TABLE 1

Compound	Yield, %	Empirical formula	N, % found	N, % calculated	Infrared spectrum (ν, cm^{-1}) C=C	Infrared spectrum (ν, cm^{-1}) C—O—C	PMR spectrum* (δ, ppm) H^2	H^4	H^6	H^7	CH_3—N
(IV)	100	$C_{21}H_{31}N_3$	12,84	12,91	2232	–	6,79	7,60	7,09	6,97	3,67
(V)	95,0	$C_{22}H_{31}N_3$	12,14	12,46	2231	–	6,69	7,60	7,04	6,90	3,53
(VI)	97,0	$C_{21}H_{29}N_3O$	12,10	12,37	2233	1121	6,75	7,59	7,07	6,96	3,66
(VII)	92,0	$C_{22}H_{31}N_3$	12,74	12,46	2233	–	6,75	7,62	7,07	6,96	3,64
(VIII)	96,7	$C_{23}H_{31}N_3$	12,31	12,02	2234	–	–	–	–	–	–
(IX)	89,5	$C_{22}H_{29}N_3O$	12,20	11,96	2234	1120	6,83	7,70	7,17	7,04	3,66
(X)	93,2	$C_{21}H_{29}N_3O$	12,60	12,37	2235	1120	–	–	–	–	–
(XI)	94,1	$C_{22}H_{29}N_3O$	12,10	11,96	2235	1121	6,75	7,64	7,09	6,95	3,60
(XII)	97,0	$C_{21}H_{27}N_3O$	12,20	11,89	2236	1120	6,79	7,64	7,11	6,98	3,70

*The PMR spectrum of (IV) has the signals of the methylene protons at the triple bond and indole ring (3.59 and 3.50).

the starting compounds (I)-(III), and also in the spectrum of N-methyl-5-ethynylindole [1]. Singlets at 6.75 and 7.6 ppm correspond to the H^2 and H^4 protons, while doublets at 7.09 and 6.96 ppm respectively correspond to the H^6 and H^7 atoms.

CONCLUSIONS

Some 3-aminomethylindoles with an aminopropynyl grouping in the 5 position of the indole ring were obtained.

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SYNTHESIS OF SOME SUBSTITUTED CYCLOPROPYLMETHANOLS

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UDC 542.91:547.512

It is known that certain allyl alcohol derivatives add dichlorocarbene, generated by the McOmie method, to give the corresponding cyclopropane derivatives [1]. However, allyl alcohol itself, dimethylvinylcarbinol, geraniol, etc. react with $:CCl_2$ in an ill-defined manner to give a complex mixture of products.

Previously [2-4] we had shown that the use of acetal and acetate protection makes it possible to obtain in good yield various gem-dichlorocyclopropylmethanol derivatives that are difficultly accessible by other methods. In the present paper this method was checked on several other examples.

The use of the ester group for protection made it possible to obtain gem-dichlorocyclopropylmethanol (II) and the corresponding carboxylic acid in good yield.

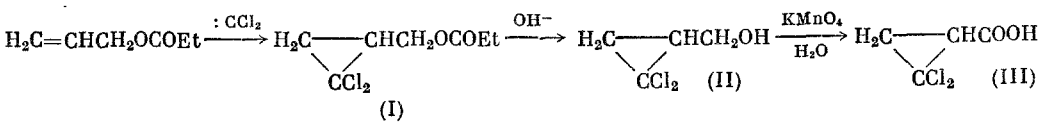

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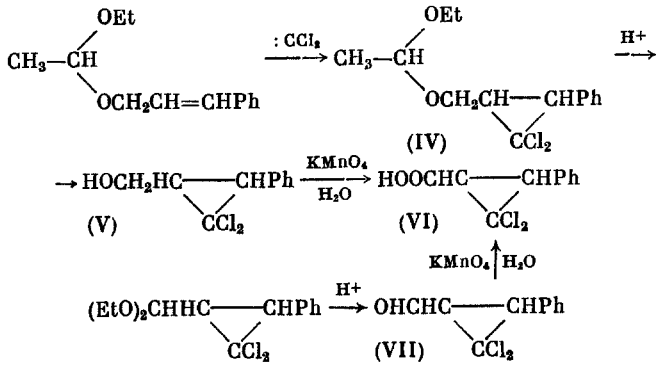
TABLE 1. Yields and Characteristics of Obtained Products

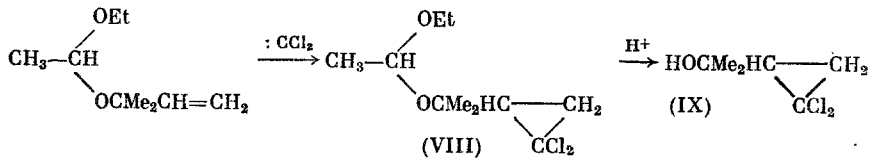
Compound	Yield, %	bp, °C (p, mm of Hg)	n_D^{20}	Found/Calc., % C	Found/Calc., % H	Empirical formula	PMR spectrum (δ, ppm; J, Hz)
(I)	56	92–94(10)	1,4600	42,71 / 42,66	5,03 / 5,12	$C_7H_{10}O_2Cl_2$	1,08 t (3H, CH_3, J=7), 1,33 m (1H, Hc*), 1,75 m (2H, 2Hc), 2,30 q (2H, CH_2, J=7), 4,10 m (2H, CH_2O)
(II)	70	77–78(10)	1,4870				1,75–2,25 m (2H, 2Hc), 2,40–2,70 m (1H, Hc), 11,3 s (1H, COOH)
(III)	61	mp 61					
(IV)	62	127–128(0,5)	1,5300				0,95–1,35 m (6H, $2CH_3$), 2,00–2,20 m (1H, Hc, 2,37 d (1H, Hc), J=8), 3,50–3,85 m (4H, $2CH_2O$), 4,65 m (1H, ), 7,10 s (5H, C_6H_5)
(V)	80	105–107(0,2)	1,5700	55,32 / 55,32	4,54 / 4,64	$C_{10}H_{10}OCl_2$	2,01–2,27 m (1H, Hc), 2,50 d (1H, Hc, J=8), 3,71 s (1H, OH), 3,75 d (2H, CH_2, J=8), 7,10 s (5H, C_6H_5)
(VI)	70	mp 108–109					1,62 d (1H, Hc, J=8), 1,94 d (1H, Hc, J=8), 7,18 s (5H, C_6H_5), 12,4 s (1H, COOH)
(VII)†	75	89–90(0,6)	1,5640	56,09 / 55,84	4,61 / 3,95	$C_{10}H_8OCl_2$	2,80 dd (1H, Hc, J=4,5 and 7,5), 3,50 d (1H, Hc, J=7,5), 7,20–7,50 m (5H, C_6H_5), 9,48 d (1H, CHO, J=4,5)
(VIII)	67	110–120(15)	1,4640				0,97–1,41 m (12H, $4CH_3$), 1,44–1,71 m (3H, 3Hc), 3,36 q (2H, CH_2O, J=7), 4,86 m (1H, )
(IX)	80	59–60(0,6)	1,4710	42,54 / 42,62	6,17 / 5,96	$C_6H_{10}OCl_2$	0,85 s, 0,97 s (6H, $2CH_3$), 1,00–1,13 m (3H, 3Hc), 2,00 s (1H, OH)

*H_c = proton of cyclopropane ring. †νCO 1720 cm^{-1} ($CHCl_3$).

The mixed ethyl cinnamyl acetal of acetaldehyde, obtained by the addition of cinnamyl alcohol to vinyl ethyl ether, adds $:CCl_2$ to give acetal (IV), which is smoothly hydrolyzed in acid medium to 1,1-dichloro-2-phenylcyclopropylmethanol (V). The oxidation of (V) with aqueous $KMnO_4$ solution leads to 1,1-dichloro-2-phenylcyclopropanecarboxylic acid (VI), which was also obtained by the oxidation of 1,1-dichloro-2-phenyl-3-formylcyclopropane (VII), which was prepared by the acid hydrolysis of its acetal [5].



We were unable to add $:CCl_2$ to dimethylvinylcarbinol acetate, but also in this case the use of acetal protection made it possible to obtain the corresponding cyclopropylmethanol derivatives (IX).



The structure of the obtained compounds was proved by elemental analysis, and also by the IR and PMR spectra. The purity of the products was verified by GLC.

EXPERIMENTAL

The GLC analysis was run on an LKhM-8 MD-5 chromatograph, using a flame-ionization detector, nitrogen as the carrier gas, and a 1.4×0.003 m glass column packed with 5% SE-30 deposited on Chromaton N-AW-DMCS. The PMR spectra were taken on Varian DA-60-IL (60 MHz) and Tesla BS-497 (100 MHz) instruments in either CCl_4 or $(CD_3)_2CO$ solution, and using TMS as the internal standard. The IR spectra were taken on a UR-20 instrument in $CHCl_3$ solution.

Propionate (I), acetals (IV) and (VIII), and also alcohols (V) and (IX) were obtained by procedures similar to those described in [2]. Alcohol (I) was obtained as described in [3]. Acids (III) and (VI) were synthesized as described in [3, 4]. Aldehyde (VII) was obtained as described in [5]. The yield and constants of compounds (I)-(IX) are given in Table 1.

CONCLUSIONS

The acetal and ester groups were used as protective agents to synthesize some difficultly available cyclopropylmethanol derivatives.

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