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"ENE" ADDUCTS OF N-SUBSTITUTED TRIAZOLINEDIONES.

3.* SYNTHESIS OF NOVEL TYPES OF IMIDOURAZOLES FROM N-SUBSTITUTED cis-CYCLOHEX-4-ENE-1,2-DICARBOXIMIDES

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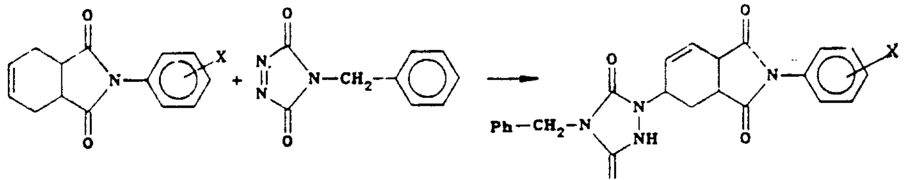
Some novel "ene" adducts of N-aryl-cis-cyclohex-4-ene-1,2-dicarboximides (N-Ar-cis-4-CHDI), and its cis,cis-3-methyl- and cis-4-methyl derivatives, to 4-benzyl-1,2,4-triazoline-3,5-dione (4-benzyl-TAD) have been prepared and characterized.

The "ene" reaction of 4-substituted TAD with olefins has been studied extensively [3-6]. Also reported has been the reaction of 4-phenyl-TAD with cyclohexene and 1-methylcyclohexene [5]. There have, however, been no reports of the reaction of 4-R-TAD with di- and trisubstituted cyclohexenes. Attempts to use N-substituted cis-4-CHDI in this reaction are of particular interest for the preparation of individual stereoisomeric compounds, and could precede a study of the mechanism of this reaction. The presence of functional groups in the adducts obtained would enable them to be used as reactive monomers in polycondensation reactions for the preparation of highly thermally stable polymers with known steric structures [7].

In earlier communications [1, 2] we referred to the reaction of 4-R-TAD with the N-arylimides of unsaturated cyclic dicarboxylic acids.

The object of the present investigation was to synthesize and establish the structures of ene-adducts of 4-benzyl-TAD (I) with N-aryl-cis-4-CHDI (IIa-h) and their 3- (IV) and 4- (VI) methyl derivatives.



IIa-h I IIIa-h

II, III a X=H, b X=p-CH$_3$, c X=m-CH$_3$, d X=o-CH$_3$, e X=p-OCH$_3$, f X=p-Br, g: X=p-Cl, h X=m-Cl

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*See [1] and [2], respectively, for Communications 1 and 2.

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TABLE 1. Properties of Products Obtained

Compound	Empirical formula	mp, °C*1	IR spectrum, cm^{-1}	Chemical shifts, δ, ppm (in deuteropyridine)*2								Yield, %
				NH	H$_{arom}$, m	NCH$_2$Ar, s	N—CH, W/O	CH=CH	α-2H*3, W/O	β-H (2H, 2 m)	other protons	
IIIa	$C_{23}H_{20}N_4O_4$	191 ... 193	3156, 1690 ... 1706, 1678	8,25 br. s	7,00 ... 7,60	4,70	4,85	5,95 W/O	3,58	2,10; 2,52	—	82
IIIb	$C_{24}H_{22}N_4O_4$	196 ... 198	3176, 1690 ... 1710, 1670	7,85 br. s	7,00 ... 7,70	4,70	4,80	5,95 W/O	3,42	2,10; 2,50	2,40 (3H, s, CH_3—Ar)	81
IIIc	$C_{24}H_{22}N_4O_4$	198 ... 199	3170, 1690 ... 1710, 1675	6,95 ... 7,40	6,95 ... 7,40	4,70	4,80	5,95 W/O	3,45	2,05; 2,45	2,30 (3H, s, CH_3—Ar)	80
IIId	$C_{24}H_{22}N_4O_4$	195 ... 196	3176, 1690 ... 1710, 1670	7,00 ... 7,50	7,00 ... 7,50	4,68	4,80	5,95 W/O	3,40	2,08; 2,45	2,30 (3H, s, CH_3—Ar)	75
IIIe	$C_{24}H_{22}N_4O_5$	193 ... 195	3180, 1690 ... 1715, 1670	9,40 s	6,60 ... 7,50	4,65	4,80	5,92 W/O	3,50	2,05; 2,50	3,40 (3H, s, Ar—OCH_3)	78
IIIf	$C_{23}H_{20}BrN_4O_4$	197 ... 198	3192, 1690 ... 1715, 1676	7,05 br. s	7,20 ... 7,80	4,70	4,85	5,95 m	3,50	2,15; 2,55	—	80
IIIg	$C_{23}H_{29}ClN_4O_4$	200 ... 202	3190, 1690 ... 1715, 1675	6,80 ... 7,20	6,80 ... 7,20	4,70	4,75	5,85 m	3,50	2,10; 2,50	—	75
IIIh	$C_{23}H_{19}ClN_4O_4$	198 ... 200	3190, 1690 ... 1715, 1675	6,70 ... 7,40	6,70 ... 7,40	4,70	4,78	5,85 m	3,45 m	2,12; 2,50	—	78
Va	$C_{24}H_{22}N_4O_4$	185 ... 187	3188, 1690 ... 1715, 1670	7,90 br. s	7,10 ... 7,60	4,60	4,45	—	3,60	2,28	1,90 (3H, s, C=C—CH_3); 5,65 (1H, br. s, CH=C)	76
VIIa	$C_{24}H_{22}N_4O_4$	185 ... 187	3190, 1690 ... 1715, 1675	7,95 br. s	7,10 ... 7,45	4,60	4,45	—	3,60	2,18	1,60 (3H, s, C=C—CH_3); 5,70 (1H, br. s, C=CH)	
VIIb	$C_{24}H_{22}N_4O_4$	211 ... 213	3190, 1690 ... 1715, 1670	7,90 br. s	7,00 ... 7,60	4,68	4,48	—	3,38	2,30; 2,60 ... 2,80*4	5,05 (2H, br. s, C=CH_2)	82*5
VIII	$C_{24}H_{22}N_4O_4$	197 ... 198	1690 ... 1715, 1675	—	7,00 ... 7,60	4,68	4,82	5,95 в. м.	3,60	2,10; 2,50	3,20 (3H, s, NCH_3)	60

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*1(IIIa-h), (Va), and (VIIa) recrystallized from chloroform–pentane (1:1), (VIIb) from acetonitrile, and (VIII) from benzene.

*2(Va) and (VIIa, b) in DMF-D$_7$.

*3Positions of protons in cyclohexane ring relative to the imide ring denoted by α- and β-.

*44H, 2m.

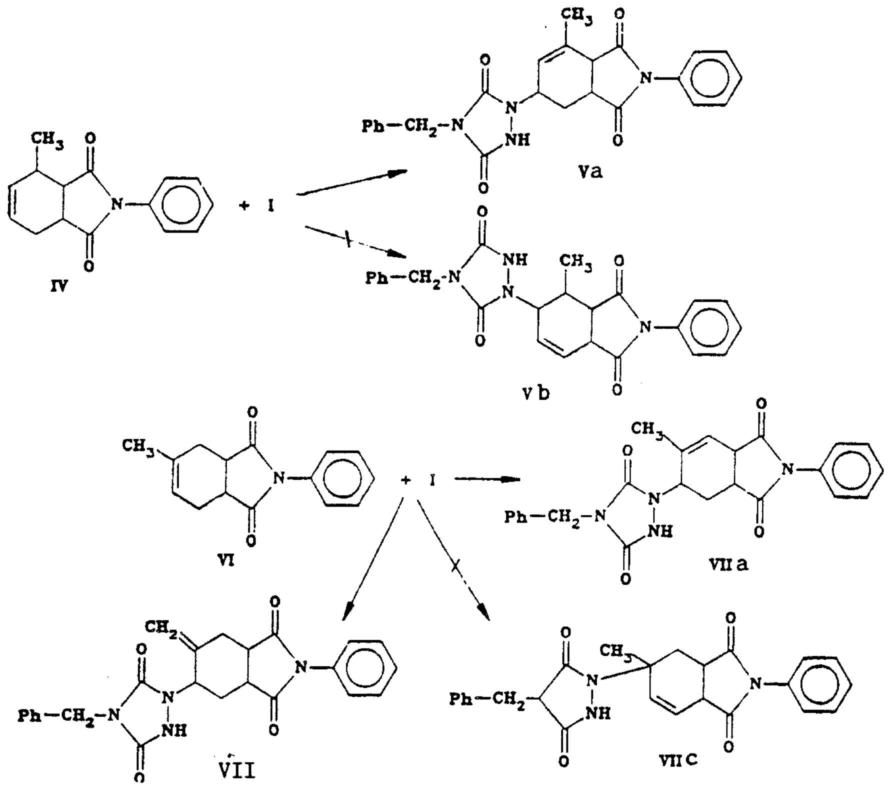
*5Overall yield of mixed isomers (VIIa) and (VIIb).

The reactions of (I) with the N-Ar-cis-4–CHDI (IIa-h) were carried out at ambient temperatures over 6-24 h (depending on the "ene" component and the solvent), and were readily followed by the changes of color of the reaction mixture, to give the adducts (IIIa-h) in high yields.

It was found that, unlike aliphatic and cycloaliphatic alkenes [5], in the present case mono-adducts were formed exclusively. The use of an excess of triazolinedione, or increasing the reaction times, did not result in formation of the bis-adduct.

When the 3- and 4-methyl-N-phenylimides (IV) and (VI) were used in the reaction, it was expected that adducts (Va) and (Vb), or (VIIa), (VIIb), or (VIIc), would be obtained respectively (Scheme 1).

Scheme 1

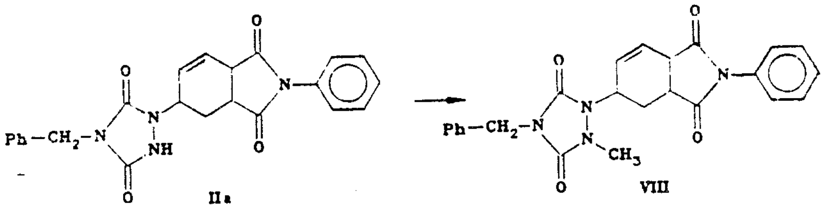


However, the PMR spectra of adducts obtained (Table 1) showed that reaction with (I) occurred at the 5-position of the methylcyclohexene moiety, to give in the first case the sole product (Va), and in the second case a mixture (1:1) of the isomeric products (VIIa) and (VIIb).

According to the spectral data, the numbers of protons in the functional groups were in exact agreement with their integral intensities.

The IR spectra of these compounds showed strong absorption for N–H at 3156-3192 cm^{-1}, which disappeared on methylation with dimethyl sulfate, as shown in the case of (VIII).

Scheme 2



EXPERIMENTAL

The IR spectra were obtained on a Specord M-80 (in Vaseline grease), and PMR spectra on a Tesla BC-487C (80 MHz), internal standard TMS.

4-Benzyl-1,2,4-triazoline-3,5-dione (I) was obtained by a standard method [8], and the corresponding 4-benzyl-1,2,4-triazolidine-3,5-dione as described in [9]. The starting N-arylcyclohex-4-en-1,2-dicarboximides (IIa-h), and their 3-Me and 4-Me derivatives (IV) and (VI), were obtained by condensing the appropriate anilines with the anhydrides at 140-150°C n DMF, as described in [10].

The elemental analysis for C, H, N, and Hal were in agreement with the calculated values.

N-Aryl-5(3,5-dioxo-4-benzyl-1,2,4-triazolidin-1-yl)cyclohex-3-ene-1,2-dicarboximides (IIIa-h) and N-phenyl-5-(3,5-dioxo-4-benzyl-1,2,4-triazolidin-1-yl)-3-methylcyclohex-3-ene-1,2-dicarboximide (Va) were obtained by reacting equimolar amounts of the addends in dry benzene, dichloromethane, or a mixture of the two (50:50) by the general method: A mixture of 0.02 mole of (I) and 0.02 mole of the imide (IIa-h) or (IV) in 50-75 ml of solvent was stirred at ambient temperature until the characteristic red color had disappeared. When benzene or the mixture of benzene and dichloromethane were used, a solid separated. This was filtered off, dried, and crystallized from a mixture of chloroform and pentane, or aqueous DMF.

When the reaction was carried out in dichloromethane, the solvent was evaporated under reduced pressure, and the viscous residual mass treated with benzene. The crystalline solid which separated was filtered off and recrystallized.

N-Phenyl-5-(3,5-dioxo-4-benzyl-1,2,4-triazolidin-1-yl)-4-methylcyclohex-3-ene-1,2-dicarboximide (VIIa) and N-Phenyl-5-(3,5-dioxo-4-benzyl-1,2,4-triazolidin-1-yl)-exo-cyclohex-4-ene-1,2-dicarboximide (VIIb). A solution of 4.82 g (0.02 mole) of N-phenyl-4-methylcyclohex-4-ene-1,2-dicarboximide (VI) and 3.78 g (0.02 mole) of (I) in 100 ml of dichloromethane was stirred vigorously at ambient temperature until the color had disappeared. The solvent was removed under reduced pressure, and the residual mass treated with a mixture of benzene and hexane. The crystalline solid which separated was filtered off and dried to give 7.05 g (82%) of a mixture of isomers (VIIa) and (VIIb), mp 180-207°C. To separate the isomers, the mixture was boiled in 150 ml of benzene, and the hot solution filtered rapidly from the solid at reduced pressure. The solid on the filter was again boiled with benzene, and filtered to give 3.05 g of (VIIb), mp 211-213°C. On cooling the mother liquors, a flocculent precipitate of the adduct (VIIa) separated (3.0 g), which was further recrystallized from a mixture of chloroform and hexane, mp 185-187°C.

N-Phenyl-5-(3,5-dioxo-2-methyl-4-benzyl-1,2,4-triazolidin-1-yl)cyclohex-3-ene-1,2-dicarboximide (VIII). A mixture of 4.3 g (0.01 mole) of (IIIa), 1.38 g of potassium carbonate, and 1.26 g (0.01 mole) of dimethyl sulfate in 75 ml of acetone was boiled under reflux for 5 h. The cooled mixture was filtered to remove the solid, then the solution was treated with 50 ml of water. The solid which separated was filtered off, dried, and twice recrystallized from benzene.

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