From the residue (20 g) we distilled another 5 g of (IV), 0.7 g of volatile compounds, and two fractions that contained (VIII): 1) 4.7 g, bp 140-159° (4 mm), purity 73%, and 2-4 g, bp 160-166° (5 mm), purity 97%. The tarry residue weighed 5 g. Redistillation of fraction 2 at 144-145° (2 mm) gave 98% pure (VIII). For analysis the product was purified by preparative GLC (column 2; 156-158°; He 8.5-9 liters/h); n_D^{20} 1.5382; d_4^{20} 1.6135. Found: C 22.26; H 2.13; Cl 75.54%; MR 63.48. $C_6H_7Cl_7$. Calculated: C 22.01; H 2.15; Cl 75.83%; MR 63.98.

The ^1H and ^{13}C NMR spectra for (VI)-(VIII) are given in Table 1.

CONCLUSIONS

In the reaction of CCl_3CH_3 with $CCl_2 = CHCH_2CH_2CH_2Cl$, and of $CCl_3CH_2CH_2Cl$ with $CCl_2 = CHCH_2Cl$, initiated by $Fe(CO)_5$ + DMF, the main addition products are respectively compounds of structure $HCCl_2CH(CCl_2CH_3)CH_2CH_2CHCl_2$ and $HCCl_2CH(CCl_2CH_2CHCl_2)CH_2Cl$. The formation of these compounds was explained by the isomerization of the radical-adducts $\dot{C}Cl_2CH(CCl_2CH_3)CH_2CH_2CH_2Cl$ and $\dot{C}Cl_2CH(CCl_2CH_2CH_2Cl)CH_2Cl$, with migration of a hydrogen atom from the CH_2Cl groups found in the 5 position to the radical center.

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TRANSFORMATIONS OF α,α-DIFLUOROCARBONYL COMPOUNDS

4.* REACTION OF POLYFLUORO KETONES WITH PHENYLHYDRAZINE

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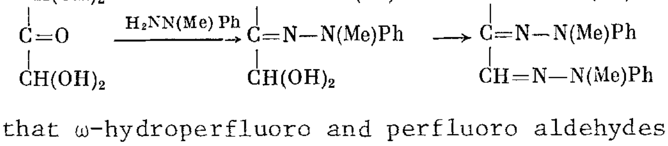
UDC 542.91:547.446:547.556.8

It is known that polycarbonyl compounds in the presence of excess methylphenyl- or phenylhydrazine, at elevated temperature, form the corresponding polyhydrazones [4, 5]:



$$\begin{matrix} CH(OH)_2 \\ | \\ C{=}O \\ | \\ CH(OH)_2 \end{matrix} \xrightarrow{H_2NN(Me)Ph} \begin{matrix} CH{=}N{-}N(Me)Ph \\ | \\ C{=}N{-}N(Me)Ph \\ | \\ CH(OH)_2 \end{matrix} \longrightarrow \begin{matrix} CH{=}N{-}N(Me)Ph \\ | \\ C{=}N{-}N(Me)Ph \\ | \\ CH{=}N{-}N(Me)Ph \end{matrix}$$

Recently we found that ω-hydroperfluoro and perfluoro aldehydes under the same conditions react with hydrazines to give polyhydrazones via all of the difluoromethylene groups. The terminal CF_3 group is not involved in the case of the perfluoro aldehydes [1-3]. Thus, β-hydrotetrafluoropropanal with excess phenylhydrazine gives the bis-, and then also the tris-

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*See [1-3] for Communications 1-3.

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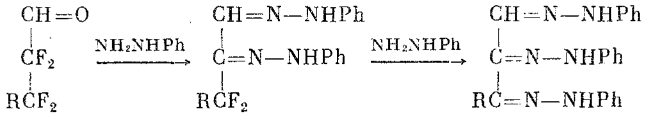
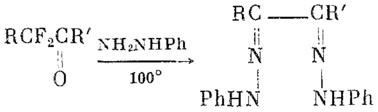
hydrazones [1], while perfluorobutanal forms the tris-phenylhydrazone of trifluoromethylmesoxalaldehyde [2]



R = H, CF_3.

The ω-hydroperfluoro and perfluoro aldehydes are formally the polycarbonyl compounds in this reaction.

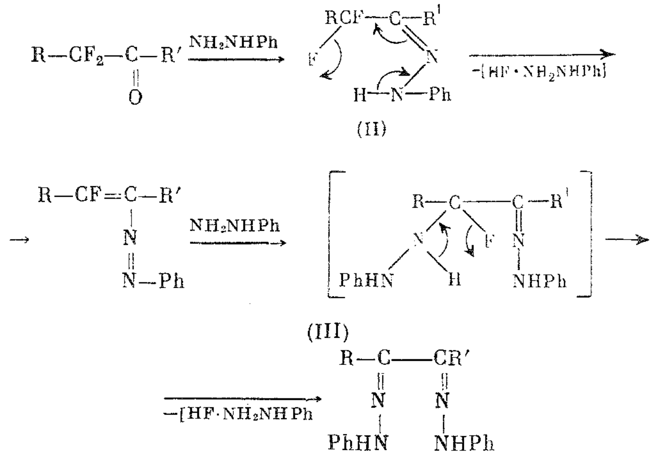
It proved that this reaction can also be extended to ketones with α-difluoromethylene groupings. Thus, the reaction of pentafluoroacetone and methyl heptafluoropropyl ketone with excess phenylhydrazine respectively gives the bis-phenylhydrazone of trifluoromethylglyoxal (Ia) and the bis-phenylhydrazone of 4,4,5,5,5-pentafluoro-2,3-pentanedione (Ib).



(Ia,b)

R=H, R′=CF_3(a); R=C_2F_5, R′=Me (b).

Like in the case of polyfluoro aldehydes, monohydrazones (II) are formed from α,α-difluoromethylene ketones, which are dehydrofluorinated by excess phenylhydrazine to the azo compounds (III). The latter add phenylhydrazine and, with subsequent dehydrofluorination, form the bis-phenylhydrazones of α-diketones (Ib-d).



(Ib–d)

R=C_2F_5, R′=Ph (b); R=CF_2H, R′=Ph (c).

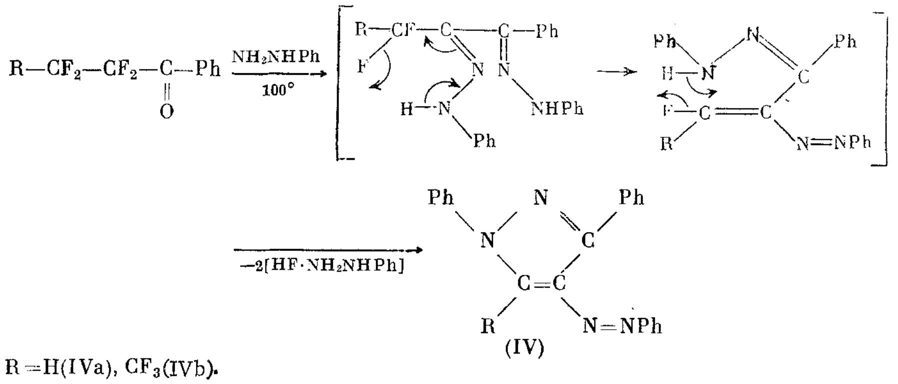
The (II) and (III) compounds can be isolated in the pure state.

The (II) monohydrazones are easily and quantitatively dehydrofluorinated by either bases (KOH, NaOH) or the $Et_3N{\cdot}BF_3$ complex. The obtained phenylazo-substituted olefins (III) are either bright red liquids or crystalline compounds that are stable when stored under room conditions (cf. [6]). The (III) compounds easily react with phenylhydrazine to give the stable bis-phenylhydrazones of the corresponding α-diketones (Ib-d).

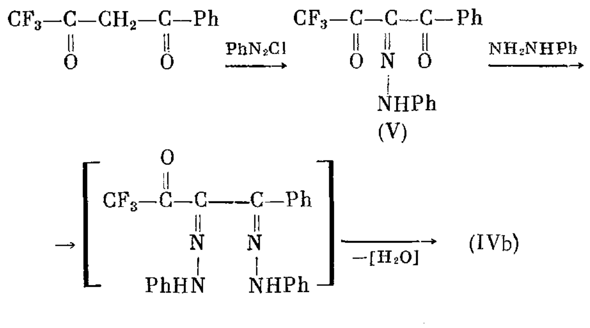
When phenylhydrazine is reacted with perfluoroalkyl phenyl ketones the intermediately formed bis-phenylhydrazones are rapidly dehydrofluorinated by the excess phenylhydrazine to give pyrazoles (IV). Thus, from 1,1,2,2-tetrafluoropropiophenone and 1,1,2,2,3,3,3-heptafluorobutyrophenone are respectively obtained 1,3-diphenyl-4-phenylazopyrazole (IVa) and 1,3-diphenyl-4-phenylazo-5-trifluoromethylpyrazole (IVb).

The formation of the pyrazoles directly from the bis-hydrazones was confirmed by special experiment. When bis-phenylhydrazones (Id) and (Ic) are heated with either phenylhydrazine or the $BF_3{\cdot}NEt_3$ complex at 100°C the pyrazoles (IVa) and (IVb) are formed in quantitative yield.

The structure of the obtained pyrazoles [on the example of (IVb)] was confirmed by synthesis from the phenylhydrazone of benzoyltrifluoromethylglyoxal (V) and phenylhydrazine.



R = H(IVa), CF_3(IVb).



EXPERIMENTAL

The PMR spectra were recorded on a Perkin—Elmer spectrometer (external standard = TMS), the ^{19}F NMR spectra were recorded on a Hitachi H-6013 spectrometer (56.456 MHz) (external standard = CF_3COOH), and the IR spectra were obtained on a UR-10 spectrometer.

1,1,2,2,3,3,3-Heptafluorobutyrophenone Phenylhydrazone (IIa). A mixture of 87 g (0.32 mole) of 1,1,2,2,3,3,3-heptafluorobutyrophenone, 44 g (0.4 mole) of phenylhydrazine, and 40 ml of 50% AcOH in 300 ml of ethanol was kept for 2 days at 20°. Then the mixture was diluted with 500 ml of water, and the lower organic layer was separated, washed with water, dried over $MgSO_4$, and vacuum-distilled. We obtained 93 g (77%) of (IIa) as a yellow oil with bp 137-138° (2 mm). Infrared spectrum (ν, cm^{-1}): 1525 s (CN), 3070 w (CH), 3325 s (NH). Found: C 52.75; H 3.06; N 7.95%. $C_{15}H_{11}N_2F_7$. Calculated: C 52.75; H 3.02; N 7.69%. Mass spectrum: M^+ 364, ($M^+ - F$) 345, ($M^+ - CF_2$) 314, ($M^+ - F - PhCN$) 242. PMR spectrum (δ, ppm): 6.7-7.4 m (Ph, NH). ^{19}F NMR spectrum (δ, ppm): 2.6 t (CF_3), 29.8 q (CF_2), 45.8 s (CF_2).

Methyl-1,1,2,2,3,3,3-heptafluoropropyl Ketone Phenylhydrazone (IIb). In a similar manner, from 26 g (0.12 mole) of the methyl heptafluoropropyl ketone, 15 g (0.14 mole) of phenylhydrazine, and 15 ml of 50% AcOH in 100 ml of ethanol we obtained 35 g (94.5%) of (IIb) as a yellow oil with bp 117-118° (8 mm). Infrared spectrum (ν, cm^{-1}): 1525 s (C=N), 2870 w (Me), 3070 w (aromatic CH), 3320 s (NH). Found: C 43.96; H 3.03; N 9.70; F 43.87%. $C_{11}H_9N_2F_7$. Calculated: C 43.71; H 2.98; N 9.27; F 44.04%. Mass spectrum: M^+ 302, ($M^+ - F$) 283, ($M^+ - CF_2$) 252, ($M^+ - F - MeCN$) 242. PMR spectrum (δ, ppm): 1.2 s (Me), 6.2-6.8 m (Ph, NH), with an integral intensity of 1:2. ^{19}F NMR spectrum (δ, ppm): 2.9 t (CF_3), 35.0 q (CF_2), 47.6 s (CF_2). $J_{CH_3-CF_2}$ = 4.3 Hz.

1,1,2,2-Tetrafluoropropiophenone Phenylhydrazone (IIc). In a similar manner, from 10 g (48 mmoles) of 1,1,2,2-tetrafluoropropiophenone, 5.6 g (52 mmoles) of phenylhydrazine, and 5 ml of 50% AcOH in 50 ml of ethanol we obtained 12 g (84%) of (IIc) as yellow crystals with mp 70-71° (from 70% ethanol). Infrared spectrum (ν, cm^{-1}): 1525 s (C=N), 3070 w (CH), 3340 s (NH). Found: C 60.16; H 4.30; N 9.36%. $C_{15}H_{12}N_2F_4$. Calculated: C 60.08; H 4.05; N 9.46%. Mass spectrum: M^+ 296, ($M^+ - HF$) 276, ($M^+ - CF_2H$) 225, ($M^+ - CF_2H - Ph$) 195. PMR spectrum (CCl_4, δ, ppm): 6.25 t.t (CF_2H), 6.8-7.7 m (Ph, NH); J^{gem}_{H-F} = 51.9, J^{vic}_{H-F} = 2.6 Hz. ^{19}F NMR spectrum (CCl_4, δ, ppm): 33.7 br.s (CF_2), 58.2 d.t. (CF_2H); J_{F-F} = 4.0 Hz.

Trifluoromethylglyoxal Bis-phenylhydrazone (Ia). Pentafluoroacetone (0.5 g, 3.6 mmoles) was passed through a solution of 3.6 g (30 mmoles) of phenylhydrazine and 2 g of AcOH in 10 ml of water, contained in a flask equipped with a CO_2 condenser. The mixture was kept for 30 min at 20°, after which the condenser was replaced by a water condenser and the mixture was refluxed for 4 h at 100°. Then the mixture was cooled, 10% AcOH solution was added until weakly acid, and the solid precipitate was separated, washed with hot water, and recrystallized twice from ethanol. We obtained 0.45 g (43%) of (Ia) as yellow crystals with mp 111-113°. Infrared spectrum (ν, cm^{-1}): 1520 and 1570 s (C=N), 3040 w (CH), 3320-3330 s (NH). Found: C 59.36; H 4.36; N 18.05; F 18.54%. $C_{15}H_{13}N_4F_3$. Calculated: C 58.82; H 4.25; N 18.30; F 18.61%. Mass spectrum: M^+ 306, (M^+ − F) 287, (M^+ − PhNH) 2.4, CF_3^+ 69. ^{19}F NMR spectrum (acetone, δ, ppm): −12.9 s (CF_3).

Phenylpentafluoroethylglyoxal Bis-phenylhydrazone (Ic). A. A solution of 7 g (20 mmoles) of (IIIc) and 5.5 g (50 mmoles) of phenylhydrazine in 50 ml of ether was kept for 2 days at 20°. Then the solution was separated from the precipitated $PhNHNH_2 \cdot HF$ and ether was evaporated. The solid residue was recrystallized twice from 80% ethanol to give 7 g (81%) of (Ic) as yellow crystals with mp 141-142°. Infrared spectrum (ν, cm^{-1}): 1525 and 1570 s (C=N), 3035-3070 w (CH), 3340 and 3450 s (NH). Found: C 61.16; H 3.95; N 12.76%. $C_{22}H_{17}N_4H_5$. Calculated: C 61.11; H 3.94; N 12.96%. Mass spectrum: M^+ 432, (M^+ − HF) 412, (M^+ − 2HF) 392, (M^+ − PhNH) 340. PMR spectrum (CCl_4, δ, ppm): 7.0-7.4 m (Ph), 8.6 s (NH), 13.3 s (NH), with an integral intensity of 15:1:1. ^{19}F NMR spectrum (CCl_4, δ, ppm): 0.9 s (CF_3), 23.0 s (CF_2).

B. A mixture of 3.0 g (8.2 mmoles) of (IIa) and 2.8 g (26 mmoles) of phenylhydrazine in 20 ml of ethanol was refluxed for 15 h. Then the mixture was cooled, diluted with 20 ml of conc. HCl, and the solid precipitate was separated, washed with hot water, and recrystallized thrice from 80% ethanol to give 1 g (29%) of product with mp 141-142°.

Methylpentafluoroethylglyoxal Bis-phenylhydrazone (Ib). A. Similar to the preceding (A), from 10 g (35 mmoles) of (IIIb) and 8 g (75 mmoles) of phenylhydrazine in 50 ml of ether we obtained 10.5 g (81%) of (Ib) as yellow crys-als with mp 103-104° (from 80% ethanol). Infrared spectrum (ν, cm^{-1}): 1535 and 1575 s (C=N), 3040 m and 3190 (CH), 3370 and 3410 m (NH). Found: C 55.66; H 4.05; N 15.32; F 25.10%. $C_{17}H_{15}N_4F_5$. Calculated: C 55.14; H 4.05; N 15.14; F 25.68%. Mass spectrum: M^+ 370, (M^+ − HF) 350, (M^+ − 2HF) 330, (M^+ − PhNH) 278. PMR spectrum (MeCN, δ, ppm): 2.5 s (Me), 6.8-7.2 m (Ph), 8.1 s (NH), 13.35 s (NH), with an integral intensity of 3:15:1:1. ^{19}F NMR spectrum (MeCN, δ, ppm): 1.3 s (CF_3), 25.2 s (CF_3).

B. A mixture of 3.1 g (14.5 mmoles) of methyl heptafluoropropyl ketone and 10 g (0.1 mole) of phenylhydrazine was kept for 5 h at 80-90°. Then the mixture was cooled, diluted with 20 ml of conc. HCl, and the solid precipitate was separated, washed with hot water, and recrystallized thrice from 80% ethanol to give 2.1 g (39%) of product with mp 103-104°.

Phenyldifluoromethylglyoxal Bis-phenylhydrazone (Id). Similar to the preceding (A), from 1 g (3.6 mmoles) of (IIIa) and 0.8 g (7.5 mmoles) of phenylhydrazine in 30 ml of ether we obtained 1 g (83%) of (Id) as yellow crystals with mp 108-109° (from 80% ethanol). Infrared spectrum (ν, cm^{-1}): 1520 and 1560 s (C=N), 3060 and 3190 w (CH), 3330 and 3450 s (NH). Found: C 69.61; H 4.65; N 15.40; F 10.13%. $C_{21}H_{18}N_4F_2$. Calculated: C 69.23; H 4.95; N 15.38; F 10.44%. Mass spectrum: M^+ 364, (M^+ − HF) 344, (M^+ − 2HF) 324, (M^+ − PhNH) 272. PMR spectrum (acetone, δ, ppm): 5.8 t (CF_2H), 6.7-7.1 m (Ph), 8.1 s (NH), 13.0 s (NH); J_{H-F} = 27.8 Hz. ^{19}F NMR spectrum (acetone, δ, ppm): 33.5 d (CF_2H).

1-Phenyl-1-phenylazohexafluoro-1-butene (IIIc). A. A mixture of 6 g (16.5 mmoles) of (IIa) and 30 ml of water was heated for 1 h at 100°, with vigorous stirring. Then a solution of 0.67 g (16.5 mmoles) of NaOH in 20 ml of water was added in drops, and the mixture was stirred for another 3 h. After cooling, the organic layer was separated, washed with water, dried over $MgSO_4$, and vacuum-distilled. We obtained 3.5 g (60%) of (IIIc) as red oil with bp 115-116° (2 mm). Infrared spectrum (ν, cm^{-1}): 1660 s (C=C), 3070 s (CH). Found: C 55.88; H 3.04; N 8.16%. $C_{16}H_{10}N_2F_6$. Calculated: C 55.81; H 2.91; N 8.14%. Mass spectrum: M^+ 344, (M^+ − CF_3) 275, (M^+ − PhN_2) 239. ^{19}F NMR spectrum (δ, ppm); 5.8 m (CF_3), 35.3 m (CF_2), 42.5 br.s (CF), with an integral intensity of 3:2:1.

B. A mixture of 50 g (0.14 mole) of (IIa) and 35 g (0.21 mole) of the $Et_3N \cdot BF_3$ complex was kept for 4 h at 80°. After cooling, the reaction mixture was washed several times with ether (a total of 100 ml), and the ether solution was washed with water and dried over $MgSO_4$. Then the ether was distilled off, while the residue was vacuum-distilled to give 39 g (81%) of product with bp 115-116° (2 mm).

1-Methyl-1-phenylazohexafluoro-1-butene (IIIb). With stirring, to 29 g (96 mmoles) of (IIb) in 200 ml of abs. ether was added in small portions 25 g (450 mmoles) of KOH powder and the mixture was stirred for 30 min. Then the ether solution was separated from the precipitate, washed with water, and dried over $MgSO_4$. The ether was distilled off, while the residue was vacuum-distilled to give 25 g (92.5%) of (IIIb) as a red liquid with bp 87-88° (8 mm). Infrared spectrum (ν, cm^{-1}): 1680 s (C=C), 2940-2980 w (Me), 3050-3080 m (aromatic

CH). Found: C 47.06; H 2.88; N 9.89%. $C_{11}H_8N_2F_6$. Calculated: C 46.81; H 2.84; N 9.93%. Mass spectrum: M^+ 282, (M^+ — CF_3) 213, (M^+ — PhN_2) 179. PMR spectrum (δ, ppm): 1.4 d.t (Me), 6.7-7.2 m (Ph), with an integral intensity of 3:5; $J_{CH_3\text{-}CF} = 3.0, J_{CH_3\text{-}CF_2} = 1.5$ Hz. ^{19}F NMR spectrum (δ, ppm): 6.8 m (CF_3), 36.0 m (CF_2), 44.5 m (CF), with an integral intensity of 3:2:1.

1-Phenyl-1-phenylazo-3-hydrotrifluoro-1-propene (IIIa). A. Similar to the preparation of (IIIc) (A), from 1.3 g (4.4 mmoles) of (IIc) and 0.175 g (4.4 mmoles) of NaOH in 20 ml of water we obtained 0.8 g (66%) of (IIIa) as red crystals with mp 85-86° (from 80% ethanol). Infrared spectrum ($\tilde{\nu}$, cm^{-1}): 1675 s (C=C), 3060-3080 w (CH). Found: C 65.10; H 3.96; N 10.13%. $C_{15}H_{11}N_2F_3$. Calculated: C 65.22; H 3.99; N 10.14%. Mass spectrum: M^+ 276, (M^+ — CF_2H) 225, (M^+ — PhN_2) 171. PMR spectrum (acetone, δ, ppm): 6.5-6.8 m (Ph), 7.15 d.t (CF_2H) $J^{gem}_{H-F} = 47.3$, $J^{vic}_{H-F} = 16.6$ Hz. ^{19}F NMR spectrum (acetone δ, ppm): 48.1 d.d (CF_2H), 52.7 d.t (CF), with an integral intensity of 2:1, $J_{F-F} = 17.3$ Hz.

B. Similar to the preparation of (IIIc) (B), from 1 g (3.4 mmoles) of (IIc) and 0.6 g (3.6 mmoles) of the $Et_3N\cdot BF_3$ complex we obtained 0.7 g (75%) of product with mp 85-86°.

C. Similar to the preparation of (IIIb), from 14 g (45 mmoles) of (IIc) and 13 g (30 mmoles) of KOH powder in 100 ml of abs. ether we obtained 12 g (92%) of product with mp 85-86°.

1,3-Diphenyl-4-phenylazo-5-trifluoromethylpyrazole (IVb). A. A mixture of 5.4 g (20 mmoles) of 1,1,2,2,3,3,3-heptafluorobutyrophenone and 26 g (24 mmoles) of phenylhydrazine in 50 ml of ethanol was refluxed for 30 h. Then the mixture was cooled, diluted with 30 ml of conc. HCl, and the solid precipitate was washed with hot water and recrystallized twice from MeCN to give 3.9 g (42%) of (IVb) as brown crystals with mp 161-162°. Infrared spectrum (ν, cm^{-1}): 1545 m (C=N), 3060-3095 w (CH). Found: C 66.62; H 3.74; N 14.23; F 14.39%. $C_{22}H_{15}N_4F_3$. Calculated: C 67.35; H 3.83; N 14.29; F 14.54%. Mass spectrum: M^+ 392, (M^+ — F) 373, (M^+ — Ph) 315. ^{19}F NMR spectrum (acetone, δ, ppm): —15.5 s (CF_3).

B. A mixture of 1 g (2.3 mmoles) of (Ic) and 2 g (18 mmoles) of phenylhydrazine was kept for 1 h at 100°. Then the mixture was cooled, diluted with 15 ml of conc. HCl, and the solid precipitate was separated, washed with hot water, and recrystallized twice for MeCN to give 0.75 g (82%) of product with mp 161-162°.

C. A mixture of 5 g (11.5 mmoles) of (Ic) and 4.5 g (27 mmoles) of the $Et_3N\cdot BF_3$ complex was kept for 2 h at 100°. Then the reaction mixture was cooled and washed several times with ether (a total of 50 ml). The ether solution was separated from the precipitate, washed with water, and dried over $MgSO_4$. The ether was evaporated, and the solid residue was recrystallized twice from MeCN to give 3.9 g (86%) of product with mp 161-162°.

D. To 3.2 g (10 mmoles) of (V) in 80 ml of ethanol was added 1.2 g (10.5 mmoles) of phenylhydrazine in 20 ml of ethanol. The mixture was kept for 1 h at 20°. The obtained precipitate was separated and recrystallized from MeCN to give 3.5 g (95%) of product with mp 161-162°.

1,3-Diphenyl-4-phenylazopyrazole (IVa). A. A mixture of 3 g (15 mmoles) of 1,1,2,2-tetrafluoropropiophenone, 11 g (105 mmoles) of phenylhydrazine, and 6 ml of AcOH was kept for 5 h at 100°. Then the mixture was cooled and diluted with 20 ml of conc. HCl. The solid precipitate was washed with hot water and recrystallized twice from 80% ethanol to give 2.7 g (57%) of (IVa) with mp 118-119°. Infrared spectrum (ν, cm^{-1}): 1535 m (C=N), 3070 w (CH). Found: C 77.45; H 4.96; N 17.60%. $C_{21}H_{16}N_4$. Calculated: C 77.78; H 4.94; N 17.23%. Mass spectrum: M^+ 324. PMR spectrum (acetone, δ, ppm): 6.9-7.5 m (Ph), 7.9 s (CH), with an integral intensity of 15:1.

B. Similar to the preparation of (IVb) (B), from 0.4 g (1.1 mmoles) of (Id) and 1 g (10 mmoles) of phenylhydrazine we obtained 0.2 g (59%) of product with mp 118-119°.

C. Similar to the preparation of (IVb) (C), from 2.5 g (7 mmoles) of (Id) and 2.5 g (15 mmoles) of the $Et_3N\cdot BF_3$ complex we obtained 2 g (90%) of product with mp 118-119°.

Benzoyltrifluoromethylglyoxal phenylhydrazone (V). With stirring, to 10 g (46 mmoles) of benzoyltrifluoroacetone in 100 ml of ethanol was added at 0-5° an aqueous solution of phenyldiazonium chloride, prepared from 6 g of $PhNH_2\cdot HCl$, 8 g of conc. HCl, 3.6 g of $NaNO_2$, and 50 g of ice and water. Then conc. aqueous NaOAc solution was added until the reaction mixture became turbid. The precipitate obtained after 1 h was separated, washed with water, and recrystallized from 80% ethanol. We obtained 10.5 g (71%) of (V) as yellow crystals with mp 116-117°. Found: C 60.44; H 3.41; N 8.55%. $C_{16}H_{11}N_2F_3O_2$. Calculated: C 60.00; H 3.44; N 8.75%. Mass spectrum: M^+ 320, $(M^+ - F)$ 301, $(M^+ - CF_3)$ 251, $(M^+ - Ph)$ 243, $(M^+ - CF_3CO)$ 223. PMR spectrum (acetone, δ, ppm): 6.8-7.1 m (Ph), 13.2 s (NH), with an integral intensity of 10:1. ^{19}F NMR spectrum (acetone, δ, ppm): −7.4 s (CF_3).

CONCLUSIONS

When reacted with phenylhydrazine, ketones with an α-difluoromethylene group form either the bis-phenylhydrazones of α-diketones or their dehydrofluorination products, and specifically substituted pyrazoles.

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REACTION OF PHTHALODINITRILE WITH AROMATIC o-CYANAMINES

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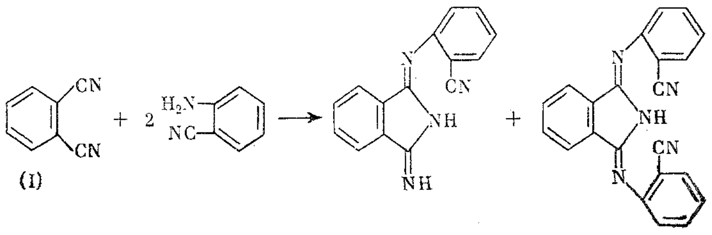
Compounds with condensed isoindole and quinazoline rings are formed when phthalodinitrile (I) is reacted with anthranilic acid and its derivatives [1], which made it possible to obtain heat-resistant polymers with isoindole and quinazoline fragments in the polycondensation chain of the tetranitriles of aromatic tetracarboxylic acids with bisanthranilic acids [2]. However, in contrast to the polymers, obtained by the polycondensation of aromatic tetracarboxonitriles with aromatic diamines in phenol [3], these polymers do not contain macroheterocycles in the polymer chain.

The purpose of the present paper was to ascertain if macroheterocyclic compounds, containing condensed isoindole and quinazoline rings, can be obtained. As the starting compounds we selected (I) and 3,3'-dicyano-4,4'-diaminodiphenylmethane (DCAM).

We first studied the condensation of (I) with anthranilonitrole (AN) using a 1:2 mole ratio of the reactants. The reaction was run in phenol at 180°C, i.e., under the conditions for the maximum formation of macroheterocycles [4, 5]. On the basis of the data for the condensation products of (I) with aniline [6] it could be assumed that the studied reaction will proceed by the following scheme:



It proved that four compounds are formed as a reaction result. Based on the mass spectral data, the molecular ions with m/e 246, 347, 492, and 502 correspond to them. The IR spectrum of the mixture has bands at 3200 (NH) and 1680, 1630 (C=N) cm^{-1} and the absorption band of the C≡N group at 2200 cm^{-1} is absent. A comparison of the IR and mass spectral data

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