CONCLUSIONS

The acylation of alkynes by α-bromobutyroyl tetrafluoroborate under "nonnucleophilic" conditions takes place as a reaction involving the conjugated addition of the acylium cation and the bromide anion from the acyl residue over the triple bond by means of a 1, 4 shift.

LITERATURE CITED

1. G. V. Roitburd, W. A. Smit, A. V. Semenovskii (Semenovsky), A. A. Shchegolev (Schegolev), V. F. Kucherov, O. S. Chizov, and V. I. Kadentsev, Tetrahedron Lett., 4935 (1972).
2. V. A. Smit, A. A. Shchegolev, and V. F. Kucherov, Izv. Akad. Nauk SSSR, Ser. Khim., 2377 (1972).
3. A. A. Shchegolev (Schegolev), W. A. Smit, G. V. Roitbird, and V. F. Kucherov, Tetrahedron Lett., 3373 (1974).
4. A. A. Shchegolev (Schegolev), W. A. Smit, V. F. Kucherov, and R. Caple, J. Am. Chem. Soc., 97, 6604 (1975).
5. G. A. Olah, H. C. Lin, and A. Germain, Synthesis, 895 (1974).
6. L. M. Jackman and S. Sternhell (editors), International Series of Monographs in Organic Chemistry, Vol. 5, Pergamon Press, New York — London (1969).
7. P. E. Peterson, R. J. Bopp, and M. M. Ajo, J. Am. Chem. Soc., 92, 2834 (1970).

INTERMEDIATES IN ELECTROPHILIC VINYL SUBSTITUTION IN 1,1-DIARYLETHYLENES AND REDUCTION OF β-SUBSTITUTED 1,1-DIARYLETHYL CATIONS BY TRIETHYLSILANE

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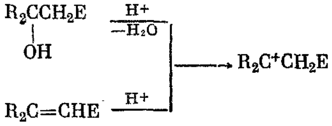
The reaction of 1,1-diarylethylenes with mercuric trifluoroacetate or mercuric nitrate in CH_3CN, ether, benzene, or another aprotonic solvent results in the substitution of the vinyl hydrogen by mercury [1]. This process is analogous to the previously known vinyl bromination reaction in [2] and several other electrophilic vinyl substitution reactions in 1,1-diarylethylenes [3].

The intermediates of mercuration and halogenation reactions have been studied with the aid of UV, ^1H NMR, and ^{13}C NMR spectroscopy [4]. The data obtained are evidence in favor of the asymmetric structure of the intermediate with predominant localization of the positive charge on one carbon atom, i.e., the open structure of β-carbonium ion $Ar_2C^+-CH_2E$, where E = $HgOCOCF_3$, Cl, Br.

The ability of carbonium ions to mediate intermolecular hydride transfer is well known. The purpose of the present work was to study hydride transfer from triethylsilane to 2-halomercuri-1,1-diarylethyl cations, which are generated from substituted olefins or alcohols and CF_3COOH according to the scheme



$$R_2C(OH)CH_2E \xrightarrow[-H_2O]{H^+} R_2C^+CH_2E \xleftarrow{H^+} R_2C{=}CHE$$

Reduction by trialkylsilanes in CF_3COOH, which is known as an ionic hydrogenation reaction [5], has not previously been applied to olefins and alcohols containing mercury or halogens.

The reactivity of β-substituted 1,1-diarylethyl cations with respect to the hydride ion should be dependent on the distribution of the positive charges in the system, which is determined by the nature of the heteroatom. The presence of a β halogen atom creates the possibility for an intramolecular nucleophilic interaction with the carbonium center. The presence of a highly polar $Hg^{\delta+}-X^{\delta-}$ bond introduces a second electrophilic center into the cation. Taking advantage of Pearson's principle of hard and soft acids and bases [6, 7], we were

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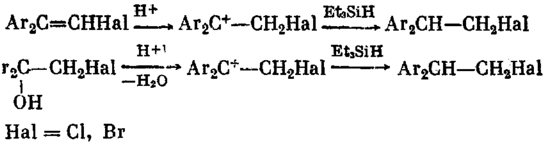
TABLE 1. Chemical Shifts and Spin—Spin Coupling Constants Calculated from Data from the PMR Spectra of 1,1-Diaryl-2-haloethanes (A_2B systems [8])

Compound	Solvent	δ, ppm		J_{AB}, Hz
		CH	CH_2	
Ph_2CHCH_2Br	CCl_4	4,35	3,83	8,0
Ph_2CHCH_2Cl	CCl_4	4,25	3,92	7,8
$(CH_3OC_6H_4)_2CH{-}CH_2Br$	CCl_4	4,20	3,73	7,6

able to a priori assume the hydride, being a soft base, should preferentially attack the β-mercurated cation at the softer mercury atom $R-Hg^{\oplus}$. In the case of the 2-halogen-substituted ion, only the C atom bearing the positive charge is an active center.

The experiment showed that 1,1-diaryl-1-hydroxy-2-haloethanes and 1,1-diaryl-2-haloethylenes containing chlorine and bromine are converted rapidly and with a high yield into 1,1-diaryl-2-haloethanes under the action of CF_3COOH and Et_3SiH according to the scheme



$$Ar_2C{=}CHHal \xrightarrow{H^+} Ar_2C^+{-}CH_2Hal \xrightarrow{Et_3SiH} Ar_2CH{-}CH_2Hal$$

$$\underset{\displaystyle OH}{Ar_2C}{-}CH_2Hal \xrightarrow[-H_2O]{H^+} Ar_2C^+{-}CH_2Hal \xrightarrow{Et_3SiH} Ar_2CH{-}CH_2Hal$$

$$Hal = Cl,\ Br$$

In the case of the formation of a stable 1,1-di(p-methoxyphenyl)-2-bromoethyl cation from 1,1-di(p-methoxyphenyl)-2-bromoethylene, the reduction proceeds so vigorously that the reaction can be carried out as a titration.

The 1,1-diaryl-2-haloethanes isolated in the experiments were characterized by elemental analysis, PMR spectra, which contained characteristic multiplets of the A_2B systems of the $CH-CH_2$ groups (Table 1), data from TLC on Silufol, and chemical conversions. 1,1-Diaryl-2-haloethanes differ with respect to their stability. The previously unknown 1,1-di(p-methoxyphenyl)-2-bromoethane is the least stable. For example, during the chromatography on Al_2O_3 it completely decomposed to form 1,1-di(p-methoxyphenyl)ethylene. From the samples of 1,1-diphenyl-2-bromoethane and 1,1-di(p-methoxyphenyl)-2-bromoethane we obtained the corresponding 2-bromomercuriethanes, which were the standards for the study of the reduction of the β-mercurated cations:

$$Ar_2CHCH_2Br \xrightarrow[\text{Ether}]{Mg} Ar_2CHCH_2MgBr \xrightarrow{HgBr_2} Ar_2CHCH_2HgBr$$

The reaction was complicated by the formation of 1,1,4,4-tetraarylbutanes, which is especially significant in the case of 1,1-di(p-methoxyphenyl)-2-bromoethane. In this case, the application of column chromatography was required for the isolation of the organomercury compound.

In the preliminary experiments it was found that mercury trifluoroacetates with the general formula $RHgOCOCF_3$, where $R = OCOCF_3$, $Ar_2C=CH$, or Ar_2CH-CH_2, react with triethylsilane in ether CH_2Cl_2, $CHCl_3$, and CH_3CN with the formation of metallic mercury. The only reduction products of the 2,2-diarylvinylmercury compounds were the corresponding olefins. In the case of the compounds with the formula Ar_2CHCH_2-$HgOCOCF_3$, the reaction was more complicated. The reaction mixture contained the 1,1-diarylethane and 1,1-diarylethylene. Such a result may be due to the radical mechanism of the reduction of the compounds under investigation. Stepwise demercuration with the intermediate formation of an unstable mercury hydride is more likely.

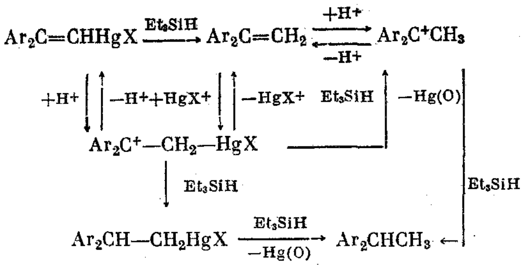
$$RHgOCOCF_3 \xrightarrow{Et_3SiH} RHgH$$

The subsequent conversions of this intermediate to form the product involve the homolytic splitting of the C—Hg bond. It should be noted that the formation of RHgH has been postulated in most communications devoted to the reduction of organomercury compounds by hydrides [9, 10].

The foregoing reactions simulate some of the processes which take place in 2,2-diarylvinylmercury salts under the conditions of ionic hydrogenation.

TABLE 2. Data from the PMR Spectra of the Products of the Ionic Hydrogenation of Mercurated 1,1-Diarylethylenes

Compound	Solvent	δ, ppm			J_{HH}, Hz
		CH	CH_2	CH_3	
$Ph_2C{=}CH_2$	Without a solvent	–	5,29	–	–
$Ph_2CH{-}CH_3$		3,92	–	1,47	7,1
$(CH_3OC_6H_4)_2C{=}CH_2$	$CHCl_3$	–	5,25	–	–
$(CH_3OC_6H_4)_2CH{-}CH_3$		4,00	–	1,55	7,0



The reduction of bis(diphenylvinyl)mercury and compounds with the general formula $(CH_3OC_6H_4)_2C=CHHgX$, where X = Cl, Br, $OCOCF_3$, or triethylsilane in CF_3COOH experimentally results in the formation of demercuration products. After the removal of the mercury, the analysis of the organic fraction by TLC and PMR spectroscopy, as postulated, showed that in all cases the main components are the corresponding 1,1,-diarylethane and 1,1-diarylethylene (Table 2). In the cases in which there were p-$CH_3OC_6H_4$ groups in the α position of the vinylmercury compounds, it was possible to establish the presence of traces of 2,2-di(p-methoxyphenyl)-ethylmercury in the mixture of reduction products by TLC on Silufol UV-254. It may be assumed that the replacement of the α-phenyl groups by anisyl groups reduces the magnitude of the effective positive charge on the carbonium C atom. The decrease in charge results in an increase in the "softness" of the carbonium center (in the sense of the principle mentioned in the foregoing), thereby making the transfer of the hydride ion to the C atom bearing the positive charge more likely.

Thus, ionic hydrogenation can be applied to the reduction of 1,1-diaryl-substituted olefins and alcohols containing Cl or Br in the β position to the corresponding 1,1-diarylethanes with the maintenance of the heteroatom. Mercury-containing compounds are demercurated under such conditions. The results are evidence of the intermediate formation of β-substituted carbonium ions.

EXPERIMENTAL

The CF_3COOH was purified by means of the Na salt [11]. The $CHCl_3$ and CH_2Cl_2 were shaken with an aqueous solution of K_2CO_3, dried, and distilled with P_2O_5 in an Ar atmosphere. The PMR spectra were recorded on Hitachi — Perkin — Elmer R-20 and Varian T-60 instruments, the internal standard being HMDS. The thin-layer and column chromatographic separations of the compounds were carried out on Silica Gel L 40/100, Silica Gel L 100/160, or Al_2O_3 (activity level II). The purity of the compounds was monitored and the chromatographic homogeneity of the products isolated was verified on Silufol UV-254 plates under standard conditions. The synthesis of the organomagnesium compounds and the reactions with them were carried out in a Hershberg apparatus in an Ar atmosphere. Triethylsilane (I) [12], 1,1-diphenyl-2-bromoethylene (II) [13], 1,1-di(p-methoxyphenyl)-2-bromoethylene (III) [14], and 2,2-diphenyl-2-hydroxyethyl chloride (IV) [15] were synthesized according to known methods. The synthesis of the 2,2-diphenylvinylmercury and 2,2-di(p-methoxyphenyl)-vinylmercury salts has previously been described in [1, 16].

2,2-Diphenyl-2-hydroxyethyl Bromide (V). A solution of 3.60 g (0.02 mole) of 1,1- diphenylethylene and 3.56 g (0.02 mole) of N-bromosuccinimide in aqueous dimethoxyethane (30 ml of dimethoxyethane and 10 ml of water) was allowed to stand at ~20°C. After 24 h, the solvent was driven off in a vacuum, and the residue was extracted with CCl_4 (three 10-ml portions). Removal of the CCl_4 and recrystallization of the resudue yielded 2.47 g (46%) of a colorless crystalline compound (V), mp 70-71.5°C (hexane). PMR spectrum (CCl_4, δ, ppm): 3.10 (broadened singlet, 1 H, OH), 4.17 (2 H (CH_2Br). Found: C, 60.30; H, 4.89; Br, 28.84%. Calculated for $C_{14}H_{13}OBr$: C, 60.66; H, 4.73; Br, 28.82%.

Bis(2,2-diphenylvinyl)mercury (VI). A 3.50-g portion (0.0076 mole) of 2,2-diphenylvinylmercury bromide was added portionwise with cooling and stirring to a solution of the Mg derivative from 3.28 g (0.012 mole) of bromide II and 0.30 g (0.012 mole) of Mg in 50 ml of absolute ether. The mixture was boiled for 5 h, after which it was treated with 70 ml of water and diluted with 50 ml of benzene. The organic layer was separated and dried by $MgSO_4$. Evaporation of the solvents in a vacuum yielded 3.1 g (73%) of a crystalline compound (VI) with mp 138.5-139°C (ethanol – benzene). TLC (Silufol, toluene eluent): R_f 0.81; for the original 2,2-diphenylvinylmercury bromide, R_f 0.71. Compound VI can be obtained by the symmetrization of 2,2-diphenylvinylmercury bromide by NaI in acetone. PMR spectrum (VI) (δ, ppm): 6.67 (=CH – Hg), $J_{^1H-^{199}Hg} = 114.3$ Hz. Found: C, 60.01; H, 3.98; Hg, 35.85%. Calculated for $C_{28}H_{22}Hg$: C, 60.15; H, 3.97; H, 35.88%.

1,1-Diphenyl-2-chloroethane (VII). A 10.30-g portion (0.09 mole) of CF_3COOH and 1.45 g (0.0125 mole) of triethylsilane were added to a solution of 2.33 g (0.01 mole) of IV in 7 ml of $CHCl_3$ at –15°C, and the mixture was stirred. Then the mixture was left to stand for 1 h. In order to isolate the reduction product, the $CHCl_3$ and the excess acid were evaporated in a vacuum. Low-temperature crystallization of the oily residue from heptane yielded 1.68 g (77%) of VII, mp 35°C (compare [17]).

1,1-Diphenyl-2-bromoethane (VIII). Reduction of II. A 10.26-g portion (0.09 mole) of CF_3COOH and 1.45 g (0.0125 mole) of triethylsilane were added with cooling by ice to a solution of 2.59 g (0.01 mole) of bromide II in 7 ml of $CHCl_3$ (or CH_2Cl_2). The mixture was held at 0°C for 1 h. The solvents were driven off in a vacuum with the temperature of the bath equal to 30°C. Low-temperature crystallization of the residue from hexane yielded 1.61 g (62%) of VIII in the form of colorless, cubic crystals, mp 61-62°C (compare [17]). TLC (Silufol, 1 : 4 benzene – hexane eluent): R_f 0.47 (VIII); R_f 0.70 (II).

Reduction of V. In analogy to the procedure for II, the reaction of 0.49 g (0.0018 mole) of V in 5 ml of $CHCl_3$ with 2.06 g (0.018 mole) of CF_3COOH and 0.29 g (0.0025 mole) of triethylsilane yielded 0.31 g (66%) of VIII, mp 61-62°C. The compounds obtained by the two methods were identical.

1,1-Di(p-methoxyphenyl)-2-bromoethane (IX). A 17.1-g portion (0.15 mole) of CF_3COOH was added to a solution of 16.00 g (0.05 mole) of bromide III in 20 ml of $CHCl_3$ with cooling and stirring. The reddish violet solution was instantaneously decolorized following the addition of 8.75 g (0.075 mole) of triethylsilane. The solvent and the excess volatile reagents were driven off in a vacuum with a temperature of the bath ≤20°C. The residue was passed through a layer of silica gel (50 g) in benzene and crystallized from hexane. The product consisted of 14.20 g (88%) of IX, mp 68-69°C. Found: C, 59.53; H, 5.48; Br, 24.99%. Calculated for $C_{16}H_{17}BrO_2$: C, 59.83; H, 5.36; Br, 24.88%. During chromatography on Al_2O_3, bromide IX was converted into 1,1-di(p-methoxyphenyl)-ethylene (X), mp 144°C. PMR spectrum of X (CCl_4, δ, ppm): 3.83 (s, 6 H, CH_3O), 5.27 (s, 2 H, CH_2=), 7.07 (m, 8 H, aromatic protons).

1,1-Diphenyl-2-bromomercuriethane (XI) (Marker). A solution of 1.88 g (0.01 mole) of dibromoethane in 25 ml of absolute ether was added to 0.85 g (0.035 mole) of Mg, and a solution of 6.50 g (0.025 mole) of bromide VIII in 25 ml of ether was added dropwise. The mixture was boiled for 12 h, filtered free of the unreacted Mg, and poured onto 5.00 g (0.014 mole) of $HgBr_2$. After the completion of the exothermic reaction, the mixture was boiled for 3 h, and the precipitate was filtered off, washed with dilute HBr and water, and dried in a vacuum. Washing with ether (three 20-ml portions) yielded 3.90 g (61%) of XI, mp 127°C (from ethanol). PMR spectrum ($CHCl_3$, δ, ppm): 4.41 (t, 1 H, CH); 2.49 (d, 2 H, CH_2Hg), $J_{^1H-^{199}Hg} = 190.0$, $J_{^1H-^1H} = 7.7$ Hz. Found: C, 36.30; H, 2.87; Br, 17.32; Hg, 43.28%. Calculated for $C_{14}H_{13}BrHg$: C 36.42; H, 2.84; Br, 17.31; Hg, 43.44%.

1,1-Di(p-methoxyphenyl)-2-bromomercuriethane (XII) (Marker). A solution of 9.63 g (0.03 mole) of bromide IX in 70 ml of ether was added dropwise to 0.73 g (0.03 mole) of Mg and 25 ml of ether. The reaction was discontinued 2 h after pouring the solution onto 5.00 g of $HgBr_2$. The mixture was stirred for 6 h, and the ethereal solution was decanted with the oily precipitate. The precipitate was washed with 20 ml of ether, and the ethereal extracts were combined. Upon cooling, 1.81 g of white crystals precipitated from the ethereal solution. An additional 2.89 g of the product, i.e., the total yield was 4.70 g, with mp 98-105°C were obtained from the precipitate formed over the course of the reaction after washing with dilute HBr and water and drying in a vacuum. According to the TLC data (Silufol, benzene eluent), the product contained two compounds: R_f 0.39 (the mercurated compound), R_f 0.24 (the mercury-free compound). The mixture was separated by chromatographing it twice in a column with silica gel, the eluent being benzene. The yield was 2.35 g (32%) of XII, mp 109-110°C (from ethanol). PMR spectrum of XII ($CHCl_3$, δ, ppm): 4.36 (t, 1 H, CH); 2.46 (d, 2 H, CH_2Hg), $J_{^1H-^{199}Hg} = 185.7$, $J_{^1H-^1H} = 8.3$ Hz; 3.68 (s, 6 H, CH_3O). Found: C, 36.63; H, 3.23; Br, 15.55; Hg, 37.88%. Calculated for $C_{16}H_{17}BrHgO_2$: C, 36.83; H, 3.28; Br, 15.31; Hg, 38.44%. The second (mercury-free) compound (0.47 g, mp 124-125°C) was determined to be 1,1,4,4-tetra(p-methoxyphenyl)butane. Found: C, 79.60; H, 7.15%. Calculated for $C_{32}H_{34}O_4$: C, 79.66; H, 7.10%.

Reduction of 2, 2-Diarylvinylmercury Compounds by Triethylsilane in CF_3COOH. Compound VI and the salts (Cl, Br, $OCOCF_3$) of 2, 2-di(p-methoxyphenyl)vinylmercury were reduced under the conditions for the synthesis of VII-IX. After the removal of the mercury, the reaction product was analyzed by TLC on Silufol UV-254 with marker XI or XII and by PMR spectroscopy.

Reduction of Trifluoroacetates by Triethylsilane. The 2, 2-diarylvinylmercury trifluoroacetates were obtained by the exchange reaction between 0.001 mole of the respective bromide in CH_2Cl_2 and an equimolar amount of $AgOCOCF_3$ in ether. The precipitated silver halide was filtered. After the evaporation of the solvents, the compound was dissolved in ether, CH_2Cl_2, $CHCl_3$, or CH_3CN, and 1 ml of triethylsilane was added. After being filtered free of mercury, the solution was analyzed by TLC.

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CONCLUSIONS

1. 1, 1-Diaryl-substituted olefins and alcohols containing a β chlorine or bromine atom are reduced by triethylsilane in CF_3COOH to 1, 1-Diaryl-2-haloethanes. Mercury-containing compounds are demercurated under these conditions.

2. The β-substituted 1, 1-diarylethyl cations formed as intermediates under the conditions of ionic hydrogenation display a pronounced carbonium character.

LITERATURE CITED

1. V. I. Sokolov, V. V. Bashilov, and O. A. Reutov, Dokl. Akad. Nauk SSSR, 188, 127 (1969).
2. P. Pfeiffer and R. Wizinger, Lieb. Ann. Chem., 461, 132 (1928).
3. P. B. D. De la Mare and R. Bolton, Electrophilic Additions to Unsaturated Systems, New York (1966).
4. V. I. Sokolov, V. V. Bashilov, P. V. Petrovskii, and O. A. Reutov, Dokl. Akad. Nauk SSSR, 213, 1103 (1973).
5. Z. N. Parnes and D. N. Kursanov, Hydride-Displacement Reactions in Organic Chemistry [in Russian], Nauka (1969).
6. T. L. Ho, Chem. Revs, 75, 1 (1975).
7. V. I. Sokolov, Dokl. Akad. Nauk SSSR, 197, 362 (1971).
8. D. Emsley, J. Feeney, and L. H. Sutcliffe, High-Resolution Nuclear Magnetic Resonance Spectroscopy, Vol. 1, Pergamon Press (1965).
9. G. M. Whitesides and J. San. Filippo, J. Am. Chem. Soc., 92, 6611 (1970).
10. E. Müller, Berichte, 109, 3804 (1976).
11. A. L. Henne and T. Alderson, J. Am. Chem. Soc., 67, 918 (1945).
12. F. C. Whitmore, E. W. Pietrusza, and L. H. Sommer, J. Am. Chem. Soc., 69, 2108 (1947).
13. P. Lipp, Berichte 56, 657 (1923).
14. F. Bergmann and J. Szmuszkowicz, J. Am. Chem. Soc., 69, 1777 (1947).
15. A. Klages and J. Kessler, Berichte, 39, 1753 (1906).
16. V. I. Sokolov, V. V. Bashilov, and O. A. Reutov, J. Organomet. Chem., 97, 299 (1975).
17. S. A. Vartanyan, A. G. Vartanyan, and E. A. Araratyan, Arm. Khim. Zh., 25, 948 (1972).