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CONJUGATED SCHIFF'S BASES—14[1]

CYCLOADDITION OF HETEROCUMULENES TO SOME 1-OXA-4-AZABUTADIENES

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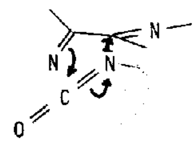
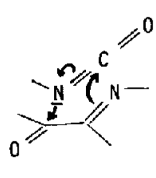
Abstract—1-Oxa-4-azabutadienes proved to be prone to react with some heterocumulenes after 1,3-cycloaddition patterns yielding various 5,5-disubstituted derivatives of 1,3-diaryl-hydanotoins as it was shown by the chemical and spectroscopic analysis. Relatively high yields, mild reaction conditions and a very weak effect of solvent polarity on the reaction rate suggested a synchroneous mechanism involving 1,2-migration of a substituent.

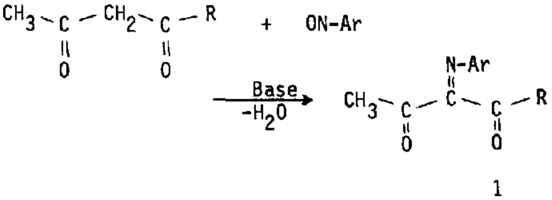
Highly substituted 1,3-heterodienes[2-4] are conspicuous from the other compounds of this kind by their atypical reactivity towards polar heteroene bonds involving formation of 5-membered heterocycles via 1,3-cycloaddition.[5,6,8] Dipolar behaviour of these reagents appears in connection with the twisted "pseudo-gauche" conformation[7] resulting from an expanding effect of large substituents conjoining the 1,3-heterodiene skeleton and forcing more or less perpendicular arrangement of the heteroene fragments. Introduction of large groups to the heterodiene system causes the higher twist of both heteroene fragments suppressing conjugation between double bonds and increasing dipolar character of the heterodiene moiety. The accepting and donating functions can be fulfilled by different centres of the 1,3-heterodiene core dependently on a charge distribution in the original reactants. Thus, 1,4-diazabutadienes are found to react with C=N double bonds of aryl isocyanates employing their N_1 nitrogen as a electron-releasing centre and C_3 carbon which plays an accepting function. The isocyanate N atom uses chiefly its n electrons to form a bond with C_3 carbon atom and here a favour of the twisted structure of 1,3-heterodienes can be seen[9]:



1-Oxa-4-azabutadienes are generally less twisted than 1,4-diazabutadienes, however they are not planar as well[10], and exhibit entirely different charge distribution. This can be shown by the π-electron density calculated using the PPP method for the selected 1-oxa-4-azabutadiene molecule.[11] In this case the CO carbon C_2 should be an acceptor whereas N_3 nitrogen seems to be nucleophilic enough to release its electrons in the cycloaddition:



In order to confront these suggestions with the experimental facts reaction of aryl isocyanates with various 1-oxa-4-aza-butadienes has been investigated. The original 1-oxa-4-aza-butadienes were synthesized by condensation of beta-dicarbonyl compounds and nitrosoarenes proceeding under the catalytic influence of bases[12]:



$$CH_3COCH_2COR + ON\text{-}Ar \xrightarrow[-H_2O]{Base} CH_3CO\text{-}C(=N\text{-}Ar)\text{-}COR$$

1

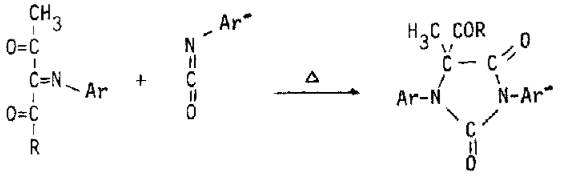
where:

1	Ar	R
a	phenyl	methyl
b	phenyl	aminophenyl
c	phenyl	2',5'-dichloraminophenyl
d	4-dimethylaminophenyl	aminophenyl
e	4-dimethylaminophenyl	2',5'-dichloraminophenyl
f	phenyl	ethoxyl
g	phenyl	morpholyl
h	phenyl	piperydyl

According to the expectations the compounds 1 reacted with aryl isocyanates. Heating of reagents in boiling benzene produced colourless crystalline products with very good yields. Elemental analyses supported the course of the reaction as a simple 1:1 addition. Inspection of the spectral properties showed explicitly the imidazolidin-2,4-dione-type structure of these substances. Thus, the IR spectra revealed sharp absorption in the CO stretching vibrations region at approximately 1780 and 1730 cm^{-1} typical for a hydantoine system.[13,14] Absorption about 1700 cm^{-1} originated from substituents containing CO groups and linking the heterocyclic ring. The ^1H NMR spectra showed a three proton singulet at 1.80 ppm corresponding to the Me group. Amide proton signals were seen by broad singlets at approximately

8.85 ppm. More information was provided by the ^{13}C NMR measurements. The ^{13}C NMR spectra were determined for two representatively chosen products resulting from the reaction of **1a** and **1g** with phenyl isocyanate. Both spectra contained similarly positioned signals attributed to carbons of the imidazolidin-2,4-dione ring. Namely, the signals observable at 72.5 and 69.0 ppm were produced by a quaternary C atom, respectively, CO C_2 carbons gave signals at 151.8 and 152.8 ppm, and CO C_4 carbons were responsible for the signals at 166.7 and 169.7 ppm, respectively. The acetyl group present in the product of **1a** caused appearance of signals at 23.1 (Me group) and 197.3 ppm (CO group). The Me group carbons attached directly to the heterocyclic ring produced signals at 15.7 and 22.9 ppm, respectively. The morpholyl fragment of the product of **1g** exhibited its carbons by signals at 44.7 and 65.9 ppm. The former were from $N(CH_2)_2$ carbons and the latter from $O(CH_2)_2$ carbons. The amide CO carbon was responsible for the signal at 163.4 ppm. Aromatic carbons produced a number of signals in the range from 116 to 134 ppm. This assessement of the C atom signals was confirmed by the complementary measurements using the "off-resonance" technique.

On the basis of these observations of 1,3-cycloaddition scheme could be ascribed to the reaction considered:



2

where:

2	Ar	Ar	R
a	phenyl	phenyl	methyl
b	phenyl	4-chlorphenyl	methyl
c	phenyl	phenyl	aminophenyl
d	phenyl	4-chlorphenyl	aminophenyl
e	4-dimethylaminophenyl	phenyl	aminophenyl
f	4-dimethylaminophenyl	phenyl	2',5'-dichloraminophenyl
g	phenyl	phenyl	2',5'-dichloraminophenyl
h	phenyl	phenyl	ethoxyl†
i	phenyl	phenyl	morpholyl
j	phenyl	phenyl	piperidyl

†The product of the proper cycloaddition added the next phenyl isocyanate molecule to its Me group.

Electron induced fragmentation of these products **2** is also evidence of their imidazolidin-2,4-dione structure. The main fragmentation patterns are fully consistent with those reported for the similar hydantoine derivatives.[15]

Formation of the 5-membered heterocyclic ring in the reaction investigated, necessitated the 1,2-migration of the Me group. Hence a question arises regarding the proper mechanism of this process. Taking into account previous theoretical considerations concerning cycloaddition of 1,4-diazabutadienes[9] it could be pointed out that the twisted structure of the 1,3-heterodiene moiety is more favourable for reactions of this very type. Then assuming the twisted "pseudo-gauche" conformation for the compounds presently investigated a synchronous concerted mechanism can be proposed. The steric arrangement of both reacting molecules in a π-complex-type transition state is shown below:

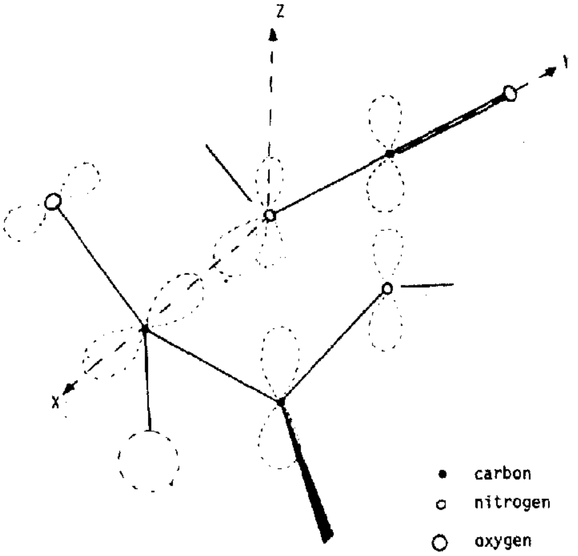
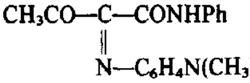


Fig. 1. The steric arrangement of the reacting molecules in the proposed π-complex-type transition state.

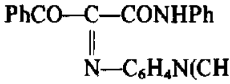
The main contacts between reacting centres are described by interactions of isocyanate N (chiefly by $2p_x$ orbital) and CO carbon (its $2p_z$ orbital) and α-azomethine N (chiefly by $2p_z$ orbital) and isocyanate carbon (its $2p_z$ orbital). Then the denating function displayed by isocyanate N is connected with its n-orbital. Such a transition state clearly shows possible synchronous 1,2-migration of a substituent linking the CO group.

For the sake of proving of the proposed synchronous concerted mechanism, measurements of the solvent polarity effect on the reaction rate were carried out. According to the predictions the reaction followed the second order kinetics and was practically independent of solvent polarity. The rate constant found for the reaction of **1d** with phenyl isocyanate occurring in xylene ($E_T = 32.3$)[16] was only twice lower as that determined in benzonitrile ($E_T = 50.8$)[16] under analogous conditions. These constants were equal to $k^{378°K}_{xylene} = 929.2 \pm 17.6 \times 10^{-6}$ and $k^{378°K}_{PhCN} = 2135.4 \pm 10.5 \times 10^{-6}/dm^3\ mol^{-1}\ s^{-1}/$. Independence of the reaction rate on solvent polarity supports a synchronous mechanism proceeding via apolar transition state. Activation parameters of this cycloaddition shed more light on the nature of the transition state. Enthalpy and entropy of activation were evaluated with the help of the Eyring's equation[17] for the following compounds:



$$CH_3CO\text{—}\underset{\underset{N\text{—}C_6H_4N(CH_3)_2}{\|}}{C}\text{—}CONHPh$$

and



$$PhCO\text{—}\underset{\underset{N\text{—}C_6H_4N(CH_3)_2}{\|}}{C}\text{—}CONHPh$$

Temp. ± 0.2°	10^6 k/dm^3 mol^{-1} s^{-1}/	
353 K	268.9 ± 2.4	91.9 ± 1.3
368 K	577.2 ± 9.2	233.5 ± 4.7
383 K	1162.4 ± 8.5	551.1 ± 6.6
$\Delta H‡$/kJ mol^{-1}/	51.92 ± 0.42	64.06 ± 0.84
$\Delta S‡$/J mol^{-1} rad^{-1}/^{1}	− 3.07 ± 0.02	− 2.62 ± 0.04

Values of both activation parameters are in good agreement with those reported for the second order reactions proceeding via a cyclic transition state.[19] Great values of $\Delta S‡$ suggest that the structure of the transition state should be similar to that of the product. Comparable values of $\Delta H‡$ can be also used in support of this concept. Differences in the reaction rates result probably from the size of the migrating substituents. The larger phenyl group causes greater steric interactions than the relatively smaller Me group that hinders to a higher degree formation of the transition state. This is exhibited also by the activation parameters.

Kinetic evidence is in good agreement with the proposed mechanism. Then the synchronous concerted mechanism including both π and n electrons seems to be entirely reasonable.

EXPERIMENTAL

1-Oxa-4-azabutadienes **1**. Condensation of various β-dicarbonyl compounds with nitrosoarenes[12,20,21] was employed for the preparation of 1-oxa-4-azabutadienes. Thus 0.02 M of a β-dicarbonyl compound[22] was dissolved in 20 to 30 ml of BuOH and a few drops of 33% t-BuOK were added. An exothermic, sometimes very violent reaction took place soon and the mixture turned from deep green to red-orange. The crude product precipitated after cooling. It was purified by repeated crystallization from t-BuOH. Liquid 1-oxa-4-azabutadienes were purified by distillation under reduced pressure. Yields varied from 60 to 80%. The chemical and spectral data are listed in Table 1.

5-Methyl-5-substituted imidazolidin-2,4-diones **2**. 0.01 M of a corresponding 1-oxa-4-azabutadiene **1** was dissolved in 5 to 10 ml dry benzene and an equimolar amount of aryl isocyanate was

Table 1.1. Yields and physical data of 1-oxa-4-azabutadienes 1

1	% Yield	M.p./b.p./°C	Formula	Analysis
a	75	/98-9/^{1mmHg}	$C_{11}H_{11}NO_2$	Calc. %C 69.8 H 5.8 N 7.4
			m.w. 189.07	Found 69.6 6.0 7.3
b	80	114-5	$C_{16}H_{14}N_2O_2$	Calc. %C 72.2 H 5.3 N 10.5
			m.w. 266.10	Found 72.1 5.2 10.8
c	78	108	$C_{16}H_{12}Cl_2N_2O_2$	Ref. 21
d	63	122	$C_{15}H_{17}N_2O_2$	Ref. 25
e	60	145-6	$C_{15}H_{15}Cl_2N_2O_2$	Ref. 26
f	65	/128-30/^{2mmHg}	$C_{12}H_{13}NO_3$	Calc. %C 65.7 H 5.9 N 6.4
			m.w. 219.09	Found 65.3 6.1 6.6
g	51	-*	$C_{14}H_{16}N_2O_3$	Calc. %C 64.6 H 6.2 N 10.8
			m.w. 260.12	Found 64.6 6.2 10.8
h	56	-*	$C_{15}H_{18}N_2O_2$	Calc. %C 69.8 H 7.0 N 10.8
			m.w. 274.13	Found 69.8 6.6 10.8

* The products 1g and 1h are heavy oils decomposing even in high vacuum, purified by repeated column chromatography using silica gel MN 60 as a filler and a mixture of benzene, cyclohexane, and chloroform /7:2:1/ as an eluent. Both original amides of acetoacetic acid, i.e., morpholide and piperidide were synthesized by condensation of ethyl acetoacetate sequently with morpholine and piperidine :

$C_8H_{13}NO_3$, m.b. 140-2°C ^{2mmHg}, Calc. %C 56.1 H 7.6 N 8.2
m.w. 171.09 Found 56.4 7.6 7.8
$C_9H_{15}NO_2$, m.b. 120-2°C ^{2mmHg}, Calc. %C 63.9 H 8.9 N 8.3
m.w. 169.11 Found 64.0 8.9 7.9 .

Table 1.2. Spectral properties of 1-oxa-4-azabutadienes **1**

$\underline{1}$*	i.r., ν_{max} cm^{-1}	^{1}H n.m.r., δ ppm	m.s., m/Z, /Int/
a	1710_{CO}, $1615_{C=N}$,	2.37 s, 6H, CH_3; 6.75-7.32 m, $5H_{ar}$	189 /13.6/, 146 /86.2/ 104 /100/, 77 /71.1/.
b	3308_{NH}, 1705_{CO}, $1650_{CO}{}^{a}$, $1638_{C=N}$	2.32 s, 3H, CH_3; 6.65-7.26 m, $10H_{ar}$ 8.11 s, 1H, NH	266 /20.9/, 223 /9.3/, 147 /73.8/, 104 /100/, 119 /28.6/, 77 /59.6/.
f	$1750_{CO}{}^{e}$, 1708_{CO}, $1618_{C=N}$	0.96 t, 3H, CH_3; 2.47 s, 3H, CH_3; 4.07 q, 2H, CH_2; 6.68-7.30 m, $5H_{ar}$	219 /24.3/, 191 /14.1/ 176 /8.4/, 147 /80.6/, 104 /100/, 77 /39.9/.
g	1708_{CO}, $1681_{CO}{}^{a}$, $1630_{C=N}$	2.15 s, 3H, CH_3; 3.70-3.76 m, $8H_{mor}$ 7.48-7.69 m, $5H_{ar}$	260 /18.1/, 217 /7.3/, 146 /83.1/, 104 /100/, 77 /62.1/, 70 /45.5/.
h	1703_{CO}, $1680_{CO}{}^{a}$, $1618_{C=N}$	0.75 t, 2H, 4-CH_2; 1.58 m, 4H, 3-CH_2 2.21 s, 3H, CH_3; 3.49 m, 4H, 2-CH_2; 7.32-7.74 m, $5H_{ar}$	274 /15.8/, 231 /6.9/, 146 /79.8/, 104 /100/, 86 /22.1/, 77 /58.9/.

***Compounds 1c, 1d, and 1e were reported previously[21,25,26].**

****Index a designates anilide, e ester, ar aromatic, mor morpholide, s singulet, t triplet, q quartet, m multiplet.**

added. The mixture was then shortly refluxed (from 15 to 45 min). After cooling 1 or 2 ml petrol ether was added to facilitate crystallization. The crude product was filtered off, washed by cold petrol ether, and recrystallized from benzene or EtOH, yields from 70 to 80%, m.ps, elemental analyses, and some spectral properties are collected in Table 2:

Kinetic measurements. Solns of the original reagents were prepared in concentrations fro 0.1 to 0.001 M using solvents of special purity. Samples were kept in a thermostat E$_1$N/VEB MLW/ maintaining temp within 0.5°. Portions of 0.2 ml were taken off from the sample at a given reaction time and mixed immediately with the 500-fold excess of cold EtOH to stop

Table 2.1. Yields and analyses of 1,3,5-trisubstituted 5-methyl-imidazolidin-2,4-diones **2**

$\underline{2}$	% Yield	M.p. °C	Formula	Analysis							
a	68	124-5	$C_{18}H_{16}N_2O_3$	Calc. %C	70.1	H	5.2	N	9.1		
			m.w. 308.12	Found	70.1		5.4		9.0		
b	70	131-2	$C_{18}H_{15}Cl\ N_2O_3$	Calc. %C	63.1	H	4.4	N	8.2	Cl	10.2
			m.w. 342.08	Found	63.1		4.4		8.1		10.1
c	72	194-6	$C_{23}H_{19}N_3O_3$	Calc. %C	71.7	H	4.9	N	10.9		
			m.w. 385.15	Found	71.6		5.1		10.9		
d	68	167-8	$C_{23}H_{18}ClN_3O_3$	Calc. %C	65.9	H	4.3	N	10.0	Cl	8.3
			m.w. 419.12	Found	65.8		4.4		10.1		8.3
e	68	202-4	$C_{25}H_{24}N_4O_3$	Calc. %C	70.1	H	5.6	N	13.1		
			m.w. 428.20	Found	69.7		5.6		13.0		
f	63	175-6	$C_{25}H_{22}Cl_2N_4O_3$	Calc. %C	60.4	H	4.4	N	11.3	Cl	14.3
			m.w. 496.10	Found	60.0		4.5		11.1		14.4
g	50	123-6	$C_{23}H_{17}Cl_2N_3O_3$	Calc. %C	60.8	H	3.7	N	9.2	Cl	15.6
			m.w. 453.06	Found	60.6		3.8		9.2		15.4
h	54	196-8	$C_{26}H_{23}N_3O_5$	Calc. %C	68.3	H	5.0	N	9.2		
			m.w. 457.17	Found	68.1		5.2		9.1		
i	71	146-8	$C_{21}H_{21}N_3O_4$	Calc. %C	66.5	H	5.5	N	11.1		
			m.w. 379.16	Found	66.7		5.5		11.2		
j	69	125-6	$C_{22}H_{23}N_3O_3$	Calc. %C	70.0	H	6.1	N	11.1		
			m.w. 377.18	Found	69.8		6.0		11.0		

Table 2.2. Spectral properties of 1,3,5-trisubstituted 5-methyl-imidazolidin-2,4-diones 2

2	i.r. ν_{max} cm^{-1}	^{1}H n.m.r., δ ppm	u.v. λ_{max}/ε/	m.s., m/Z, /Int/
a	1783_{2CO}, 1730_{4CO}, 1715_{CO}	1.70 s,3H,CH_3;2.33 s,3H,CH_3;7.48-7.22 m,10H_{ar}	244 /16 750/	308 /21.1/,265 /6.2/ 119 /26.4/,118 /100/
b	1786_{2CO}, 1740_{4CO}, 1717_{CO}	1.74 s,3H,CH_3;2.32 s,3H,CH_3;7.47-7.19 m,9H_{ar}	245 /30 020/	342 /18.6/,344 /6.4/ 299 /8.4/,301 /3.0/ 155 /7.6/,153 /23.1/ 154 /18.0/,152 /46.1/ 119 /23.8/,118 /100/
c	3303_{NH}, 1775_{2CO}, 1730_{4CO}, $1710_{CO}{}^{a}$	1.83 s,3H,CH_3;7.55-7.08 m,15H_{ar};8.44 s,1H,NH	233 /37 600/	385 /2.1/,266 /100/ 118 /74.2/,119 /19.2/
d	3315_{NH}, 1784_{2CO}, 1720_{4CO}, $1695_{CO}{}^{a}$	1.85 s,3H,CH_3;7.52-7.03 m,14H_{ar};8.63 s,1H,NH	237 /35 800/	419 /1.3/,300 /100/ 302 /33.4/,153 /12.5/ 155 /4.1/,119 /22.4/ 118 /69.8/
e	3390_{NH}, 1785_{2CO}, 1715_{2CO}, $1695_{CO}{}^{a}$	1.80 s,3H,CH_3;2.93 s,6H,N/CH_3/$_2$;6.80-6.60 m,2H_{ar};7.55-7.05 m,12H_{ar} 8.56 s,1H,NH	259 /35 550/	428 /1.1/,309 /100/ 294 /86.2/,159 /12.1/ 144 /18.1/,119 /14.5/ 118 /26.3/
f	3300_{NH}, 1792_{2CO}, 1730_{4CO}, $1700_{CO}{}^{a}$	1.97 s,3H,CH_3;3.01 s,6H,N/CH_3/$_2$;7.67-6.78 m,11H_{ar};8.51 d,1H_{ar};9.02 s,1H,NH	261 /4 550/ 216 /6 700/	496 /1.1/,309 /100/ 294 /86.6/,189 /18.9/ 187 /28.2/,159 /14.1/ 144 /17.3/,119 /15.2/ 118 /19.1/
g	3302_{NH}, 1770_{2CO}, 1725_{4CO}, $1700_{CO}{}^{a}$	1.94 s,3H,CH_3;7.51-6.98 m,12H_{ar};8.40 d,1H_{ar};8.85 s,1H,NH	238 /21 400/	453 /1.6/,455 /1.0/ 266 /100/,189 /17.9/ 187 /26.3/,119 /22.4/ 118 /70.1/
h	3300_{NH}, 1738_{2CO}, $1710_{CO}{}^{e}$, 1700_{4CO}, $1640_{CO}{}^{a}$, 1210_{OC},	1.10 t,3H,CH_3;4.07 q,2H,CH_2;5.26 s,2H,CH_2;,7.37-6.98 m,15H_{ar};7.77 s,1H,NH	281 /23 600/ 232 /38 700/	457 /12.1/,338 /26.4/ 310 /14.8/,266 /100/ 119 /16.9/,118 /79.5/ 429 /11.4/,385 /94.7/
i	1760_{2CO}, 1705_{4CO}, 1695_{CO}	1.80 s,3H,CH_3;3.50-3.75 m,8H_{mor};7.10-7.53 m,10H	225 /17 000/ 212 /16 520/	379 /24.6/,265 /81.0/ 119 /20.4/,118 /100/ 77 /46.0/,70 /34.7/
j	1750_{2CO}, 1700_{4CO}, $1690_{CO}{}^{a}$	0.70-0.78 m,2H_p;1.58-1.62 m,4H_p;1.81 s,3H,CH_3;3.41-3.59 m,4H_p;7.19-7.46 m,10H_{ar}	256 /8.000/ 225 /15 900/	377 /28.3/,265 /96.4/ 119 /21.1/,118 /100/ 112 /8.6/,86 /40.3/

Indexes a, ar, e, mor, s, t, q and m have the same meanings as those mentioned in Table 1.2. Index p designates piperidine and d doublet.

the course of the cycloaddition due to the rapid conversion of aryl isocyanate into an inactive urethane occurring under influence of alcohol. Reaction progress was controlled by detection of the concentration decrease of the 1-oxa-4-azabutadiene used. This was calculated with the help of the Lambert-Beer equation[23] employing as an analytical wavelength the characteristic very intense absorption (ϵ_{max} 15,000–21,000) appearing in the visible region at 426 to 430 nm. Rate constants and activation parameters were deduced using statistics.[24] The former were found by the graphic method from the slope of the linear regression of the concentration changes vs reaction time (r = 0.995) and the latter from the Eyring's equation[17] (r = 0.999).

Apparatus. The UV spectra were determined on a VSU-2P Zeiss Jena spectrophotometer using 1- and 0.5- cm silica transmission cells. The IR spectra were recorded on an IR-75 Zeiss Jena spectrophotometer in hexachlorobutadiene and Nujol mulls. The ^{1}H NMR spectra were determined on a Jeol 100 spectrometer in $CDCl_3$ as solvent and TMS as internal standard. The ^{13}C NMR spectra were determined on a Beckmann spectrometer in $CDCl_3$ using $[(CH_3)_3Si]_2O$ as standard. The MS spectra were recorded on an LKB 9000S spectrometer under the following conditions: voltage 70 eV, accelerating voltage 3.5 kV, ion source temp 250°, direct inlet temp 60 to 90°, trap current 60 A.

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