CONCLUSIONS

It was shown that the triscyclopentadienyl complexes of the zirconium and hafnium hydrides of type Cp_3MH, and also bis(cyclopentadienyl)zirconium hydride $Cp_2ZrCl(H)$ reduce CCl_4 and $CHCl_3$ in toluene to $CHCl_3$ and CH_2Cl_2, respectively.

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EFFECT OF REACTION CONDITIONS AND SUBSTRATE STRUCTURE ON DIRECTION OF ADDING BROMOMALONIC ESTER TO α,β-UNSATURATED ALDEHYDES

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547.381

Bromomalonic ester (I) reacts with acrolein in the presence of sodium alcoholate [1] to give 1,1-diethyoxycarbonyl-2-formylcyclopropane. With crotonaldehyde this reaction proceeds not only at the double bond, but also at the carbonyl group, and leads to 3-methyl-2-(1,2-oxido-2,2-diethoxycarbonylethyl)-1,1-diethoxycarbonylcyclopropane. By using the standard two-phase catalysis method [50% aqueous NaOH solution, triethylbenzylammonium chloride (TEBAC), solvent] it becomes possible to add (I) not only to acrolein [2, 3], but also to a series of β-substituted α,β-unsaturated aldehydes (crotonaldehyde, cinnamaldehyde, fumaraldehyde monoacetal) and dienals (sorbaldehyde, 5-phenylpentadienal, 5,5-dichloropentadienal) and obtain the corresponding cyclopropane derivatives. The same reaction of (I) with acrolein can also be run in another liquid—solid phase catalytic system, and specifically K_2CO_3—DMF—TEBAC (LSCS). However, an attempt to transfer to other α,β-unsaturated aldehydes proved unsuccessful; only tetraethoxycarbonylethylene [4] was obtained as a result.

In the present paper we used the LSCS to generate carbanions in the case of the reaction of (I) with 3,3-dichloroacrolein (II) and 5,5-dichloro-2,4-pentadienal (III). It proved that when the LSCS is used the reaction of (II) and (III) with (I) proceeds exclusively on the type of the Darzens condensation to give glycidyl esters (IV) and (V). In the case of (III) the formation of diene oxide (V) is accompanied by partial HCl cleavage, and as a result (V) and epoxy ester (VI) are obtained in a 7:3 ratio. As a result, it can be seen on the example of (III) that, depending on the selected two-phase catalysis conditions, the reaction of (I) can proceed either at the activated double bond [3] or at the carbonyl group, leading as the result of subsequent HBr cleavage to the cyclopropane in the first case, and to the oxide in the second case.

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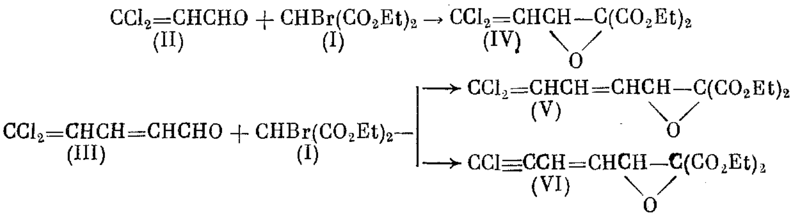
TABLE 1. Yields and Characteristics of Obtained Products

Compound	Yield, %	bp, ℃ (p, mm Hg)	n_D^{20}	$\frac{\text{Found}}{\text{Calculated}}$, %			Infrared spectrum, ν, cm^{-1}	PMR spectrum (δ, ppm), J, Hz
				C	H	Cl		
(IV)	48	107–109 (0,25)	1,4755	42,04 / 42,43	4,23 / 4,27	26,03 / 25,64	1750	1,27 m (6H, 2CH$_3$ est., J=7), 4,08 d (1H, CH, J=8), 4,21 qu (4H, 2CH$_2$ est., J=7), 5,6 d (1H, CH=, J=8)
(V)+(VI)	52	140–142 (0,2)	1,5000	47,51 / 48,00	4,90 / 4,60	19,92 / 20,45	1740 2400	1,17 t (CH$_3$ est., J=7), 3,9 d (CH, J=8), 4,2 qu (CH$_2$est., J=7), 5,75–6,25 m (CH=), 6,3–7,0 m (=CHCH=)
(XII)	51	158–160 (0,5)	1,5375	64,12 / 64,14	5,91 / 5,70		1622 1672 1745	0,75 t, 1,27 t (6H, 2CH$_3$ est., J=7), 3,52 m, 4,23 m (4H, 2CH$_2$ est.), 5,1 d (1H, CH, J=2), 7,15 s (5H, Ph), 7,45 d (1H, CH=, J=3), 9,5 s (1H, HCO)
(XIII) *	60	197–199 (0,5)	1,5345	58,27 / 57,88	4,77 / 4,85	10,28 / 10,05	1623 1673 1745	0,84 t, 1,28 t (6H, 2CH$_3$ est., J=7), 3,66 m, 4,28 m (4H, 2CH$_2$ est.), 5,15 d (1H, CH, J=2), 7,0–7,35 m (4H, C$_6$H$_4$), 7,55 d (1H, CH, J=2), 9,5 s (1H, CHO)
(XIV) †	74	mp 69–70 (hexane)		62,22 / 62,06	5,98 / 5,79		1620 1670 1740	0,8 t, 1,2 t (6H, 2CH$_3$ est., J=7), 3,6 m, 4,2 m (4H, 2CH$_2$ est.), 3,65 s (3H, CH$_3$O), 5,1 d (1H, CH, J=2), 6,6–7,1 m (4H, C$_6$H$_4$), 7,5 d (1H, CH=, J=2), 9,4 s (1H, CHO)
(XV) ‡	55	mp 111–112 (hexane)		66,68 / 66,27	5,81 / 5,85		1620 1675 1745	1,1 t, 1,3 t (6H, 2CH$_3$ est., J=7), 4,1 qu, 4,3 qu (4H, 2CH$_2$ est., J=7), 4,8 d.d (1H, CH, J=8, 2), 5,9 d.d (1H, CH=, J=16, 8), 6,6 d (1H, CH=, J=16), 7,25 s (5H, Ph), 7,4 d (1H, CH=, J=2), 9,7 s (2H, CHO)
(XVI)	75	170–175 (0,5)	1,5313	55,27 / 55,54	5,07 / 4,97	9,54 / 9,88	1620 1670 1740	0,9 t, 1,3 t (6H, 2CH$_3$ est., J=7), 3,75 qu, 4,25 qu (4H, 2CH$_2$ est., J=7), 5,4 d (1H, CH, J=2), 6,7–7,2 m (3H, 3CH$_{\text{arom}}$) 7,5 d (1H, CH=, J=2), 9,5 s (1H, CHO)

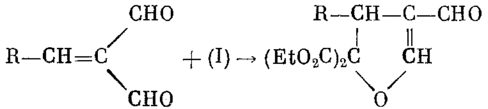
*UV spectrum, $\lambda_{\max}$, nm (ε): 255(13,044), 233(13,587), 201(26,631).

†UV spectrum, $\lambda_{\max}$, nm (ε): 255(10,385), 230 (10,513), 201(25,290).

‡UV spectrum, $\lambda_{\max}$, nm (ε): 256(21,962), 204(18,155).



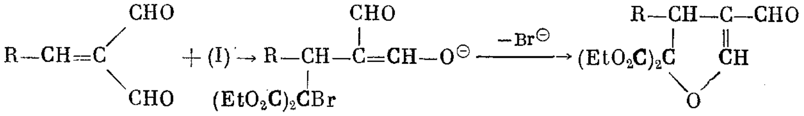
It was interesting to react (I) with arylidenemalonic dialdehydes of type (VII)-(XI), for which the addition of carbanion is equally probable to both the C=C and the C=O bond. We reacted (I) with (VII)–(XI) in the LSCS and obtained functionally substituted dihydrofurans (XII)–(XVI), i.e., products that correspond to still another possible direction for the addition of (I) to α,β-unsaturated aldehydes besides the formation of cyclopropanes and oxides. The structure of the obtained compounds was proved by their UV and PMR spectral data (Table 1). Thus, the UV spectra of (XIII)-(XV) lack absorption that corresponds to the cinnamaldehyde system. The signals of four protons are most informative in the PMR spectrum of (XV): a doublet at 7.4 ppm with a small J = 2 Hz (long-range spin-spin coupling constant) belongs to the isolated olefinic proton of the dihydrofuran ring; the olefinic proton, attached to the carbon of the phenyl ring, is manifested by a doublet at 6.6 ppm with J = 16 Hz; its vicinal olefinic proton gives a double doublet at 5.9 ppm with J = 16 and 8 Hz; the presence of the same SSCC, i.e., J = 8 Hz, for the doublet at 4.8 ppm confirms the fact that the latter belongs to the cyclic methine proton.



(VII)–(XI) (XII)–(XVI)

R = C_6H_5 (VII), (XII); p-ClC_6H_4 (VIII), (XIII); p-$CH_3OC_6H_4$ (IX), (XIV); PhCH=CH (X), (XV);  (XI), (XVI)

The formation of (XII)-(XVI) probably occurs via the initial addition of the $\bar{C}Br(CO_2Et)_2$ carbanion on the type of the Michael reaction and stabilization of the obtained intermediate carbanion by the ejection of bromine and 1,5-cyclization.



This reaction is the first example of forming dihydrofurans by the Michael addition to α,β-unsaturated aldehydes. The structure of the obtained compounds was confirmed by elemental analysis and the IR, UV, and PMR spectra.

EXPERIMENTAL

The GLC analysis was run on an LKhM-8MD-5 instrument equipped with a flame-ionization detectors. The carrier gas was nitrogen and the 1.4 × 0.003 m glass column was packed with 5% SE-30 deposited on Chromaton N-AW-DMCS. The PMR spectra were obtained on Varian DA-60-IL (60 MHz) and Tesla BS-497 (100 MHz) instruments in CCl_4 solution, and the chemical shifts are given on the δ scale, using TMS as the internal standard. The IR spectra were taken on a UR-20 instrument in $CHCl_3$ solution. The UV spectra were taken on a Specord instrument in alcohol solution.

The arylidenemalonic aldehydes (VII)-(XI) were obtained as described in [5]. The reaction of (I) with (II), (III), and (VII)-(XI) was run as described in [4]. The yields and characteristics of the obtained products are given in Table 1.

CONCLUSIONS

1. The use of the K_2CO_3—DMF—TEBAC system instead of NaOH—CH_2Cl_2—TEBAC for running the reaction of bromomalonic ester with 3,3-dichloroacrolein and 5,5-dichloro-2,4-pentadienal changes the direction of the reaction and leads to obtaining the oxide (Darzens reaction product) instead of the cyclopropane (Michael reaction product).

2. On the example of arylidenemalonic aldehydes, we discovered a new type of adding bromomalonic ester under two-phase conditions (K_2CO_3—DMF—TEBAC) to give dihydrofurans.

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PHENYL-2-CARBORANYLIODONIUM FLUOBORATE

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Recently we described the preparation of some phenyl-9-o- and phenyl-9-m-carboranyliodonium salts [1] and their reaction with nucleophiles [2-4].

The present paper is devoted to the synthesis and some reactions of a new member of this class of compounds, namely phenyl-2-p-carboranyliodonium fluoborate (I). This salt was obtained in 80% yield as described in [1] by the oxidative condensation of 2-iodo-p-carborane (II) with benzene using $K_2S_2O_8$ in an $(MeCO)_2O$—conc. H_2SO_4 mixture.

$$\underset{(II)}{2\text{-}p\text{-}C_2H_2B_{10}H_9I} + PhH + K_2S_2O_8 \xrightarrow[2.\ HBF_4]{1.\ H_2SO_4} \underset{(I)}{[2\text{-}p\text{-}C_2H_2B_{10}H_9\overset{+}{I}Ph]BF_4^-}$$

Based on the PMR spectra (100 MHz in acetone-d_6), (I) resembles phenyl-9-m-carboranyl- (III) and phenyl-9-o-carboranyliodonium (IV) fluoborates [2]. The signals of the protons at the C atoms of the p-carborane nucleus (3.9 and 4.5 ppm) are shifted strongly downfield when compared with the unsubstituted p-carborane and its 2-chloro and 2,11-dichloro derivatives [5]. Multiplets in the 8.2-8.4 (o-H) and 7.5-8.0 ppm (m- and p-H) regions correspond to the aromatic protons of (I).

In their properties (solubility, stability toward air and light, decomposition temperature, etc.) (I) resembles (III) and (IV) [1]. However, in contrast to (IV) and similar to (III), (I) is stable toward water [4], alcohol, and DMSO [2].

It seemed of interest to compare the behavior of (I) and (III) in reactions with nucleophilic reagents. Previously we had shown that, depending on the nature of the nucleophile, (III) reacts with cleavage of either the $B—\overset{+}{I}$ or $C—\overset{+}{I}$ bond. Nucleophilic substitution on the B atom of the carborane nucleus is probably realized in the first case [2]. In the second case the nucleophile apparently first forms a complex with the iodonium cation, which then decomposes homolytically [3]. The competition of ionic and radical reactions that proceed in parallel is usually observed when diaryliodonium salts react with nucleophiles [6, 7], whereas the combination of two ligands of such different nature as phenyl and carboranyl in one onium I atom leads to the situation that the ionic reactions of phenylcarboranyliodonium salts are realized selectively with cleavage of the more polar B—I bond, while the radical reactions are also realized selectively, but with cleavage of the less polar C—I bond.

As is known, the following rule is observed in the series of diaryliodonium salts: The more electron-deficient the ligand, attached to the onium center, the easier is the nucleo-

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