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FORMATION OF HETEROCYCLIC ISOSTERES OF INDENONE IN THE REACTION OF THE σ DERIVATIVES OF IRON WITH TOLANE

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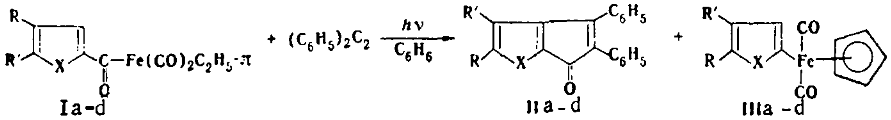
In a number of cases the reaction of σ derivatives of transition metals with acetylenes is accompanied by cyclization reactions, in which one or several molecules of the acetylene and various fragments of the organometallic compound participate. Often it is the formation of new C—C bonds which becomes the main direction of these reactions [1]. In the literature there are few data on the reactions of alkyl and aryl σ derivatives of iron leading to the formation of the products from cyclooligomerization in the coordinated and free state [2-4].

In order to study the reactivity of our previously synthesized heterocyclic σ derivatives of π-cyclopentadienyldicarbonyliron [5] we investigated the reaction of these compounds and of the isosteric σ-benzoylcyclopentadienylcarbonyliron [6] with diphenylacetylene (tolane). It was found that the photochemical reaction of the acyl σ derivatives (Ia-d) with tolane gives 2,3-diphenylindenone (IIa) and its hetero analogs (IIb-d) and also the products from photochemical decarbonylation (IIIa-d):



I—III a $R=R'=H$, $X=-CH=CH-$; b $R=R'=H$, $X=S$; c $R=CH_3$, $R'=H$, $X=O$;
d $RR'=-CH=CH-CH=CH-$, $X=O$

Under these conditions the furoyl σ derivative (Ie) (R = R' = H, X = O) does not react with tolane, and the only product is the decarbonylated σ derivative (IIIe).

Until now the heterocyclic analogs of indenone have been unknown. The published data [7-9] concern the isosteres of indanones containing a hydrogenated five-membered ring.

The structure of compounds (IIb-d) is confirmed by elemental analysis and IR, UV, and mass spectra (Table 1). In the IR spectra of compounds (IIa-d) at 1710 cm^{-1} there is a strong absorption band corresponding to the stretching vibrations of the CO group. In the UV spectra the thia- and oxaindenones (IIb-d), like 2,3-diphenylindenone (IIa), have a strong absorption maximum at about 265 nm and a low-intensity absorption maximum in the visible region. Substitution of the benzene ring by the heterocycle gives rise to a bathochromic shift of the long-wave absorption maximum by 30-35 nm for the oxaindenones (IIc, d) and by 60 nm for the thiaindenone (IIb) in comparison with the spectrum of compound (IIa). The

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TABLE 1. Heteroanalogs of 2,3-Diphenylindenone

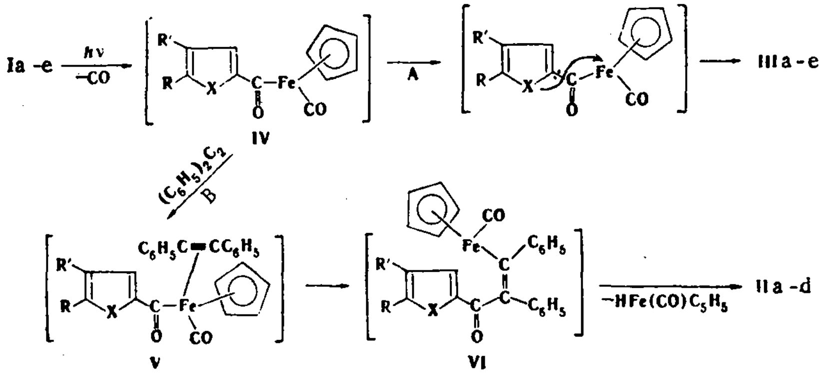
Compound	mp, °C	Molecular formula	IR spectrum, $\nu_{C=O}$, cm^{-1}	UV spectrum, λ_{max}, nm (lg ε)	Mass spectrum, m/e (relative intensity, %)	Yield of indenone, %	Yield of decarbonylated product, %
IIa	149—150*	$C_{21}H_{14}O$	1712	263 (4,56) 436 (3,22)	—	43	22
IIb	161—162	$C_{19}H_{12}OS$	1710	267 (4,40) 510 (3,16)	288 (100), 287 (37), 259 (19), 258 (20), 215 (14)	52	32
IIc	80—81	$C_{20}H_{14}O_2$	1713	267 (4,47) 470 (3,66)	286 (100), 271 (12), 244 (50), 243 (17), 215 (54), 213 (18)	30	35
IId	136—137	$C_{23}H_{14}O_2$	1710	259 (4,59) 263 (4,58) 464 (3,88)	322 (100), 294 (22), 293 (28), 265 (17), 215 (16)	48	20
IX	86—87	$C_{19}H_{12}OS$	1706	267 (4,67) 448 (3,44)	288 (100), 287 (54), 259 (20), 258 (25), 215 (18), 129 (14)	19	—

*Published data [10], mp 150-151°C.

formation of the tricyclic condensed system in compound (IId) leads to the appearance of a new absorption maximum at 259 nm.

Maximum-intensity peaks for the molecular ions are observed in the mass spectra of compounds (IIb-d), and their m/e values correspond to the molecular formulas of the proposed structures. A common direction of decomposition under electron impact for compounds (IIa, b, d) is the ejection of CO and COH groups from the molecular ion. A feature of the fragmentation of compound (IIc) is the initial elimination of the methyl substituent, which is followed by ejection of the CO and COH groups. The presence of stable molecular ions confirms the aromatic character of compounds (IIb-d).

A possible mechanism for the reaction of acyl derivatives of iron with tolane is given in the following scheme:

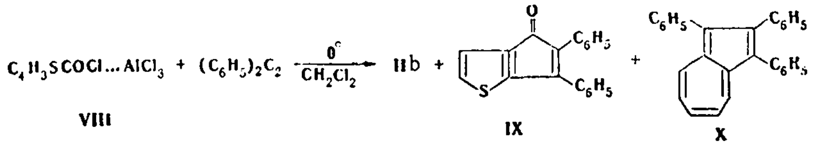


Irradiation of the acyl σ derivative of iron with UV light, as shown in [11], leads to the elimination of the terminal carbonyl group and to the formation of the electronically and coordinationally unsaturated intermediate (IV). The vacant coordination position in the intermediate (IV) can be filled in two directions. The first direction (A) consists of the migration of the aryl radical to the metal atom and conversion of the bridging CO to a terminal CO. This leads to the formation of the decarbonylated σ derivatives (IIIa-e). In the second direction (B) the intermediate (IV) adds the nucleophilic tolane molecule, and the unstable π complex (V) which forms is converted into the indenone derivative as a result of intramolecular cyclization. The formation of 2,3-diphenylindenone from the stable tolane π complex of iron was observed earlier [12]. It should be noted that derivatives of type (III) are not formed during irradiation of the acyl σ derivatives of iron in the presence of the stronger nucleophile triphenylphosphine [11]. In this case the vacant position in the intermediate (IV) is extinguished on account of the electron pair of the phosphorus and not on account of rearrangement.

The closure of the indenone ring probably goes through entry of the tolane molecule at the Fe—C σ bond [the intermediate (VI)]. Analogous products from insertion (occurring as cis-addition at the triple bond) were obtained in the stable form for derivatives of manganese

[13] and rhodium [14]. In the investigated case the low stability of the organoiron complexes does not make it possible to fix the formation of the intermediate products (V) and (VI). We suppose that it is coordination of the tolane of the π and σ type in the intermediates (V) and (VI) which excludes isomerization, and cyclization occurs strictly specifically with the formation of the 6H derivatives for compounds (IIb, c) and the 3H isomer for compound (IId). The unstable coordinationally unsaturated hydride (VII) decomposes under the reaction conditions.

The heteroanalogs of indenone can also be obtained by condensation of tolane with the chlorides of the respective acids [15]. We realized an alternative synthesis of 6-thiaindenone (IIb) by the reaction of tolane with thiophenecarbonyl chloride in the presence of aluminum chloride:



In this case the structural isomer 5,6-diphenyl-4H-cyclopenta[b]thiophen-4-one (IX) is formed in addition to 6-thiaindenone (IIb). In addition, the adduct (VIII), like the complexes of arenesulfenyl chlorides with aluminum chloride [16], catalyzes the dimerization of tolane to 1,2,3-triphenylazulene (X). The isomer (IX) is evidently formed as a result of rearrangement of a spirothiophenonium ion similar to the intermediate proposed in [15].

The difference in the structure of the isomers (IIb) and (IX) determines their different physicochemical characteristics. 4-Thiaindenone (IX) has a lower melting point and a lower R_f value than compound (IIb), and this makes it possible to separate the isomers with a sufficient degree of purity by chromatography. In the UV spectrum of compound (IX) the absorption maximum in the visible region is shifted toward the short-wave region by 52 nm, and this gives rise to the different color of the isomers, i.e., red for compound (IX) and dark-violet for compound (IIb). The position of the carbonyl group in the IR spectrum of compound (IX) compared with the spectrum of compound (IIb) hardly changes at all. The mass spectrum of compound (IX) is similar to the spectrum of compound (IIb) (Table 1).

Comparison of the methods for the synthesis of heteroanalogs of indenone given in the present work shows that it is advantageous to use the organoiron compounds, which permit selective synthesis of isomers having specific structures with relatively high yields.

EXPERIMENTAL

The photochemical reactions were carried out in apparatus of the Schlenk tube type in an inert atmosphere with cooling by running water. For irradiation we used a 200-W PRK-4 quartz lamp with a wavelength of 365 nm. The IR spectra were recorded in tablets with potassium bromide on a UR-20 instrument. The mass spectra were obtained on an MS-30 mass spectrometer with a DS-50 data-processing system (inlet temperature 30°C, source temperature 180°C, ionizing potential 70 eV). The UV spectra were measured on a Perkin–Elmer 402 spectrophotometer in methylene chloride. Neutral aluminum oxide of grade 2 activity and silica gel L-100-250 μ were used for chromatography.

2,3-Diphenylindenone (IIa). A solution of 1.6 g (5.7 mmole) of compound (Ia) and 1.0 g (5.7 mmole) of tolane in 100 ml of benzene was irradiated for 4 h. The solvent was then evaporated, and the reaction mixture was chromatographed on a column of aluminum oxide. The column was eluted with petroleum ether (bp 40-45°C) with the gradual addition of diethyl ether. From the colorless band 1 we isolated 0.2 g (20%) of tolane. From the yellow band 2 by crystallization of the dry residue from pentane we obtained 0.33 g (22%) of the decarbonylated derivative (IIIa). From the orange band 3 by recrystallization from hexane we isolated 0.7 g (43%) of 2,3-diphenylindenone (IIa). Compounds (IIa) and (IIIa) were identified by comparison of the IR spectra with the spectra of authentic samples [5, 6] and by the absence of a melting-point depression.

4,5-Diphenyl-6H-cyclopenta[b]thiophen-6-one (IIb). Compound (IIb) was obtained similarly to (IIa) with a 52% yield. The product formed dark-violet needles; mp 161-162°C (from a 20:1 mixture of hexane and methylene chloride). Found %: C 78.8; H 4.0; S 11.1. $C_{19}H_{12}OS$. Calculated %: C 79.1; H 4.2; S 11.1. At the same time, we obtained 0.36 g (32%) of compound (IIIb), which was identified by its IR spectrum and melting point [6].

2-Methyl-4,5-diphenyl-6H-cyclopenta[b]furan-6-one (IIc). Compound (IIc) was obtained similarly to compound (IIa). The yield was 48%, and the product formed bright-red needles; mp 80-81°C (from hexane). Found %: C 83.6; H 5.3. $C_{20}H_{14}O_2$. Calculated %: C 83.9; H 5.0. At the same time, we obtained 0.46 g (35%) of compound (IIIc), which was identified by its IR spectrum [6].

1,2-Diphenyl-3H-cyclopenta[b]benzofuran-3-one (IId). Compound (IId) was obtained similarly to compound (IIa) with a 48% yield. The product formed bright-red needles; mp 136-137°C (from hexane). Found %: C 85.4; H 4.6. $C_{23}H_{14}O_2$. Calculated %: C 85.7; H 4.6. At the same time, we obtained 0.17 g (20%) of compound (IIId), which was identified by its IR spectrum [6] and by the absence of a melting-point depression with an authentic sample.

σ-Furylcyclopentadienyldicarbonyl Iron (IIIe). A solution of 1 g (3.7 mmole) of compound (Ie) and 0.66 g (3.7 mmole) of tolane was irradiated for 6 h. By chromatography of the reaction mixture on a column of aluminum oxide we eluted the following bands: 1) with petroleum ether, colorless; 2) with a 20:1 mixture of petroleum ether and diethyl ether, yellow. From band 1 we isolated 0.6 g (92%) of tolane, and from band 2 we isolated 0.55 g (60%) of a yellow oil identical with compound (IIIe) in its IR spectrum and R_f value [6].

Reaction of Thiophenecarbonyl Chloride with Tolane. In a dropping funnel we mixed 3.8 g (26 mmole) of thiophenecarbonyl chloride, 2.5 g (17 mmole) of aluminum chloride, and 10 ml of methylene chloride. The solution was added with cooling to 0°C to a solution of 3.1 g (17 mmole) of tolane in 10 ml of methylene chloride. The mixture was stirred for 30 min and poured onto ice. A 20-ml portion of concentrated hydrochloric acid was added, and the organic layer was separated, washed with water (2 × 20 ml) and dried over calcium chloride. The solvent was evaporated, and the residue was chromatographed on a column of silica gel. The following bands were eluted: 1) with a 20:1 mixture of petroleum ether and methylene chloride, blue; 2) with a 5:1 mixture of petroleum ether and methylene chloride, violet; 3) with a 1:1 mixture of petroleum ether and methylene chloride, red. From band 1 by crystallization from a 10:1 mixture of hexane and methylene chloride we isolated 1.7 g (28% calculated on the tolane) of blue crystals of 1,2,3-triphenylazulene (X), which was identified by its melting point [16] and by elemental analysis. From fraction 2 by recrystallization from the same mixture we isolated 0.75 g (15%) of dark-violet crystals, which did not give a melting-point depression with compound (IIb). From band 3 by recrystallization from a 10:1 mixture of hexane and ether we obtained 0.95 g (19%) of red needles of compound (IX); mp 86-97°C. Found %: C 78.6; H 4.2; S 11.1. $C_{19}H_{12}OS$. Calculated %: C 79.1; H 4.2; S 11.1.

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