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Distribution of the Products of Benzhydryl Bromide Heterolysis in the Presence of Triphenylverdazyl in Aprotic Solvents

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Abstract—The distribution of products of benzhydryl bromide heterolysis in the presence of triphenylverdazyl in anhydrous nitrobenzene and propylene carbonate, as well as in anhydrous acetonitrile in the presence of benzyltriethylammonium chloride was studied. In kinetic experiments the contribution of verdazyl alkylation was always minor, and verdazyl was mostly consumed in the reaction with HBr evolved during solvolysis. Thus, triphenylverdazyl is not an indicator of the solvent-separated ion pair of benzhydryl bromide. **DOI:** 10.1134/S1070363206050239

Dvorko and co-workers [1, 2] have put forward and substantiated the hypothesis that triphenylverdazyl (I) in aprotic solvents selectively and quantitatively reacts with solvent-separated ion pairs formed on monomolecular heterolysis of substrates [reaction (1)]. By contrast, our data [3] on the product distribution in benzhydryl bromide heterolysis in anhydrous acetonitrile in the absence of salts show that in these conditions verdazyl prefers to react with the acid formed by solvolysis of the substrate [reaction (2)].



As an argument in favor of their theory [1] Dvorko and Ponomareva have adduced the correlation of the rate of consumption of verdazyls with their concentration and structure, observed in heterolysis of a series of substrates in the presence of certain salts. The referees explained this effect in terms of verdazyl–salt competition the cationoid intermediate, but did not find out product distribution under those conditions. To our knowledge, the benzhydryl system exhibited such behavior in the heterolysis of benzhydryl bromide in acetonitrile in the presence of benzyltriethylammonium chloride or tetraethylammonium iodide [4].

Proceeding with this discussion, we have studied the distribution of products in the above reaction system. As seen from Table 1 (exp. nos. 1 and 2), substrate solvolysis is still always prevailing, while increased concentration of verdazyl in the presence of salt actually slightly increases the initial reaction rate. Thus, the observed dependence of reaction rate on verdazyl concentration is not associated with verdazyl– salt competition for the cationoid intermediate.

It is known that preparative reactions of certain compounds with triphenylverdazyl in acetonitrile give products comprising a solvent molecule. Even though

Exp. no.	[RX], M	$c_{\text{init}} \times 10^4$, M	$c_0 \times 10^4$, M	$c_{ m min} imes 10^4 \ { m M}$	$c_{\max} \times 10^4$ M	α	$k \times 10^6,$ s^{-1}	$k \times 10^6,$ s^{-1}			
Acetonitrile, 25°C											
1	0.053	2.05	2.00	0.23	1.87	0.90^{d}	0.98 ± 0.03	0.86^{c}			
2	0.056	0.822	0.797	0.115	0.720	0.86 ^d	0.85 ± 0.05	0.76 ^c			
				Propylene of	carbonate, 25	5°C					
3	0.022	1.27	1.22	0.26	1.22	0.97^{d}	4.25 ± 0.10	4.61±0.07 [5]			
4	0.020	1.25	1.14	0.26	1.19	0.92^{d}	4.39 ± 0.06				
Nitrobenzene, 40°C											
5	0.050	1.26	1.11	0.22	1.06	0.65 ^e	0.185 ± 0.011	0.16 [†]			
6	0.050	1.25	1.21	0.44	1.14	0.82 ^e	0.21 ± 0.04				

Table 1. Product distribution in heterolysis of benzhydryl bromide in the presence of triphenylverdazyl in acetonitrile,^a propylene carbonate, and nitrobenzene^b

^a In the presence of Et₃PhCH₂NCl (*c* 3.11×10⁻⁴ M). ^b For denotations of concentrations, see the legend for formula (3). ^c Interpolated over data in [4]. ^d By formula (3). ^e By formula (4). ^f Interpolated over data in [6].

this circumstance has no effect on reaction kinetics and product distribution [2, 7], we also studied the product distribution in benzhydryl bromide heterolysis in the presence of triphenylverdazyl in chemically inert solvents [8], viz. anhydrous propylene carbonate and nitrobenzene. For reducer in propylene carbonate we used the same reagent as in acetonitrile [3] (Table 2, exp. nos. 1–4). The contribution of pathway (2) in the apparent rate constant in this solvent was calculated by formula (3).

$$\alpha = \frac{2(\Delta c - \Delta c_{\rm r} + \Delta c_0)}{\Delta c} \,. \tag{3}$$

Here $\Delta c_0 = c_{\text{init}} - c_0$ is the jumpwise fall of the verdazyl concentration on addition of benzhydryl bromide; $\Delta c = c_0 - c_{\text{min}}$, verdazyl consumption during the reaction; and $\Delta c_r = c_{\text{max}} - c_{\text{min}}$, increase of the radical concentration on addition of reducer.

In nitrobenezene, satisfactory results were obtained with *N*,*N*-dimethyl-*p*-anisidine as a reducer. This reducer provides quantitative regeneration of verdazyl from salt (Table 2, exp. nos. 8 and 9), but the degree of regeneration of the radical from its reaction products with HCl is slightly lower in this case (r 0.94, Table 2, exp. nos. 5–7).¹ With this in mind, the contribution of pathway (2) can be calculated by formula (4).

$$\alpha = \frac{2\Delta c_{\rm r} - 2r\Delta c_0 - \Delta c}{\Delta c(2r - 1)} \,. \tag{4}$$

As seen from Table 1 (exp. nos. 3–6), our measured rate constants of benzhydryl bromide heterolysis in both the solvents fairly fit those reported in [5, 6]. However, in our case, too, the substrate hydrolysis still remains the prevailing pathway. The slightly larger contribution of verdazyl alkylation in nitrobenzene is probably explained by the fact that this solvent contains slightly less water.

Table 2. Regeneration of triphenylverdazyl for its reaction products with HCl and from triphenylverdazylium bromide in propylene carbonate at 25° C and in nitrobenzene at 40° C

Exp. no.	Starting compound	$c_{\text{init}} \times 10^4,$ M	$c_{\min} \times 10^4$, M	$c_{\max} \times 10^4,$ M	r^{a}						
Propylene carbonate (Reducer A) ^b											
1	I + HCl	1.35	0.329	1.33	0.98						
2		1.35	0.395	1.33	0.98						
3	IIIc	1.39	_	1.44	1.00						
4		1.32	_	1.31	0.99						
Nitrobenzene (Reducer B) ^b											
5	$\mathbf{I} + \mathbf{HCl}$	3.16	0.96	3.01	0.93						
6		1.04	0.56	1.02	0.95						
7		0.97	0.23	0.92	0.93						
8	III ^c	1.36	_	1.33	0.98						
9		0.53	—	0.52	0.98						

^a (*r*) Degree of regeneration of compound **I**, $r = \Delta c_r / \Delta c$. ^b (*A*) One drop of 33% *p*-anisidine and 10% morpholine in propylene carbonate per 1 ml of the reaction mixture; (*B*) 2.5 mg of *N*,*N*-dimethyl-*p*-anisidine per 1 ml of the reaction mixture.

^c Triphenylverdazylium bromide, initial concentration by the absorption at 540 nm.

¹ Reduction with a mixture of *N*,*N*-dimethyl-*p*-anisidine and *N*-methylmorpholine in nitrobenzene was not studied. With pure *N*,*N*-dimethyl-*p*-anisidine in propylene carbonate, an unsatisfactory result was obtained (*r* 0.59).

Thus, under conditions of conventional kinetic experiments triphenylverdazyl cannot serve as indicator on the solvent-separated ion pair of benzhydryl bromide. In our opinion, there are no reasons why in all other cases in the absence of special protection from moisture one would expect complete capture of cationoids with verdazyl. Since with most substrates the above method is unsuitable for studying the product distribution [2], we consider the theory in question experimentally unsubstantiated and problematic for wide verification.

EXPERIMENTAL

All experiments were performed as described in [3]. Propylene carbonate was purified as described in [5]. Nitrobenzene was twice distilled in a vacuum over P_2O_5 and once over BaO. Benzyltriethylammonium chloride was prepared from triethylamine and benzyl chloride in acetonitrile, recrystallized from the same solvent, and dried in a vacuum at 100°C. The measurement errors were calculated at a 95% confidence level.

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