1-BENZOYL-2-ARYL-3-ARYLMETHYL-1,3-DIAZACYCLANES — NEW PRODUCTS OF THE ACYLATION OF BIS-AZOMETHINES

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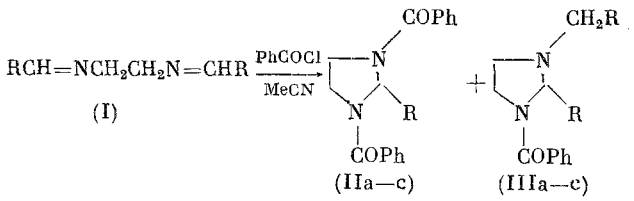
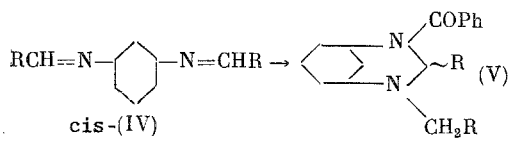
The acylation of bis-azomethines, $RCH{=}N(CH_2)_nN{=}CHR$ by the acid chlorides of aromatic acids in polar media is a convenient method for the synthesis of previously unavailable 1,3-bis-acyl-1,3-diazacyclanes [1, 2].

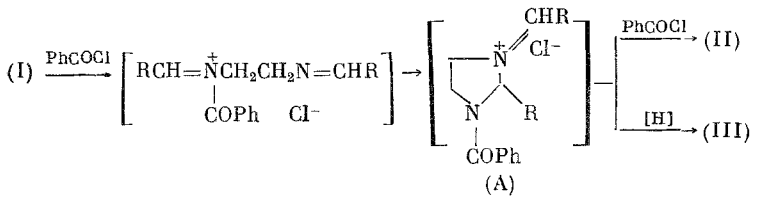
In the present work, we showed that the benzoylation of (I) gives the bis-acylation product (II) and the monoacylation product (III), while cis-1,3-di(p-methoxybenzylidenamino) cyclohexane (IV) gives (V).





Here and subsequently, R = Ph (a), C_6H_4OMe-p (b), (IV), (V), $C_6H_4NO_2$-p (c).

The yields of (III) and (V) do not exceed 13%. In benzene, which is a nonpolar medium, (Ia)-(Ic) gave (IIa)-(IIc), while the monoacyl derivatives (IIIa)-(IIIc) were not detected in the reaction mixtures by thin-layer chromatography on Silufol using 3:1 benzene–ether as the eluant. The transformations (I) → (III) and (IV)→ (V) are apparently achieved through cyclic immonium intermediate (A)



The reduction of salt (A) may proceed with the participation of the starting azomethine (I). It is interesting to note that the yield of (III) is virtually independent of the nature of R, reagent concentration and (I)/PhCOCl ratio but depends on the polarity of the medium. The separation of (II) and (III) was carried out by column chromatography on silica gel with benzene and benzene–ether mixtures as eluants. Products (III) have higher chromatographic mobility than (II) and are eluted first. Products (IIb), (IIc), (IIIa)-(IIIc), (IV) and (V) had not been described. Products (IIb) and (IIIb) could not be separated and their ratio in the mixture was evaluated by PMR spectroscopy. Product (IIc) is an amorphous powder, while (IIIa), (IIIc) and (V) are crystalline comopunds with sharp melting points (in contrast to the corresponding (II)). All products (III) are soluble in 1-10% hydrochloric acid. These solutions are rapidly hydrolyzed and become turbid; an aldehydic odor arises.

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EXPERIMENTAL

The melting points were determined on a Boetius heating block. The mass spectra were taken on a Varian MAT CH-6 spectrometer. The ^1H and ^{13}C NMR spectra were taken on a Bruker WM-250 spectrometer relative to TMS as the internal standard. The signal multiplicity in the ^{13}C NMR spectra were determined by off resonance. The chromatographic separation was carried out on (100-160 μ) silica gel with elution initially by benzene and then by benzene–ether mixtures in various ratios. The chromatographically uniform fractions (monitored on Silufol plates with elution by 3:1 benzene–ether) were combined and evaporated. The residues were recrystallized. The elemental analyses of all the compounds obtained corresponded to the theoretical values.

1,3-Dibenzoyl-2-phenylimidazolidine (IIa) and 1-benzyl-3-benzoyl-2-phenylimidazolidine (IIIa). A sample of 127 mmoles PhCOCl was added dropwise for 40 min to a mixture of 63.6 mmoles (Ia) 400 mmoles Et_3N and 50 ml abs. acetonitrile, heated at reflux for 3 h and evaporated in vacuum. Chloroform was added. The mixture was washed with cold water, dried over Na_2SO_4 and subjected to chromatography to give 8.6 g (38.0%) (IIa), mp ∿70-90°C (from Et_2O–MeOH) [1], R_f 0.2 (3:1 benzene–ether) and 2.78 g (12.8%) (IIIa), mp 123.5-124.0°C (from MeOH at –70°C), R_f 0.4 (3:1 benzene–ether). PMR spectrum in $CDCl_3$ (δ, ppm, J, Hz): multiplets 2.5-4.2 (6H, CH_2) containing 3.38 d (1H, NCH_2Ph, J = 13.5), 3.89 d (1H, NCH_2Ph, J = 13.5), 5.11 and 5.42 s (1H, NCH), 7.0-7.75 m (15H, Ph). ^{13}C NMR spectrum in $CDCl_3$: 48.8 t, 50.7 t, 56.1 t (CH_2), 79.9 d (CH), 126.4 d, 127.0 d, 127.6 d, 127.9 4, 128.1 d, 128.3 d, 128.6 d, 130.3 d (CH arom.), 135.7 s, 137.7 s, 139.9 s (quaternary arom. C), 169.3 (CO).

1,3-Dibenzoyl-2-p-methoxyphenylimidazolidine (IIb) and 1-p-methoxybenzyl-3-benzoyl-2-p-methoxyphenylimidazolidine (IIIb). The reaction was carried out by analogy to the above procedure using 23.6 mmoles (Ib), 47.2 mmoles PhCOCl, and 150 mmoles Et_3N. R_f 0.3 (IIb) and (IIIa). A sample of 127 mmoles PhCOCl was added dropwise for 40 min to a mixture of 63.6 mmoles (Ia), graphy, while (IIb) was isolated. The yield of (IIb) was 3.37 g (37%) as an amorphous powder, R_f 0.3 (1:1 benzene–ether). PMR spectrum in $CDCl_3$: 3.77 s (3H, OCH_3), 3.80-3.95 m (4H, NCH_2), 6.8-7.5 m (15H, NCHN arom.). ^{13}C NMR spectrum in $CDCl_3$: 45.1 t (CH_2), 55.0 q (OCH_3), 72.2 d (NCHN), 114.0 d (C_6H_4OMe), 126.1 d, 127.0 d, 127.3 d, 128.1 d, 130.2 d (CH arom.), 131.6 s, 135.3 s, 159.6 s (quaternary arom. C), 168.8 (C=O). The PMR spectrum indicates that the (IIIb)/(IIb) ratio in the reaction mixture is 26:74. Hence, the calculated yield was 13% for (IIIb). In the mass spectrum of the reaction mixture, (IIIb): M^+ m/z 402, $[M - PhCO]^+$, $[M - C_6H_4OMe]^+$, $[M - CH_2C_6H_4OMe]^+$.

1,3-Dibenzoyl-2-p-nitrophenylimidazolidine (IIc) and 1-p-nitrobenzyl-3-benzoyl-2-p-nitrophenylimidazolidine (IIIc). This reaction was carried out by analogy to the above using 21.5 mmoles (Ic), 43.0 mmoles PhCOCl, and 150 mmoles Et_3N to give 4.43 g (51.5%) (IIc) as an amorphous powder, R_f 0.3 (1:1 benzene–ether) and 0.65 g (7.0%) (IIIc), mp 228-233°C (3:1 $CHCl_3$–MeOH), R_f 0.4 (1:1 benzene–ether). PMR spectrum of (IIc) in $CDCl_3$: 3.8-4.1 br. (4H, NCH_2), 7.1-8.3 m (15H, phenyl and NCH). ^{13}C NMR spectrum of (IIc) in $(CD_3)_2CO$: 47.7 t (NCH_2), 72.4 d (NCH), 124.3 d, 128.2 d, 128.9 d, 129.2 d, 130.4 d, 130.6 d, 131.3 d (CH arom. COPh groups are inequivalent), 136.6 s, 148.3 s, 148.7 s (quaternary arom. C), 169.6 s (C=O). PMR spectrum of (IIIc) in $CDCl_3$: 2.6-4.0 m (6H, CH_2), 5.15 and 5.50 s (1H, NCH), 7.1-8.3 m (13H, arom.).

1,3-Dibenzoyl-2-p-methoxyphenyl-1,3-diazabicyclo[3.3.1]nonane (VI) and 1-p-methoxybenzyl-3-benzoyl-2-p-methoxyphenyl-1,3-diazabicyclo[3.3.1]nonane (V). This reaction was carried out by analogy with the above using 34.7 mmoles (IV), 69.4 mmoles PhCOCl, and 70 mmoles Et_3N to give 9.31 g (61.0%) (VI), mp 271.5-272.0°C and 0.95 g (6.0%) (V), mp 146.5-148.0°C (from ethyl acetate), R_f 0.4 (3:1 benzene–ether). PMR spectrum in $CDCl_3$: 1.2-2.8 m (8H, ring CH_2), 3.5-4.6 m (10H, NCH, NCH_2 and MeO), 6.9-7.5 m (14H, NCHN and arom.). ^{13}C NMR spectrum in $CDCl_3$: 17.6 t, 28.8 t, 30.2 t (ring CH_2), 47.4 d, 48.7 d (NCH), 54.7 q (OCH_3), 55.2 t (NCH_2), 70.9 d (NCHN), 113.4 d, 126.3 d, 126.8 d, 127.9 d, 128.7 d, 129.6 d (arom. CH), 130.8 s, 137.0 s, 137.9 s, 158.3 s, 158.5 s (quaternary arom. C), 170.3 (C=O).

CONCLUSION

The benzoylation of bis-azomethines derived from ethylenediamine and cis-1,3-diaminocyclohexane gives 1,3-dibenzoyl-1,3-diazacyclanes and 1-benzoyl-3-benzyl-1,3-diazacyclanes.

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ALKYLATION OF AROMATIC HYDROCARBONS BY 1-FLUOROMETHYL-o,m-CARBORANES BY THE ACTION OF $AlCl_3$

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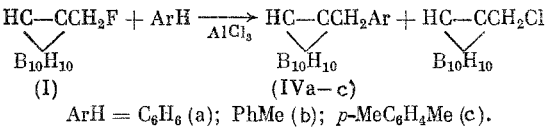
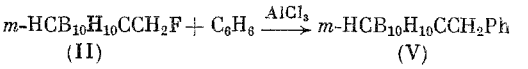
In our previous work [1], we showed that 1-chloromethyl- and 1-bromomethyl-o-carboranes, in contrast to 1-(β-chloroethyl)- and 1-(β-chloropropyl)-o-carboranes, do not alkylate benzene in the presence of $AlCl_3$ upon prolonged heating. The reactivity of primary alkyl halides in the alkylation of benzene in the Friedel–Crafts reaction increases in the series RI < RBr < RCl < RF [2]. In this regard, we studied the alkylation of aromatic hydrocarbons by 1-fluoromethyl-o-carborane (I) and found that, in contrast to 1-chloromethyl-o-carborane, it alkylates benzene, toluene and p-xylene in the presence of $AlCl_3$.



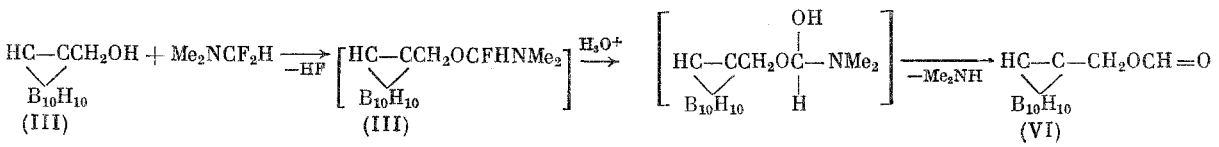
ArH = C_6H_6 (a); PhMe (b); p-MeC_6H_4Me (c).

The reaction proceeds at 60°C. In addition to 1-arylmethyl-o-carboranes (IVa)-(IVc), some amount of 1-chloromethyl-o-carborane is formed due to the exchange reaction between (I) and $AlCl_3$ which does not react with aromatic hydrocarbons. 1-Fluoromethyl-m-carborane (II) also alkylates benzene by the action of $AlCl_3$.



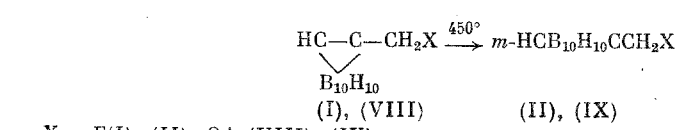
Thus, in the series of 1-halomethyl-o,m-carboranes, the rather highly polarized $RCH_2F...AlCl_3$ capable of the electrophilic alkylation of aromatic hydrocarbons is formed only in the case of 1-fluoromethyl-o,m-carborane due to the high polarity of the C–F bond.

Carborane (I) was synthesized in our previous work from 1-hydroxymethyl-o-carborane (III) and SF_4 [3]. In the present work, we attempted to obtain (I) by the reaction of (III) with α-fluoroalkylamines which are commonly used for the substitution of the hydroxyl group by fluorine [4]. However, the following transformations proceed in this case:



The reaction of bis(hydroxymethyl)-o-carborane with the Yarovenko reagent leads to the formation of 3,4-carborano-2,5-tetrahydrofuran (VII) [15].

Carborane (II) was obtained in our previous work in low yield [3]. We have found that (II) is formed in high yield upon passing (I) through a quartz tube in vacuum:



X = F(I), (II); OAc(VIII), (IX).

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