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1,3-Dipolar Character of Six-membered Aromatic Rings. XIII.*,[1] 2-(2',4'-Dinitrophenyl)-4-oxidoisoquinolinium

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The title compound reacts as a 1,3-dipole across the 1- and 3-positions with olefinic and acetylenic dipolarophiles. The stereochemistry of the adducts is deduced from nuclear magnetic resonance spectra.

Introduction

We previously reported[3] that the betaine, 2-methyl-4-oxidoisoquinolinium (**1**) displays 1,3-dipolar reactivity with acrylonitrile and methyl acrylate. In other series[4] the replacement of N-methyl by an N-aryl substituent as with 1-(2',4'-dinitrophenyl)-3-oxidopyridinium (**4**), greatly enhances the 1,3-dipolar reactivity of the betaine. Undheim and Hansen[5] recently described the preparation of 2-benzyl-4-oxidoisoquinolinium (**3**) by dissociation of the HBr salt in the mass spectrometer. We now report on 2-(2',4'-dinitrophenyl)-4-oxidoisoquinolinium (**2**). 2-(2',4'-Dinitrophenyl)-4-hydroxyisoquinolinium chloride (**5**) and triethylamine were used to prepare 2-(2',4'-dinitrophenyl)-4-oxidoisoquinolinium (**2**) *in situ*.

Reactions with Olefins

The reaction of compound (**2**) with N-phenylmaleimide gave a single adduct (**6**). The bicyclic structure was demonstrated by the nuclear magnetic resonance (NMR) spectrum (Table I and II): the bridgehead protons H-1 and H-3 appear as doublets due to coupling with H-9 and H-10 respectively, thus establishing the *endo*-configuration of the N-phenylmaleimide grouping and the stereospecificity of the cycloaddition. Similarly Lown and Matsumoto have reported the exclusive formation of the *endo*-cycloadducts when either the isoquinolinium imine[6] (**7**) or the pyrylium oxide[7] (**8**) was reacted with N-phenylmaleimide. Two alternative double-layer transition states[8] [(**9a**) and (**9b**)] (Figure) are conceivable, but repulsion between the aryl groups is large in structure (**9b**), which favours *endo*-addition. This behaviour contrasts with that of 1-methyl-3-oxidopyridinium[9] which yields the *exo*-cycloadduct.

The relatively unreactive[10] dipolarophile, styrene, reacted with 2-(2',4'-dinitrophenyl)-4-oxidoisoquinolinium (**2**) to produce two regioisomers, 6-*endo*-cycloadduct (**11**) mp 245—246° and 7-*endo*-cycloadduct (**12**) mp 250—251°. In both regioisomers, the bridgehead protons appear as doublets with $J \geqslant 6$ Hz, therefore the phenyl substituent has in each case an *endo*-configuration. The lanthanide shift reagent, $Eu(fod)_3$, demonstrated that for isomer (**11**),

* Dedicated to the memory of Prof. Eiji Ochiai.

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the doublet at δ 4.92 (no LIS) was the bridgehead, H-1 while for isomer (**12**), the doublet at δ 4.74 (large LIS) was the bridgehead, H-3. In regioisomer (**11**), the low field multiplet at δ 4.32 is coupled to the bridgehead proton, H-1 as shown by double resonance, thus the phenyl substituent must be 9-*endo*. Similarly, the low field multiplet at δ 4.34 of regioisomer (**12**), is coupled to the bridgehead proton, H-3, thus the phenyl substituent is 10-*endo*. Again, as in the case of the N-phenylmaleimide cycloaddition above, repulsion between the aryl groups is large in the double layer transition states and *endo*-addition is favoured.

Both dimethyl maleate and dimethyl fumarate react with the betaine (**2**) in the presence of triethylamine, to yield the same two isomeric cycloadducts (**13**), mp 185—186° and (**14**), mp 183—184°. The orientation and stereochemistry of the two isomeric adducts were determined by NMR. In both (**13**) and (**14**), one of the bridgehead protons is a doublet while the other is a singlet, which establishes the *trans*-nature of the carbomethoxy-groups. In cycloadduct (**13**), the doublet, H-3 suffers a large LIS with the addition of $Pr(fod)_3$ while the singlet, H-1 is unaffected. For cycloadduct (**14**), the singlet for the bridgehead, H-3 suffers a large LIS while the doublet for the bridgehead, H-1 is unaffected. In the reaction of dimethyl maleate with the betaine (**2**), the expected [*cf.* 1-(5′-nitropyrid-2′-yl)-3-oxidopyridinium[11]] *cis*-isomers (**15**) and (**16**) were not obtained. Presumably (**15**) and (**16**) were initially formed but in the presence of excess base. Et_3N, were epimerised[12] to the *trans*-isomers (**13**) and (**14**).

Cycloadducts were also obtained from the betaine (**2**) with acrylic acid derivatives. Unlike 1-methyl-3-oxidopyridinium,[9] the cycloaddition of the betaine with acrylonitrile and methyl acrylate were not regiospecific and all four possible isomers were produced in each case (TLC). Only one isomer, the 9-*endo*-cyano-cycloadduct (**10**) was isolated. In the NMR spectrum (Table I and II), both bridgehead protons are doublets. The doublet at δ 5.42 was assigned to H-1 while that at δ 4.89 was assigned to H-3 since, in the presence of $Pr(fod)_3$ the doublet at δ 4.89 suffers a strong LIS. On irradiation at the frequency of H-1, the low field octet due to H-9-*exo* collapsed to a quartet.

Table I. H^1-NMR Chemical Shifts of Cycloadducts

	H-1	H-3	H-9		H-10		Phenyl	CO_2Me	CH_2	CH_3
			exo	*endo*	*exo*	*endo*				
6[a]	5.86[b]	5.10[b]	4.58[c]	—	4.36[c]	—	7.24—8.00[d]	—	—	—
10[e]	5.42[b]	4.89[b]	4.07[f]	—	3.36[f]	2.31[g]	7.30—8.00[d]	—	—	—
11[e]	4.92[b]	4.74[b]	4.32[d]	—	3.18[d]	2.16[g]	7.16—7.93[d]	—	—	—
12[e]	5.06[b]	4.74[b]	3.22[d]	2.27[g]	4.34[d]	—	6.80—7.90[d]	—	—	—
13[e]	5.30[h]	4.87[c]	—	3.62[b]	4.37[g]	—	7.30—8.04[d]	3.69, 3.90[h,h]	—	—
14[e]	5.27[b]	4.96[h]	4.30[c]	—	—	3.64[b]	7.20—8.06[d]	3.55, 3.85[h,h]	—	—
17[e]	5.68[h]	5.09[b]	—	—	6.60[b]		7.30—8.00[d]	—	—	—
18[e]	5.36[b]	5.39[h]	7.06[h]		—	—	7.10—7.94[d]	—	—	—
19[e]	5.55[h]	5.27[e]	—	—	—	—	7.26—8.00[d]	3.82, 3.86[h,h]	—	—
20[e]	5.54[h]	5.36[e]	—	—	—	—	7.20—8.00[d]	—	—	—
21[e]	6.67[h]	5.78[e]	—	—	—	—	7.50—8.1[d]	—	4.10[g]	1.15[e]

δ in ppm relative to Me_4Si as internal standard; coupling constant in Hz

a) In DMSO-d_6
b) doublet
c) triplet
d) multiplet
e) in $CDCl_3$
f) octet
g) quartet
h) singlet

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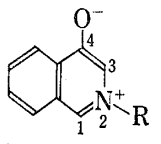
Reactions with Acetylenes

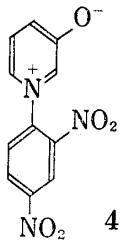
1-Methyl-3-oxidopyridinium[9] and 2-methyl-4-oxidoisoquinolinium[3] give resinous products with acetylenic dipolarophiles such as dimethyl acetylenedicarboxylate (DMAD). However treating the betaine salt (**5**) with NEt_3 in the presence of acetylenic dipolarophiles led to suc-

TABLE II. Coupling Constants (Hz)

	Compounds							
	6	**10**	**11**	**12**	**13**	**14**	**17**	**18**
3, 10_{exo}	8.5	8.0	8.0	8.0	8.0	—	3.5 ($J_{3,10}$)	—
1, 9 *exo*	6.0	6.0	6.0	6.0	—	6.0	—	3.5 ($J_{1,9}$)
9_{exo}, 10_{endo}	—	7.0	7.0	—	—	7.0	—	—
9_{exo}, 10_{exo}	9.0	10.0	10.0	11.0	—	—	—	—
10_{endo}, 10_{exo}	—	14.0	14.0	—	—	—	—	—
9_{exo}, 9_{endo}	—	—	—	13.5	—	—	—	—
9_{endo}, 10_{exo}	—	—	—	5.0	6.0	—	—	—



1 : R=Me
2 : R=2, 4-diNO_2−Ph
3 : R=CH_2−Ph



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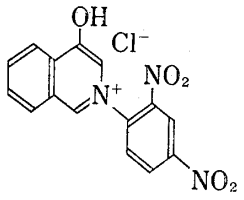

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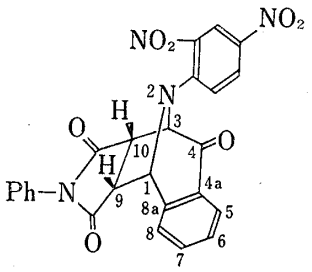

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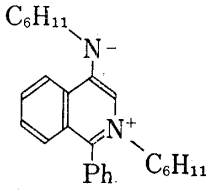

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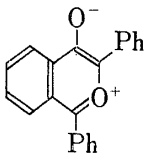

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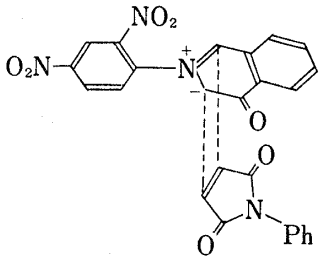

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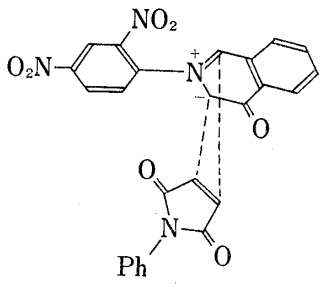

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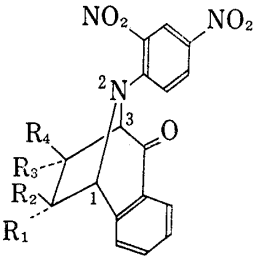
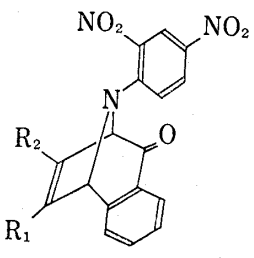
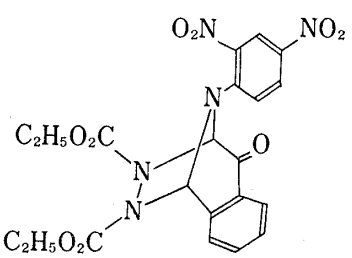


10 : R_1=CN, R_2=R_3=R_4=H
11 : R_1=Ph, R_2=R_3=R_4=H
12 : R_1=R_2=R_4=H, R_3=Ph
13 : R_1=R_4=H, R_2=R_3=CO_2Me
14 : R_1=R_4=CO_2Me, R_2=R_3=H
15 : R_1=R_3=CO_2Me, R_2=R_4=H
16 : R_2=R_4=CO_2Me, R_1=R_3=H



17 : R_1=Ph, R_2=H
18 : R_1=H, R_2=Ph
19 : R_1=R_2=CO_2Me
20 : R_1=R_2=Ph



21

Ph=phenyl

cessful cycloadditions. Phenylacetylene yielded two regioisomeric cycloadducts (**17**), mp 166—167° and (**18**), mp 178—179°. The cycloadduct (**17**) has a doublet at δ 5.09 which suffers a large LIS in the presence of $Pr(fod)_3$, thus the phenyl group is at C-9. For cycloadduct (**18**), the same bridgehead proton, H-3 (large LIS) is a singlet since the phenyl group is on the adjacent C-10. Again the betaine-phenylacetylene cycloaddition is not regiospecific. The reaction of betaine (**2**) with DMAD produced a single cycloadduct (**19**), mp 188—189°, and diphenylacetylene yielded cycloadduct (**20**), mp 140—142°.

2-(2′,4′-Dinitrophenyl)-4-oxidoisoquinolinium (**2**) reacted with diethyl azodicarboxylate in refluxing acetonitrile to yield a single cycloadduct, (**21**), mp 190—191°. The adduct analysed for $C_{21}H_{19}N_5O_9$ and had a parent peak at *m/e* 485. The infrared (IR) spectrum showed an ester (ν 1750) and an α,β-unsaturated ketone (ν 1710).

The betaine also reacted with *cis*-stilbene, chloral, diphenylketone, phenyl isocyanate and phenyl isothiocyanate to form cycloadducts which could not be isolated since they rapidly underwent cyclo-reversion.

Experimental

The melting points were determined with a Reichert apparatus. Spectra were recorded with a Perkin-Elmer model 257 grating spectrophotometer, a Hitachi-Perkin-Elmer RMU-6E mass spectrometer, a Unicam SP-800A spectrophotometer, and a Varian HA-100 MHz NMR spectrometer. Compounds were purified until they were observed as single spots on thin-layer chromatography, using Kieselgel (PF 254) and chloroform as eluant.

2-(2′,4′-Dinitrophenyl)-4-hydroxyisoquinolinium Chloride (5)——4-Hydroxyisoquinoline (4.0 g, 0.028 mol.) was added in small aliquots to a well-stirred solution of tetrahydrofuran (50 ml) containing 1-chloro-2,4-dinitrobenzene (6.0 g, 0.03 mol.) which was heated under reflux (64°) for 8 hr. The pale-orange solid (6.0 g, 60%) which deposited was filtered and washed thoroughly with tetrahydrofuran. Recrystallisation (from chloroform-diethyl ether) gave the chloride salt (**5**) as pale-orange crystals, mp 213—215° (Found: C, 51.3; H, 3.2; N, 12.1. $C_{15}H_{10}N_3O_5Cl$ requires C, 51.8; H, 2.9; N, 12.1%); ν_{max} (Nujol) 3300 (OH), 1605 (arom. C=C), 1525 (asym. NO_2), 1330 (sym. NO_2) cm^{-1}. Mass Spectrum *m/e*: 311 (M^+-HCl).

Reaction of 2-(2′,4′-Dinitrophenyl)-4-oxidoisoquinolinium (2)——(i) With N-Phenylmaleimide: 2-(2′,4′-Dinitrophenyl)-4-oxidoisoquinolinium chloride (5 g, 0.014 mol.) and N-phenylmaleimide (4 g, 0.02 mol.) in dry acetonitrile (40 ml) were heated under reflux (82°). Triethylamine (5 ml) was added dropwise to the refluxing solution over 0.5 hr. The betaine salt dissolved and a dark brown solution remained. After 18 hr, the reaction mixture was chloroform-extracted (3×50 ml) and the solvent removed *in vacuo*. The solid residue was purified by thick-layer chromatography [Kieselgel PF 254; light petroleum-chloroform (80: 20)]. 2-(2′,4′-Dinitrophenyl)-1,3-ethano-1,2,3,4-tetrahydro-4-*oxo*-N-phenylisoquinoline-9,10-*endo*-dicarboximide (**6**) was obtained as yellow prismatic needles (4.4 g, 72%), mp 259—260° [chloroform: light petroleum (60—80°), (50: 50)] (Found: C, 62.3; H, 3.6; N, 11.5. $C_{25}H_{16}N_4O_7$ (requires C, 62.0; H, 3.3; N, 11.6%). ν_{max} ($CHBr_3$) 1720 (α,β unsaturated ketone, C=O), 1600 (C=C), 1525 (antisym. NO_2), and 1335 (sym, NO_2) cm^{-1}. λ_{max} (EtOH) 208 (ε 1.56×10^4) and 337.5 (5.85×10^3) nm. Mass Spectrum *m/e*: 484.

(ii) With Styrene: 2-(2′,4′-Dinitrophenyl)-4-hydroxyisoquinolinium chloride (5 g, 0.014 mol.) and styrene (4 g, 0.04 mol.) in dry acetonitrile (40 ml) were treated as above with triethylamine (5 ml). The solid reaction product (3.8 g, 68%) was a mixture of two components (TLC) which were separated by preparative thick-layer chromatography [Kieselgel PF 254, ethyl acetate–light petroleum (60—80°) (20: 80)]. The first regioisomer to be eluted was 2-(2′,4′-dinitrophenyl)-1,3-ethano-1,2,3,4-tetrahydro-4-*oxo*-9-*endo*-phenylisoquinoline (**11**) (1.52 g, 26%) as yellow prismatic plates, mp 245—246° [chloroform–light petroleum (60—80°) (50: 50)] (Found: C, 66.3; H, 4.2; N, 9.9. $C_{23}H_{17}N_3O_5$ requires C, 66.5; H, 4.1; N, 10.1%). ν_{max} ($CHBr_3$) 1700 (α,β-unsaturated ketone, C=O), 1610 (C=C), 1525 (antisym. NO_2) and 1335 (sym. NO_2) cm^{-1}. λ_{max} (EtOH) 208 (ε 1.65×10^4) and 350 (7.00×10^3) nm. Mass Spectrum *m/e*: 415. The second regioisomer, 2-(2′,4′-dinitrophenyl)-1,3-ethano-1,2,3,4-tetrahydro-4-*oxo*-10-*endo*-phenylisoquinoline (**12**) (2.28 g, 40%) was eluted next as yellow prismatic plates, mp 250—251° [chloroform–light petroleum (60—80°) (50: 50)] (Found: C, 66.5; H, 4.1; N, 10.1. $C_{23}H_{17}N_3O_5$ requires C, 66.5; H, 4.1; N, 10.1%). ν_{max} ($CHBr_3$) 1700 [α,β-unsaturated ketone, C=O), 1610 (C=C), 1525 (antisym. NO_2) and 1335 (sym. NO_2) cm^{-1}, λ_{max} (EtOH) 208 (ε 1.68×10^4) and 350 (7.06×10^3) nm. Mass Spectrum *m/e*: 415.

(iii) With Acrylonitrile: Compound (**5**) (5 g, 0.014 mol.) and acrylonitrile (1.2 g, 0.02 mol.) in dry acetonitrile (40 ml) were heated under reflux (82°) and treated as above with triethylamine (5 ml). The solid reaction product (3.31 g, 65%) was obtained as a mixture of four components (TLC). Chromatography on Kieselgel PF 254 [light petroleum (60—80°)–ethyl acetate (4: 1)] gave 2-(2′,4′-dinitrophenyl)-1,3-ethano-1,2,3,4-tetrahydro-4-oxoisoquinoline-9-*endo*-carbonitrile (**10**) (1.0 g, 20%) as yellow hexagonal plates, mp

94—95° [chloroform–light petroleum (60—80°) (50: 50)] (Found: C, 59.1; H, 3.4; N, 15.2. $C_{18}H_{12}N_4O_5$ requires C, 59.3; H, 3.3; N, 15.4%). ν_{max} ($CHBr_3$) 1690 (α,β-unsaturated ketone, C=O), 1600 (C=C), 1525 (antisym. NO_2) and 1335 (sym. NO_2) cm^{-1}. λ_{max} (EtOH) 208 (ε 1.58×10^4), 225 (1.30×10^4), 295 (5.75×10^3) and 337.5 (4.85×10^3) nm. Mass Spectrum *m/e*: 364.

(iv) With Dimethyl Fumarate or Dimethyl Maleate: The salt (**5**) (5 g, 0.01 mol.) and dimethyl fumarate (or dimethyl maleate) (3.0 g, 0.02 mol.) in dry acetonitrile (40 ml) were treated as above with triethylamine (5 ml). The reaction product was obtained as a mixture of two components (by TLC), which were separated by preparative thick-layer chromatography [Kieselgel PF 254, light petroleum (60—80°)–ethyl acetate (80: 20)]. The first isomer to be eluted was dimethyl 2-(2′,4′-dinitrophenyl-1,3-ethano-1,2,3,4-tetrahydro-4-oxoisoquinoline-9-*endo*-10-*exo*-dicarboxylate (**14**) (1.40 g, 22%) as yellow prisms, mp 183—184° [chloroform–light petroleum (60—80°), (50: 50)] (Found: C, 55.1; H, 3.9; N, 9.1. $C_{21}H_{17}N_3O_9$ requires C, 55.4; H, 3.8; N, 9.2%). ν_{max} ($CHBr_3$) 1730 (ester, C=O), 1700 (α,β-unsaturated ketone, C=O), 1600 (C=C), 1525 (antisym. NO_2) and 1335 (sym. NO_2) cm^{-1}. λ_{max} (EtOH) 207.5 (ε 250×10^4), 237.5 (1.36×10^4) and 3.41 (1.00×10^4) nm. Mass Spectrum *m/e*: 455. The second isomer to be eluted was dimethyl 2-(2′,4′-dinitrophenyl)-1,3-ethano-1,2,3,4-tetrahydro-4-oxoisoquinoline-9-*exo*-10-*endo*-dicarboxylate (**13**) (1.33 g, 21%) as yellow prisms [chloroform–light petroleum (60—80°), (50: 50)] mp 185—186° (Found: C, 55.1; H, 3.9; N. 9.4. $C_{21}H_{17}N_3O_9$ requires C, 55.4; H, 3.8; N, 9.2%). ν_{max} ($CHBr_3$) 1730 (ester, C=O), 1700 (α,β-unsaturated ketone, C=O), 1600 (C=C), 1525 (antisym. NO_2) and 1335 (sym. NO_2) cm^{-1}. λ_{max} (EtOH) 208 (ε 2.55×10^4), 238 (1.40×10^4) and 340 (1.01×10^4) nm. Mass Spectrum *m/e*: 455.

(v) With Phenylacetylene: 2-(2′,4′-Dinitrophenyl)-4-hydroxyisoquinolinium chloride (**5**) (5 g, 0.014 mol.) and phenylacetylene (3 g, 0.03 mol.) in dry acetonitrile (30 ml) were heated under reflux (82°) and treated with triethylamine (5 ml) as above. The solid reaction product (3.5 g, 62%) was obtained as a mixture of two regioisomers (TLC) which were separated by preparative thick-layer chromatography [Kieselgel PF 254, light petroleum (60—80°)–ethyl acetate (80: 20)]. The first regioisomer to be eluted was 2-(2′,4′-dinitrophenyl)-1,3-etheno-1,2,3,4-tetrahydro-4-*oxo*-9-phenylisoquinoline (**17**) (1.48 g, 26%) as yellow plates, mp 166—167° [chloroform–light petroleum (60—80°) (50: 50)] (Found: C, 66.7; H, 3.6; N, 10.1. $C_{23}H_{15}N_3O_5$ requires C, 66.8; H, 3.7; N, 10.2%). ν_{max} ($CHBr_3$) 1700 (α,β-unsaturated ketone, C=O), 1600 (C=C), 1525 (antisym. NO_2) and 1335 (sym. NO_2) cm^{-1}. λ_{max} (EtOH) 225 (ε 2.45×10^4), 250 (2.40×10^4) and 347.5 (1.21×10^4) nm. Mass Spectrum *m/e*: 413. The second regioisomer, 2-(2′,4′-dinitrophenyl)-1,3-etheno-1,2,3,4-tetrahydro-4-*oxo*-10-phenylisoquinoline (**18**) (1.44 g, 25%) was eluted next as yellow hexagonal plates, mp 178—179° [chloroform–light petroleum (60—80°) (50: 50)] (Found: C, 66.7; H, 3.8; N, 10.1. $C_{23}H_{15}N_3O_5$ requires C, 66.8; H, 3.7; N, 10.2%). ν_{max} ($CHBr_3$) 1700 (α,β-unsaturated ketone, C=O), 1600 (C=C), 1525 (antisym. NO_2) and 1335 (sym. NO_2) cm^{-1}. λ_{max} (EtOH) 225 (ε 2.50×10^4), 250 (2.44×10^4) and 344 (1.20×10^4) nm. Mass Spectrum *m/e*: 413.

(vi) With Dimethyl Acetylenedicarboxylate: Compound (**5**) (5 g, 0.014 mol.) and DMAD (4.3 g, 0.03 mol.) in dry acetonitrile (30 ml) were treated with triethylamine (5 ml) as above. The solid residue was purified by thick-layer chromatography [Kieselgel PF 254, light petroleum (60—80°)–chloroform (50: 50)]. Dimethyl 2-(2′,4′-dinitrophenyl)-1,3-etheno-1,2,3,4-tetrahydro-4-oxoisoquinoline-9,10-dicarboxylate (**19**) was obtained as yellow prisms (3.7 g, 60%), mp 188—189° (ethanol) (Found: C, 55.9; H, 3.5; N, 9.4. $C_{21}H_{15}N_3O_9$ requires C, 55.6; H, 3.3; N, 9.3%). ν_{max} ($CHBr_3$) 1725 (ester, C=O), 1700 (α,β-unsaturated ketone, C=O), 1600 (C=C), 1525 (antisym. NO_2) and 1335 (sym. NO_2) cm^{-1}. λ_{max} (EtOH) 207.5 (ε 1.64×10^4), 232 (1.36×10^4) and 330 (6.65×10^3) nm. Mass Spectrum *m/e*: 453.

(vii) With Diphenylacetylene: Compound (**5**) (5 g, 0.014 moll.) and diphenylacetylene (3.5 g, 0.02 mol.) in dry acetonitrile (30 ml) were treated with triethylamine (5 ml) as above. The brown reaction product was chromatographed on Kieselgel PF 254 and eluted with light petroleum (60—80°)–chloroform (50: 50) to give 2-(2′,4′-dinitrophenyl)-1,3-etheno-1,2,3,4-tetrahydro-4-*oxo*-9,10-diphenylisoquinoline (**20**) (1.9 g, 35%) as yellow hexagonal prisms, mp 140—142° [chloroform–light petroleum (60—80°) (50: 50)]. ν_{max} ($CHBr_3$) 1700 (α,β-unsaturated ketone, C=O), 1640 (C=C), 1600 (arom. C=C), 1525 (antisym. NO_2) and 1335 (sym. NO_2) cm^{-1}. Mass Spectrum *m/e*: 489. A satisfactory analysis could not be obtained due to instability of the compound.

(viii) With Diethyl Azodicarboxylate: Compound (**5**) (5 g, 0.014 mol.) and diethyl azodicarboxylate (5 g, 0.03 mol.) in acetonitrile (30 ml) was treated with triethylamine (5 ml) as above. The reaction product was purified by chromatography on Kieselgel PF 254 [light petroleum (60—80°)–ethyl acetate (4: 1)] to give 1,3-(N,N′-bisethoxycarbonylhydrazo)-2-(2′,4′-dinitrophenyl)-1,2,3,4-tetrahydro-4-oxoisoquinoline (**21**) (3.42 g, 65%) as pale yellow prisms, mp 190—191° [light petroleum (60—80°)–chloroform]. (Found: C, 51.9; H, 4.2; N, 14.4. $C_{21}H_{19}N_5O_9$ requires C, 52.0; H, 4.0; N, 14.4%). ν_{max} ($CHBr_3$) 1740 (ester, C=O), 1710 (α,β-unsaturated ketone, C=O), 1600 (C=C), 1525 (antisym. NO_2) and 1335 (sym. NO_2) cm^{-1}. λ_{max} (EtOH) 210 (ε 2.68×10^4), 245 (1.69×10^4) and 292.5 (1.11×10^4) nm. Mass Spectrum *m/e*: 485.

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