precipitate was filtered off, washed with water, dried, extracted with benzene, and chromatographed on Al_2O_3 deactivated in air for 2 h. 0.2 g (26% of theoretical) of substance II was obtained in the form of dark raspberry-colored crystals. M.p. (with decomposition) 204–205° (from benzene).

Found, %: C 60.32; 60.51; H 4.24; 4.23; N 15.75; 15.88
$C_{13}H_{11}O_3N_3$. Calculated, %: C 60.69; H 4.31; N 16.34

IR spectrum (in Vaseline oil and perfluorohydrocarbon, NaCl prism): 1590, 1560, 1515, 1429, 1370, 1332, 1313, 1279, 1248, 1212, 1187, 1164, 1106, 1072, 1057, 1020, 935, 870, 844, 804, 764, 748, 687 cm^{-1}.

A mixed sample with the substance previously obtained by us [4] from diacetylferrocene melted without depression. The IR spectra of the two substances are identical.

Complex of substance I with $CdCl_2$. To a solution of 0.1 g (0.00047 mole) of $CdCl_2 \cdot 2H_2O$ in 0.1 ml of warm water was added a 5-fold volume of alcohol, and the resulting solution was poured into a saturated alcoholic solution of 0.1 g (0.00047 mole) of I. The brown needle-shaped crystals that separated after 48 h were filtered off, washed with alcohol, and dried in vacuo. Weight 0.14 g. From the filtrate, a further 0.04 g of the complex was isolated. The total yield of the complex of I with $CdCl_2$ was 0.18 g (quantitative). The complex of I with $CdCl_2$ does not melt; it decomposes at 240–250°; on treatment with water it liberates I quantitatively.

Found, %: C 39.21; 39.15; H 2.85; 2.74; N 7.10; 7.24; Cl 17.55; 17.91
$C_{13}H_{12}N_2OCdCl_2$. Calculated, %: C 39.47; H 3.06; N 7.08; Cl 17.93

Hydrogenation of I. 4.58 g (0.021 mole) of I was hydrogenated in glacial CH_3COOH (70 ml) over Pt (from 0.07 g of PtO_2). After 9 h, 1186 ml of H_2 (0.048 mole, 17°, 741 mm) had been absorbed. The solution was filtered, diluted with 300 ml of water, neutralized with 20% alkali, and repeatedly extracted with ether. The ethereal solution was dried over $MgSO_4$. The ether was distilled off in vacuo. The residue was extracted repeatedly with n-pentane. After evaporation of the n-pentane, the remaining 5-methyl-3,4-cyclopentano-1-phenylpyrazole (IV) was distilled in vacuo (2 mm, bath temperature 120°). Yield 2.77 g (65% of theoretical). M.p. 78-79°. IV is a white crystalline substance.

substance, is readily soluble in organic solvents (somewhat less so in petroleum ether) and in acids.

Found, %: C 79.04; 79.05; H 7.14; 7.14; N 13.95; 14.09
$C_{13}H_{14}N_2$. Calculated, %: C 78.75; H 7.12; N 14.13

IR spectrum (in vaseline oil, NaCl prism) 700, 763, 909, 1022, 1057, 1360, 1458, 1506, 1590, 2920 cm^{-1}.

Hydrogenation of II. This was carried out analogously to that described above. From 2.4 g (0.009 mole) of II, 1.2 g (66% of theoretical) of 5-methyl-3,4-cyclopentano-1-(*n*-aminophenyl)-pyrazole (V) was obtained. V is readily soluble in acids, hot water, $CHCl_3$, and alcohol; less soluble in benzene; poorly soluble in petroleum ether; recrystallized from a mixture of benzene and petroleum ether. M.p. 135–136°.

Found, %: C 73.63; 73.37; H 7.27; 7.13; N 19.27
$C_{13}H_{15}N_3$. Calculated, %: C 73.21; H 7.08; N 19.70

Synthesis of IV and VII from acetylcyclopentanone⁽⁶⁾ **(VI) and phenylhydrazine.** To a solution of 8.6 g (0.08 mole) of freshly distilled phenylhydrazine in 11 ml of 28% H_2SO_4, 10.1 g (0.08 mole) of VI was gradually added. The mixture was heated for 2 h at 90–95°, then neutralized with 10% NaOH and extracted with ether. From the ethereal solution 15 g of a mixture of IV and VII was isolated (95% of theoretical yield). 6.0 g of this mixture was chromatographed on Al_2O_3. VII is eluted with petroleum ether. Yield 5.85 g (97.5% of the mixture). M.p. 57–58° (from petroleum ether).

Found, %: C 78.60; 78.61; H 7.26; 7.21
$C_{13}H_{14}N_2$. Calculated, %: C 78.75; H 7.12

IV is eluted with benzene. Yield 0.15 g (2.5% of the mixture). M.p. 78–79°. A mixed sample with IV obtained by hydrogenation of I melted without depression. The IR spectra of both preparations are identical.

5-Methyl-3,4-cyclopentano-1-(*n*-nitrophenyl)-pyrazole (VIII). 0.3 g (0.0015 mole) of VIII was added in portions to ice-cooled HNO_3, sp. gr. 1.51 (3 ml). After 2 h the solution was poured into 50 ml of ice water. VIII separated as a yellow precipitate. Yield of VIII 0.3 g (83% of theoretical). VIII is readily soluble in acetone and $CHCl_3$, somewhat less soluble in benzene and ether; it crystallizes from alcohol and from aqueous alcohol. M.p. 137–138°.

Found, %: C 64.15; 63.96; H 5.62; 5.64
$C_{13}H_{13}N_3O_2$. Calculated, %: C 64.18; H 5.38

Reduction of 5-methyl-3,4-cyclopentano-1-(*n*-nitrophenyl)-pyrazole (VIII). 0.66 g (0.0027 mole) of VIII was reduced with hydrogen in alcohol at room temperature over Pd charcoal for 8 h. The alcohol was distilled off in vacuo under N_2. Yield of 5-methyl-3,4-cyclopentano-1-(*n*-aminophenyl)-pyrazole (V), 0.57 g (quantitative). M.p. 136–136.5° (after recrystallization from water and petroleum ether). A mixed sample with the substance obtained by hydrogenation of II melted without depression.

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