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A PMR STUDY OF EXCHANGE REACTIONS INVOLVING DIARYLTRIAZENES AND THEIR PHENYLMERCURY DERIVATIVES

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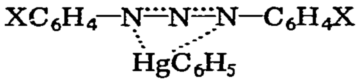
Summary

Exchange reactions involving 2′-methylbenzenesulphonanilide, substituted diaryltriazenes and their C_6H_5Hg derivatives have been studied by the PMR method in chlorobenzene solution. On the basis of the data obtained, values of equilibrium constants for the exchange reactions involving substituted diaryltriazenes and their C_6H_5Hg derivatives have been calculated. Analysis of the finding has shown that the position of equilibrium is governed by the polar and steric effects of the substituents and the relative intensity of intramolecular coordination of hydrogen and the phenylmercury group with the substituent in the 2-position of the diaryltriazene system. Consideration of the results obtained suggests a non-mesomeric structure for C_6H_5Hg derivatives of diaryltriazenes undergoing rapid metallotropic rearrangement.

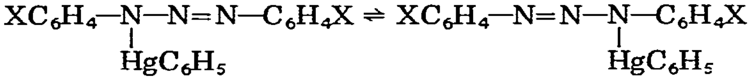
Introduction

It has been shown earlier by ^{19}F-$\{^1H\}$ and ^{13}C-$\{^1H\}$ NMR methods [1] that arylmercury derivatives of diaryltriazenes in solution, either have a mesomeric structure (A), or undergo rapid metallotropic rearrangement occurring mainly by an intramolecular mechanism (B).



$$\underset{HgC_6H_5}{XC_6H_4-N\overset{...}{-}N\overset{...}{-}N-C_6H_4X}$$

(A)



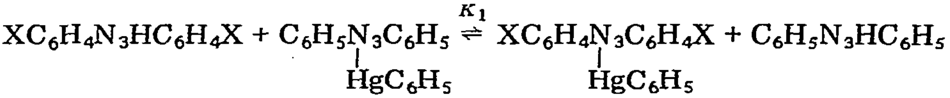
$$XC_6H_4-\underset{HgC_6H_5}{\underset{|}{N}}-N=N-C_6H_4X \rightleftharpoons XC_6H_4-N=N-\underset{HgC_6H_5}{\underset{|}{N}}-C_6H_4X$$

(B)

This ambiguity demands further studies on how the organomercury group is bonded to the diaryltriazene moiety.

Results and discussion

The present work has as its purpose a study of the structure of the phenylmercury derivatives of diaryltriazenes in solution; determination of the relative stability of diaryltriazenes and their C_6H_5Hg derivatives with respect to electronic and steric effects of the substituents and the virtual formation of chelate rings in the *ortho*-substituted diaryltriazenes and their C_6H_5Hg derivatives. Owing to the fact that in solutions of mixtures of diaryltriazenes and their C_6H_5Hg derivatives a metal—proton type rapid exchange occurs, we have adopted for our purposes the method of exchange equilibria together with the PMR method. These methods have been used with succes previously to study steric effects and intramolecular coordination in substituted benzenesulphonanilides and their C_6H_5Hg derivatives [2]. In this connection we have studied the effect of the nature and position of the substituent in the aromatic ring on the position of exchange equilibria involving substituted diaryltriazenes and their C_6H_5Hg derivatives (eq. 1).



$$XC_6H_4N_3HC_6H_4X + \underset{\displaystyle |\atop HgC_6H_5}{C_6H_5N_3C_6H_5} \overset{K_1}{\rightleftharpoons} \underset{\displaystyle |\atop HgC_6H_5}{XC_6H_4N_3C_6H_4X} + C_6H_5N_3HC_6H_5 \qquad (1)$$

Unfortunately, direct determination of equilibrium constants for reaction 1 turned out to be impossible as a result of a rapid, on the PMR time-scale, intermolecular exchange of the proton and the phenylmercury group in the mixture of 2,2′-dimethyldiphenyltriazene and its C_6H_5Hg derivative (chlorobenzene solution, temp. 34° C, concn. 0.05 *M*). By contrast, an exchange of this type in the mixture of 2′-methylbenzenesulphonanilide and its C_6H_5Hg derivative, under similar conditions, proceeds slowly [2]. Therefore, in order to determine the equilibrium constant K_1 for exchange reaction 1 we used the equilibrium con-

TABLE 1

EQUILIBRIUM CONSTANTS K_2 FOR THE REACTION OF $XC_6H_4N_3HC_6H_4X$ WITH $C_6H_5SO_2N(HgC_6H_5)C_6H_4CH_3$-2 IN CHLOROBENZENE (EQ. 2)

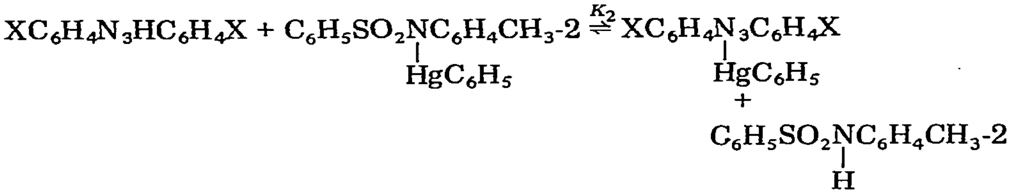
X	K_2
H	7.6 ± 0.3
4-CH_3	5.3 ± 0.3
4-OCH_3	3.2 ± 0.9
4-F	12.3 ± 0.7
3-F	30.5 ± 2
2-CH_3	1.0 ± 0.05
2-OCH_3	23.0 ± 3
2-F	8.3 ± 1.4
2-Cl	90.0 ± 10
2-Br	149.0 ± 16
2-I	406.0 ± 60

TABLE 2

EQUILIBRIUM CONSTANTS K_1 FOR THE REACTION OF $XC_6H_4N_3HC_6H_4X$ WITH $C_6H_5N_3(HgC_6H_5)C_6H_5$ IN CHLOROBENZENE (EQ. 1)

X	K_1
H	1
4-CH_3	0.7 ± 0.1
4-OCH_3	0.4 ± 0.1
4-F	1.6 ± 0.2
3-F	4.0 ± 0.4

stant K_2 obtained experimentally for reaction 2 (see Experimental). The values of K_1 and K_2 are presented in Tables 1—3.



$$XC_6H_4N_3HC_6H_4X + C_6H_5SO_2\underset{HgC_6H_5}{\underset{|}{N}}C_6H_4CH_3\text{-}2 \overset{K_2}{\rightleftharpoons} XC_6H_4\underset{HgC_6H_5}{\underset{|}{N_3}}C_6H_4X + C_6H_5SO_2\underset{H}{\underset{|}{N}}C_6H_4CH_3\text{-}2 \quad (2)$$

Consideration of the data obtained shows the dependence of K_1 on the type and position of the substituent. A more detailed analysis reveals that in reactions involving 3,3′- and 4,4′-substituted diaryltriazenes a good correlation of ln K_1 with the Hammett constants of the substituents is observed.

This correlation is expressed by eq. 3.

$$\ln K = \rho \times \sigma + \gamma \qquad (3)$$

It follows then that in the reactions under study the eqilibrium position depends largely on the substituent polar effects. Since this dependence exists its positive value means that the increase in electron-accepting properties of the substituents stabilizes the C_6H_5Hg derivative of diaryltriazene with respect to the corresponding diaryltriazene.

Calculation of the equilibrium constants for reactions involving 2,2′-dimeth-

TABLE 3

EQUILIBRIUM CONSTANTS K_1 FOR THE REACTION OF 2-$XC_6H_4N_3HC_6H_4X$-2 WITH $C_6H_5N_3(HgC_6H_5)C_6H_5$ IN CHLOROBENZENE (EQ. 1) TOGETHER WITH EQUILIBRIUM CONSTANTS K_c FOUND BY CALCULATION FROM THE TWO-PARAMETER CORRELATION (EQ. 4)

X	K_1	K_c	$\Delta(\Delta G)$ (kcal/mol) [a]
F	1.1 ± 0.2	1.4	—0.1
Cl	12 ± 2	1.2	1.4
Br	20 ± 3	1.0	1.8
I	50 ± 10	0.9	2.5
CH_3	0.13 ± 0.01		
OCH_3	3.1 ± 0.3	0.05	2.5

[a] Difference in the free energies as established by eq. 3.

yldiphenyltriazene using eq. 1 and making allowances only for the substituent polar effect (σ_0) gives a value $K_e = 0.71 \pm 0.06$ which is much higher than the experimental value. This fact can probably be attributed to the steric effect of the *ortho*-methyl groups. The presence of such an effect, in turn, points indirectly away from a symmetric mesomeric structure of the C_6H_5Hg derivative of diaryltriazene since a structural analysis of the C_6H_5Hg derivative of 2,2′-dimethyldiphenyltriazene, carried out on a Stewart-Brigleb model, demonstrates that in the case of a mesomeric structure (A) there is no Van der Waals interaction between the phenylmercury and *ortho*-methyl groups for any conformation caused by rotation about the C—N bonds. On the other hand, for an asymmetric structure (B), with certain fixed conformations, intense overlap of the Van der Waals spheres of the mercury atom and *ortho*-methyl group occurs. Thus, it is most likely that in solution C_6H_5Hg derivatives of diaryltriazenes possess an asymmetric structure where the mercury atom is bonded mainly to one or other of the terminal nitrogen atoms of the triazene chain, and which undergoes rapid metallotropic transformations.

So it may be reasonable to suggest that intermolecular exchange of arylmercury groups, observed earlier [1] in solutions of arylmercury derivatives of diaryltriazenes, is likely to proceed through an eight-membered transition state and represents an intermolecular tautomeric process. Thus, in the case of arylmercury derivatives of diaryltriazenes in solution, metallotropy is expected to occur by intramolecular and intermolecular mechanisms simultaneously but at different rates.

Turning now to a discussion of the systems involving *ortho*-substituted diaryltriazenes and their C_6H_5Hg derivatives containing *ortho*-substituents which have an unshared pair of electrons, it should be noted that in earlier studies there were indications that in the C_6H_5Hg derivatives of 2′-substituted benzenesulphonanilides there exists intramolecular coordination of the mercury atom with the *ortho*-substituent [2]. Owing to the fact that the structures of the corresponding fragments of the *ortho*-substituted phenylamine group in 2′-substituted benzenesulphonanilide and in 2,2′-disubstituted diaryltriazene are approximately the same, it is possible to analyse the magnitudes of the equilibrium constants for the reactions involving 2,2′-dihalo- and 2,2′-dimethoxy-substituted diaryltriazenes on the assumption that, as in the previous cases, the position of the equilibria under study are likely to be affected mainly by the following three factors: the polar effect of the substituents, its steric requirements, and the relative intensity of the hydrogen atom and phenylmercury intramolecular coordination with the *ortho*-substituent. The effect of the polar and steric factors can be allowed for by using eq. 4 which is a two-parameter correlation equation, where ρ and β are the constants which account for

$$\ln K = \rho \times \sigma_0 + \beta \times V_x + \gamma \qquad (4)$$

the contributions of the corresponding effects to the equilibrium constant value, and σ_0 and V_x are, respectively, the polar constant [3] and the Charton steric parameter [4] of the substituent and characterize its electronic effect and steric requirements [4]. It has been shown by Charton [4] that correlation equations of this type are well satisfied by a great many series of reactions in which the reaction rate or the equilibrium position is affected by the steric and polar effects of the substituents. When determining the coefficients in eq. 4 we assumed that the electronic effect of the *ortho*-substituent influences the equilibrium position with the same intensity as in the case of *para*- and *meta*-positions and that the magnitude of the equilibrium constant for reactions involving 2,2′-dimethyldiphenyltriazene is affected only by the polar and steric properties of the substituents. The following coefficient values were obtained: $\rho = 1.6, \beta = -1.4, \gamma = 0.06$. They were used for calculating the equilibrium constant K_c for the exchange reactions involving 2,2′-dihalo- and 2,2′-dimethoxy-substituted diphenyltriazenes. The data obtained are listed in Table 3 together with the corresponding values of σ_0 and the Charton V parameters. A comparison of the constants obtained with those obtained experimentally reveals that the calculated constant agrees with the experimentally derived constant only for the reaction involving 2,2′-difluorodiphenyltriazene, while in the other cases the calculated and experimental values differ by at least one order of magnitude. It is obvious that introduction of chlorine, bromine, iodine and methoxy group into the 2- and 2′-positions of diphenyltriazene stabilizes phenomenally the C_6H_5Hg derivatives when compared with the substituted diphenyltriazene and to a far greater extent than could be expected for the action of only the polar and steric effects of these substituents. This can be attributed to the fact that there exists in the C_6H_5Hg derivatives an intramolecular coordinative bond of the halogen or oxygen atom with the C_6H_5Hg group that is far stronger than the corresponding virtual intramolecular hydrogen bond in *ortho*-substituted diphenyltriazene.

The data obtained correspond essentially to already published results concerning the relative strength of chelate rings formed by the hydrogen atom and phenylmercury group in 2′-substituted benzenesulphonanilides and their C_6H_5Hg derivatives [2].

Consideration of the Stewart-Brigleb molecular models for symmetric mesomeric structures of the C_6H_5Hg derivatives of 2,2′-disubstituted diphenyltriazene shows that in this case intramolecular coordinative interaction of the phenylmercury group with the oxygen or halogen atom is impossible because there is no overlap of the Van der Waals spheres of the mercury atom and the corresponding *ortho*-substituents. The intramolecular coordination found in the compounds under study is thus an indirect indication of the fact that the C_6H_5Hg derivatives of diaryltriazenes have an asymmetric structure, in which the C_6H_5Hg group is bonded to one terminal atom of the triazene chain and which undergoes rapid metallotropic transformations.

The results obtained make it possible to calculate the difference in the free energies of the formation of the mercury—halogen or —oxygen coordinative intramolecular bond and the virtual intramolecular hydrogen bond by eq. 5

$$\Delta(\Delta G) = 2.3RT(\ln K_1 - \ln K_c) \qquad (5)$$

where R is the gas constant (1.99 cal/mol · degree), T is the experimental temperature (307 K). The results of calculations are given in Table 3.

Consideration of the $\Delta(\Delta\ G)$ values demonstrates that, as in the case of benzenesulphonanilides and their C_6H_5Hg derivatives, the intramolecular coordinative bond between Cl, Br or I and the methoxy group turns out to be stronger for the phenylmercury group than for the hydrogen atom.

TABLE 4

MELTING POINTS AND ANALYTICAL DATA FOR SUBSTITUTED DIARYLTRIAZENES AND THEIR PHENYLMERCURY DERIVATIVES

Compound	M.p. (°C) (dec.)	Analyses (found (calcd.) (%))		
		C	H	N
$(2\text{-BrC}_6\text{H}_4)_2\text{N}_3\text{H}$	111	40.59 (40.60)	2.56 (2.56)	11.89 (11.35)
$(2\text{-IC}_6\text{H}_4)_2\text{N}_3\text{H}$	143	32.01 (32.09)	2.00 (2.02)	9.10 (9.36)
$(3\text{-FC}_6\text{H}_4)_2\text{N}_3\text{HgC}_6\text{H}_5$	178—179	42.32 (42.36)	2.63 (2.55)	7.58 ((7.49)
$(4\text{-CH}_3\text{C}_6\text{H}_4)_2\text{N}_3\text{HgC}_6\text{H}_5$	209—210	47.87 (47.85)	3.93 (3.79)	8.48 (8.37)
$(2\text{-CH}_3\text{C}_6\text{H}_4)_2\text{N}_3\text{HgC}_6\text{H}_5$	159—160	48.26 (47.81)	3.80 (3.79)	8.52 (8.37)
$(4\text{-CH}_3\text{OC}_6\text{H}_4)_2\text{N}_3\text{HgC}_6\text{H}_5$	148	45.67 (44.98)	3.53 (3.59)	8.04 (7.87)
$(2\text{-ClC}_6\text{H}_4)_2\text{N}_3\text{HgC}_6\text{H}_5$	166—167	39.79 (39.82)	2.39 (2.41)	8.37 (7.74)
$(2\text{-BrC}_6\text{H}_4)_2\text{N}_3\text{HgC}_6\text{H}_5$	167	33.55 (34.18)	1.97 (2.06)	6.61 (6.65)
$(2\text{-IC}_6\text{H}_4)_2\text{N}_3\text{HgC}_6\text{H}_5$	188	29.84 (29.79)	1.79 (1.81)	5.81 (5.79)
$(2\text{-CH}_3\text{OC}_6\text{H}_4)_2\text{N}_3\text{HgC}_6\text{H}_5$	136—137	44.35 (44.98)	3.37 (3.58)	7.86 (7.87)

Experimental

Equilibrium constants for reaction 2 were determined from the integrated intensities of the PMR signals of the *ortho*-methyl groups of 2-methylbenzenesulphonanilide and its C_6H_5Hg derivatives. PMR spectra were obtained on R-20 Hitachi-Perkin-Elmer and R-32 Perkin-Elmer spectrometers. Concentrations of the starting reagents were all 0.05 *M*. Chlorobenzene purified by a conventional technique, was used as the solvent.

Calculations of the equilibrium constants for reaction 1 were based on the simple assumption that if one knows the equilibrium constants K_1 and K_2 of the reactions

$$\mathrm{MA} + \mathrm{M^{*}B} \overset{K_1}{\rightleftharpoons} \mathrm{MB} + \mathrm{M^{*}A}$$

and

$$\mathrm{MC} + \mathrm{M^{*}B} \overset{K_2}{\rightleftharpoons} \mathrm{MB} + \mathrm{M^{*}C}\,,$$

then the constant K_3 of the reaction

$$\mathrm{MA} + \mathrm{M^{*}C} \overset{K_3}{\rightleftharpoons} \mathrm{MC} + \mathrm{M^{*}A}$$

may be derived from

$K_3 = K_2/K_1$

The substituted diphenyltriazenes were obtained by diazoization of the substituted anilines and subsequent reaction of the resultant aryldiazonium salt with the corresponding aniline [3].

The C_6H_5Hg derivatives of the diaryltriazenes under study were synthesized by the action of phenylmercury hydroxide on the corresponding triazenes [1].

The melting point of the previously reported substituted diaryltriazenes and their C_6H_5Hg derivatives showed a good agreement with the published data. Melting points and analytical results for the substituted diaryltriazenes and their phenylmercury derivatives that have not been described in the literature are listed in Table 4.

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