HEXAHYDROTETRAZINES FROM AZOMETHINEIMINES

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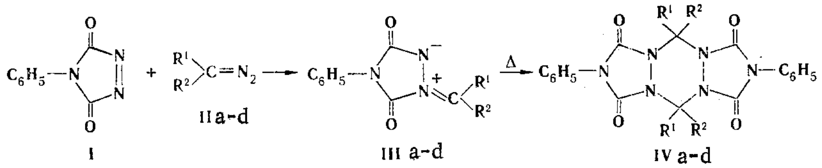
The thermal and photochemical decomposition of azomethineimines obtained from 4-phenyl-1,2,4-triazoline-3,5-dione and a number of diaryldiazomethanes leads to the formation of the corresponding dimers, viz., perhydrobis(1,2,4-triazolo[1,2-a;1,2-d]1,2,4,5-tetrazinyls). Dimerization is irreversible in both cases.

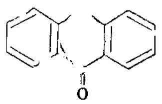
It is known that azomethineimines are inclined to undergo thermal dimerization [1-4], but, at the same time, there has been only one report of a similar sort of transformation under conditions of UV irradiation of azomethineimines [1], which, however, are not capable of dimerization in the ground state.

We have observed both thermal and photochemical dimerization of azomethineimines obtained from 4-phenyl-1,2,4-triazoline-3,5-dione (I) and aryl-substituted diazo compounds of the aliphatic series (IIa-d) [5]:



II—IV a $R^1=R^2=Ph$; b $R^1=Ph$, $R^2=C_6H_4OCH_3$-*p*; c $R^1=Ph$, $R^2=1$- naphthyl;

d $R^1—R^2=$



Thus colorless substances (Table 1) were isolated after removal of the solvent when benzene solutions of azomethineimines IIIa-d were refluxed until the intense color of the starting compounds had vanished; the results of elementary analysis of these products, the results of determination of their molecular masses, and their spectral characteristics made it possible to assign to them the structure of dimers, which are evidently formed by "head-to-tail" drawing together of the starting molecules.

In the IR spectra of the dimers the absorption bands of the carbonyl groups are shifted to the short-wave region by several tens of reciprocal centimeters, and this constitutes evidence for the disappearance of the dipolar character in the transformation products [5] (see Table 2). The UV spectra of dimers IVa-d do not contain the absorption bands in the

TABLE 1. Perhydrobis(1,2,4-triazolo[1,2-a; 1,2-d]1,2,4,5-tetrazinyl) Derivatives IVa-d

Compound	mp, °C	Found, %			Empirical formula	Calc., %			Yield, %
		C	H	N		C	H	N	
IVa	219—221	73,8	4,8	12,5	$C_{21}H_{15}N_3O_2$	73,8	4,4	12,3	100
IVb	123—124	71,2	5,0	11,0	$C_{22}H_{17}N_3O_3$	71,2	4,6	11,3	100
IVc	122—123	76,8	4,5	10,6	$C_{25}H_{17}N_3O_2$	76,7	4,4	10,7	100
IVd	175—176	71,9	3,6	11,4	$C_{22}H_{13}N_3O_3$	72,1	3,6	11,3	75

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TABLE 2. Position of the νCO Band in the IR Spectra of Azomethineimines IIIa-d and Their Dimers IVa-d

Compound	νC=O, cm^{-1}	Compound	νC=O, cm^{-1}
IIIa	1720 1815	IVa	1770 1820
IIIb	1725 1810	IVb	1765 1820
IIIc	1715 1810	IVc	1765 1820
IIId	1720 1820	IVd	1765 1820

long-wave region that are characteristic for starting azomethineimines IIIa-d.

Azomethineimines IIIa-c are converted virtually quantitatively to the corresponding dimers, which are the only reaction products here. In the case of azomethineimine IIId, a polymerization product (25%) is formed in addition to the dimer.

Ultraviolet irradiation of azomethineimines IIIa-d leads to the formation of multicomponent mixtures, in the composition of which dimers IVa-d were detected. In the case of azomethineimine IIIb the dimer was isolated in 11% yield. The constants of the isolated compound and its spectral characteristics were in complete agreement with the properties of dimer IVb obtained via the thermal route. No melting-point depression was observed for a mixture of the two substances.

Let us note that, in contrast to the photodimerization of azomethineimines described in [1], dimerization is irreversible in this case.

EXPERIMENTAL

The IR spectra of solutions of the compounds in chloroform were recorded with a UR-20 spectrometer. The UV spectra of solutions in chloroform were recorded with a Perkin–Elmer M-402 spectrophotometer. Ultraviolet irradiation was carried out by means of a Hanau S-81 high-pressure mercury lamp (110-125 W) in an apparatus with a quartz filter ($\lambda > 210$ nm) in tetrahydrofuran.

2,5,5,8,11,11-Hexaaryl-1,3,7,9-tetraoxoperhydrobis(1,2,4-triazolo[1,2-a;1,2-d]-1,2,4,5-tetrazinyls) (IVa-c). A solution of 0.4 mmole of the corresponding azomethineimine (III) [5] in 40-70 ml of benzene was refluxed for 2-3.5 h until the color changed from dark red to light yellow. The benzene was removed in the vacuum created by a water aspirator. Colorless crystals of dimers IVa-c were precipitated when a mixture of hexane with a small amount of ether was added to the residual oil. Analytically pure samples were obtained by means of column chromatography on L 40/100 silica gel with ether–hexane (1:3) at the eluent.

Hexahydrotetrazine IVd. A solution of 0.4 mmole of azomethineimine IIId [5] in 40 ml of benzene was refluxed until the color changed from dark cherry-red to light yellow (1.5 h), during which a polymer precipitated. The precipitate was removed by filtration, and the reaction mixture was then worked up as described for IVa-c.

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