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Abstract

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PREPARATION OF SUBSTITUTED METHYLTROPYLIDENES BY THE REACTION OF ALKYLBENZENES WITH CHLOROCARBENE AND METHYLLITHIUM

Previously (^{1,2}), the ability of : CHCl and other monohalocarbenes to add to benzene with formation of the corresponding tropylium halides and products of their subsequent transformations was demonstrated.

In the present work we have investigated the reaction of monochlorocarbene, generated from CH_2Cl_2 under the action of CH_3Li, with benzene and a series of alkylbenzenes (toluene, *n*-xylene, cumene, tert-butylbenzene), and have also studied some properties of the substituted tropylidenes formed under these conditions.

All experiments on the synthesis of methyltropylidenes were carried out by adding an ethereal solution of methyllithium to a mixture of methylene chloride and an aromatic hydrocarbon (molar ratio 1 : 1 : 6–20) at various temperatures (from −20 to 100°). According to chromatographic studies, from benzene there was indeed formed, along with other products, only one isomeric methyltropylidene (^{2}), whereas from alkylbenzenes mixtures of isomeric methylalkyltropylidenes were obtained. Thus, for example, from toluene a mixture of three isomeric dimethyltropylidenes was obtained, and the ratio among them, depending on the experimental conditions, varied from 1 : 1 : 2 to 1 : 1 : 6. Rapid conduct of the interaction leads to a sharp increase in the content in the dimethyltropylidenes formed of, probably, the highest-boiling isomer, which has the greatest retention time in chromatography.

As was shown by experiments with benzene and toluene, the optimal conditions for formation of tropylidenes by this reaction are a temperature of 30–40° and slow addition of the organolithium compound, not requiring external cooling of the mixture. Under these conditions the yield of methyltropylidene from C_6H_6 was 30% of the theoretical, whereas at the boiling temperature of the reaction mixture it did not exceed 20% (^{2}). Similarly, the yield of the mixture of isomeric dimethyltropylidenes from toluene at 34–36° was 40% of the theoretical, at the boiling temperature of the reaction mixture (100–40°) it was 20%, and at 0 and −20° only 12%. A decrease in the yield of isomeric dimethyltropylidenes (to 20%), together with a change in their ratio, was also caused by an increase in the rate of addition of CH_3Li to the mixture of CH_2Cl_2 and toluene (temperature of the reaction mixture ~ 35°, cooling bath ~ 10°). The yields of dimethyltropylidenes were also lowered by using an excess of CH_2Cl_2 relative to CH_3Li, whereas changing the molar ratio CH_3Li :toluene from 1 : 7 to 1 : 20 had practically no effect on the results of this interaction. In contrast to toluene, the other alkylbenzenes (cumene, tert-butylbenzene, *n*-xylene) under optimal conditions (~ 35°) gave the corresponding isomeric alkylmethyltropylidenes in lower overall yields (10-25% of the theoretical). The structure of the hydrocarbons obtained as derivatives of cycloheptatriene-1,3,5 is confirmed by data from quantitative hydrogenation over freshly prepared Raney nickel at ~ 20° and a hydrogen pressure of 1 atm (each mole of hydrocarbon absorbs exactly 3 moles of H_2), and also by the formation, upon boiling them with equimolar amounts of maleic anhydride in xylene, of the corresponding 1 : 1 adducts in 80-90% yields. The UV and NMR spectra* data for the methyltropylidene obtained from C_6H_6

Table 1

Properties of substituted tropilidenes

Hydrocarbons	Yield, % of theory	B.p., °C (mm)	n_D^{20}	d_4^{20}	MR_D, found	MR_D, calculated	Found, % C	Found, % H	Gross formula	Calculated, % C	Calculated, % H	UV spectrum (in *n*-hexane), λ_{max}, mμ
Methyltropilidene (I)*	30	131 (764)	1.5032	0.8712	35.34	35.38	90.19 90.22	9.46 9.40	C_8H_{10}	90.50	9.50	257-258
Dimethyltropilidene (II)**	40	63-64 (30)	1.5095	0.8744	41.03	41.30	89.81 89.72	10.20 10.00	C_9H_{12}	89.93	10.07	260, 263
Methylisopropyltropilidene (III)	20	67-68 (8)	1.4998	0.8832	49.33	49.41	88.80 88.72	10.92 10.90	$C_{11}H_{16}$	89.12	10.88	260, 266

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* UV spectrum (in *n*-hexane): λ_{max} 257-258 mμ (ε 3440); NMR spectrum (in m.d. relative to the signal of tetramethylsilane, taken as 0): doublet—1.18 and 1.30 (CH_3 group); quartet—1.45, —1.55, —1.65 and —1.90 (saturated CH group); quartet—4.80, —4.90, —4.95 and —5.05 (vinyl protons at $C_{(1)}$ and $C_{(6)}$); triplet—5.87, —6.05 and —6.08 (vinyl protons at $C_{(2)}$ and $C_{(5)}$); triplet—6.40, —6.45 and —6.50 (vinyl protons at $C_{(3)}$ and $C_{(4)}$). Contrary to the UV data.

Hydrocarbons	Yield, % of theory	B.p., °C (mm)	n_D^{20}	d_4^{20}	MR_D, found	MR_D, calculated	Found, % C	Found, % H	Gross formula	Calculated, % C	Calculated, % H	UV spectrum (in n-hexane), $\lambda_{\max}$, mμ
Methyl-*tert*-butyltropilidene (IV)	25	69–71 (8)	1.5032	0.8821	54.39	54.56	88.78 88.69	10.90 10.97	$C_{12}H_{18}$	88.81	11.19	258,265, 272
Trimethyltropilidene (V)	10	70 (12)	1.5170	0.9043	44.90	44.70	89.21 89.17	10.42 10.50	$C_{10}H_{14}$	89.41	10.59	248

* According to (2), 7-methylcycloheptatriene-1,3,5 has b.p. 132.5°, n_D^{20} 1.5030, $\lambda_{\max}$ (in C_2H_5OH) 257 mμ (ε3600).
** Ratio of isomers 1 : 1 : 3.

tropilidene are in complete agreement with the structure assigned to it (2), namely 7-methylcycloheptatriene-1,3,5. In contrast to the latter, mixtures of isomeric methylalkyltropilidenes had two or three absorption maxima in their UV spectra, apparently corresponding to different isomers (Table 1).

The structures of the latter were also confirmed by NMR spectral data, which, as was to be expected, were of a rather complex character. Analysis of the proton spectrum of the simplest of the methylalkyltropilidenes—dimethyltropilidene, obtained from toluene—confirmed the presence in it of three isomers: 1,7-dimethylcycloheptatriene-1,3,5 in predominant amount, and 2,7- and 3,7-dimethylcycloheptatrienes-1,3,5 in approximately equal amounts. It should be noted that the results of chromatographic analysis also indicate a predominant content in the mixture of dimethyltropilidenes of the most strongly retained and, evidently, highest-boiling isomer, which, by analogy with the isomeric xylenes (4), should indeed be the 1,7-isomer.

All these data support the mechanism proposed earlier (1, 2) for the formation of tropilidenes from benzene and chlorocarbene, which includes the intermediate formation of the chlorotropylium ion. According to this mechanism, replacement of benzene by toluene or another monoalkylbenzene should lead to three isomeric 7-methyl-X-alkylcycloheptatrienes-1,3,5, as is in fact observed:

$$CH_2Cl_2 \xrightarrow{CH_3Li} LiCHCl_2 \xrightarrow{-LiCl} :CHCl,$$

$$\text{alkylbenzene } (R{-}C_6H_5) \xrightarrow{:CHCl} \text{chloronorcaradiene intermediate} \longrightarrow \text{alkyl-substituted chlorotropylium ion}$$

1,7-methylalkylcycloheptatriene-1,3,5 + 2,7-methylalkylcycloheptatriene-1,3,5 + 3,7-methylalkylcycloheptatrie

and NMR spectra, an intense band at 2920 cm^{-1} was found in the IR spectra of methyltropilidene and methylalkyltropilidenes; this band is characteristic of a saturated CH_2 group, which is present only in methylcycloheptatrienes-1,3,5 with an unsubstituted 7-position. Possibly this is connected with the ease of migration of multiple bonds in methyltropilidenes, similarly to methyl-substituted cyclopentadienes (3).

Table 2

Properties of adducts of methyltropylidenes with maleic anhydride

Starting hydrocarbon (see Table 1)	b.p., °C (mm)	n_D^{20}	d_4^{20}	MR_D, found	MR_D, calculated	Found, % C	Found, % H	Empirical formula	Calculated, % C	Calculated, % H
I	m.p. 127–128°	–	–	–	–	70.26 70.18	5.71 5.70	$C_{12}H_{12}O_3$	70.57	5.92
II	145 (2)	1.5185	1.2117	54.62	55.25	71.50 71.47	6.70 6.50	$C_{13}H_{14}O_3$	71.08	6.46
III	138 (1)	1.5120	1.1349	65.11	64.51	72.96 73.15	7.23 7.43	$C_{15}H_{18}O_3$	73.14	7.36
IV	140 (3)	1.5150	1.1328	69.29	69.20	73.50 73.45	7.68 7.61	$C_{16}H_{20}O_3$	73.81	7.74
V	142 (3)	1.5148	1.1667	60.02	59.90	71.98 71.92	6.96 7.05	$C_{14}H_{16}O_3$	72.39	6.94

The methyltropylidenes obtained by us are mobile liquids with a pungent odor, readily oxidized and polymerized during handling and storage. The properties of these hydrocarbons are given in Table 1, and those of their adducts with maleic anhydride in Table 2.

Along with substituted tropylidenes, in all the experiments we carried out there also occurred the formation of a number of alkyl and chloroalkyl derivatives of benzene. Thus, from benzene there were formed (especially when the reaction was carried out rapidly) small amounts of toluene and *o*-, *m*-, and *p*-xylenes (content in the reaction products 1-3%) and somewhat larger amounts of ethylbenzene and benzyl chloride (up to 10% in the reaction products). In similar fashion, products obtained from alkylbenzenes contained traces of methylalkylbenzenes and appreciable amounts of chloromethylalkyl- and ethylalkylbenzenes. The formation of these benzene derivatives is evidently connected mainly with addition of the arising : CHCl not only to $C = C$, but also to the $C—H$ bonds of the benzene ring, which in the case of alkylbenzenes apparently proceeds more readily than for benzene itself:

$$\mathrm{RC_6H_5} \xrightarrow{\mathrm{:CHCl}} \mathrm{RC_6H_4CH_2Cl} \xrightarrow[\mathrm{-LiCl}]{\mathrm{CH_3Li}} \mathrm{RC_6H_4CH_2CH_3}.$$

This ability of : CHCl, first detected by us, to insert into $C—H$ bonds once again indicates that, in its reactivity, chlorocarbene occupies an intermediate position between : $\mathrm{CH_2}$ and : $\mathrm{CCl_2}$ (^{2,5}), which, as is known (^{6}), does not add to aromatic $C = C$ and $C—H$ bonds. In addition, in the case of cumene, by analogy with its behavior in reaction with dichlorocarbene (^{7}), insertion of : CHCl into the $C—H$ bond of the tertiary carbon atom of the isopropyl group is also possible. The formation from benzene and its homologs of mono- and polymethyl derivatives of benzene (toluene, xylenes, etc.) may be explained either by partial participation of the chloromethylbenzenes formed in metalation reactions, or by the formation of : $\mathrm{CH_2}$ through slight metalation of $\mathrm{CH_2Cl_2}$ at the Cl atom:

$$\mathrm{RC_6H_4CH_2Cl} \xrightarrow{CH_3Li} \mathrm{RC_6H_4CH_2Li} \xrightarrow{CH_2Cl_2}$$

$$\mathrm{CH_2Cl_2} \xrightarrow{CH_3Li} \mathrm{CH_2Cl(Li)} \xrightarrow[-LiCl]{} : \mathrm{CH_2} \xrightarrow{RC_6H_5} \mathrm{RC_6H_4CH_3}.$$

Under the conditions adopted by us, tropylidene-benzene isomerization of the methyltropylidenes formed is less probable.

The gaseous products liberated during the interaction of $\mathrm{CH_3Li}$ with $\mathrm{CH_2Cl_2}$, as was to be expected (^{2}), consisted mainly of methane (60-70%) and ethylene (40-30%), formed as a result of insertion of : CHCl into the $C—Li$ bond of methyllithium (under our conditions, the main reaction of chlorocarbene).

Experimental section

Chromatographic determinations were carried out chiefly by V. L. Polinin on a gas-liquid chromatograph with a capillary column

0.3 mm × 35 m, packed with triethylene glycol dibutyrate, at 70-90° using nitrogen as the carrier gas (^{4}).

The UV spectra of the substituted tropilidenes were recorded in *n*-hexane solution on an SF-4 spectrophotometer. The NMR spectra were recorded on a high-resolution YNM radiospectrometer at a frequency of 60 MHz at 20° relative to tetramethylsilane as an internal standard.

Synthesis of methyltropilidenes. To a stirred solution of CH_2Cl_2 in an excess of benzene or alkylbenzene was added a 1.5-3 *M* ethereal solution of CH_3Li (molar ratio to CH_2Cl_2, $1:1$) at such a rate that the temperature of the reaction mixture was maintained at 34-36° without additional cooling. The addition of CH_3Li was accompanied by vigorous evolution of a gas containing 60-70% CH_4 and 40-30% C_2H_4. After the entire amount of methyllithium had been added, the reaction mixture was stirred until gas evolution ceased, diluted with water, and worked up in the usual manner. Ether and unchanged benzene (alkylbenzene) were distilled off on a column at atmospheric pressure; the residue was distilled in vacuo and analyzed by gas-liquid chromatography. The results of the experiments performed and the properties of the methyltropilidenes obtained, purified by repeated vacuum fractionation, are given in Table 1.

Catalytic hydrogenation of methyltropilidenes. 2.3 g (21 mmoles) of methyltropilidene (see Table 1) in 20 ml of dry cyclohexane was hydrogenated to saturation in a "duck" over 1 g of freshly prepared Raney nickel at ~20° and an H_2 pressure of 770 mm Hg. After 1.5 h of hydrogenation, 1410 ml of H_2 had been absorbed (the theoretically required amount, 1411 ml). Distillation of the hydrogenation products gave 2.1 g (91%) of methylcycloheptane, b.p. 134° (758 mm), n_D^{20} 1.4415, d_4^{20} 0.8033, MR_D found 36.90, calculated 37.00.

Found, %: C 85.29, 85.39; H 14.08, 14.09
C_8H_{16}. Calculated, %: C 85.62; H 14.38

According to (8), b.p. 133-135° (760 mm), n_D^{20} 1.4410, d_4^{20} 0.8052.

In a similar manner, catalytic hydrogenation was carried out on 2.3 g (19 mmoles) of a mixture of isomeric dimethyltropilidenes (see Table 1). In 75 min of hydrogenation, 1280 ml of H_2 was absorbed, corresponding to the theoretically required amount (1277 ml). The yield of the mixture of isomeric dimethylcycloheptanes was 2.0 g (82%), b.p. 142-143° (740 mm), n_D^{20} 1.4630, d_4^{20} 0.8128, MR_D found 41.59, calculated 41.65.

Found, %: C 85.20, 85.43; H 14.10, 14.00
C_9H_{18}. Calculated, %: C 85.62; H 14.38

Preparation of adducts of methyltropilidenes with maleic anhydride. A solution of 3.4 g (32 mmoles) of methyltropilidene (see Table 1) and 3.4 g (34 mmoles) of maleic anhydride in 20 ml of xylene was boiled for 30 h, evaporated almost to dryness, and diluted with *n*-hexane. The precipitate that separated was filtered off and reprecipitated three times from a benzene solution with hexane. The yield of the adduct was 5.6 g (86%), m.p. 127-128°. The maleic anhydride adducts with methylalkyltropilidenes obtained in a similar manner were very viscous liquids and were isolated by vacuum distillation; yields 80-

90%. The properties and elemental-analysis data for the adducts are given in Table 2.

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