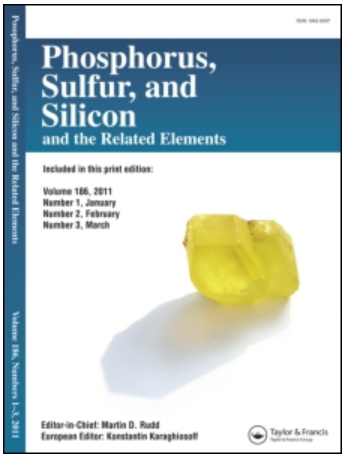

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OLEFIN SYNTHESIS VIA THE LITHIUM DERIVATIVE OF THE *N,N,N′,N′*-TETRAMETHYLDIAMIDES OF ARYLMETHANEPHOSPHONIC ACIDS. 3 SYNTHESIS OF SOME β-DISUBSTITUTED STYRENES

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OLEFIN SYNTHESIS VIA THE LITHIUM DERIVATIVE OF THE *N,N,N',N'*-TETRAMETHYLDIAMIDES OF ARYLMETHANEPHOSPHONIC ACIDS. 3
SYNTHESIS OF SOME β-DISUBSTITUTED STYRENES

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The reaction of Li-derivatives of *N,N,N',N'*-tetramethyldiamides of arylmethanephosphonic acids (**1**-Li) with alkanones, cycloalkanones, alkylaryl- and diarylketones **2a–h** is studied. It is found that in THF at −70°C adducts **3**-Li and **4**-Li are formed, the corresponding hydroxyl compounds **3** and **4** being isolated in 36–81% yields, while by elevated temperatures the reaction is completely shifted to the starting **1**-Li and **2**. By thermolysis of **3** and **4** in neutral medium olefins **5** and **6** are obtained even from readily enolysable ketones. The stereochemistry of the addition reaction with nonsymmetrical ketones as well as the influence of the substituents at the carbonyl groups on the conformation and adsorption properties of the adducts are discussed.

INTRODUCTION

In previous papers[1,2] we proposed a convenient way for the synthesis of (*Z*)-stilbenes and (*Z*)-β-substituted styrenes by highly erythro-stereoselective addition of α-Li-*N,N,N',N'*-tetramethyldiamides of arylmethanephosphonic acids to aldehydes and subsequent stereospecific thermal olefination of the obtained hydroxyphosphonamide adducts. We also showed the advantages of this synthetic approach over the known methods for the preparation of (*Z*)-alkenes from analogous hydroxyphosphonamide[3] and phosphinoxide[4,5] adducts.

In the present work the interaction of the tetramethyldiamides of arylmethanephosphonic acids with ketones was studied with a view to synthesize and investigate the respective hydroxyphosphonamide adducts as well as their transformation into β,β-disubstituted styrenes. It is known that ketones are less reactive towards phosphonate carbanions as compared with aldehydes,[6] which is usually related to steric effects.[7] The yields of olefins in the case of enolyzable ketones such as acetophenone and cyclopentanone are low.[8–10] The direct olefination of nonsymmetrical ketones with diphenylbenzylphosphinoxide carbanions[11] proceeds (*E*)-stereospecifically.

RESULTS AND DISCUSSION

We have studied the interaction of Li-derivatives of *N,N,N',N'*-tetramethyldiamides of phenyl- and 4-chlorophenylmethanephosphonic acids **1a,b**

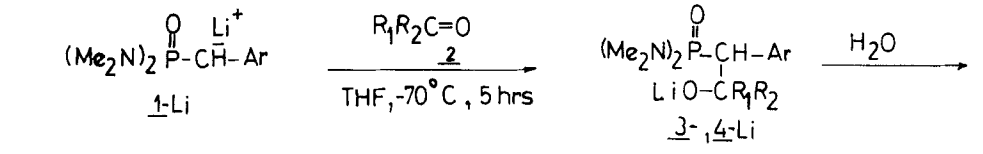
(**1a**: Ar = C_6H_5; **1b**: Ar = C_6H_4—Cl-(4)) with some alkanones, cycloalkanones, alkylaryl- and diarylketones **2a–h**. The metallation of **1a,b** was carried out by BuLi in THF at −70°C, and then the reaction of **1**-Li thus obtained with **2** was conducted for 5 hours at −70°C (citation 1, procedure A). After hydrolysis, adducts of **1** and **2**, i.e. *N,N,N′,N′*-tetramethyldiamides of 1-aryl-2,2-dialkyl-(aryl)-2-hydroxyethanephosphonic acids **3**, **4a–h** were obtained with yields of 36–81% (Scheme 1, Table I).

Unlike the reaction of **1** with aldehydes where the rise of the reaction temperature from −70°C to +20°C leads to highly erythro-stereoselective addition (citation 1, procedure B), the attempt to carry out an analogous reaction of **1a** with acetophenone **2g** failed because even at −20°C it is completely shifted toward the starting **1a** and **2g** and no adducts were isolated (Table II). The same result was obtained in more polar solvent (THF:HMPT = 85:15) even at −70°C. A similar retroaldol decomposition to the starting reactants has been observed by treatment of adducts of phosphinoxides and ketones with bases.[12]

Further, by thermal olefination of the newly obtained adducts **3**, **4a–h**, the corresponding β,β-disubstituted styrenes **5**, **6a–e**, α-methylstilbene **5g** and α-phenylstilbene **5h** were obtained (Scheme 1, Table III).

By olefination of the adducts **3e** and **4e**, simultaneous elimination of hydrogen chloride takes place, leading to the formation of the corresponding arylidenecyclohexenes **5e** and **6e** (Scheme 2).

In contrast to the reaction of 1-methylthioalkylphosphonate carbanions with



2	ketones
a	CH_3COCH_3
b	$C_2H_5COC_2H_5$
c	$CH_3COC_2H_5$
d	
e	
f	
g	$CH_3COC_6H_5$
h	$C_6H_5COC_6H_5$

1a, 3, 5 Ar = C_6H_5

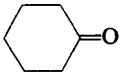
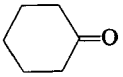
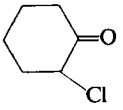
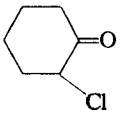
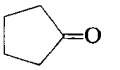
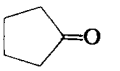
1b, 4, 6 Ar = C_6H_4Cl-(4)

5e, 6e R_1R_2C = 

SCHEME 1

TABLE I

Yields and constants of the compounds **3** and **4** obtained from **1** and **2**

No	Ar	Ketone	Yields% **3**, **4**	Er./thr. **3**, **4**	M.P.* °C
3a	C_6H_5	CH_3COCH_3	66	—	128–130
4a	C_6H_4—Cl-(4)	CH_3COCH_3	42	—	133–135
3b	C_6H_5	$C_2H_5COC_2H_5$	36	—	127–129
4b	C_6H_4—Cl-(4)	$C_2H_5COC_2H_5$	48	—	131–132
3c	C_6H_5	$CH_3COC_2H_5$	61	50/50**	88–91
3d	C_6H_5		60	—	127–128
4d	C_6H_4—Cl-(4)		62	—	142–143
3e	C_6H_5		66	—	161–163
4e	C_6H_4—Cl-(4)		81	20/80	132–134
3f	C_6H_5		58	—	108–109
4f	C_6H_4—Cl-(4)		71	—	139–141
3g	C_6H_5	$CH_3COC_6H_5$	55	24/76	157–159***
3h	C_6H_5	$C_6H_5COC_6H_5$	49	—	211–212

The elemental analyses for **3** and **4** are in good agreement with the theoretical values. IR (nujol): 970–980 cm^{-1} (ν_{P-N}), 1140–1200 cm^{-1} ($\nu_{P=O}$), 3200–3400 cm^{-1} (ν_{OH} bonded).

* M.p. of recrystallised compounds **3**, **4a–h**.

** For the determination of Er/Thr. ratio the signals ^1H (80 MHz) were used as follows: 3c (δ): 5.58 and 5.82; **4e**: 3.95 and 4.52 (the relative configuration of the isomers is not determined); **3g**: 3.74 and 3.64.

*** M.p. of the pure threo-isomer, obtained after two recristallisations from ether.

cyclopentanone and acetophenone, yielding very low quantities (if any) of olefinic products (7–10% and 0%, respectively)[10] in our case the reaction of **1a**,**b** with the same ketones affords the corresponding adducts and respective olefins **5**, **6f**,**g** with very good yields. Thus the conduction of the aldol step of the reaction at low temperature and the subsequent thermal olefination of the isolated hydroxyadducts represents a convenient synthetic pathway for the preparation of alkenes from enolyzable ketones.

The adducts **3c**, **3e** and **3g** obtained with nonsymmetrical ketones **2c**, **2e** and **2g**, represent diastereomeric mixtures. By double recrystallization of the mixture **3g**

TABLE II

Reaction conditions and products of the reaction of **1a** with **2g**

No	Reaction conditions	**3g** Yield	**3g** erythro:threo
1.	5 hrs at −70°C, THF	55	24:76
2.	5 hrs at −70°C, ether	28	12:88
3.	2 hrs at −70°C, THF	38	26:74
4.	5 hrs at −70°C, 1/2 hr to room temperature, THF	—	—
5.	2 hrs at −70°C, 1 hr to room temperature, THF	—*	—
6.	5 hrs at −20°C, THF	—*	—
7.	5 hrs at −70°C, THF/HMPA 85:15	—	—

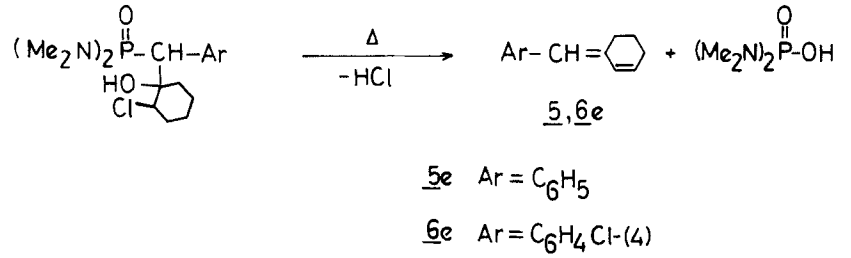
* The quantity of the recovered **2g** (as 2,4-dinitrophenylhydrazon) is 90% and 92% resp.

TABLE III

Yields of the olefins **5**, **6**

No	Olefin	Yield	Ref.
5a	$C_6H_5CH{=}C(CH_3)_2$	76	18
6a	(4)-Cl-$C_6H_4CH{=}C(CH_3)_2$	72	19
5b	$C_6H_5CH{=}C(C_2H_5)_2$	80	20
6b	(4)-Cl—$C_6H_4CH{=}C(C_2H_5)_2$	79	—
5c	$C_6H_5CH{=}C(CH_3)C_2H_5$	83*	21
5d	$C_6H_5CH=$ 	65	22
6d	(4)-Cl—$C_6H_4CH=$ 	60	22
5e	$C_6H_5CH=$ 	66	23
6e	(4)-Cl—$C_6H_4CH=$ 	69	—
5f	$C_6H_5CH=$ 	84	24
6f	(4)-Cl—$C_6H_4CH=$ 	82	—
5g	$C_6H_5CH{=}C(CH_3)C_6H_5$	86*	25
5h	$C_6H_5CH{=}C(C_6H_5)_2$	85	26

* **5c**: Z/E ratio 50:50.
5g: Z/E ratio 16:84.



SCHEME 2

in ether, pure threo-*N,N,N',N'*-tetramethyldiamide of 1,2-diphenyl-2-methyl-2-hydroxyethanephosphonic acid† was isolated. The IR-spectrum of threo-**3g** in a diluted tetrachloromethane solution (10^{-3} M) indicates the absence of T_3-conformation without intramolecular hydrogen bond P=O···HO— at about 3300 cm^{-1}.

On the basis of the *J*-constant value for the methyl group of the ketonic rest ($^3J_{CH} = 6.4$ Hz) and taking into account the application of the Karplus dependence of *J* on the dihedral angle,[13,14] it can be assumed that the T_2-conformation is prevailing (i.e. $T_2 \gg T_1$ and T_3). A similar prevalance of conformations with gauche hydrogen atoms was observed also in the case of threo-phosphonamide adducts obtained from aldehydes having ortho-substituted benzene ring.

In both cases (ketones and ortho-substituted aldehydes) the prevalance of the T_2-conformation is probably due to steric effects.

A peculiarity observed with diastereomeric erythro-**3g** and threo-**3g** is the higher R_f-value of the threo-adduct as compared with the R_f-value of the erythro-adduct **3g**, while all investigated phosphonamide adducts obtained with aldehydes show $R_{f\text{er.}} > R_{f\text{thr.}}$. Assuming that the adsorption of **3g** on silicagel is dicentric (via both polar groups – OH and O=P[N(CH$_3$)$_2$]$_2$), as so far accepted for phosphonate adducts, one can explain the weaker adsorption of the threo-adduct in T_2-conformation with the greater steric hindrance of the adsorbed polar groups[16] by the two bulky phenyl groups as compared with erythro-**3g** (E_1 and E_2).

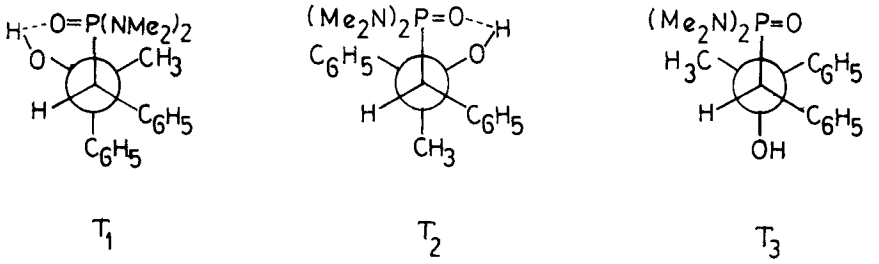


FIGURE 1 Possible conformations of threo-**3g**.

† Its configuration was proven by thermal olefination,[3] yielding pure (*E*)-**5g**.

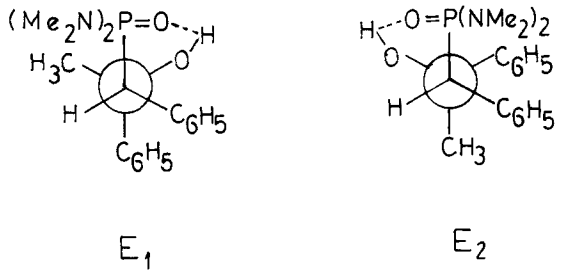


FIGURE 2 Conformations of the erythro-**3g** by dicentric absorbtion.

Furthermore, the type of the mobile phase does not influence the relative retention of the diastereomeric pair **3g**- the order $R_{fthr.} > R_{fer.}$ is kept also when ethylacetate/hexane 2:1, benzene/acetonitrile 2:1 and cyclohexane/acetone 1:1 are used. The choice of the latter two phases is made by means of a microcomputer programme enabling the selection of mobile phases showing the same value of solvent strength ($\varepsilon = 0.442$).[17]

EXPERIMENTAL

The reaction of **1** and **2** was carried out under dry argon in anhydrous THF. The ketones were destilled before use. The spectra of the adducts **3**, **4** as well as of the olefins **5**, **6** were recorded on TESLA-BS-487 spectrometer and in some cases on JEOL-JNM-100 spectrometer with TMS as internal standard and using $CDCl_3$ as solvent. The olefins were determined using ^{1}H-NMR, UV and IR-spectroscopy. They were purified by chromatography on Al_3O_3 with hexane. The qualitative TLC investigation were carried out on silicagel 60 F_{254} (aluminium sheets "Merck") using ethylacetate-hexane 2:1 as a mobile phase (for adducts) or hexane (for olefins).

Synthesis of N,N,N',N'-tetramethyldiamides of 1-aryl-2,2-dialkyl(aryl)-2-hydroxyethanephosphonic acides **3**, **4**

General procedures[1] To a solution of **1** (5 mmol) in 12 ml anhydrous THF, cooled to −70°C, buthyllithium (5 mmol, 1.6 M in hexane), diluted with 2 ml THF is added under argon. The mixture is stirred ½ hr, the ketone **2** (5 mmol)† in 2 ml THF is added and stirring continued for another 5 hrs at −70°C. The mixture is hydrolyzed with 5 ml water, then extracted with CH_2Cl_2 (3 × 10 ml), the extract washed with water and dried with magnesium sulfate. After evaporation of the solvent the crude reaction products **3**, **4** were studied by ^{1}H-NMR and tlc (Table IV).

The crude **3**, **4** were purified by washing with ether/hexane (1:2) and recrystallized from ether or ether/hexane prior to determining their physical constants and elemental analysis.

Conversion of the Hydroxyphosphonamide Adducts into Olefins

Thermal olefination of the adducts **3**, **4** into olefins **5**, **6**

General procedure. A mixture of 1 mmol **3**, **4**, silicagel (weighting three times more then **3**, **4**) and toluene (3–5 ml) is refluxed with stirring 5 hrs. After cooling the reaction mixture is filtered and the silicagel washed with ether (2 × 15 ml), the combined filtrates washed with water (2 × 5 ml), and dried over $MgSO_4$. The solvents are evaporated in vacuum and the residue is purified by column chromatography on alumina using hexane as eluent.

† In the experiments with **2a**, **2b** and **2c** 5–10% excess of ketone was used.

TABLE IV

^{1}H-NMR spectral data of the adducts **3**, **4** in $CDCl_3$

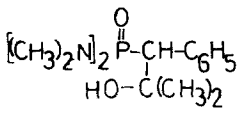
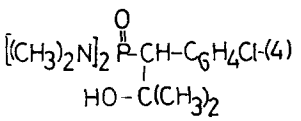
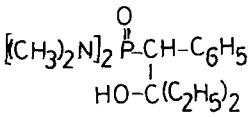
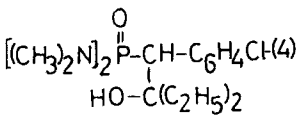
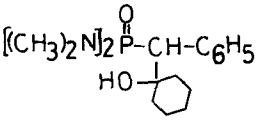
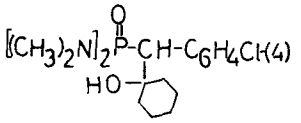
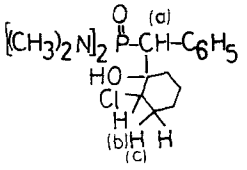
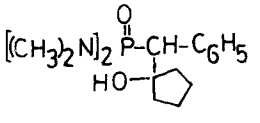
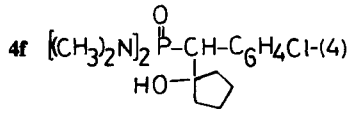
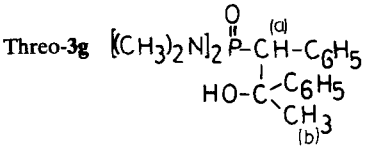
3a		δ 1.08 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 2.16 (d, $^3J_{PH}$ = 8 Hz) and 2.70 (d, $^3J_{PH}$ = 8 Hz, 12H, NCH_3), 3.35 (d, $^2J_{pH}$ = 16 Hz, 1H, CH), 5.70 (s, 1H, OH), 6.80–7.90 (m, 5H, C_6H_5).
4a		δ 1.00 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 2.00 (d, $^3J_{PH}$ = 8 Hz) and 2.60 (d, $^3J_{PH}$ = 8 Hz, 12H, NCH_3), 3.20 (d, $^2J_{PH}$ = 16 Hz, 1H, CH), 5.52 (s, 1H, OH), 6.50–7.70 (m, 4H, C_6H_4—).
3b		δ 0.68 (t, J = 8 Hz, 3H, CH_3), 0.94 (t, J = 8 Hz, 3H, CH_3), 0.98–1.90 (m, 4H, CH_2), 2.04 (d, $^3J_{PH}$ = 8 Hz) and 2.72 (d, $^3J_{PH}$ = 8 Hz, 12H, NCH_3), 3.50 (d, $^2J_{PH}$ = 16 Hz, 1H, CH), 5.80 (s, 1H, OH) 6.84–8.00 (m, 5H, C_6H_5).
4b		δ 0.70 (t, J = 8, Hz, CH_3), 0.96 (t, J = 8 Hz, 3H, CH_3), 1.04–2.04 (m, 4H, CH_2), 2.14 (d, $^3J_{PH}$ = 8 Hz) and 2.80 (d, $^3J_{PH}$ = 8 Hz, 12H, NCH_3), 3.48 (d, $^2J_{pH}$ = 16 Hz, 1H, CH), 5.58 (s, 1H, OH), 6.87–8.03 (m, 4H, C_6H_4—).
3d		δ 0.75–2.06 (m, 10H, CH_2), 2.25 (d, $^3J_{PH}$ = 8.5 Hz) and 2.83 (d, $^3J_{PH}$ = 9.5 Hz, 12H, NCH_3), 3.47 (d, $^2J_{PH}$ = 15 Hz, 1H, CH), 5.60 (S, 1H, OH), 6.87–8.06 (m, 5H, C_6H_5).
4d		δ 0.75–2.04 (m, 10H, CH_2), 2.23 (d, $^3J_{PH}$ = 8.5 Hz) and 2.78 (d, $^3J_{PH}$ = 9 Hz, 12H, NCH_3), 3.44 (d, $^2J_{PH}$ = 15 Hz, 1H, CH), 5.47 (s, 1H, OH), 6.38–7.97 (m, 4H, C_6H_4—).
3e		δ 1.37–2.12 (m, 8H, CH_2), 2.22 (d, $^3J_{PH}$ = 8.5 Hz) and 2.81 (d, $^3J_{PH}$ = 9.5 Hz, 12H, NCH_3), 3.92 (d, $^2J_{H}a_{P}$ = 17 Hz, 1H, H^a), 4.2 (t, $^3J_{H}b_{H}c$ = 5 Hz, 1H, H^b), 5.1 (s, 1H, OH), 6.87–8.07 (m, 5H, C_6H_5).
3f		δ 1.34–2.07 (m, 8H, CH_2), 2.22 (d, $^3J_{PH}$ = 9 Hz), and 2.84 (d, $^3J_{PH}$ = 9 Hz, 12H, NCH_3), 3.46 (d, $^2J_{PH}$ = 14.5 Hz, 1H, CH), 5.60 (s, 1H, OH) 6.93–8.12 (m, 5H, C_6H_5).

TABLE IV

(*continued*)

4f 	δ 1.25–2.12 (m, 8H, CH_2), 2.23 (d, $^3J_{PH}$ = 8.5 Hz) and 2.85 (d, $^3J_{PH}$ = 8.5 Hz, 12H, NCH_3), 3.42 (d, $^2J_{PH}$ = 14.5 Hz, 1H, CH), 5.53 (s, 1H, OH), 6.87–8.17 (m, 4H, C_6H_4—).
Threo-**3g** 	δ 1.24 (s, 3H, H^b), 2.06 (d, $^3J_{PH}$ = 6.6 Hz) and 2.09 (d, $^3J_{PH}$ = 6.17 Hz, 12H, NCH_3), 3.64 (d, $^2J_{PH}a$ = 15.3 Hz, 1H, H^a), 7.10 (s, 1H, OH), 7.16–7.58 (m, 10H, C_6H_5).

1-Chloro-4-(2-ethyl-1-butenyl)-benzene **6b**. $C_{12}H_{15}Cl$ (195.7) Calc.%: c, 74.02; H, 7.77. Found: C, 74.30; H, 7.82. λ_{max} 253 nm (ethanol). ^{1}H-NMR ($CDCl_3$); δ 1.00 (t, J = 8. Hz, 3H, CH_3), 1.05 (t, J = 8 Hz, 3H, CH_3), 2.00–2.30 (m, 4H, CH_2), 6.10 (s, 1H, CH), 6.98–7.25 (m, 4H, C_6H_4).

1-Chloro-4-(2-cyclohexen-1-ylidene methyl)-benzene **6e**. $C_{13}H_{13}Cl$ (204.7) Calc.%: C, 76.28; H, 6.70. Found: C, 75.92; H, 6.46; λ_{max} 285 nm, ^{1}H-NMR ($CDCl_3$); δ 1.43–2.81 (m, 6H, CH_2), 5.75–6.38 (m, 3H, CH=), 7.00–7.63 (m, 4H, C_6H_4—); IR (nujol) 1495 cm^{-1} ($\nu_{CH\text{-}aryl}$), 1645 cm^{-1} ($\nu_{C=C}$).

1-Chloro-4-(cyclopentylidenemethyl)-benzene **6f**. $C_{12}H_{13}Cl$ (192.7) Calc.%: C, 74.80; H, 6.80. Found: C, 74.98; H, 7.20. λ_{max} 264 nm (ethanol). ^{1}H-NMR ($CDCl_3$); δ 0.75–2.00 (m, 8H, CH_2), 6.30 (s, 1H, CH), 7.10–7.50 (m, 4H, C_6H_4—). IR (nujol) 1495 cm^{-1} ($\nu_{CH\text{-}aryl}$), 1590 and 1600 cm^{-1} ($\nu_{C=C}$).

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