

Reaction of Aryldiazonium Chlorides with 1,3,5-Triketones. An Evidence for the Azohydrazone Conversion

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The coupling reactions of diazonium chlorides with *sym*-1,3,5-triketones are described. The azo-form of the products is rearranged into the hydrazo-form during this reaction. Dihydrazones (I) were formed in the sodiumacetate buffered solution while in the sodium hydroxide solution both (I) and monohydrazones (II) were formed. The spectroscopic analysis, based on the data from infrared and ultraviolet spectra, indicates that dihydrazones exist in the double *syn*-form with an intramolecular hydrogen bond.

It is well known that β -diketones in the presence of a weak base readily react with a diazonium ion to yield monohydrazones¹. Only two cases of such coupling are known for compounds having two active methylene groups where the cleavage of the new molecule does not take place^{2,3}. The coupling of aryldiazonium salts with 1,6-diaryl-1,3,4,6-hexanetetrone gave only formazans⁴.

We wish to describe coupling reactions of the diazonium salts with diaroyl acetones (*sym*-1,3,5-triketones). In these reactions the azo-form is rearranged into the tautomeric hydrazo-form during the coupling and diarylhydrazones of pentaoxo compounds were obtained. Such compounds with five cumulated carbonyl groups are not described yet. The structures of new compounds have been elucidated by spectroscopic methods.

RESULTS AND DISCUSSION

The coupling reactions of diazonium ions with *sym*-1,3,5-triketones were carried out in a sodium acetate buffered solution according to Scheme 1. The series of compounds (I) was obtained (Table I). The colour of the products varied from yellow to red.

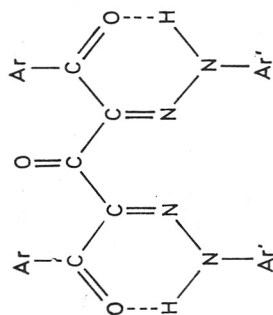
The coupling reaction of 1,5-di-(*p*-tolyl)-1,3,5-pentanetrione with benzenediazonium chloride in an excess of sodium hydroxide was also performed. A mixture of hydrazone (Ib) and monohydrazone (II) resulted (Scheme 1).

The yields and elementary analyses for all the new products prepared are given in Table I.

* Taken in part from the M. Sc. Thesis.

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TABLE I
1,5-Diaryl-1,2,3,4,5-pentamptone 2,4-diarylhvdrzones*



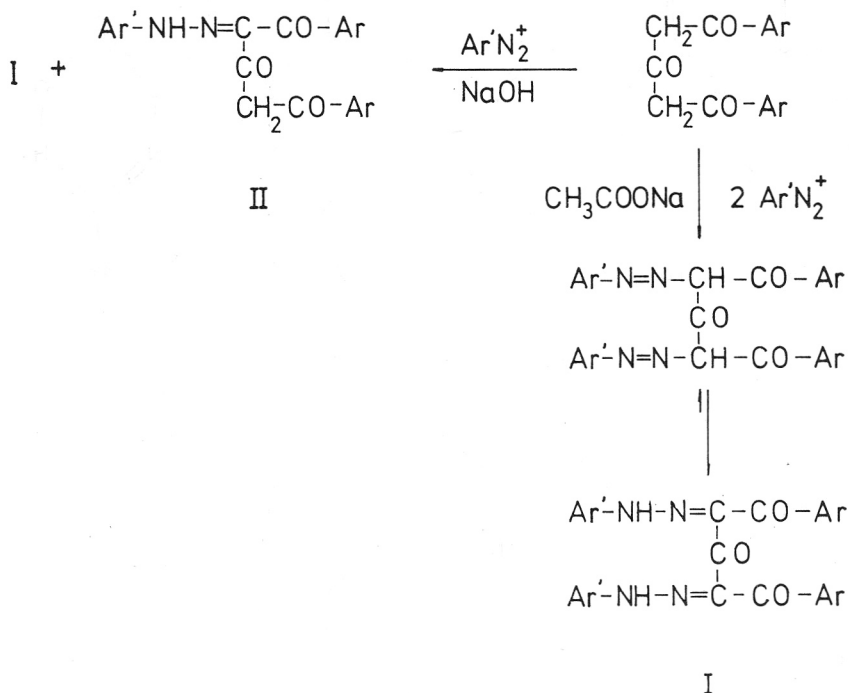
No.	Ar	Ar'	M. p./°C	Formula	Calc'd. %				Found %			
					C	H	N	Cl	C	H	N	Cl
Ia**	C ₆ H ₅ —	C ₆ H ₅ —	84	C ₃₀ H ₂₈ N ₄ O ₄	71.13	5.17	11.06	—	71.42	5.14	11.21	—
Ib	<i>p</i> -CH ₃ C ₆ H ₄ —	C ₆ H ₅ —	82	C ₃₁ H ₂₆ N ₄ O ₃	74.08	5.22	11.15	—	74.20	5.02	11.42	—
Ic	C ₄ H ₉ S—	C ₆ H ₅ —	81	C ₂₅ H ₁₈ N ₄ S ₂ O ₄	61.71	3.73	11.52	13.18	61.99	4.01	11.24	12.93
Id	<i>p</i> -CH ₃ OC ₆ H ₄ —	C ₆ H ₅ —	75	C ₃₁ H ₂₆ N ₄ O ₅	69.65	4.90	10.48	—	69.87	5.15	10.76	—
Ie	<i>p</i> -ClC ₆ H ₄ —	C ₆ H ₅ —	77	C ₂₉ H ₂₀ N ₄ Cl ₂ O ₃	64.09	3.71	10.58	—	64.29	4.01	10.58	13.33
If***	C ₆ H ₅ —	<i>p</i> -CH ₃ C ₆ H ₄ —	90	C ₃₁ H ₂₆ N ₄ O ₃	74.08	5.22	11.15	—	74.21	5.51	11.44	—
Ig	<i>p</i> -CH ₃ C ₆ H ₄ —	<i>p</i> -CH ₃ C ₆ H ₄ —	81	C ₃₃ H ₃₀ N ₄ O ₃	74.69	5.70	10.56	—	74.59	5.94	10.69	—

* Except for the If, which was recrystallized from glacial acetic acid, for all other compounds the solvent was *o*-xylene.

** Corresponds to semiketal structure on the central carbon atom.

*** Deuterated If was prepared by recrystallization from CD₃COOD. M.p. was the same as for the nondeuterated If.

Scheme 1



Although the products of the described coupling reactions are hydrazones, there are some difficulties in the elucidation of their structure. First, it is possible that azo-compounds (III) which are initially formed are in an equilibrium with corresponding enols (IIIa) which could form an intramolecular hydrogen bond. Another structural problem is a possible existence of geometrical (*syn*- and *anti*-) isomers. All possible structural forms are presented in Fig. 1.

Due to the very poor solubility of the products it was not possible to record n. m. r. spectra. Therefore, we have analysed i. r. spectra in detail, and supported this investigation with u. v. spectra.

Infrared spectra

From the previous studies of Korobkov⁵ and Shapiro *et al.*⁶ and a number of other similar investigations⁷⁻¹¹ it was concluded that, if a six-membered ring containing conjugated C=O and C=N groups was formed in phenylhydrazones, strong hydrogen bonding took place. Therefore, we have assumed, that our compounds exist in the form IV (double *syn*-form).

Since numerous i. r. absorption bands of such molecules overlap, it is difficult to make an assignment even in the case of products obtained from monoketones. Thus, a band in the 3300 cm⁻¹ region can be assigned to both NH and OH stretching, and it is practically impossible to distinguish between them if a hydrogen bond exists¹². However, if a band in the C=O stretching

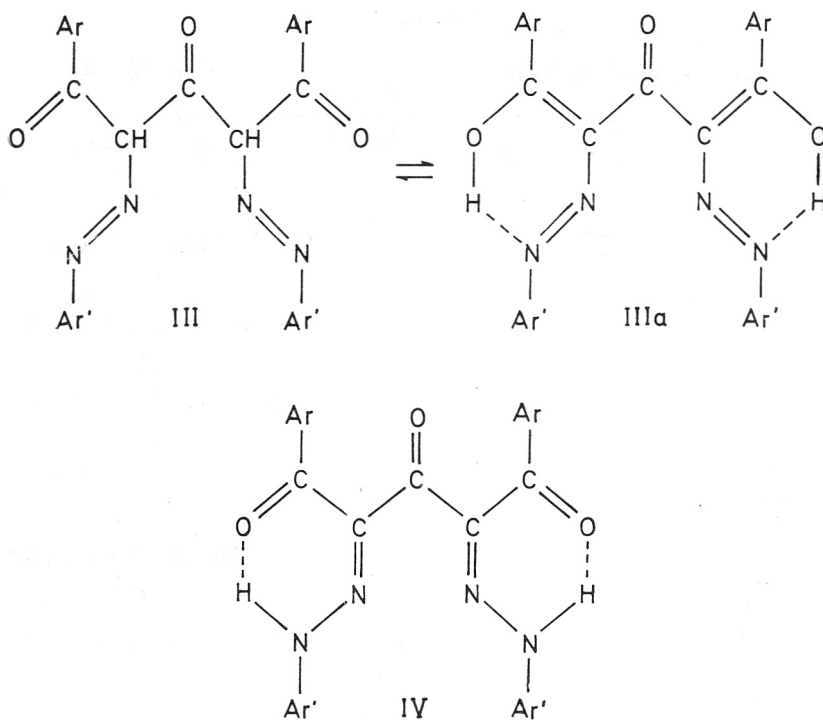


Fig. 1.

region is found, the band in the 3300 cm^{-1} region is due to the NH stretching, and NH deformation bands should support the existence of the hydrazone. In the case of the azo-form there is no absorption in the $\text{C}=\text{O}$ stretching region and the band in the 3300 cm^{-1} region can be attributed to the OH stretching.

We have observed bands in the range $3197\text{--}3150\text{ cm}^{-1}$ which we assigned to the hydrogen bonded NH stretches. This is in agreement with other cases of the $\text{NH}\dots\text{O}$ bonds^{11,13-17} in structurally similar compounds. A free NH group absorbs in the $3500\text{--}3200\text{ cm}^{-1}$ region¹⁸ as proved by cases where no hydrogen bond¹⁹ or where both forms exist¹³.

The double *syn*-form of our dihydrazones was confirmed by the band assignment in the $1700\text{--}1400\text{ cm}^{-1}$ region. In this region two infrared active $\text{C}=\text{O}$ stretching modes are expected. The intensive bands between 1652 cm^{-1} and 1629 cm^{-1} were assigned to the stretching of the central carbonyl group. Since this group is conjugated with two $\text{C}=\text{N}$ groups, its stretching wavenumber is lower than that for nonconjugated $\text{C}=\text{O}$ group in azo-compounds²⁰. The absorption in the 1650 cm^{-1} region could also correspond to form IIIa, but in this case there would be no absorption characteristic for the $\text{Ar}-\text{CO}$ group (see later). This band for enols is very broad and shifted to a lower wavenumber, as for β -diketones¹⁶.

$\text{ArC}=\text{O}$ stretching wavenumbers were found between 1610 and 1585 cm^{-1} and overlapped with benzene ring absorption bands. The carbonyl stretching

bands are more shifted towards lower values than in double conjugated ketones due to the carbon—oxygen link weakened by the hydrogen bond. However, the bands did not become broad and less intensive as one could expect. They stayed narrow and intensive. The same was noticed in β -diketones²¹, in compounds with conjugated C=O and C=N bonds⁶, in phenyl hydrazones of 1,2-diketones²², and in enaminketones²³. Such an effect is due to a conjugate hydrogen-bonded system with the ionic structure IVa (Fig. 2).

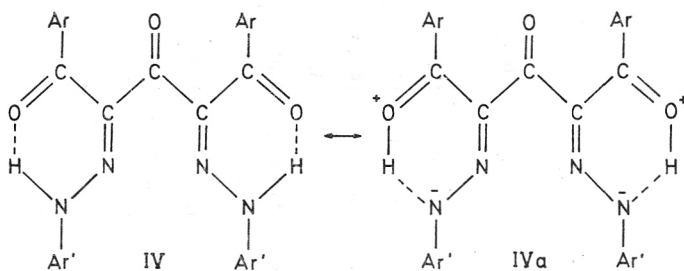


Fig. 2.

The C=N stretching band is not easy to assign, because it appears in a region where many other bands appear. The bands in the 1577—1565 cm^{-1} range was assigned to this mode, which is in accordance with the assignments of other authors^{9,11,14} for structurally similar compounds. This band position is not affected by the substitution in aromatic rings.

The bands in the 1500 cm^{-1} region are also difficult to assign. Hadži^{7,24} claims that they are the combination bands of the NH deformation and of some skeletal modes. Mecke and Funk²⁵ attributed these bands to the stretching of the conjugated skeleton.

To make this point clear, we compared the spectrum of the deuterated If compound* with that of the normal species. The band at 1500 cm^{-1} of the normal species disappeared and the new band in the deuterated compound at 1099 cm^{-1} appeared. Other bands preserved their positions. Hence, we assigned the former band to the NH deformation and the later one to the skeletal vibration.

Other bands at 1500 cm^{-1} and 1450 cm^{-1} were assigned to aromatic ring vibrations. Bands in the 1312 and 1302 cm^{-1} regions which were not present in triketones were assigned to Ar'-N stretches^{13,26}.

Infrared data are summarized in Table II.

Ultraviolet and visible spectra

The data for u. v. and vis. spectra are presented in Table III.

The band at 271—287 nm, due to conjugated C=O and C=N chromophores, is very strong. For Ia, Ig, and II it appears as the shoulder, whereas it is a »pure« band for Ic and Id, and does not appear for Ib, Ie, and If. One could expect it at higher wavelengths but here the $\pi \rightarrow \pi^*$ transition effect is probably suppressed by the hydrogen bonding effect. It decreases the

* See Table I.

TABLE II

No.	Ar	Ar'	$\tilde{\nu}/\text{cm}^{-1}$						
			ν_{NH}	$\nu_{\text{C=O}}$ (central)	$\nu_{\text{C=O}}$ (ArCO)	$\nu_{\text{C=N}}$	δ_{NH}	skeletal	$\nu_{\text{Ar-N}}$
Ia	C ₆ H ₅ —	C ₆ H ₅ —	3197 w	1652 vs	1600 m	1577 m	1510 s	1461 s	1305 s
Ib	<i>p</i> -CH ₃ C ₆ H ₄ —	C ₆ H ₅ —	3177 w	1645 vs	1604 s	1569 m	1497 s	1452 s	1308 s
Ic	C ₄ H ₉ S—	C ₆ H ₅ —	3190 w	1629 vs	1593 m	1569 m	1498 s	1452 s	1302 m
Id	<i>p</i> -CH ₃ OC ₆ H ₄ —	C ₆ H ₅ —	3180 w	1644 vs	1598 vs	1573 m	1502 s	1452 s	1309 m-s
Ie	<i>p</i> -ClC ₆ H ₄ —	C ₆ H ₅ —	3190 w	1649 vs	1585 vs	1565 m-s	1501 s	1452 s	1305 s
If	C ₆ H ₅ —	<i>p</i> -CH ₃ C ₆ H ₄ —	3150 w*	1643 vs	1610 vs	1572 m	1500 s**	1451 s	1312 s
Ig	<i>p</i> -CH ₃ C ₆ H ₄ —	<i>p</i> -CH ₃ C ₆ H ₄ —	—	1642 vs	1602 vs	1568 m	1493 s	1452 s	1308 s
II	<i>p</i> -CH ₃ C ₆ H ₄ —	C ₆ H ₅ —	3180 w	1651 vs	1608 vs	1569 m	1509 s	1460 s	1302 s

* For the deuterated if a weak $\nu(\text{ND})$ band appeared at 2340 cm⁻¹.** For the deuterated if a strong $\delta(\text{ND})$ band appeared at 1099 cm⁻¹.

TABLE III*

No.	$\lambda_{\max.}/\text{nm}$ (u. v)				$\lambda_{\max.}/\text{nm}$ (vis.)
	E	B			
Ia	—	249	280 sh	—	419
Ib	218	257	—	—	423
Ic	224	—	271	—	410
Id	229	255	287	—	418
Ie	—	257	—	—	422
If	233	248	—	344**	430
Ig	—	255	282 sh	—	425
II	222	253	282 sh	—	418

* See text.

** Observed only for this compound.

energy of the n -electron level and so this band has not a great bathochromic shift.

The band at 410—430 nm in the visible region of the spectrum is very strong for all the compounds. It is caused by the pronounced conjugation of the entire system (cf. formula IV). Five chromophores are mutually conjugated — three C=O and two C=N groups — or even seven if one accounts the conjugation of aromatic rings with C=O groups.

This system is additionally stabilized by the hydrogen bond which increases its resonance energy. The resonant structures and the possibility of polar forms (Fig. 2) are dominating in comparison with the weak inductive effect. That is obvious from the fact that maxima are only slightly shifted. Therefore we consider this as the additional support to our conclusion that compounds studied exist as diarylhydrazones in the double *syn*-form. Elguero *et al.*²⁷ and Venien¹⁴ came to similar conclusions.

EXPERIMENTAL

The melting points were determined on a Kofler heating microscope and are uncorrected. The i. r. spectra were recorded as KBr pellets with a Perkin-Elmer Model 221 spectrophotometer between 4000 and 667 cm^{-1} . The u. v. and vis. spectra in dioxane were recorded on Perkin-Elmer UV/VIS models 137 and 124, respectively.

Coupling reactions in sodium acetate buffered solution (Ia—Ig)

General procedure: The sym-1,3,5-triketone* (0.01 mol) was dissolved in a 250 ml flask in 80 ml methanolic solution of 0.8 g NaOH and 6.4 g sodium acetate. After diluting with water to 160 ml, this mixture was stirred and cooled to 0—5 °C. A diazonium chloride solution was prepared by dissolving the aromatic amine (0.02 mol) in 16 ml of 5 M HCl, cooling to 0 °C, and adding sodium nitrite (1.4 g) in a saturated water solution at 0 °C.

The diazonium salt solution was added dropwise to the triketone solution. Almost instantaneously upon addition, a yellow product was formed, which became orange and red in the course of the reaction. After the addition of the diazonium salt solution was completed, the mixture was stirred for 30 min at low temperature, followed by 3 hours at room temperature, and then left to stand overnight. The crude product was filtered off, washed with methanol and dried in air. The crude

* Prepared according to ref. 28.

products were obtained in good yields. After recrystallizations from the corresponding solvent pure products were obtained.

The data for dihydrazones (Ia—Ig) are summarized in Table I.

Coupling reaction with the excess of sodium hydroxide (II)

To prepare the monohydrazone (II), 2.49 g (0.01 mol) of 1,3-di(*p*-methylbenzoyl)acetone was dissolved in 130 ml of methanol to which a solution of 2.1 g (0.052 mol) of NaOH in 100 ml of water was added with stirring in a 500 ml flask. The mixture was cooled to 0–5 °C and a diazonium chloride solution was added dropwise.* The colour of the solution changed from yellow to red, and then an orange product was formed which turned to red in the course of the reaction.

After the addition of the diazonium chloride solution was completed, the mixture was stirred for 30 min at low temperature and for 1 and 1/2 hours at room temperature, and then left to stand overnight. The crude product was filtered off and dried in air. This product was dissolved in 8 ml of chloroform, gently warmed and stirred with 80 ml of petroleum ether added from a dropping funnel in 8 ml portions. The precipitate was separated and again treated with chloroform and petroleum ether, respectively. Combined dark red solutions after cooling overnight gave yellow needles in 30% yield, m.p. 125–130 °C. The recrystallization from absolute alcohol gave yellow needles, m.p. 131–134 °C (II). The residue in the flask was recrystallized from *o*-xylene to give 42% of reddish crystals, m.p. 192–206 °C (Ib)**.

1,5-Di(*p*-tolyl)-1,2,3,5-pentantetrone 2-phenylhydrazone (II) yellow needles, yield 30%, m.p. 131–134 °C.

Anal. C₂₅H₂₂N₂O₃ (298.44) calc'd: C 75.36; H 5.57; N 7.03%
found: C 75.22; H 5.58; N 7.05%

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* Prepared by dissolving of 3.92 g (0.04 mol) of aniline in 32 ml 5 N HCl, cooling to 0 °C and adding sodium nitrite (2.8 g) in saturated water solution at 0 °C.

** By multiple recrystallizations from *o*-xylene one obtains a product with m.p. 215–219 °C. Its i.r. spectrum is identical with Ib obtained in the sodium acetate buffered solution. The mixed melting point shows no decrease.

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SAŽETAK

Reakcija arildiazonijevih klorida s 1,3,5-triketonima. Dokaz azo-hidrazonske pretvorbe

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Reakcijom arildiazonijevih klorida sa simetričnim 1,3,5-triketonima nastaju di-arilhidrazoni 1,5-diaril-1,2,3,4,5-pentanpentona kao produkt pretvorbe početnoga azo-oblika u tautomerni hidrazonski oblik. U suvišku natrijeva hidroksida uz diarilhidrazone nastaju i monoarilhidrazoni 1,5-diaril-1,2,3,5-pentantetrona. Analizom infracrvenih i ultraljubičastih spektara određena je struktura produkata.

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