Anal. Calcd for $C_{21}H_{21}ClN_2$: C, 74.88; H, 6.28; N, 8.32. Found: C, 74.96; H, 6.39; N, 8.38.

4-Methoxy-*N*-[1-phenyl-3-(phenylamino)propyl]aniline (6g): IR ($CHCl_3$) 3420 (NH) cm^{-1}; NMR ($CDCl_3$) δ 2.05 (q, 2, J = 6 Hz, CH_2C), 3.2 (t, 2, J = 6 Hz, CH_2N), 3.7 (s, 3, CH_3), 3.75 [br s, 2, $(CNH)_2$], 4.45 (t, 1, J = 6 Hz, CH), 6.4-7.35 (m, 14, aromatic H).

Anal. Calcd for $C_{22}H_{24}N_2O$: C, 79.48; H, 7.28; N, 8.43. Found: C, 79.59; H, 7.16; N, 8.49.

***N*-[1-Phenyl-3-(phenylamino)butyl]aniline (6h)**: IR ($CHCl_3$) 3420 (NH) cm^{-1}; NMR ($CDCl_3$) δ 1.15 (d, 3, J = 6 Hz, CH_3), 1.95 (t, 2, J = 6 Hz, CH_2), 3.4-3.65 (m, 1, $CHCH_3$), 3.95 [br s, 2, $(CNH)_2$], 4.6 (t, 1, J = 6 Hz, CHPh), 6.45-7.4 (m, 15, aromatic H).

Anal. Calcd for $C_{22}H_{24}N_2$: C, 83.50; H, 7.64; N, 8.85. Found: C, 83.59; H, 7.53; N, 8.91.

***N*-[1,3-Diphenyl-3-(phenylamino)propyl]aniline (6i)**: IR (Nujol) 3380 (NH) cm^{-1}; NMR ($CDCl_3$) δ 2.3 (t, 2, J = 6 Hz, CH_2), 3.9 [br s, 2, $(CNH)_2$], 4.45 [t, 2, J = 6 Hz, $(CH)_2$], 6.25-7.35 (m, 20, aromatic H).

Anal. Calcd for $C_{27}H_{26}N_2$: C, 85.67; H, 6.92; N, 7.40. Found: C, 85.72; H, 6.88; N, 7.46.

4-Chloro-*N*-[1,3-diphenyl-3-(phenylamino)propyl]aniline (6j): IR ($CHCl_3$) 3400 (NH) cm^{-1}; NMR ($CDCl_3$) δ 2.3 (t, 2, J = 6 Hz, CH_2), 3.7 [br s, 2, $(CNH)_2$], 4.45 [t, 2, J = 6 Hz, $(CH)_2$], 6.25-7.35 (m, 19, aromatic H).

Anal. Calcd for $C_{27}H_{25}ClN_2$: C, 78.53; H, 6.10; N, 6.78. Found: C, 78.62; H, 6.01; N, 6.86.

4-Methoxy-*N*-[1,3-diphenyl-3-(phenylamino)propyl]aniline (6k): IR ($CHCl_3$) 3370 (NH) cm^{-1}; NMR ($CDCl_3$) δ 2.1-2.35 (m, 2, CH_2), 3.65 (s, 3, CH_3), 4.15 [br s, 2, $(CNH)_2$], 4.3-4.6 [m, 2, $(CH)_2$], 6.35-7.35 (m, 19, aromatic H).

Anal. Calcd for $C_{28}H_{28}N_2O$: C, 82.32; H, 6.91; N, 6.86. Found: C, 82.41; H, 7.02; N, 6.94.

Registry No. 1 (R' = Ph; Y = O), 67931-44-6; 1 (R', = Ph; Y = PhN), 55552-57-3; 1 (R = Me; Y = PhN), 52969-24-1; 1 (R' = H; Y = PhN), 52969-23-0; **3** (R' = Ph; Y = O), 68090-83-5; **3** (R' = H; Y = PhN), 68110-48-5; **3** (R' = Me; Y = PhN), 71912-91-9; **3** (R' = Ph; Y = PhN), 68090-82-4; **4a**, 1126-78-9; **4b**, 2655-27-8; **4c**, 4746-32-1; **4d**, 2716-62-3; **4e**, 80865-89-0; **4f**, 80865-90-3; **4g**, 62740-72-1; **4h**, 80865-91-4; **5a**, 6943-87-9; **5b**, 80865-92-5; **5c**, 7714-93-4; **5d**, 80865-93-6; **5e**, 80865-94-7; **5f**, 80865-95-8; **5g**, 80865-96-9; **5h**, 80865-97-0; **6a**, 4566-58-9; **6b**, 4293-32-7; **6c**, 4274-54-8; **6d**, 80865-98-1; **6e**, 80865-99-2; **6f**, 80866-00-8; **6g**, 80866-01-9; **6h**, 80866-02-0; **6i**, 80866-03-1; **6j**, 80866-04-2; **6k**, 80866-05-3; ethyl bromide, 74-96-4; propyl bromide, 106-94-5; butyl bromide, 109-65-9; PhCH=NPh, 1013-88-3; $PhCH{=}NC_6H_4Cl$-4, 41839-60-5; $PhCH{=}NC_6H_4OMe$-4, 5291-46-3; EtCPh=NPh, 14752-72-8.

Conformational Behavior of 1-Alkyl-1,2,3,4-tetrahydroazocin-2-ones

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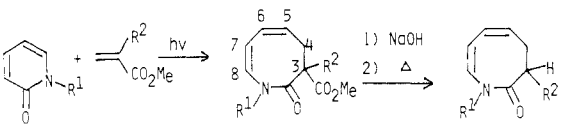
Received August 26, 1981

Several of the title compounds were synthesized, and their ^1H NMR spectra were studied at various temperatures. When the temperatures were lowered, simple patterns due to 3-CH_2 and N-CH_2 geminal protons and the N-β-$(CH_3)_2$ group on 1-mehyl- (**1**), 1-ethyl- (**2**), and 1-isobutyl-1,2,3,4-tetrahydroazocin-2-ones (**3**) became sharp multiplets after passing through the coalescence points. The T_c (-60 to -40 °C) and ΔG_c^* (10.3-10.9 kcal/mol) values were reasonably explained as being due to the ring inversion associated with rotation of the N-C(α) bond. ^1H NMR spectra of **2** with a large 3-substituent were also temperature dependent. The temperature-dependent chemical shifts were concluded to be due to population changes in the chiral azocinone ring systems, where steric hindrance due to the 3-substituent plays a major role.

Conformational processes of medium-ring compounds are rather complex, since a number of relatively weak interactions are involved. Several eight-membered rings compounds have been studied, and the roles of pseudorotation as well as the ring inversions have been elucidated.[1] From this aspect, eight-membered unsaturated lactams (azocinones) and the irhomologues are also expected to afford valuable information on conformational processes. In the previous paper, the present authors have reported that several geminal protons of N-alkyl groups in 3-substituted 1-alkyl-1,2,3,4-tetrahydroazocin-2-ones are in nonequivalent magnetic environments as detected by ^1H NMR spectra.[2] N-α-geminal protons of the 1-ethyl group of the corresponding azocinone without a 3-substituent, however, are located in an equivalent environment.[2] The temperature-dependent ^1H NMR spectra were suggested to be due to the restricted rotation around N(1)-C(α) bond in combination with ring inversion. As to the experimental observation, however, Anet has given a new interpretation: the temperature-dependent chemical shift is explained by the population changes between the rapidly equilibrating rotamers associated with the tetrahydroazocinone ring interconversion between two nonplanar forms.[3]

Scheme I



R^1	R^2
Me	H
Et	Me
i-Bu	

	R^1	R^2
4:	Me	H
5:	Et	H
6:	i-Bu	H
7:	Et	Me

	R^1	R^2
1:	Me	H
2:	Et	H
3:	i-Bu	H
8:	Et	Me

(1) F. A. L. Anet and M. Ghiaci, *J. Org. Chem.*, **45**, 1224 (1980).
(2) K. Somekawa, S. Kumamoto, T. Matsuo, and I. Ueda, *Tetrahedron*, **36**, 81 (1980).
(3) F. A. L. Anet, *Tetrahedron Lett.*, 2133 (1980).

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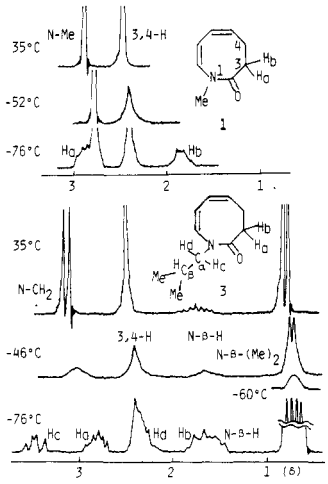
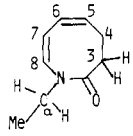


Figure 1. Temperature-dependent ^1H NMR spectra of 1 and 3.

Table I. Temperature-Dependent ^1H NMR Chemical Shifts[a]



temp, °C	$\delta_{3\text{-H}}$	$\Delta\nu_3$, Hz	$\delta_{4\text{-H}}$	$\delta_{\text{N-CH}_2(\alpha)}$	$\Delta\nu_\alpha$, Hz	$\delta_{\text{N-C-Me}}$
35	251 s		251 s	339		101
−47	248 br		248 br s	332 br q		99
−49	248 br		248 br s	329 br		99
−59	293, 198	95	249	371, 296	75	99
−74	297, 193	104	248	373, 286	87	99
−94	297, 191	106	247	378, 284	94	97

[a] CS_2-$CDCl_3$ (3:1) as solvent.

In order to clarify the effects of ring inversion and rotation around the N–C(α) bond, we prepared the title compounds, and the temperature-dependent ^1H NMR spectra were carefully studied as described in this paper.

Results and Discussion

The compounds studied in this paper are shown in Scheme I. 1-Methyl- (1) and 1-isobutyl-1,2,3,4-tetrahydroazocin-2-ones (3) were prepared by the same method as previously described for 1-ethyl analogue 2[2] (Scheme I). The photoaddition of 1-ethyl-2-pyridone to methyl methacrylate afforded 7, which was converted to 8 by pyrolysis. Marked changes in the ^1H NMR patterns, which are typical to dynamic NMR, were observed with the 3-CH_2 protons of on 1–3, with the N-CH_2 protons of 2 and 3, and also with the N-β-$(CH_3)_2$ protons of 3. Examples are shown in Figure 1. When the temperatures were lowered, the simple patterns due to the 3-CH_2 and N-CH_2 geminal protons and the N-β-$(CH_3)_2$ group gradually became broad signals and finally turned into two groups of sharp multiplets after passing through the respective coalescence points. The chemical shifts and assignments for 2 are summarized in Table I, and the rest are given in the Experimental Section.

The temperature dependences of chemical shift separations ($\Delta\nu$, Hz) for the geminal protons and N-β-$(CH_3)_2$ groups are shown in Figure 2. The $\Delta\nu_3$ values for the

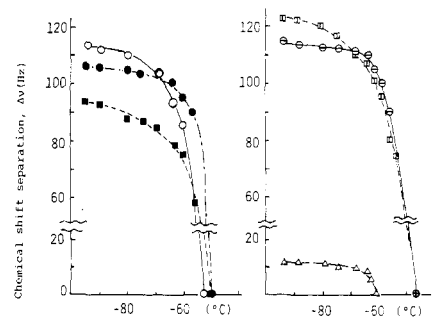


Figure 2. Temperature-dependent chemical shift separations of geminate and dimethyl protons in 1 [3-CH_2 (○)], 2 [3-CH_2 (●), N-CH_2 (■)], and 3 [3-CH_2 (⊖), N-CH_2 (open box with vertical bar), N-β-$(CH_3)_2$ (△)].

Table II. Activation Parameters for Conformational Process of 1-Alkyl-1,2,3,4-tetrahydroazocin-2-ones

compd (alkyl)	proton	T_c, °C	$\Delta\nu$, Hz	J, Hz	$\Delta G_c^\ddagger$, kcal/mol
1 (Me)	3-CH_2	−52	115	14.0	10.3
2 (Et)	3-CH_2	−49	106	14.0	10.5
	N-CH_2	−49	94	14.0	10.6
3 (i-Bu)	3-CH_2	−46	115	14.0	10.6
	N-CH_2	−46	122	14.0	10.6
	N-β-$(CH_3)_2$	−60	11.5	0	10.9

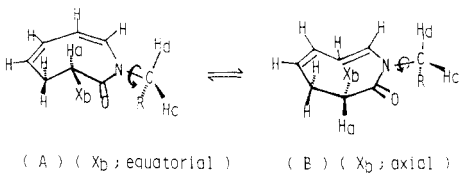
3-CH_2 protons of 1–3 are nearly equal. However, the corresponding values for the N-CH_2 protons of 3 are considerably larger than those for 2. The coalescence temperatures (T_c) are located between -60 and -46 °C; the more bulky the N-alkyl groups are, the higher the T_c. The activation parameters for the coalescence are summarized in Table II. The $\Delta G_c^\ddagger$ values were calculated as previously described.[2] As far as the $\Delta G_c^\ddagger$ values are concerned, no significant difference between the 3-CH_2 and N-CH_2 groups is observed. The $\Delta G_c^\ddagger$ values (10.3–10.9 kcal/mol) thus indicate that the conformational change of the ring is mainly responsible for the dynamic NMR as explained below.

Since the three staggered conformers of the N-CH_3 group of 1 are isoenergetic, they must be equally populated, whether or not some group is restricting their motion. As no temperature dependence was observed with the N-CH_3 signal, it is clear that the rotation around the N–C(α) bond is not essentially restricted. In the presence of bulky groups at the C(α) position, however, the rotamer population with respect to the N–C(α) bond will become nonequivalent because of the chiral conformation of the rigid ring at low temperatures. On an average, the geminal proton of N-CH_2 and the N-β-$(CH_3)_2$ protons are in nonequivalent electromagnetic environments due to the chiral ring system, which involves a magnetically anisotropic amide group as discussed in the previous paper.[2] As the temperature is raised, the above nonequivalence of the geminal protons will be removed by the onset of active conformational processes such as ring inversion, which is also clearly detected by the coalescence of the 3-CH_2 signals.

The stable conformation of the azocinone ring at the low temperatures will be close to the distorted boat conformation as given for the 3-cyano analogue.[4] It should be also noticed that the $\Delta G_c^\ddagger$ values in Table II are not far from those for ring-inversion processes of 2,4,6-cycloctatrienone (11.9 kcal/mol)[5] and cyclohexane (10.1

(4) I. Ueda, K. Somekawa, S. Kumamoto, and T. Matsuo, *Acta Crystallogr., Sect. B*, **B35**, 778 (1979).

Scheme II



(A) (Xb ; equatorial) (B) (Xb ; axial)

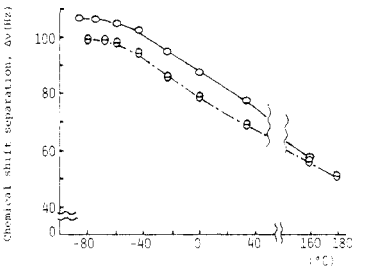


Figure 3. Temperature-dependent chemical shift separations of N-CH_2 protons in **5** (Θ) and **8** (O).

kcal/mol).[6] Hence, a conformational exchange process as shown in Scheme II may be suggested to explain the above dynamic NMR. The ring inversion brings the H(a) proton at the axial position in form A (X = H) to the equatorial position in form B. The average electromagnetic environments for the H(c) and H(d) protons are also exchanged with each other by the same conformational change.

Temperature-dependent ^1H NMR signals of 3-substituted azocinones show fairly different behaviors in comparison with those of the unsubstituted analogues. The $\Delta\nu$ value of the N-CH_2 protons in **5**, for example, starts from ca. 100 Hz at −80 °C and gradually decreases to 50 Hz at 180 °C. At the temperatures below −70 °C, the $\Delta\nu$ values reach an asymptotic value. No coalescence of N-CH_2 signals was observed in the investigated temperature ranges. Essentially the same phenomena were observed with **8** as shown in Figure 3.

The relative rotamer population around the N–C(α) bond will not be affected by the presence of the substituent at the 3-position. It is quite likely, however, that the conformation of the azocinone ring is strongly controlled by the bulky substituent. In the case of **8**, the most stable conformation of the azocinone ring must be a distorted boat form, as suggested by x-ray crystallography,[4] where the 3-methyl group is at the equatorial position [form A (X = CH_3) in Scheme II]. On the other hand, the 3-methyl group at the axial position is expected to introduce large steric hindrance due to transannular interactions [form B (X = CH_3) in Scheme II].

On the basis of these discussions, it is strongly suggested that the 3-substituted azocinones (**5** and **8**) will predominantly take the form A conformation. Then, the chirality of the azocinone ring in form A dominates over that of form B in the equilibrium, and the average electromagnetic environments for the geminal protons of the N-CH_2 group should remain nonequivalent. In agreement with this expectation, significantly large $\Delta\nu$ values were observed with the N-CH_2 protons in the 3-substituted azocinones up to 160 °C (Figure 3). The $\Delta\nu$ values increase at the lower temperatures as expected from the ratio between form A and B under rapid-exchange conditions. It is also suggested that the energy of activation for the transformation from A to B would be hardly affected by the presence of a substituent at the 3-position, since no steric strain is involved. Then, the ring inversion as suggested in unsubstituted azocinones will also account for the presence of a break-off point in $\Delta\nu$ values for 3-substituted azocinones at ca. −70 °C. The energy of activation for the transformation from form B to A, on the other hand, seems to be appreciably reduced by the 3-substituent, since no signals due to form B could be clearly detected even at −80 °C.

In short, the strange temperature dependence of $\Delta\nu$ in 3-substituted azocinones could be also reasonably explained by conformational changes of the chiral azocinone ring where the partitions between form A and form B are controlled by the steric hindrance due to the substituent at the 3-position. The experimental evidence and conclusion thus advanced in this paper are essentially in agreement with the Anet's explanation.[3]

Experimental Section

All melting points were measured on a Yanagimoto Mel-temp apparatus and are uncorrected. Spectral data were recorded with the following spectrometers: JASCO Model A-3 (IR), JEOL Model JNM MH-100 (^1H NMR, 100 MHz), JEOL Model JMS-01SG (mass spectra). ^1H NMR spectra were obtained with Me_4Si as an internal standard and deuteriochloroform as the solvent unless otherwise indicated. Reported values are in reciprocal centimeters for IR spectra and in δ values for ^1H NMR spectra. The temperature dependence of ^1H NMR spectra between −100 and +180 °C was investigated with a carbon disulfide–deuteriochloroform mixed solvent (3:1) at low temperatures and with 1,2,4-trichlorobenzene solution at high temperatures. The temperature was determined by the use of methanol and 1,3-propandiol as standard samples.

1-Methyl-1,2,3,4-tetrahydroazocin-2-one (1). Methyl 1-methyl-1,2,3,4-tetrahydro-2-oxo-3-azocinecarboxylate (**4**,[7] 1.7 mmol) in 5 mL of methanol was mixed with 20% NaOH (0.5 mL). After reflux for 2 h, the solution was concentrated at reduced pressure and acidified with 6 N HCl. The precipitate was collected, washed with water, and dried to give the acid: mp 181–184 °C; 64% yield. The acid (1.1 mmol) was heated in a glass tube for 40 min at 180 °C. The residue was chromatographed on a silica gel column (benzene, diethyl ether, and acetone), and the solvent (diethyl ether) was removed to give **1**: oil; 20% yield; IR (film) 1660, 1648; ^1H NMR 2.49 (s, 4, 3,4-H), 2.88 (s, 3, α-H), 5.5–5.9 (m, 4, 5-H through 8-H); mass spectrum, m/e (relative intensity) 137 (55, M^+).

Anal. Calcd for $C_8H_{11}NO$: C, 70.04; H, 8.08; N, 10.21. Found: C, 69.88; H, 8.05; N, 10.09.

1-Isobutyl-1,2,3,4-tetrahydroazocin-2-one (3). Analogously to **1**, methyl 1-isobutyl-1,2,3,4-tetrahydro-2-oxo-3-azocinecarboxylate (**6**,[2] 1.3 mmol) gave the acid (mp 139–143 °C; 86%), which was successively converted to **3** (oil, 50%) on pyrolysis: IR (film) 1660, 1643; ^1H NMR 0.77 (d, J = 7 Hz, 6, β-CH_3), 1.72 (m, 1, α-H), 2.46 (s, 4, 3,4-H), 3.11 (d, J = 7 Hz, 2, α-H), 5.4–5.9 (m, 4, 5-H through 8-H); mass spectrum, m/e (relative intensity) 179 (30, M^+).

Anal. Calcd for $C_{11}H_{17}NO$: C, 73.70; H, 9.56; N, 7.81. Found: 73.40; H, 9.44; N, 7.56.

Methyl 1-Ethyl-3-methyl-1,2,3,4-tetrahydro-2-oxo-3-azocinecarboxylate (7) and 1-Ethyl-3-methyl-1,2,3,4-tetrahydroazocin-2-one (8). A solution of 1-ethyl-2-pyridone (40 mmol) and methyl methacrylate (200 mmol) in 200 mL of methanol was irradiated for 21 h with a 400-W high-pressure mercury lamp. After the precipitate was removed by filtration, the filtrate was evaporated to dryness, and the residue was chromatographed on a silica gel column (diethyl ether, acetone). The material from the first fraction was repeatedly purified by chromatography (diethyl ether) to give **7** (oil, 7%). **7** (1.7 mmol) in 5 mL of methanol was mixed with 20% NaOH (1.0 mL). After

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(6) F. A. L. Anet, "Dynamic Nuclear Magnetic Resonance Spectroscopy", L. M. Jackman and F. A. Cotton, Eds., Academic Press, New York, 1975, p 579.

(7) K. Somekawa, T. Shimou, H. Muta, and S. Kumamoto, *Nippon Kagaku Kaishi*, 1443 (1976).

being refluxed for 2 h, the solution was concentrated at reduced pressure and acidified with 6 N HCl. The precipitate was washed with water and dried to give the acid (mp 159–160 °C, 50%). The acid (0.5 mmol) was heated to 170 °C in a glass tube for 1 h and chromatographed on a silica-gel column (diethyl ether) to give 8 (oil, 85%).

7: IR (film) 1745, 1647, 1445; ^{1}H NMR 1.05 (t, J = 7 Hz, 3, β-H), 2.87 (m, 1, 4-H), 1.34 (s, 3, 3-CH_3), 2.33 (m, 1, 4-H), 3.08 (sextet, J = 7, 14 Hz, 1, α-H), 3.81 (sextet, J = 7, 14 Hz, 1, α-H), 3.62 (s, 3, OCH_3), 5.7–5.9 (m, 4, 5-H through 8-H); mass spectrum, m/e (relative intensity) 223 (30, M^+).

Anal. Calcd for $C_{12}H_{17}NO$: C, 64.55; H, 7.67; N, 6.27. Found: C, 64.19; H, 7.75; N, 6.07.

8: IR (film) 1660–1620, 1440, 1380; ^{1}H NMR 1.00 (d, J = 7 Hz, 3, 3-CH_3), 1.03 (t, J = 7 Hz, 3, β-H), 2.34 (br, 2, 4-H), 3.04 (sextet, J = 7, 14 Hz, α-H), 3.82 (sextet, J = 7, 14 Hz, α-H), 3.38 (m, 1, 3-H), 5.7–5.9 (m, 4, 5-H through 8-H); mass spectrum, m/e (relative intensity) 165 (80, M^+).

Anal. Calcd for $C_{10}H_{15}NO$: C, 72.69; H, 9.15; N, 8.48. Found: C, 72.34; H, 9.14; N, 8.32.

Acknowledgment. We express our thanks to Professor Ikuhiko Ueda of Kyushu University for his valuable suggestions. The financial aid by the Asahi Glass Foundation for Industrial Technology is also deeply acknowledged.

Registry No. 1, 80753-91-9; 2, 74142-27-1; 3, 80753-92-0; 4, 61856-34-6; 4 acid, 80753-93-1; 5, 74142-22-6; 6, 74142-24-8; 6 acid, 80753-94-2; 7, 80753-95-3; 7 acid, 80753-96-4; 8, 80753-97-5; 1-ethyl-2-pyridone, 13337-79-6; methyl methacrylate, 80-62-6.

Effects of α Substitution on the Carbonyl Stretching Frequencies of Phenyl Carboxylates

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Received September 2, 1981

The infrared carbonyl stretching frequencies for several esters of the general formula $R^1R^2R^3C$—COOPh were determined in carbon tetrachloride. The σ^* and E_s Taft parameters as well as the $\nu_{Charton}$ parameters for the same esters were determined. The carbonyl stretching frequencies are well correlated by a dual substituent parameter treatment: $\nu_{C=O} = \nu^0_{C=O} + \rho^*\sigma^* + \delta E_s$ or $\nu_{C=O} = \nu^0_{C=O} + \rho^*\sigma^* + \Psi\nu_{Charton}$. In both cases the steric parameter is much larger than the polar parameter, suggesting that the effect of the substituents on the carbonyl stretching frequencies is of a steric nature, although a small contribution of the polar effect is observed.

An earlier investigation reported the effect of substitution at the α-position of phenyl carboxylates on the carbonyl stretching frequencies of the esters in carbon tetrachloride and chloroform solutions[2]. In continuation of this work, we have prepared several phenyl esters of allylacetic acid mono- and disubstituted at the α-position, with the general formula CH_2=$CHCH_2CR^1R^2COOPh$. These include phenyl allylacetate, phenyl allylethylacetate, phenyl allylphenylacetate, phenyl allylisopropylacetate, phenyl allylmethylacetate, phenyl allyldimethylacetate, phenyl allylethylphenylacetate, and phenyl allyldiphenylacetate. The Taft[3] and Charton[4] parameters of the groups CH_2=$CHCH_2$—$\dot{C}R^1R^2$ were determined, as were the carbonyl stretching frequencies of the esters in carbon tetrachloride. Our investigations were undertaken in order to obtain quantitative information pertinent to the steric and/or electronic effects on the carbonyl stretching frequencies of the esters caused by substituents at the α-position of the phenyl allylacetate.

Experimental Section

Materials. Allylacetic acid, butyric acid, isobutyric acid, isovaleric acid, phenylacetic acid, and phenyl acetate were obtained commercially and were either redistilled or recrystallized before use. Phenyl allylacetate, phenyl allylphenylacetate, and phenyl allyldiphenylacetate were prepared previously in our laboratories.[2]

Preparation of α-Substituted Allylacetic Acids. Allylethylacetic acid was prepared in accordance with the procedure of Pfeffer et al.[5] with some modifications: 108 mmol of n-butyllithium (2 M solution in hexane) was added to a solution of 96 mmol of diisopropylamine in 30 mL of THF. A solution of 48 mmol of butyric acid in 10 mL of THF was added slowly. After 15 min, 10 mL of HMPT was added and the solution stirred for 15 min. Allyl bromide (104 mmol) was then added. After stirring at room temperature for 2 h, followed by distillation of the solvent, the residue was poured into water and extracted with petroleum ether. The water layer was acidified and extracted with ethyl ether. The ether solution was washed with cold water and dried with $MgSO_4$. After removal of the ether, the crude acid was purified by the use of a silica gel column, employing ether/chloroform (4:1). The purified product was distilled to give the required acid. The same procedure was employed for the preparation of the acids shown in Table I.

Preparation of α-Substituted Phenyl Allylacetates. Phenyl allylethylacetate was prepared in accordance with the procedure of Kanaoka et al.[6] with some modifications: 112 mmol of P_2O_5 was added to 113 mmol of ethyl ether and 204 mmol of chloroform. Then, 15 mmol of allylethylacetic acid and 26 mmol of phenol were added. The reaction mixture was stirred during 24 h at room temperature. After removal of the solvents, the residue was poured into ice and almost neutralized with a 10% water solution of NaOH. The final neutralization was made with $NaHCO_3$. The water solution was extracted with chloroform. The chloroform solution was washed with a $NaHCO_3$ water solution and with water and then dried with $MgSO_4$. After removal of the chloroform, the crude ester was purified by the use of a silica

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