Notes

Stereoselective Synthesis of 1-Substituted 2,6-Dicyanopiperidines and Transformation of 2,6-Dialkylated Products of 1-Phenyl-2,6-dicyanopiperidine to δ-Diketones and Cyclohexenones

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α-Amino nitriles are the masked acyl anion equivalents and useful reagents for preparation of ketones.[1] Several synthetic methods have been reported for the preparation of 1-alkyl- and 1-amino-2,6-dicyanopiperidines,[2] being cyclic α-amino nitriles. There is, however, no information about their utility as the masked diacyl dianions equivalents of glutaraldehyde. Furthermore, their stereochemistry[2a] has not been explicitly elucidated. We report here that a modified Strecker reaction of glutaraldehyde with primary aryl- and benzylamines affords 1-phenyl-, 1-(*p*-methoxyphenyl)-, and 1-benzyl-2,6-dicyanopiperidines (**1a**, **1b**, and **1c**) in good yields (Scheme I), that the configuration of the two cyano groups of **1** is assigned to axial–axial, and that hydrolysis of 2,6-dialkylated products **2** of **1a** gives δ-diketones **3** and α,β-unsaturated cyclohexenones **4** in good yields.

A modified Strecker reaction of glutaraldehyde with aniline, *p*-anisidine, and benzylamine using sodium hydrogen sulfite and sulfurous acid gave, under the optimum conditions, **1a**, **1b**, and **1c** in 74%, 86%, and 67% yields, respectively. The yield of **1** depended critically on the concentration of glutaraldehyde. The highest yields of **1a**, **1b**, and **1c** were obtained with the concentration of 0.03, 0.05, and 0.06 mol/L, respectively. The formation of polymers increased at higher glutaraldehyde concentrations. The use of sulfurous acid and sulfur dioxide provides the following advantages: (i) The formation of colored byproducts is suppressed; (ii) water-insoluble amines are transformed to soluble ammonium hydrogen sulfites; (iii) sulfurous acid is gradually removed from the reaction mixture, evolving sulfur dioxide.

In the case of **1b**, two kinds of stereoisomers were isolated in a mole ratio of 98:2. The configuration of the two cyano groups of each stereoisomer was examined by ^{1}H NMR (see Figure 1 and Table I). Since the axial proton is generally more shielded than its equatorial counterpart,[3] the chemical shift difference between the axial and equatorial methine protons, α to the CN group, of the two isomers suggests their respective CN group configuration. More definitive evidence for the CN configuration is provided by the spin–spin coupling constant between the methine and the vicinal methylene protons. The methine protons of the major product (**1b**-a) afford two overlapping

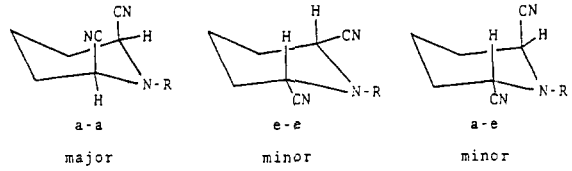
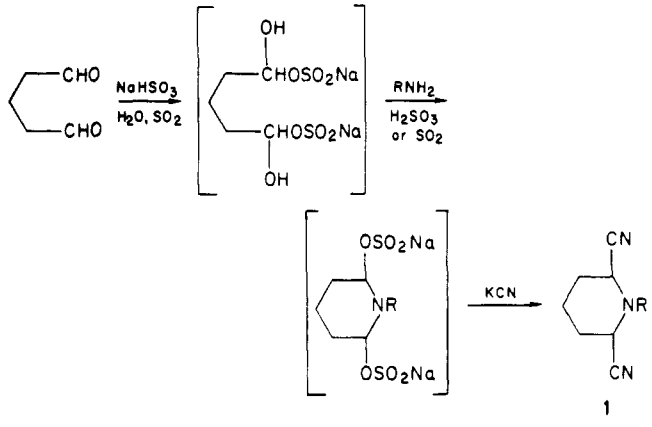


Figure 1. Configuration for two CN groups of each stereoisomer.

Scheme I



doublets (J < 3 Hz). The axial methine protons of the minor product (**1b**-e), on the other hand, give rise to two distinguishable doublets with coupling constants of 6.9 and 3.9 Hz, which are similar to the reported J_{ax-ax} and J_{ax-eq} of *N,N'*-dimethylpiperazine, i.e., 7.41 and 2.4 Hz.[4] The configuration for the two CN groups of **1b**-a is thus assigned to axial–axial and that of **1b**-e to equatorial–equatorial.

In the case of **1a**, a single stereoisomer (**1a**-a) was obtained, and its axial–axial configuration is determined likewise. In the case of **1c**, three stereoisomers were obtained. The major product was isolated in a mole ratio of 97%. The other two minor products were obtained in a mole ratio of 3% as a mixture and could not be isolated. In our unpublished work, the trans isomer (**1c**-ae) has been isolated, and its axial–equatorial configuration of CN groups has been confirmed: The unequivalent benzyl methylene protons give two distinguishable doublets (J = 13 Hz)[5] (see Table I). Thus, the configuration of the two CN groups of **1c** is assigned as follows: The major product (**1c**-a) is axial–axial, and each of the two other minor products is equatorial–equatorial and axial–equatorial, respectively.

When **1b**-a in ethanol was heated at 70 ± 5 °C for 40 h until thermal decomposition of **1b**-a occurred, partial conversion of **1b**-a to **1b**-e (27%) and the corresponding trans isomer (**1b**-ae) (30%) was confirmed by means of high-pressure liquid chromatography and ^{1}H NMR spectroscopy. Under similar conditions, **1b**-e was also converted to **1b**-a (10%) and **1b**-ae (22%). When the heating time was within 1 h, the conversion was not observed. This suggests that **1b**-a is obtained under kinetically controlled

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Table I. Characteristic ^1H NMR Spectra of Stereoisomers 1a-1c

compd.	configuration for CN	ratio, %	^1H NMR ($CDCl_3/Me_4Si$), δ CH_2 (benzyl)	CH (α position to CN)
1a	cis			
	1a-a	100		e-H, 4.66 (2 H, t-like, J = ca. 2.3 Hz)[a]
	1a-e	0[b]		a-H, 4.29 (2 H, dd, J = 6.9, 3.9 Hz)[a]
	trans			
	1a-ae	0[b]		e-H, 4.66 (1 H, t-like, J = ca. 2.3 Hz)[a]
				a-H, 4.29 (1 H, dd, J = 6.9, 3.9 Hz)[a]
1b	cis			
	1b-a	98		e-H, 4.42 (2 H, t-like, J < 3 Hz)[a]
	1b-e	2		a-H, 4.20 (2 H, dd, J = 6.9, 3.9 Hz)[a]
	trans			
	1b-ae	0[b]		e-H, 4.42 (1 H, t-like, J < 3 Hz)
				a-H, 4.20 (1 H, dd, J = 6.9, 3.9 Hz)
1c	cis			
	1c-a	97	3.91 (2 H, s)	e-H, 3.89 (2 H, t-like, J < 3 Hz)[a]
	1c-e	3[d]	3.55 (2 H, s)	a-H, 3.58 (2 H, br m)
	trans[c]			
	1c-ae	*d*	4.43 (1 H, d, J = 13 Hz)	e-H, 3.87 (1 H, br m)
			3.39 (1 H, d, J = 13 Hz)	a-H, 3.58 (1 H, br-m)

[a] Measured by ^1H NMR spectrometer (270 MHz). [b] Obtained after equilibration experiment (see Text). [c] Isolated in our other work. [d] Obtained as a mixture of **1c**-e and **1c**-ae.

Table II. Di- and Monoalkylations of 2,6-Dicyanopiperidine 1a

1	RX[a] (molar equiv)	LDA, molar equiv	time, h	yield, % 2	5
a	$CH_3(CH_2)_4Br$ (2.2)	2.1	0.5	96	0
b	MeI (3.5)	4.0	2.0	99	0
c	$PhCH_2Br$ (2.2)	2.5	2.5	68	22
	(3.7)	4.0	1.0	96	0
d	$CH_2{=}CHCH_2Br$ (2.1)	2.1	0.5	57	39
	(2.6)	2.6	6.0	72	20
	(3.5)	3.5	2.0	100	0

[a] RX = $R'CH_2X$.

conditions and thermodynamically converted to **1b**-e and **1b**-ae. Likewise, **1a**-a was converted to **1a**-e (1%) having the equatorial–equatorial configuration and **1a**-ae (7%) corresponding to the trans isomer. Similarly, **1c**-a was converted to **1c**-e (4%) and **1c**-ae (40%) together with a unknown product (2%).

The stereoselective formation is presumed to be due to the following reasons: The two bulky sodium sulfite groups of the intermediate shown in Scheme I are likely to be in equatorial–equatorial orientation. An S_N2 displacement of the sulfite group by cyanide ion is thus presumed to give the cis (axial–axial) isomer of **1**. The configuration of 1-alkyl-2,6-dicyanopiperidines has been suggested to be equatorial–equatorial,[2a] but the reaction pathway greatly differs from that employed here: These piperidines have been prepared via cyanohydrination of glutaraldehyde followed by displacement of hydroxy groups by amines.

The alkylation of **1a** was carried out at −78 °C by adding lithium diisopropylamide (LDA) dropwise to **1a** and alkyl halides dissolved in a mixture of tetrahydrofuran and hexamethylphosphoramide (HMPA) (Scheme II). Under the optimum conditions, the reaction of **1a** with pentyl bromide, methyl iodide, benzyl bromide, and allyl bromide gave 2,6-dipentyl-, 2,6-dimethyl-, 2,6-dibenzyl-, and 2,6-diallyl-2,6-dicyano-1-phenylpiperidines (**2a**, **2b**, **2c**, and **2d**) in 96–100% yields, respectively (see Table II). No attempt was made to determine the configuration of **2**, although a single isomer of **2** was formed.

Except the case of **2d**, all dialkylated products **2** were easily hydrolyzed in an aqueous solution of 15% hydrochloric acid using THF as a cosolvent and converted to the corresponding α,β-unsaturated cyclohexenones **4** in high yields (see Table III). It is obvious that the product **4** is

Scheme II

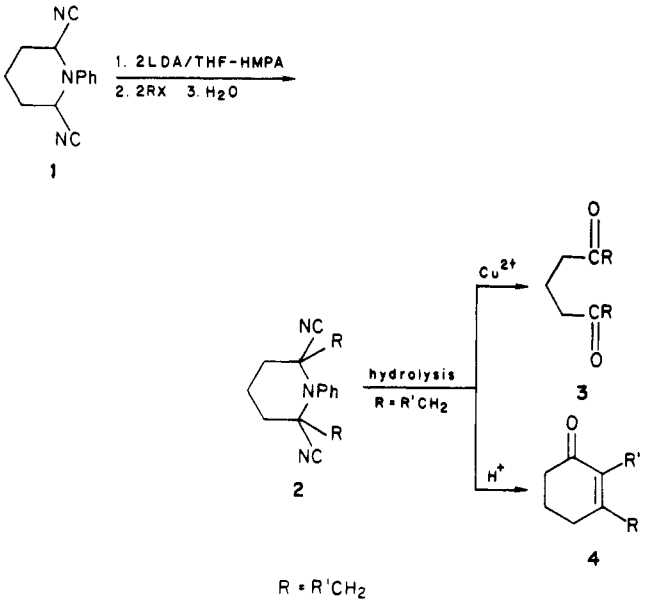

Table III. Conversion of 2,6-Dialkyl-2,6-dicyanopiperidines 2 to α,β-Unsaturated Cyclohexenones 4 and δ-Diketones 3

2	R'[a]	conditions	time, h	yield, % 3	4
a	$CH_3(CH_2)_3$	1% HCl–THF	24	18	78
		0.5% HCl–THF	47	76	20
		15% HCl–THF	26	0	100
b	H	15% HCl–THF	3	0	62[b]
c	Ph	15% HCl–THF	16	0	100
		30% $(COOH)_2$–THF	26	51	31
d	$CH_2{=}CH$	15% HCl–THF	5	0	0

[a] R = CH_2R'. [b] Isolated as the 2,4-dinitrophenyl hydrazone of **4b**.

obtained by intramolecular condensation of δ-diketones **3**, since the formation of **3** was noted in the initial period by means of thin-layer chromatography. On the other hand, when the hydrolysis was carried out in an aqueous solution of cupric sulfate or cupric acetate containing dioxane or ethanol as a cosolvent, δ-diketones **3** were selectively obtained in good yields, and the formation of **4** was not detected at all. Cupric ion presumably removes

Table IV. Conversion of 2,6-Dialkyl-2,6-dicyano-1-phenylpiperidines 2 to δ-Diketones 3 Using Cupric Salt

2	R	conditions: Cu^{2+} [a]	solvent (v/v)	temp, °C	time, h	yield of 3, %
a	$CH_3(CH_2)_4$	$Cu(OAc)_2$	dioxane–H_2O (1:1)	50	2.5	94
		$Cu(OAc)_2$	EtOH–H_2O (95:5)	50	3	57
b	CH_3	$CuSO_4 \cdot 5H_2O$	EtOH–H_2O (4:1)	50	18	74
c	$PhCH_2$	$CuSO_4 \cdot 5H_2O$	dioxane–EtOH–H_2O (5:5:1)	80	5	71
d	$CH_2{=}CHCH_2$	$CuSO_4 \cdot 5H_2O$	EtOH–H_2O (2:1)	70	3	0 [b]
		$Cu(OAc)_2$	dioxane–H_2O (1:1)	50	1	0 [b]

[a] Cupric salts of 3 equimolar amounts based on 2 were used. [b] The product corresponding to 3 was not obtained.

cyanide from 2 by precipitating insoluble $[Cu(CN)_4]^{3-}$ salts,[6] and then the hydrolysis takes place to give 3. Thus, the use of cupric salts suppresses the intramolecular condensation (see Table IV).

The work using 1 as synthetic reagents for preparation of useful diketones and piperidine alkaloids is in progress and will be reported.[7]

Experimental Section

All melting points were taken on a Yanagimoto micromelting point apparatus and are uncorrected. ^1H NMR spectra were determined with Hitachi R-24 (60 MHz) and JEOL FX-270 (270 MHz) nuclear magnetic resonance spectrometers using tetramethylsilane as an internal standard. IR and mass spectra were taken with diffraction grating infrared (Japan Spectroscopic Co. LTD., A-202 type) and high-resolution mass spectrometers (Hitachi, RMU-7M type), respectively. Microanalytical data were obtained with a Perkin-Elmer 240 elemental analyzer.

(I) Preparation of 1-Substituted 2,6-Dicyanopiperidines. Synthesis of 1-Phenyl-2,6-dicyanopiperidine (1a) as a Typical Example. To a mixture of sodium hydrogen sulfite (6.24 g, 0.06 mol) dissolved in 200 mL of water was added 50% aqueous solution of glutaraldehyde (6.01 g, 0.03 mol). The solution was stirred for 1 h at room temperature and then diluted to 800 mL with water. After 2 L of sulfur dioxide was bubbled into the diluted solution, an aqueous solution (200 mL) of anilinium hydrogen sulfite, previously prepared by adding 6% sulfurous acid to aniline (2.79 g, 0.03 mol), was added dropwise to the solution. The solution was stirred for 16 h at room temperature and neutralized with sodium carbonate. Solid potassium cyanide (3.91 g, 0.06 mol) was then added to the solution. After being stirred for 6 h, the solution was extracted with dichloromethane (5 × 150 mL). The combined organic layers were washed with brine and dried over anhydrous sodium sulfate. After removal of the solvent, the residue was purified by means of column chromatography (silica gel/benzene). Thus, **1a**-a was obtained in 73% yield (4.62 g): mp 186–187 °C; IR (KBr) ν_{CN} 2250 cm^{-1}; ^1H NMR ($CDCl_3/Me_4Si$, 60 MHz) δ 1.80–2.35 (br m, 6 H), 4.66 (br s, 2 H), 7.05–7.45 (m, 5 H); mass spectrum (70 eV), *m/e* (relative intensity) 211 (M^+, 71), 185 (31), 130 (61), 104 (64), 77 (100). Anal. Calcd for $C_{13}H_{13}N_3$: C, 73.90; H, 6.20; N, 19.89. Found: C, 73.96; H, 6.21; N, 19.99.

1-(*p*-Methoxyphenyl)-2,6-dicyanopiperidine (1b). By the same procedure, the Strecker reaction of glutaraldehyde (8.00 g, 0.04 mol) with *p*-anisidine (4.92 g, 0.04 mol) was carried out to give two kinds of stereoisomers of **1b** [**1b**-a (8.20 g, 84.3%) and **1b**-e (0.18 g, 1.7%)].

1b-a: mp 135.5–136 °C; IR (KBr) ν_{CN} 2250 cm^{-1}; mass spectrum (70 eV), *m/e* (relative intensity) 241 (M^+, 100), 174 (20), 161 (44), 122 (22); ^1H NMR ($CDCl_3/Me_4Si$, 60 MHz) δ 1.70–2.30 (br m, 6 H), 3.79 (s, 3 H), 4.42 (br m, 2 H), 6.82 (d, *J* = 9 Hz, 2 H), 7.13 (d, *J* = 9 Hz, 2 H). Anal. Calcd for $C_{14}H_{15}N_3O$: C, 69.69; H, 6.27; N, 17.42. Found: C, 69.83; H, 6.27; N, 17.37.

1b-e: mp 95.5–96 °C; IR (KBr) ν_{CN} 2260 cm^{-1}; mass spectrum (70 eV), *m/e* (relative intensity) 241 (M^+, 100), 174 (23), 161 (49), 122 (29); ^1H NMR ($CDCl_3/Me_4Si$, 60 MHz) δ 1.70–2.30 (br m, 6 H), 3.79 (s, 3 H), 4.20 (br s, 2 H), 6.88 (d, *J* = 9 Hz, 2 H), 7.20 (d, *J* = 9 Hz, 2 H). Anal. Calcd for $C_{14}H_{15}N_3O$: C, 69.69; H, 6.27; N, 17.42. Found: C, 69.65; H, 6.26; N, 17.42.

1-Benzyl-2,6-dicyanopiperidine (1c). By the same procedure, the Strecker reaction of glutaraldehyde (12.02 g, 0.06 mol) with benzylamine (6.42 g, 0.06 mol) was carried out to give three kinds of stereoisomers of **1c** [**1c**-a (8.79 g, 65%) and a mixture of **1c**-e and **1c**-ae (0.27 g, 2%)].

1c-a: mp 81–82 °C; IR (KBr) ν_{CN} 2250 cm^{-1}; mass spectrum (70 eV), *m/e* (relative intensity) 225 (M^+, 7), 148 (14), 134 (24), 91 (100); ^1H NMR ($CDCl_3/Me_4Si$, 60 MHz) δ 1.80–2.10 (br m, 6 H), 3.89 (br s, 2 H), 3.91 (s, 2 H), 7.36 (s, 5 H). Anal. Calcd for $C_{14}H_{15}N_3$: C, 74.64; H, 6.71; N, 18.65. Found: C, 74.54; H, 6.74; N, 18.58.

The mixture of **1c**-e and **1c**-ae was an oil. Physical properties of the mixture are as follows: mass spectrum (70 eV), *m/e* (relative intensity) 225 (M^+, 10), 148 (17), 134 (30), 91 (100); ^1H NMR ($CDCl_3/Me_4Si$, 60 MHz) δ 1.60–2.00 (br m, 12 H), 3.39 (d, *J* = 13 Hz, 1 H), 3.55 (s, 2 H), 3.58 (br s, 3 H), 3.87 (br s, 1 H), 4.43 (d, *J* = 13 Hz, 1 H), 7.28 (s, 10 H).

(II) Preparation of 1-Phenyl-2,6-dialkyl-2,6-dicyanopiperidines 2. Typical Procedure: Preparation of 2,6-Dicyano-2,6-dipentyl-1-phenylpiperidine (2a). Under nitrogen atmosphere, a mixture of **1a** (0.423 g, 2 mmol) and *n*-amyl bromide (0.664 g, 4.4 mmol) was dissolved in a mixture of THF (10 mL) and HMPA (5 mL) and cooled to −78 °C. To the mixture was added dropwise 4.2 mmol of LDA dissolved in THF (5 mL). The reaction mixture was stirred for 0.5 h at −78 °C, poured into an aqueous saturated ammonium chloride (20 mL), and extracted with diethyl ether (3 × 30 mL). The combined ether layers were washed with brine and dried with anhydrous sodium sulfate. After the ether was distilled off, the residue was purified by means of column chromatography. Thus, **2a** was obtained in 96% yield (0.676 g, 1.92 mmol). Physical properties are summarized in Table V.

2,6-Dicyano-2,6-dimethyl-1-phenylpiperidine (2b). By the same procedure, the reaction of **1a** (0.423 g, 2.0 mmol) with methyl iodide (0.994 g, 7.0 mmol) using LDA (8.0 mmol) was carried out to give 0.474 g (99% yield) of **2b** (see Table V).

2,6-Dibenzyl-2,6-dicyano-1-phenylpiperidine (2c). By the same procedure, the reaction of **1a** (1.465 g, 6.93 mmol) with benzyl bromide (4.383 g, 25.6 mmol) using LDA (28 mmol) was carried out to give 2.595 g (96% yield) of **2c** and 1.06 g (5.88 mmol, 23% yield based on benzyl bromide) of *trans*-stilbene (mp 123.5–124 °C, lit.[8] mp 122–124 °C). Physical properties of **2c** are summarized in Table V.

2,6-Diallyl-2,6-dicyano-1-phenylpiperidine (2d). By the same procedure, the reaction of **1a** (0.423 g, 2.0 mmol) with allyl bromide (0.847 g, 7.0 mmol) using LDA (8.0 mmol) was carried out to give 0.583 g (100% yield) of **2d** (see Table V).

2-Benzyl-2,6-dicyano-1-phenylpiperidine (5c). By the same procedure, the reaction of **1a** (0.634 g, 3.0 mmol) with benzyl bromide (1.129 g, 6.6 mmol) using LDA (7.5 mmol) was carried out to give 0.798 g (68% yield) of **2c** and 0.204 g (22% yield) of **5c** (see Table V).

2-Allyl-2,6-dicyano-1-phenylpiperidine (5d). By the same procedure, the reaction of **1a** (1.048 g, 5.0 mmol) with allyl bromide (1.573 g, 13 mmol) using LDA (13 mmol) was carried out to give 1.037 g (72% yield) of **2d** and 0.251 g (20% yield) of **5d** (see Table V).

(III) Preparation of δ-Diketones 3. The typical procedure is as follows: A mixture of **2a** (0.456 g, 1.1 mmol) and cupric

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Table V. Physical Properties of Di- and Monoalkylated Products 2 and 5

compd	mp, °C	IR (KBr) ν_{CN}, cm^{-1}	^{1}H NMR ($CDCl_3$/Me_4Si), δ	microanalysis found (calcd) C	H	N
2a	59–60	2220	0.82 (t, J = 5 Hz, 6 H), 1.0–1.6 (m, 16 H), 1.7–2.6 (m, 6 H), 6.1–7.1 (br m, 1 H), 7.1–7.7 (m, 3 H), 8.0–8.4 (br m, 1 H)	for $C_{23}H_{33}N_3$ 78.82 (78.58)	9.35 (9.46)	12.07 (11.95)
2b	116–117	2230	1.20 (s, 6 H), 1.6–2.4 (m, 6 H), 7.00 (br s, 1 H), 7.38 (s, 3 H), 8.12 (br s, 1 H)	for $C_{15}H_{17}N_3$ 75.12 (75.28)	7.10 (7.16)	17.60 (17.56)
2c	220–221	2230	1.75 (br s, 6 H), 2.50 (d, J = 13 Hz, 2 H), 2.79 (d, J = 13 Hz, 2 H), 7.24 (s, 5 H)	for $C_{27}H_{25}N_3$ 83.07 (82.83)	6.53 (6.44)	10.62 (10.73)
2d	119–120	2230	1.50–2.10 (m, 6 H), 2.15 (d, J = 7 Hz, 4 H), 4.98 (dd, J = 17, 2 Hz, 2 H), 5.15 (dd, J = 9, 2 Hz, 2 H), 5.36–6.15 (m, 2 H), 7.10 (br s, 1 H), 7.20–7.70 (br m, 3 H), 8.24 (br s, 1 H)	for $C_{19}H_{21}N_3$ 78.38 (78.32)	7.25 (7.26)	14.42 (14.42)
5c	179–180	2225	1.40–2.30 (m, 6 H), 2.52 (d, J = 13 Hz, 1 H), 3.00 (d, J = 13 Hz, 1 H), 4.28 (br s, 1 H), 7.05–8.00 (m, 10 H)	for $C_{20}H_{19}N_3$ 79.70 (79.70)	6.38 (6.35)	13.88 (13.94)
5d	104–105	2220	1.35–2.70 (m, 6 H), 2.27 (d, J = 7 Hz, 2 H), 4.22 (br s, 1 H), 5.01 (dd, J = 18, 2 Hz, 1 H), 5.10 (dd, J = 8, 2 Hz, 1 H), 5.35–6.0 (m, 1 H), 7.20–7.75 (m, 5 H)	for $C_{16}H_{17}N_3$ 76.49 (76.46)	6.84 (6.82)	16.53 (16.72)

acetate (0.646 g, 3.3 mmol) dissolved in a solution of 20 mL each of dioxane and water was warmed to 50 °C for 2.5 h. After the mixture was filtered, the solution layer was extracted with diethyl ether (3 × 20 mL). The ether layer was dried with anhydrous sodium sulfate. After the ether was distilled off, the residue was purified by means of column chromatography. Thus, 6,10-pentadecanedione (**3a**) was obtained in 94% yield (0.268 g): mp 68.0–68.5 °C; IR (KBr) ν_{CO} 1705 cm^{-1}; ^{1}H NMR ($CDCl_3$/Me_3Si, 60 MHz) δ 0.90 (t, J = 5 Hz, 6 H), 1.1–1.6 (br m, 12 H), 1.6–2.1 (m, 2 H), 2.39 (t, J = 6 Hz, 4 H), 2.43 (t, J = 6 Hz, 4 H). Anal. Calcd for $C_{15}H_{28}O_2$: C, 74.95; H, 11.74. Found: C, 74.80; H, 11.54.

2,6-Heptanedione (3b). By the same procedure, the hydrolysis of **2b** (0.241 g, 1.0 mmol) using ethanol (20 mL) and cupric sulfate (0.749 g, 3.0 mmol) instead of dioxane and cupric acetate, respectively, was carried out to give **3b** (0.095 g, 74% yield): colorless oil (lit.[9] mp 29–32 °C). The ^{1}H NMR spectrum agreed with that reported in the literature.[9]

1,7-Diphenyl-2,6-heptanedione (3c). By the same procedure, the hydrolysis of **2c** (0.791 g, 2.0 mmol) using 20 mL each of dioxane and ethanol, and cupric sulfate (0.999 g, 4 mmol) was carried out to give **3c** (0.520 g, 93% yield): mp 41.5–42.5 °C; IR (KBr) ν_{CO} 1710 cm^{-1}; ^{1}H NMR ($CDCl_3$/Me_4Si, 60 MHz) δ 1.72 (pent, J = 6 Hz, 2 H), 2.37 (t, J = 6 Hz, 4 H), 3.57 (s, 4 H), 7.20 (br s, 10 H). Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19. Found: C, 81.50; H, 7.17.

(IV) Preparation of α,β-Unsaturated Cyclohexenones 4 by Hydrolysis. The typical procedure is as follows: A mixture of **2a** (0.342 g, 1.0 mmol) dissolved in a solution of 10 mL of THF and 5 mL of 15% aqueous hydrochloric acid was gently refluxed for 26 h and then extracted with diethyl ether (3 × 20 mL). The ether layer was washed with brine and dried with anhydrous sodium sulfate. After the solvent was distilled off, the residue was purified by means of column chromatography. Thus, **4a** was obtained in 100% yield (0.215 g): colorless oil; IR (neat) ν_{CO} 1665 cm^{-1}; ^{1}H NMR ($CDCl_3$/Me_4Si, 60 MHz) δ 0.92 (t, J = 5 Hz, 6 H), 1.11–1.68 (m, 10 H), 1.70–2.58 (m, 10 H). Anal. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 80.90; H, 11.58.

3-Methyl-2-cyclohexenone (4b). By the same procedure, the hydrolysis of **2b** (0.566 g, 2.4 mmol) was carried out. However, **4b** is volatile and is isolated as its 2,4-dinitrophenyl hydrazone: After the hydrolysis was done, the reaction solution was neutralized with sodium hydrogen carbonate, and then to the reaction solution was added a mixture of 2,4-dinitrophenylhydrazine (0.961 g, 4.85 mmol) dissolved in a mixture of sulfuric acid (4 mL), water (6 mL), and 95% ethanol (6 mL). The solution was stirred for 24 h at room temperature. The hydrazone was extracted with benzene (100 mL) and purified by means of column chromatography. Thus, the 2,4-dinitrophenyl hydrazone of **4b** was obtained in 62% yield (0.426 g): mp 179–180 °C (lit.[10] mp 175 °C).

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3-Benzyl-2-phenyl-2-cyclohexenone (4c). By the same procedure with the case of **4a**, the hydrolysis of **2c** (0.743 g, 1.9 mmol) was carried out to give **4c** (0.498 g, 100% yield): mp 117–118 °C; IR (KBr) ν_{CO} 1662 cm^{-1}; ^{1}H NMR ($CDCl_3$/Me_4Si, 60 MHz) δ 1.54–2.20 (m, 2 H), 2.29 (t, J = 6 Hz, 2 H), 2.47 (t, J = 6 Hz, 2 H), 3.42 (s, 2 H), 6.90–7.50 (m, 10 H). Anal. Calcd for $C_{19}H_{18}O$: C, 86.99; H, 6.92. Found: C, 86.69; H, 6.90.

Registry No. *cis*-**1a**, 98217-26-6; *trans*-**1a**, 98217-27-7; *cis*-**1b**, 98217-28-8; *trans*-**1b**, 98217-29-9; *cis*-**1c**, 98195-08-5; *trans*-**1c**, 98217-30-2; **2a**, 98217-31-3; **2b**, 98217-32-4; **2c**, 98217-33-5; **2d**, 98217-34-6; **3a**, 22633-24-5; **3b**, 13505-34-5; **3c**, 97388-62-0; **4a**, 98217-35-7; **4b**, 1193-18-6; **4b** (2,4-dinitrophenylhydrazone), 3234-76-2; **4c**, 98217-36-8; **5c**, 98217-37-9; **5d**, 98217-38-0; glutaraldehyde, 111-30-8; aniline, 62-53-3; *p*-anisidine, 104-94-9; benzylamine, 100-46-9; *n*-amyl bromide, 110-53-2; benzyl bromide, 100-39-0; allyl bromide, 106-95-6; *trans*-stilbene, 103-30-0.

(10) Birch, A. J.; Shookry, E. M. A.; Stansfield, F. *J. Chem. Soc.* **1961**, 5376.

The Electronic Structure of Triazolinediones. Photoelectron Spectroscopic Investigations†

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The *N*-alkyl-or *N*-aryltriazolinediones are probably the most reactive dienophiles available today.[1a] Besides this high dienophilicity they also react with various olefins,[1b] acetylenes,[1c] and electron-rich π-systems.[1d] Furthermore a strong selectivity in proper model systems like propellanes has been observed.[2] The sequence of the frontier orbitals as well as the ionization energies of triazolinediones are useful in judging their reactivity and selectivity. To

† Dedicated to Professor David Ginsburg on the occasion of his 65th birthday.

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