

ELECTROPHILIC VINYL MERCURATION OF 1,1-DIARYLETHYLENES

V.I. SOKOLOV, V.V. BASHILOV* and O.A. REUTOV

Institute of Organoelement Compounds of the Academy of Sciences of the U.S.S.R., Moscow (U.S.S.R.)

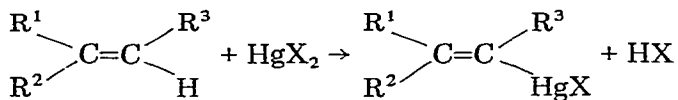
(Received June 28th, 1978)

Summary

A full report is given on the previously described reaction between 1,1-diarylethylenes and mercury(II) salts which results in the formation of vinylic organomercurials. Experimental procedures and NMR spectra are described in detail. Special attention is paid on the nature of the intermediate common to both substitution and addition in this system. The structure of this intermediate can best be interpreted as β -mercurated carbenium ion.

Introduction

It is well known that alkenes form mercurinium ions or neutral π -complexes with mercury(II) salts, which, when attacked by a suitable nucleophile, turn into addition products (conjugate mercuration) [1]. In some instances mercury(II) is reduced, and products of oxidation of olefin substrate are formed (Denigès—Treibs reactions) [2]. It was discovered several years ago that the interaction between some olefins and mercury salts in a conjugated mercuration [3—5] or under the conditions of a Treibs reaction [6—8] gives vinylmercury compounds. The reaction may be considered, at least formally, to be similar to the well known aromatic mercuration. The overall process may be represented by the following general scheme:



The kinetics of vinyl mercuration was studied by PMR by considering steroid systems [8]. The reaction may be satisfactorily described by second order equations. The kinetic results have not permitted us, however, to state unambiguously which stage, the addition of the HgX^+ particle or the elimination of hydrogen, governs the rate of the process as a whole.

From spectral investigations of ionic particles formed from 1,1-diarylethylenes

(continued on p. 274)

TABLE I
 PRODUCTS OF VINYL MERCURATION OF 1,1-DIARYLETHYLENES

Original olefin	Solvent	Mercurating agent	Reaction product	Yield (%)	T_m (°C) solvent	Analysis found (calcd.) (%)						
						C	H	Br	Cl	F	Hg	
I	Benzene or acetonitrile	Hg(OCOCF ₃) ₂	2,2-Diphenylvinylmercuri- bromide (VII)	85	157, from ethanol	36.49 (36.58)	2.41 (2.41)	17.29 (17.38)				43.83 (43.63)
			2,2-Diphenylvinylmercuri- chloride (VIII)	78	143 from benzene	40.74 (40.50)	2.68 (2.67)		8.35 (8.53)			47.31 (48.29)
II	Benzene	Hg(OCOCF ₃) ₂	2,2-Di(<i>p</i> -tolyl)- vinylmercuri- chloride (IX)	91 ^a	181.5-182 from ethanol	43.28 (43.35)	3.46 (3.41)		7.90 (7.98)			44.56 (45.25)
II	Benzene	Hg(OCOCF ₃) ₂	2,2-Di(<i>p</i> -tolyl)- vinylmercuri- bromide (X)	74	156 from ethanol	39.44 (29.40)	3.23 (3.10)	16.27 (16.38)				40.92 (41.12)
III	Diethyl ether	Hg(OCOCF ₃) ₂ + BF ₃ Me ₂ O	2,2-Di(<i>p</i> -chloro- phenyl)vinyl- mercuri- chloride (XI)	95 ^a	182 from CCl ₄	34.69 (34.73)	1.88 (1.87)		22.29 (21.98)			41.12 (41.43)

V	Acetonitrile	Hg(NO ₃) ₂	Mixture of Z and E isomers of 2- <i>p</i> -fluorophenyl-2- <i>p</i> -anisylvinylchloride (XIII)	80	121-122 from ether	39.19 (38.89)	2.74 (2.61)	4.12 (4.10)
VI	Acetonitrile	Hg(NO ₃) ₂	Mixture of Z and E isomers of 2- <i>p</i> -chlorophenyl-2- <i>p</i> -tolylvinylmercurichloride (XIV)	61	186.5-187 from CCl ₄	38.65 (38.85)	2.67 (2.61)	15.73 (15.29)
V	Acetonitrile	Hg(NO ₃) ₂	2- <i>p</i> -Fluorophenyl-2- <i>p</i> -anisyl-1,1-di(chloromercuri)ethylene (XV)	16	263 (dec.) from acetone	25.75 (25.79)	1.76 (1.59)	2.39 (2.72)
II	Acetonitrile	Hg(NO ₃) ₂	2,2-Di(<i>p</i> -tolyl)-1,1-di(chloromercuri)ethylene dissolved in DMC (XVI)	54	189-191 (dec.)	28.71 (28.58)	2.71 (2.66)	52.30 (53.03)
			id. dissolved in acetone (XVII)		244-246 (dec.)	31.39 (31.00)	2.84 (2.74)	53.63 (54.47)

^a Yield of non-purified product.

and mercury trifluoroacetate, a mechanism of vinyl mercuration has been previously suggested, which includes the intermediate formation of asymmetric particles, β -mercurated carbenium ions [9,10].

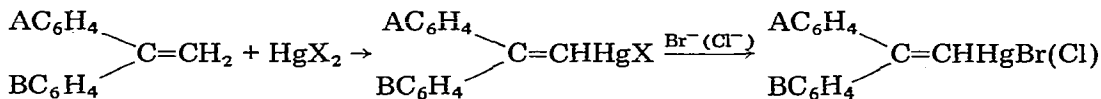
The present report covers the results of a detailed study of vinyl mercuration of 1,1-diarylethylenes. The aim was to determine the requirements upon a mercurating agent, to investigate the part played by, and the effect upon the course of the reaction of, the nature of the olefin substrate and of the solvent.

Results and discussion

The effect of a mercury salt anion confirms the ionic mechanism of vinyl mercuration [9]. Thus, covalent mercury halogens (HgCl_2 and HgBr_2) and the substantially covalent mercury acetate give no products of vinyl mercuration with 1,1-diarylethylenes. The reaction involves mercury salts having a weakly nucleophilic anionoid fragment and, therefore, possessing a highly electrophilic mercury: trifluoroacetate, nitrate, borofluoride. To compare the reactivities of mercury borofluoric and trifluoroacetate, these salts were prepared *in situ* by an exchange reaction between silver borofluoride and trifluoroacetate with HgBr_2 in a mixture with tetrahydrofuran and diethyl ether (1/10 v/v). The concentration of the solutions was $3.78 \times 10^{-2} \text{ mol l}^{-1}$. Equimolar quantities of 1,1-diphenylethylene were added to the solutions. After 15 min the reaction was stopped by treating the reaction mixture with an aqueous solution of KBr . With mercury borofluoride, the transformation of olefin into the vinyl mercury derivative amounts to 17%. Mercury trifluoroacetate is obviously much less active, as 2,2-diphenylvinylmercuribromide is formed in trace amounts detected by thin-layer chromatography. Thus, the order of the activities of salts in the vinyl mercuration reaction corresponds to suggestions on the electrophilic properties of mercurating agents: $\text{HgBr}_2 \approx \text{HgCl}_2 < \text{Hg}(\text{OAc})_2 \ll \text{Hg}(\text{OCOCF}_3)_2 < \text{Hg}(\text{NO}_3)_2 \leq \text{Hg}(\text{BF}_4)_2$.

Mercury borofluoride is inconvenient to use practically. It is best to use mercury nitrate in a polar solvent such as acetonitrile. The most convenient mercurating agent is mercury trifluoroacetate, as it is readily soluble in most organic solvents.

Products of substituting hydrogen for mercury were obtained from I, 1,1-diphenylethylene, and its five analogs containing substituents in the *para*-position on the phenyl groups: II, 1,1-di-(*p*-tolyl)ethylene, III, 1,1-di-(*p*-chlorophenyl)ethylene, IV, 1,1-di-(*p*-methoxyphenyl)ethylene, V, 1-*p*-fluorophenyl-1-methoxyphenylethylene and VI, 1-*p*-chlorophenyl-1-*p*-tolylethylene.



(X = OCOCF_3 ; NO_3)

The solvents used were benzene, acetonitrile and diethyl ether. The course of the reaction may be controlled using these conditions. As vinyl mercuration proceeds, the signal of the original olefin protons at $\delta \sim 5$ ppm disappears in the PMR spectrum, while that at $\delta \sim 6$ ppm, corresponding to reaction product, increases in

TABLE 2

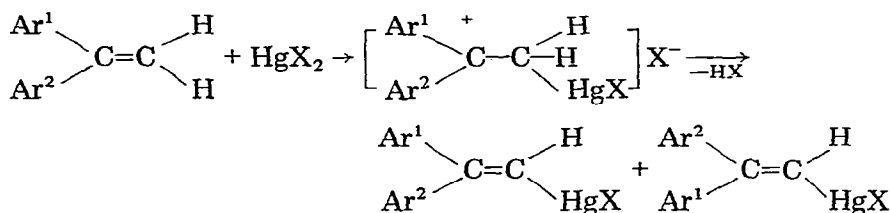
PMR SPECTRA OF PRODUCTS OF THE VINYL MERCURATION OF 1,1-DIARYLETHYLENES
(Ar¹Ar²C=CHHgX)

Ar ¹	Ar ²	X	Solvent	δ, ppm (=CH—Hg)	J(¹ H— ¹⁹⁹ Hg) a(Hz)
C ₆ H ₅	C ₆ H ₅	Cl	(CH ₃) ₂ SO	6.44	184.8
C ₆ H ₅	C ₆ H ₅	OCOCF ₃	CH ₃ CN	6.22	
C ₆ H ₅	C ₆ H ₅	Br	(CH ₃) ₂ SO	6.52	199.3
C ₆ H ₅	C ₆ H ₅	Cl	[(CH ₃) ₂ N] ₃ PO	6.48	183.3
CH ₃ C ₆ H ₄	CH ₃ C ₆ H ₄	Cl	[(CH ₃) ₂ N] ₃ PO	6.44	
CH ₃ C ₆ H ₄	CH ₃ C ₆ H ₄	OCOCF ₃	CH ₃ CN	6.21	
ClC ₆ H ₄	ClC ₆ H ₄	Cl	(CH ₃) ₂ SO	6.59	169.8
CH ₃ OC ₆ H ₄	CH ₃ OC ₆ H ₄	Cl	(CH ₃) ₂ SO	6.17	198.0
ClC ₆ H ₄	CH ₃ C ₆ H ₄	Cl	(CH ₃) ₂ SO	6.45	179.0
ClC ₆ H ₄	CH ₃ C ₆ H ₄	Cl	CHCl ₃	6.19; 6.24(1/1)	
FC ₆ H ₄	CH ₃ OC ₆ H ₄	Cl	(CH ₃) ₂ CO	{ 6.35 6.39 } ^{1/1}	210.2 208.5
CH ₃ C ₆ H ₄	CH ₃ C ₆ H ₄	Br	(CH ₃) ₂ SO	6.49	

intensity. The acid formed in the course of vinyl mercuration corresponds to the signal at δ ~11 ppm.

Vinylmercury compounds were separated and identified as chlorides or bromides. The results are presented in Table 1. All the compounds obtained were analysed by PMR spectra. Presence of signals in the range of δ 6.0—6.5 ppm indicates the formation of vinylmercury compounds. An additional confirmation of product structure was the observation of spin—spin coupling of the signal of olefin protons on nuclei ¹⁹⁹Hg, J(¹H—¹⁹⁹Hg) (Table 2).

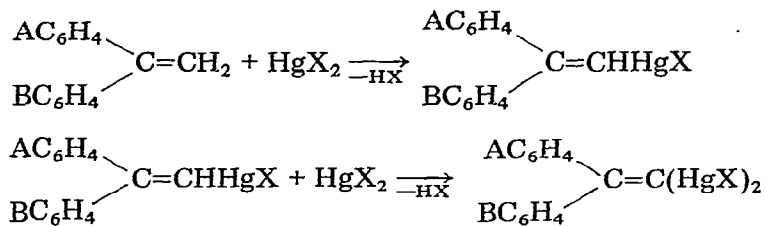
The mercuration of asymmetrically substituted olefins V and VI which have non-equivalent atoms of hydrogen in the methylene group, results, as PMR tends to indicate, in an equimolar mixture of *Z* and *E* isomers. The absence of stereoselectivity in substitution is probably related to the transition state of the reaction which is of such a character that the paths of formation of *Z* and *E* isomers are indistinguishable. This correlates well with the mechanism we have suggested for the reaction via the β-mercurated carbenium ion [9,10], in which rotation about the C—C bond is substantially free.



Carbenium ion is stabilized in the absence of strong nucleophiles by the elimination of the β-hydrogen atom with retention of the C—Hg bond.

A degree of similarity may be noted between vinyl mercuration and substitution of hydrogen for mercury in aromatic substrates. It is known that electrophilic aromatic mercuration may lead to the formation of di- and polymercurated

products [11]. It is then natural to expect the same process to occur for 1,1-diarylethylenes having two atoms of hydrogen on the terminal carbon atom and the formation of dimercury derivatives by the second equivalent of mercury salt. Actually, dimercurated products in the form of chlorides, resulting from stage-by-stage substitution, were separated for olefins II and V (Table 1).



(A = CH₃, B = CH₃; A = F, B = CH₃O)

Double vinyl mercuration is another way of synthesizing compounds with two mercury atoms and an olefin carbon atom. Previously Matteson has obtained 1,1-dimercurated olefins by substituting mercury for boron [12].

An increase in the number of substituents at a double bond usually tends to lower its reactivity with respect to mercury salts. However, asymmetric diarylethylenes exhibit increased reactivity in the ground state due to polarization of the double bond. As stated above, the substitution of a single vinyl hydrogen by mercury has no adverse effect upon subsequent dimercuration. The effect of the third substitute upon the reactivity of the olefin double bond in 1,1-diarylethylenes for vinyl mercuration by mercury trifluoroacetate in benzene or acetonitrile has been studied by considering XVIII, 2,2-diphenylvinylbromide, XIX, 1,1,2-triphenylethylene, and XX, 1,1-diphenylpropylene. These olefins, even after prolonged holding of the reaction mixture (24 h, 20°C), fail to give vinylmercury derivatives. Olefins containing electron-acceptor groups, bromine or phenyl, were not substituted. This corresponds to the electrophilic nature of vinyl mercuration. More complicated is the case of XX, 1,1-diphenylpropylene. For solutions in benzene, containing XX and mercury trifluoroacetate in ratios of 1/1 and 1/3, the PMR spectra show two quadruplets at δ 6.04 ppm and 6.14 ppm with a constant coupling with methyl group protons (δ 1.74 ppm) J 7.1 Hz. The difference in chemical shifts of the methyl groups is less than 1 Hz (for a working frequency of the apparatus of 60 MHz). The quadruplet at 6.14 ppm is from initial olefin. The absence of any substantial differences between spectra of the starting olefin XX and the compound formed in the presence of the mercury salt suggests a reversible formation of a complex between mercury trifluoroacetate and the olefin. It should be noted that the ratio of the signal intensities of the two quadruplets indicates qualitatively a dependence of the amount of the complex upon the mercury salt/olefin ratio. The quantity of the complex-included olefin increases with the relative proportion of mercury trifluoroacetate.

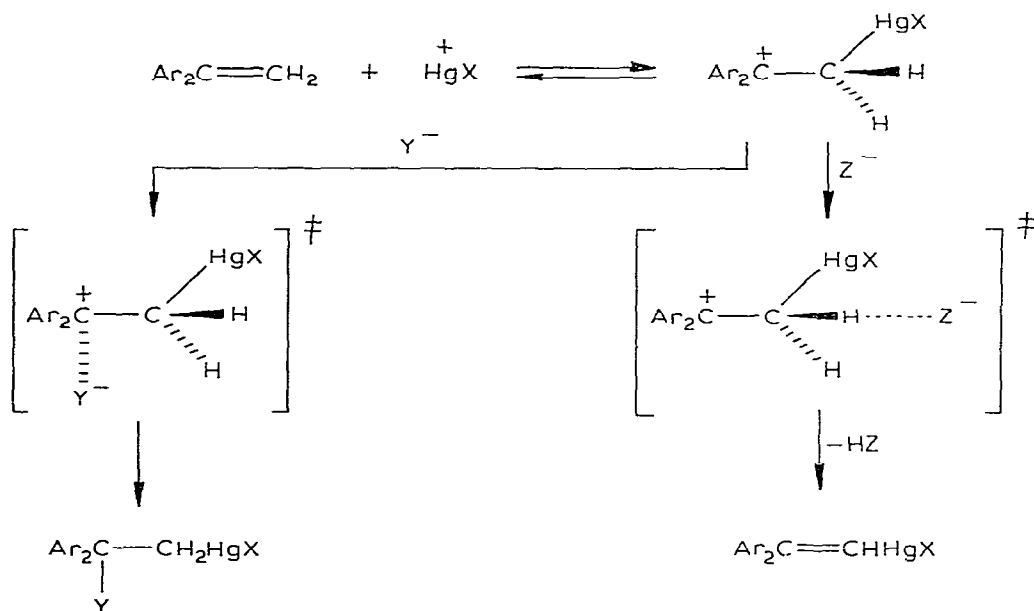
The spectroscopic criterion of the progress of vinyl mercuration of olefin XX should be the transformation of the doublet of the methyl group into a singlet and a simultaneous disappearance of the olefin proton quadruplet. Absence of such changes in the PMR spectrum after 24 h suggests that XX fails

to yield a vinyl mercury compound as in the vinyl mercuration of 1,1-diarylethylenes. It may thus be inferred that the introduction of a third substituent, irrespective of its nature, into the 1,1-diarylethylene substantially lowers the ability of olefin to take part in vinyl mercuration.

We have considered the effects of the type of mercurating agent and of the olefin substrate upon vinyl mercuration. No less important a factor is the solvent.

It is known that in water, methanol and hydrogen peroxide, mercury(II) acetate and 1,1-diphenylethylene, yield only solvomercuration (conjugate addition) products [13–15]. Therefore, for the same olefin substrate, the choice of solvent and mercury salt directs the reaction towards either vinyl substitution or addition. It seems highly probable that both substitution and addition with highly electrophilic mercury salts pass through the same intermediate, β -mercurated 1,1-diarylethylene cation. This intermediate may be stabilized with the C–Hg bond retained in the product through interaction with a nucleophilic solvent with the formation of solvomercuration products, and through elimination of the β -hydrogen atom.

SCHEME 1



The concurrent (dual) reactions of 1,1-diphenylethylene were discovered in a thin-layer chromatography analysis of products of its mercuration by mercury trifluoroacetate in methanol. As well as the main 2-methoxy-2,2-diphenylethylmercuribromide, XXI, R_f 0.23 (silufol, eluent toluene/hexane 2/1), there was also present on the chromatogram a less intensive spot which corresponds to the vinylmercury compound VII, R_f 0.44. Methoxymercuration of 1,1-di(*p*-tolyl)ethylene (II) under standard conditions (15 min) led to a mixture consisting of the starting olefin II (42%), vinylmercury compound VII (36.5%) and methoxymercuration product XXI (31.5%). Methyl groups in phenyl rings

TABLE 3

EFFECT OF CH₃OH CONTENT UPON THE COMPOSITION OF REACTION PRODUCTS OF 1,1-DIPHENYLETHYLENE AND Hg(OCOFCF₃)₂ IN BENZENE^a

No. of experiment	Molar ratio Hg(OCOFCF ₃) ₂ /CH ₃ OH	Total yield of VII and XX	T _m (°C)	δ (ppm) (CDCl ₃)
1	1/1	85	157	6.43
2	1/3	82	127 (dec.)	3.08; 2.93 (2.08H); 6.43 (1H)
3	1/10	80	158 (dec.)	3.08 (3H); 2.93 (2H)
4	1/1 Mixture of substances from experiments 1 and 3		128 (dec.)	

^a Original concentration of reagents c₀ 0.93 mol l⁻¹; 20°C; reaction time in each experiment 15 min.

promote delocalization of the positive charge in the ionic intermediate by stabilizing it. This is probably one of the reasons for the decreased reactivity of the carbon carbenium atom in the methoxymercuration reaction II.

The stabilization of the intermediate β-mercured carbenium ion through elimination of the β-hydrogen atom, being an intramolecular process, is independent of the nucleophilic solvent concentration. As the ratio of the amount of products formed in each path is governed by the ratio of the rates of methoxymercuration and elimination reactions, it is possible to vary the ratio of product by varying the quantity of alcohol in the reaction mixture.

Data on the effect of the quantity of alcohol in the reaction mixture upon vinyl mercuration were obtained for the 1,1-diphenylethylene/Hg/(OCOFCF₃)₂/CH₃OH system in benzene. In the experiments, the olefin/mercury ratio was maintained at 1/1, while the quantity of CH₃OH was varied (Table 3).

For a Hg(OCOFCF₃)₂/CH₃OH ratio of 1/1, the main product of the reaction was the vinyl mercury compound VII. Preferential formation of adduct XXI was observed for a 1/10 ratio. A triple excess in the reaction mixture of CH₃OH with respect to Hg(OCOFCF₃)₂, resulted, according to PMR spectra data, in a mixture of XXI and VII in a ratio of 7/5.

It is thus clear that the absence of strong nucleophiles is not a necessary precondition for vinyl mercuration, as was suggested previously [3].

Decreasing the concentration of a strong nucleophile in the reaction mixture is equivalent to using structurally similar, but weaker nucleophilic molecules. Bethell and Howard have quantitatively evaluated the nucleophilic activity of various alcohols in the reaction with the secondary 1,1-di(*p*-chlorophenyl)methylium cation [16]. Compared to CH₃OH, the secondary butanol and the tertiary butanol were respectively 10 and 40 times less active.

Accordingly, if the reaction between Hg(OCOFCF₃)₂ and 1,1-diphenylethylene is conducted under standard conditions (Table 4) in secondary and tertiary butanols, the result is a vinyl mercuration product VII only, the lesser nucleophilic properties of the tertiary butanol manifesting themselves through a higher yield of VII.

TABLE 4

EFFECT OF SOLVENT UPON VINYL MERCURATION OF 1,1-DIPHENYLETHYLENE AND $\text{Hg}(\text{OCOCF}_3)_2$ ^a

No. of experiment	Solvent	ϵ	Yield VII (%)	Relative effective electrophilic properties of $\text{Hg}(\text{OCOCF}_3)_2$ ^b
1	Benzene	2.3	84	1.0
2	Tert-butanol	10.9	32	0.38
3	Acetonitrile	37.5	20	0.24
4	Sec-butanol	15.8	12	0.14
5	Tetrahydrofuran	7.6	6	0.07
6	Dimethylformamide	36.7	1	0.01

^a Original concentration of reagents c_0 0.93 mol l^{-1} ; 20°C ; reaction time in each experiment 15 min.^b Values calculated on yield of VII.

On the whole, any external nucleophilic interaction inhibits vinyl substitution in the reaction between highly electrophilic mercury salts and 1,1-diarylethylenes. Two pathways may be pointed out for nucleophilic inhibition by a solvent. One way has been discussed above. It consists in the formation of an addition product from the double bond. The other way of nucleophilic inhibition is related to the ability of solvent molecules to form complexes with a mercury salt. In a complex formation with coordination unsaturated mercury salt, the solvent competes with olefin and thus lowers the effective electrophilic properties of the mercurating agent with respect to olefin through delocalization of the positive charge in the complex.

The effect of solvents upon vinyl mercuration has been studied semi-quantitatively in 6 examples (Table 4). The fastest reaction was in weakly solvating benzene, but practically fails to proceed in dimethylformamide. The effect of the dielectric constant (ϵ) of the solvent upon the vinyl mercuration is probably very weak. Thus, benzene and tetrahydrofuran, although having close values of ϵ , differ widely in their action upon mercury salts. The relative effective electrophilic properties of $\text{Hg}(\text{OCOCF}_3)_2$ are 14 times higher in benzene than in tetrahydrofuran.

Nucleophilic inhibition of vinyl mercuration through complex formation is most apparent for mercury(II) nitrate. Attempts to conduct vinyl mercuration of 1,1-diarylethylenes in bipolar aprotic solvents, benzonitrile and phosphoric acid hexamethyltriamide (HMPTA), have failed. However, stable complexes whose compositions are XXII, $(\text{C}_6\text{H}_5\text{CN})_2\text{Hg}(\text{NO}_3)_2$, and $(\text{HMPTA})_2\text{Hg}(\text{NO}_3)_2$ have been separated from the reaction mixture.

The filling of the coordination sphere of mercury atom by strongly bonded ligands, solvent molecules, substantially lowers the electrophilic properties of mercury(II) in the reaction with olefins.

Therefore, the data on the effect of the solvent upon the reaction of vinyl mercuration permit the conclusion that the main property of a solvent governing the vinyl mercuration is its nucleophilic properties with respect both to mercury and the carbon atom carrying a positive charge.

Experimental

Reactions were carried out with anhydrous solvents: acetonitrile, benzene, diethyl ether, tetrahydrofuran, methanol and dimethylformamide. The purity of substances and chromatographic homogeneity of separated products were verified on Silufol UV-254 plates under standard conditions. PMR spectra were recorded on Varian-T-60 and Hitachi-Perkin-Elmer R-20 apparatus with a working frequency of 60 MHz.

Silver trifluoroacetate was obtained from silver oxide and trifluoroacetic acid [17].

Silver borofluoride was obtained through a reaction between boron trifluoride etherate and silver oxide in benzene [18,19].

Mercury(II) nitrate. A commercially available chemically pure compound was used after drying in a vacuum exsiccator in the presence of KOH and P₂O₅.

Mercury(II) trifluoroacetate was produced by the reaction of equimolar quantities of yellow mercury oxide and trifluoroacetic acid anhydride in trifluoroacetic acid [20]. CF₃COOH was driven out of the product in vacuum in the presence of P₂O₅, melting point 156–158°C.

Boron trifluoride etherate, BF₃(CH₃)₂O, Fluka A.G. was distilled, prior to use, in argon with calcium hydride, boiling point, 125–129°C.

Original 1,1-diarylethylenes

I, 1,1-diphenylethylene, II, 1,1-di(*p*-tolyl)ethylene, [22], III, 1,1-di(chlorophenyl)ethylene, [23], IV 1,1-di(*p*-methoxyphenyl)ethylene, [21], XIX, 1,1,2-triphenylethylene, [24] and XX, 1,1-diphenylpropylene [25] were obtained according to standard procedures via organomagnesium compounds. V, 1-*p*-fluorophenyl-1-*p*-methoxyphenylethylene, and VI, 1-*p*-chlorophenyl-1-*p*-tolylethylene, were obtained for the first time.

1-*p*-Fluorophenyl-1-*p*-methoxyphenylethylene

An organomagnesium solution composed of 16.0 g (9.1×10^{-2} mol) of *p*-fluorobromobenzene and 2.22 g (9.1×10^{-2} mol) of magnesium in 100 ml ether was mixed with a solution of 13.7 g (9.0×10^{-2}) of *p*-methoxyacetophenone in 35 ml of ether. The reaction mixture was boiled for 2 h. After treatment of the reaction mixture by 30 ml of water and 15 ml of concentrated HCl, the product was extracted by means of ether. Ether extracts were vaporized in vacuum. The residue was distilled in vacuum to drive off the 163–166°C fraction (8 mmHg). The product was 9.37 g of olefin V (45%) in the form of colourless crystals, m.p. 73–74°C (from methanol). Found: C, 78.85; H, 5.67; F, 8.16. C₁₅H₁₃FO calcd.: C, 79.01; H, 5.70; F, 8.33%. PMR spectrum (CCl₄, δ, ppm): 3.67 (s, 3H, CH₃O); 5.20 (quadr, 2H, =CH₂) J^{hem} 1.22 Hz; 7.2 (m, 8H, arom.).

Similarly to V, VI was obtained from *p*-tolylmagnesium bromide and *p*-chloroacetophenone with a yield of 69%; boiling point 187–190°C/16 mmHg; melting point 55–57°C (from ethanol). PMR spectrum (CCl₄, δ, ppm): 2.27 (s, 3H, CH₃); 5.24 (quadr., 2H, =CH₂); 7.2 (m, 8H, arom.).

General procedure for the vinyl mercuration of 1,1-diarylethylenes by mercury trifluoroacetate

A solution of Hg(OCOFCF₃)₂, c 0.3–0.45 mol l⁻¹ in benzene or acetonitrile,

was mixed at 20°C with an equimolar amount of corresponding olefin. After 1 h, the reaction mixture was stirred with a 2 M aqueous solution of KBr or NaCl. Once the organic solvent was removed, the solid residue was washed with water, then with hexane to separate unreacted olefin. The product was extracted by cold chloroform (30 ml per gram) to remove sparingly soluble dimercury derivative impurity. The solution was filtered and dry-vaporized in vacuum. The analytically pure monomercurated derivative was obtained by recrystallizing the residue from the corresponding solvent (Table 1). This procedure was applicable to all the 1,1-diarylethylenes investigated in the present work.

The vinyl mercuration by mercury trifluoroacetate, in the presence of the activating additive, $\text{BF}_3(\text{CH}_3)_2\text{O}$, was described previously [26].

Vinyl mercuration of 1,1-diarylethylenes by mercury nitrate

Mercuration by mercury nitrate differs from that by mercury trifluoroacetate in that the reaction was conducted heterogeneously with shaking. The solvent was acetonitrile. The completion of the reaction was determined by the complete dissolution of the mercury nitrate suspension. The method is suitable for 1,1-diphenylethylene, 1-*p*-chlorophenyl-1-*p*-tolylethylene and 1-*p*-fluorophenyl-1-*p*-methoxyphenylethylene (Table 1).

*2-*p*-Fluorophenyl-2-*p*-methoxyphenyl-1,1-di(chloromercuri)ethylene (XV)*

A solution of 1.17 g of V in 5 ml CH_3CN was mixed with 1.67 g (5.1×10^{-3} mol) of mercury nitrate. After 20 min the reaction mixture was treated with an aqueous solution of NaCl. The oily substance which was precipitated crystallized on standing. Thin-layer chromatography (silufol, eluent benzene) of the sediment showed traces of the original olefin (R_f 0.71). The main components of the mixture were as follows: monomercurated olefin, XIII, (R_f 0.49) and a dimercury derivative, XV, (R_f 0.19). To precipitate XV, the sediment was washed with ether and recrystallized from a mixture of acetone/benzene/petroleum ether (1/1/2 v/v). The product was 0.59 g (16%) XV, m.p. 263°C (Table 1).

Mercury nitrate complex with benzonitrile XXII

1.80 g (5.5×10^{-3} mol) of mercury nitrate were dissolved in 5 ml of benzonitrile. After 1 h crystals were precipitated from the clear solution. After 12 h the sediment was filtered, washed with ether and acetone, and then dried. The product was 2.35 g (80%) of a light-yellow crystalline substance, XXII, m.p. 134°C. Found: C, 31.56; H, 2.05; Hg, 37.50; N, 10.81. $\text{Hg}(\text{NO}_3)_2 \cdot 2 \text{C}_6\text{H}_5\text{CN}$ calcd.: C, 31.66; H, 1.90; Hg, 37.80; N, 10.55%.

Mercury nitrate complex with phosphoric acid hexamethyltriamide (PAHMTA) (XXIII)

Similarly to XXII, complex XXIII was obtained from mercury nitrate and PAHMTA. The product was precipitated from the solution by a mixture of ether/hexane (1/6). A colourless crystalline substance, m.p. 101–103°C (decomposes at 110°C), was obtained. Found: C, 20.53; H, 5.28; P, 9.00. $\text{Hg}(\text{NO}_3)_2 \cdot 2 (\text{CH}_3)_6\text{N}_3\text{P}=\text{O}$ calcd.: C, 21.29; H, 5.28; P, 9.09%. Complex XXIII may be prepared from XXII by treatment with an excess of PAHMTA.

2,2-Diarylvinyliodide from products of vinyl mercuration

2,2-Diphenylvinyliodide (XXIV), was obtained by the reaction of equimolar quantities of iodine, 3.24 g, and 5.30 g of VIII in 150 ml of chloroform. After 2 h the solution was filtered of the mercury halide sediment, washed with 3×20 ml of 20% aqueous solution of KI and dried with $MgSO_4$. The residue, after vaporization of $CHCl_3$, was crystallized by cooling from 50 ml of methanol. The product was 3.20 g of XXIV (82%), m.p. 40–41°C. Found: C, 55.02; H, 3.70; I, 41.37. $C_{14}H_{11}I$ calcd.: C, 54.92; H, 3.62; I, 41.46%.

PMR spectrum (C_6F_6): δ 6.60 ppm (s, 1H, =CH–I).

2,2-Di(*p*-chlorophenyl)vinyliodide (XXV), was obtained similarly to XXIV from 2,2-di(*p*-chlorophenyl)vinylycerchloride with a yield of 83%, m.p. 62°C (from alcohol). Found: C, 44.82; H, 2.50. $C_{14}H_9Cl_2I$ calcd.: C, 44.84; H, 2.42%.

References

- 1 O.A. Reutov, I.P. Beletskaya and V.I. Sokolov, *Organometallic Compound Reaction Mechanisms*, "Khimiya" Publishers, Moscow, 1972, p. 222.
- 2 H. Arzoumanian and J. Metzger, *Synthesis*, (1971) 527.
- 3 V.I. Sokolov, V.V. Bashilov and O.A. Reutov, *Dokl. Akad. Nauk SSSR*, 188 (1969) 127.
- 4 J.M. Coxon, M.P. Hartshorn and A.J. Lewis, *Tetrahedron Lett.*, (1969) 3521.
- 5 J.M. Coxon, M.P. Hartshorn and A.J. Lewis, *Tetrahedron*, 26 (1970) 3755.
- 6 M. Kočor and M. Gumulka, *Tetrahedron Lett.*, (1960) 3067.
- 7 M. Kočor and M. Gumulka, *Roczn. Chem.*, 45 (1971) 1003.
- 8 R.G. Smith, H.E. Ensley and H.E. Smith, *J. Org. Chem.*, 37 (1972) 4430.
- 9 V.I. Sokolov, V.V. Bashilov, P.V. Petrovskii and O.A. Reutov, *First IUPAC Conference on Physical Organic Chemistry*, Switzerland, 1972, Abstr., p. 148.
- 10 V.I. Sokolov, V.V. Bashilov, P.V. Petrovskii and O.A. Reutov, *Dokl. Akad. Nauk SSSR*, 213 (1973) 1103.
- 11 L.G. Makarova and A.N. Nesmeyanov, *Organoelemental Chemistry Methods*, "Nauka" Publishers, Moscow, 1965.
- 12 D.S. Matteson and D.B. Tripethy, *J. Organometal. Chem.*, 21 (1970) P6.
- 13 A.N. Nesmeyanov and I.F. Lutsenko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1942) 366.
- 14 V.I. Sokolov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1972) 1089.
- 15 S. Patai, M. Harnik and E. Hoffman, *J. Amer. Chem. Soc.*, 72 (1950) 923.
- 16 D. Bethell and R.D. Howard, *Chem. Commun.*, (1966) 94.
- 17 D. Janssen and Ch. Wilson, *Org. Synth.*, 36 (1956) 47.
- 18 H. Meerwein, V. Hederich and K. Wunderlich, *Arch. Pharm.*, 291 (1958) 541.
- 19 K. Heyns and H. Paulsen, *Angew. Chem.*, 72 (1960) 349.
- 20 D.A. Shearer and G.F. Wright, *Can. J. Chem.*, 33 (1955) 1002.
- 21 P. Pfeiffer and R. Wizinger, *Liebigs. Ann. Chem.*, 461 (1928) 132.
- 22 R. Anschütz and A. Hilbert, *Ber.*, 57 (1924) 1697.
- 23 F. Bergmann and J. Szmuszkowicz, *J. Amer. Chem. Soc.*, 70 (1948) 2748.
- 24 W. Schlenk and E. Bergmann, *Lieb. Ann. Chem.*, 463 (1928) 1.
- 25 A. Klages, *Ber.*, 35 (1902) 2646.
- 26 V.I. Sokolov, V.V. Bashilov and O.A. Reutov, *J. Organometal. Chem.*, 97 (1975) 299.