Chemistry

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Abstract

Full Text

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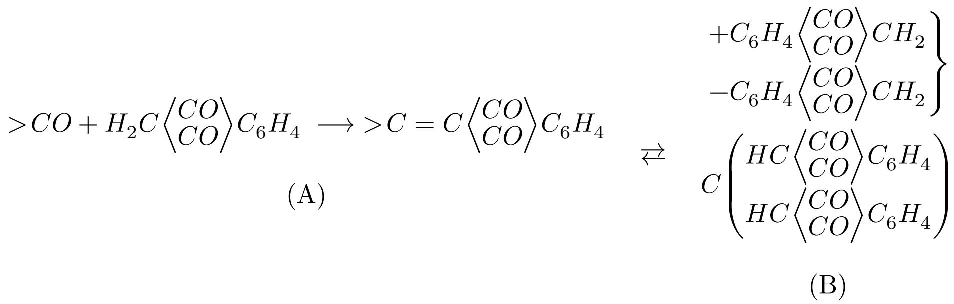
GEMINAL DIINDANDIONYLALKANES

In a number of works (see (^{1}) and the literature cited there) we have studied the condensation of indandione-1,3 with certain quinones and aromatic aldehydes and have shown that, depending on the reaction conditions and on the quinone or aldehyde used, both ylidene compounds (A) and diindandionyl compounds (B) may be formed, according to the general scheme



$$>CO + H_2C\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_4 \longrightarrow >C=C\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_4 \quad \rightleftarrows \quad \left.\begin{matrix}+C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle CH_2\\ -C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle CH_2\end{matrix}\right\} \quad C\left(\begin{matrix}HC\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_4\\ HC\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_4\end{matrix}\right)$$

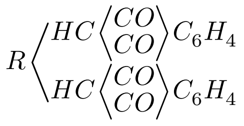
(A)

(B)

With aliphatic aldehydes this reaction has been little studied. By condensing indandione-1,3 with formaldehyde, Radulescu (^{2}) prepared methylenebisindandione, or diindandionylmethane—a white crystalline substance with m.p. about 201°. With acetaldehyde in pyridine solution he obtained a finely crystalline pink substance with m.p. 227°, which he regarded as diindandionylethane, but did not characterize further. Later Ionescu (^{3}) noted that diindandionylethane is yellow and melts at 254°, but he also did not investigate it further. Therefore the question arises whether the authors mentioned had one and the same substance, and, if not, which of them had diindandionylethane.

Table 1

Geminal diindandionylalkanes



$$R\left\langle\begin{matrix}HC\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_4\\ HC\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_4\end{matrix}\right.$$

Fig. 1

Figure 1: Fig. 1

No.	Name	R	M.p., °C	Found, % C	Found, % H	Calculated, % C	Calculated, % H	Yield, %	UV absorption curves $CHCl_3$	UV absorption curves NaOH
—	Diindandionylmethane	CH_2	201 (2)	—	—	—	—	—	—	—
I	Dnd*-ethane	CH_3CH	155	75.50	4.61	75.48	4.40	79.8	1	8
II	Dnd-propane	$CH_3 \cdot CH_2 \cdot CH$	140 – 142	75.98	4.88	76.08	4.94	58.1	2	9
III	Dnd-butane	$CH_3(CH_2)_2 \cdot CH$	115 – 117	76.30	5.17	76.30	5.20	73.0	3	10
IV	Dnd-isobutane	$(CH_3)_2 \cdot CH \cdot CH$	170 – 172	76.28	5.27	76.30	5.20	68.0	4	11
V	Dnd-pentane	$CH_3(CH_2)_3 \cdot CH$	92.5 – 94.5	76.75	5.50	76.67	5.55	50.0	5	12
VI	Dnd-isopentane	$(CH_3)_2 \cdot CH \cdot CH_2 \cdot CH$	120 from CH_3OH	76.54	5.61	76.67	5.55	45.0	6	13
VII	Dnd-isohexane	$(CH_3)_2CH(CH_2)_2 \cdot CH$	163 decomp.	77.03	5.84	77.00	5.88	58.60	7	14

* Dnd = diindandionyl.

According to Radulescu' s opinion (4), alkylidenebisindandiones can be obtained only up to ethylidenebisindandione, because with higher homologs of aldehydes the self-condensation of indandione to anhydrobisindandione or bindone proceeds faster than the condensation of indandione with the aldehyde. Indeed, when condensing indandione with aliphatic aldehydes beginning with propionic aldehyde, Ionescu (3) obtained only alkylideneindandionebindones and alkylidenebisbindones. Diindandionylalkanes were not obtained.

Fig. 1

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

Fig. 2

Having established experimentally that diindandionyl compounds often readily split off a molecule of indandione (B → A) in alcoholic or acetic-acid solution, whereas in alkalis these compounds are stable, we condensed aliphatic aldehydes with indandione in an alkaline medium. Although aldehydes in an alkaline medium readily enter into aldol condensation and undergo resinification, under certain conditions (at low temperature, which retards the self-condensation of indandione and the resinification of the aldehyde, but does not affect the condensation of indandione with aldehydes), it is possible to direct the reaction toward the predominant formation of diindandionyl compounds. In the condensation of aliphatic aldehydes that are sparingly soluble in water, mechanical stirring must be used.

Thus, we successfully condensed indandione with acetic, propionic, butyric, valeric, and caproic aldehydes.

In this case, salts of the corresponding geminal diindandionylalkanes are formed, readily soluble in water. Upon acidification of the solution, the free diindandionylalkanes are isolated. Diindandionylethane (I), m.p. 155°, was obtained in good yield; it differs from the above-mentioned diindandionylethanes described by Radulescu and Ionescu. It is possible that they isolated the product of anhydrization of diindandionylethane—the corresponding pyran.

Fig. 3

Fig. 4

The diindandionylalkanes obtained (see Table 1) are white crystalline substances, readily soluble in organic solvents. Their solubility increases with increasing length of the aliphatic chain. Diindandionylpentane and diindandionylhexane are also readily soluble in ether, so that their isolation and purification are difficult. In the light, the diindandionylalkanes turn yellow.

Since diindandionyl compounds have characteristic absorption in the short-wavelength region of the UV spectra (5), to confirm the structures of the diindandionylalkanes obtained (I–VII, see Table 1), their UV absorption spectra

Fig. 4

Figure 4: Fig. 4

were recorded in chloroform solution (curves 1-7) and in alkali (curves 8-14), in Figs. 1-4. The character of the curves obtained coincides with the absorption-spectrum curves of diindandionylarylmethanes (5), but in chloroform the more intense maximum of the diindandionylalkanes is split into two peaks: at 240 and 248 mμ ($\varepsilon = 2.1 \cdot 10^4$—$2.3 \cdot 10^4$). Splitting of the characteristic maximum is observed to a greater or lesser extent also in other diindandionyl compounds (5). In the region 293-332 mμ there appears a maximum, small in intensity ($\varepsilon =\sim 0.2 \cdot 10^4$), but characteristic of diindandionyl compounds and their derivatives.

In alkaline solution, the character of the absorption spectra of diindandionylalkanes (curves 8-14) coincides with the spectra of the enolate-anion form of other diindandionyl compounds (^{5}). Here, upon formation of another chromophoric system—an α,β-unsaturated ketone—a small bathochromic shift appears and the intensity of the characteristic maximum increases by approximately a factor of 2 ($\varepsilon = 4 \cdot 10^4$–$5.5 \cdot 10^4$).

Experimental Part

Diindandionylalkanes (I-VII). 10 g (0.07 mole) of indandione-1,3 is dissolved in 100 ml of 5% KOH with cooling by ice; 3-5 ml (0.035 mole) of a pure aliphatic aldehyde is added to the cold solution, and the mixture is stirred for several hours. In the case of acetic and propionic aldehydes, 4 hours of stirring is sufficient; for valeric and caproic aldehydes, 12 hours are necessary. The dark-red solution is filtered, diluted to 500 ml with water, and poured dropwise, with stirring, into 200 ml of dilute HCl. A yellow precipitate forms. In the case of propionic and butyric aldehydes, an oil may separate. It is dissolved in methanol, from which crystals of the condensation product precipitate. If the precipitate contains bindone (the alkaline solution of the precipitate is colored red-violet), it is dissolved in 10% KOH and the precipitated potassium salt of bindone is filtered off. The salt of the diindandionylalkane remains in solution. Acidification of the solution gives the diindandionylalkane.

For purification, the dry diindandionylalkane (I-IV) is treated with ether; the residue is dissolved in chloroform and, by precipitation with ether, white crystals of diindandionylalkane are obtained. Diindandionylpentanes (V and VI) and diindandionylhexane (VII) are better treated with CCl_4, since the solubility of the substances in ether becomes appreciable. The residue after treatment with CCl_4 is crystallized from ether. From the ethereal filtrate the substance can be precipitated with petroleum ether.

Condensation of acetic and propionic aldehydes with indandione proceeds well even without stirring, if the alkaline solution of both components is left for 24 hours in a refrigerator.

Diindandionylalkanes dissolve readily in alkalis with a red-orange coloration, and in concentrated sulfuric acid with a red-violet coloration.

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

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