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

V. V. Grushin, T. P. Tolstaya, and I. N. Lisichkina UDC 542.91:547.1'127

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.

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

Based on the PMR spectra (100 MHz in acetone-d₆), (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-I or C-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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A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow; M. V. Lomonosov Moscow State University. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 2165-2168, September, 1983. Original article submitted February 8, 1983.

philic substitution of this ligand and the smaller is the formation of radical reaction products [6, 7]. Based on the data in [8, 9], the 2-p-carboranyl group is much more electrondeficient than the 9-m-carboranyl group.* Consequently, starting with an analogy in the behavior of our salts and diaryliodonium salts, and taking into account the approximately same steric conditions in salts (I) and (III), it could be expected that the rate of nucleophilic substitution on the B atom in (I) will be higher than in (III), while the rates of the radi-

cal reactions (with cleavage of the C-I bond) for (I) and (III) will be approximately equal and close to the analogous reactions of the diaryliodonium salts. Actually, (I) reacts with azide ion approximately five times faster than (III), and forms the previously unknown 2-p-carboranyl azide in 91% yield.

$$(I) + N_3 \rightarrow 2 - p - C_2 H_2 B_{10} H_9 N_3 + PhI$$

The "p-carboranylation" of fluorine anion also proceeds quickly and smoothly, and leads to the previously unknown 2-fluoro-p-carborane in quantitative yield.

$$(I) + F^- \rightarrow 2 - p - C_2 H_2 B_{10} H_9 F + PhI$$

Previously, we had found that the "m-carboranylation" of the ambident NO_2 and $ArSO_2$ anions by salt (III) leads to unexpected⁺ products, and specifically 9-hydroxy-m-carborane and the 9-m-carboranyl esters of arenesulfinic acids, respectively [2]. Probably, in the given case, due to the steric hindrance created by the carborane ligand, attack of the iodonium cation at the B atom by the central atom of the reacting anion (N or S) is impossible. Therefore, it is evident that the nitrite and arenesulfinate anions attack the B atom, attached to the onium center, only by the O atom. Starting with the above, it could be expected that when (I) is reacted with NaNO₂ it should also give the corresponding hydroxy derivative, but more easily than (III). Actually, (I) reacts with NaNO₂ to give 2-hydroxyp-carborane at a lower temperature and more quickly than (III).

$$(I) + NO_2^- \rightarrow 2 - p - C_2 H_2 B_{10} H_9 OH + PhI + NO + NO_2$$

$$(77\%)$$

On the other hand, the reaction of (I) with PPh_3 , judging by the presence of benzene and diphenyl in the products, is realized by the radical mechanism and proceeds, as was to be expected, similar to the reactions of (III) and (IV), with a retention of the B-I bond and at approximately the same rate [3].

 $(I) + PPh_3 \rightarrow Ph_4 \dot{P}BF_4^- + 2 - p - C_2 H_2 B_{10} H_9 I + PhH + Ph_2 \\ \approx 1\%^{\ddagger} + C_2 H_2 B_{10} H_9 I + PhH + Ph_2 \\ \sim 1\%^{\ddagger} + Ph_2 \\ \text{traces} \ddagger$

To obtain (I) we developed a new and convenient method for the synthesis of (II) by the iodination of p-carborane with iodine in the presence of CF_3CO_2Ag in dichloroethane. A fivefold excess of the Ag salt with respect to the p-carborane is needed to complete the reaction. The yield of the desired product is high, and only about 10% of diiodo products is formed.

EXPERIMENTAL

<u>2-Iodo-p-carborane (II).</u> A mixture of 3.1 g of p-carborane, 10 g of CF_3CO_2Ag and 6.3 g of I_2 in 35 ml of dry dichloroethane was refluxed for 36 h, adding 3 g each of CF_3CO_2Ag and I_2 at 6-h intervals until the condensate retained a weak color. The reaction was checked by TLC (Silufol, pentane). The reaction mixture was cooled to 20°C, shaken with 50 ml of water, and the AgI was filtered. The organic layer was washed with NaHSO₃ solution and evaporated. A pentane solution of the residue was passed through an Al_2O_3 bed and the pentane was removed in vacuo. Product (II) was recrystallized from pentane (+30 to -50°). Yield 4.7 g (81%), mp 57-59° (cf. [11]).

^{*}For example, from [9] for the 9-m-carboranyl group: $\sigma_I = -0.12$ to -0.17, $\sigma_R = -0.02$ to -0.03; and for the 2-p-carboranyl group: $\sigma_I = +0.02$ to -0.04, $\sigma_R = +0.02$ to +0.002. +Under these conditions, $Ph_2I^+Bf_4^-$ reacts with NaNO₂ and p-MeC₆H₄SO₂Na to respectively give nitrobenzene and phenyl p-tolyl sulfone [10]. **‡**Based on the GLC data.

Phenyl 2-p-Carboranyliodonium Fluoborate (I). To a mixture of 49 ml of Ac₂O, 91 ml of conc. H_2SO_4 , 3.7 g of (II), and 18 ml of benzene at -12° was added in portions 10 g of finely ground $K_2S_2O_8$ and the reaction mixture was stirred for 1 h at $0-5^{\circ}$, 7 h at 20°, and then it was poured into 300 g of ice. The subsequent workup was the same as in the preparation of (III) [1]. Product (I) was purified by passing a CH_2Cl_2 (DCM) solution through an Al_2O_3 bed. Yield 4.77 g (80%), mp 175° (decomp.). Found, %: C 22.43; H 3.68. $C_8H_{16}B_{11}F_4I$. Calculated, %: C 22.14; H 3.72.

Reaction of (I) with Sodium Azide. A mixture of 0.7 g of (I), 0.3 g of NaN₃, 7 ml of DCM, and 6 ml of water was stirred vigorously for 15 min at 20°. The residue from the evaporation of the organic layer was passed as a pentane solution through an Al_2O_3 bed and then the solution was poured into a Petri dish. After evaporation of the pentane and iodobenzene the residual 2-p-carboranyl azide was sublimed thrice in vacuo. Yield 0.27 g (91%), mp 59-60°. Found, %: N 22.52. C₂H₁₁B₁₀N₃. Calculated, %: N 22.69. IR spectrum (v, cm⁻¹): 2160 (N₃), 1355 (BN).

Reaction of (I) with Sodium Fluoride. A mixture of 0.7 g of (I), 0.2 g of NaF, 5 ml of DCM, and 4 ml of water was stirred vigorously for 35 min at 20°. The residue from the evaporation of the organic layer was passed as a pentane solution through an Al_2O_3 bed and the pentane was removed. A solution of the residue (a mixture of 2-fluoro-p-carborane and PhI) in 4 ml of dry CCl₄ was saturated with chlorine at 5°, then the CCl₄ was removed in vacuo, while the mixture of PhICl₂ and 2-fluoro-p-carborane was treated with pentane. Yield of PhICl₂ 0.31 g (70%). The pentane solution of the product was passed through an Al_2O_3 bed and then evaporated to give 0.26 g (100%) of 2-fluoro-p-carborane, mp 256° (after a double sublimation in vacuo). Found, %: F 11.74. $C_2H_{11}B_{10}F$. Calculated, %: F 11.71.

<u>Reaction of (I) with Sodium Nitrite.</u> A mixture of 0.7 g of (I), 0.7 g of NaNO₂, 5 ml of DCM, and 4 ml of water was stirred vigorously for 50 min at 20°. The organic layer was evaporated in vacuo, the residue was dissolved in 20 ml of 5% NaOH solution, and the alkaline solution was washed with pentane and treated with 20% HCl solution until acid. The obtained precipitate was sublimed in vacuo to give 0.198 g (77%) of 2-hydroxy-p-carborane, mp 301° (benzene-hexane) (cf. [12]).

Reaction of (I) with Triphenylphosphine. A solution of 0.3 g of (I) and 0.36 g of PPh₃ in 3.5 ml of acetone in an ordinary glass test tube, fitted with a reflux condenser, was illuminated on an aluminum foil background with an electric lamp (60 W) at a distance of 15 cm. A precipitate of Ph₄PBF₄ began to deposit after 40 min, and the reaction was ended in 7 h. The reaction mixture was treated with excess ether. Yield of Ph₄PBF₄ 0.249 g (85%), mp 340° (cf. [3]). The filtrate from the Ph₄PBF₄ separation was evaporated, the residue was refluxed for 1 h with a solution of 1 ml of MeI in 3 ml of ether, and then the reaction mixture was passed as a pentane solution through an Al₂O₃ bed and evaporated to dryness. Yield of (II) 0.169 g (91%), mp 60-61° (cf. [11]).

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CONCLUSIONS

Phenyl-2-p-carboranyliodonium fluoborate was obtained for the first time by the oxidative condensation of 2-iodo-p-carborane with benzene. It reacts with N_3 , F⁻, and NO_2 with cleavage of the B-I bond, while with PPh₃ it reacts with cleavage of the C-I bond.

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