Studies of Saturated Heterocyclic Compounds. II.[1] The Preparation and PMR Spectroscopic Study of Mono- and Di-substituted-1,3-dioxolan-4-ones

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The relationship of the configurations and the magnitude of the long-range spin coupling constants between the 2-H and 5-H, $J_{2,5}$, of 1,3-dioxolan-4-ones has been elucidated, the $J_{2,5}(trans)$ value being always larger than the $J_{2,5}(cis)$ value. Geometrical isomers of several 2,5-disubstituted derivatives have been separated by means of preparative tlc and assigned by means of PMR spectroscopy, especially by the use of their $J_{2,5}$ values. The sign of the $J_{2,5}$ values for a 2-trichloromethyl derivative has been determined by a partial decoupling experiment, both $J_{2,5}$ (*cis*) and $J_{2,5}$' (*trans*) being positive.

In a previous paper,[1] we reported that the magnitudes of the long-range coupling constants between 2-H and 5-H, $J_{2,5}$, of 1,3-dioxolan-4-ones may be useful for determining the configurations of geometrical isomers of 2,5-disubstituted derivatives because the derivatives containing phenyl and trichloromethyl groups showed fairly large $J_{2,5}$ values as a result of a dual-path mechanism[2,3] between 2-H and 5-H across the oxygen atoms, $J_{2,5}(trans)$ being larger than $J_{2,5}$ (cis).[4] Since stereochemical studies of 1,3-dioxolan-4-ones have been left undeveloped because of the difficulty of the isolation and identification of each isomer,[5-8] the measurement of the $J_{2,5}$ can be expected to be an effective method of their stereochemical assignments. Therefore, a detailed study has now been made with other derivatives.

In this paper, we will first examine whether configurational assignments using differences in phenyl-proton chemical-shifts in some *p*-substituted phenyl derivatives agree with those[1] previously obtained by using the spectral patterns of phenyl protons. Secondly, we will elucidate the relationship between the $J_{2,5}$ values and the configurations of these compounds. Next, the configurational assignments for geometrical isomers of several 2,5-disubstituted derivatives by PMR spectroscopy will be reported. Finally, the determination of the signs of $J_{2,5}(cis)$ and $J_{2,5}(trans)$ for a 2-trichloromethyl derivative by means of a partial decoupling experiment will be described.

Experimental**

*Preparation of Materials.**** 5-Substituted- and 2,5-disubstituted-1,3-dioxolan-4-ones were prepared from the corresponding *dl*-α-hydroxycarboxylic acids and aldehydes; each isomer of the 2,5-disubstituted derivatives was separated from the reaction mixture by means of preparative tlc.[1] The physical constants of these compounds are listed in Table 1. 2-Trichloromethyl-1,3-dioxolan-4-one (Bp 94.5—96 °C/7 mmHg, Mp 40—41 °C) was prepared by the reaction of glycolic acid and chloral.[7,9] All the sample were purified by repeated distillations or by recrystallization from suitable solvents before the measurement, and the 1,3-dioxolan-4-one ring was identified by means of its IR spectra ($\nu_{C=O}$).

Measurements. The PMR spectra were measured with a Varian A-60 spectrometer and a JNM 4H-100 spectrometer at room temperature. Carbon tetrachloride, chloroform-*d*, and acetone-d_6 were used as solvents (concentration: *ca.* 40—50 mg/0.5 ml), and TMS was used as an internal reference. The chemical shifts and coupling constants were recorded in δ and Hz respectively. The solutions were degassed for the partial decoupling experiments, but were not degassed for the other measurements. The mass spectra were measured with a Hitachi RMU-7M spectrometer (ionizing potential: 70 eV; chamber temperature: 150 °C), and the millimass data were calculated against the standard peaks (PFK or *n*-eicosane), using a Hitachi 002-type datalizer connected with the spectrometer. Since, in the low-mass spectra, no distinguishable difference between the geometrical isomers was observed under the present conditions, the measurements of the millimass spectra were carried out with only one of each pair. The IR spectra were measured using a Hitachi-Perkin Elmer 225 spectrometer in a carbon tetrachloride solution (*ca.* 0.2 mol/l, 0.1 mm KRS-5 cell) or KBr discs.

Results and Discussion

Table 2 shows the PMR spectral data for the phenyl protons of several 5-*p*-substituted phenyl derivatives; a higher-field part of the spectrum was used in an approximate analysis of the AA'BB' system in order to avoid complications due to additional larger couplings caused by 5-H. Moreover, the ring protons were assigned by the use of their benzylic couplings with 5-H: the higher-field part of the AA'BB' spectrum was attributable to the protons (A protons) *ortho* to the substituent group, while the lower-field part was attributable to the *meta*-protons (B protons).

By comparing the differences in chemical shifts between the A and B protons $|\Delta\delta_{AB}|$ obtained for the 2-trichloromethyl-5-*p*-substituted phenyl derivatives (Compounds **5** and **6**) in $CDCl_3$, the $|\Delta\delta_{AB}|$ values of the isomers with lower R_f values were found to be larger than those with higher R_f values, which are similar to the $|\Delta\delta_{AB}|$ values of 5-*p*-substituted phenyl derivatives (Compounds **2** and **3**). The same trend continues in the other solvents, although the chemical

** All the melting points and boiling points are uncorrected.

*** All the compounds except for the Compound **1** and the 2-trichloromethyl derivative are unknown.

Table 1. Physical constants of 1,3-dioxolan-4-ones

No.	Compound 2-R	5-R′		Bp, °C/mmHg (Mp, °C)	Millimass, M^+ (*m/e*) Found (Calcd)	$\nu_{C=O}$ cm^{-1}	R_f Value[c]
1	H	C_6H_5		124—125/5	—	1825[a]	0.31
2	H	*p*-Cl·C_6H_4		141/4	198.0084 ($C_9H_7ClO_3$=198.0083)	1825[a], 1790	0.35
3	H	*p*-$CH_3OC_6H_4$		137/1	194.0588 ($C_{10}H_{10}O_4$=194.0576)	1825[a], 1795	0.19
4	H	$C_6H_5CH_2$		112—113/1	178.0638 ($C_{10}H_{10}O_3$=178.0629)	1805[a]	0.31
5	CCl_3	*p*-Cl·C_6H_4	*cis*	needles (105—105.5)	313.9067 ($C_{10}H_6Cl_4O_3$=313.9071)	1837[a]	0.58
			trans	needles (102—102.5)	—	1835[a]	0.69
6	CCl_3	*p*-$CH_3OC_6H_4$	*cis*	needles (110—112)	—	1835[a], 1815	0.40
			trans	powder (52)	309.9581 ($C_{11}H_9Cl_3O_4$=309.9566)	1832[a]	0.51
7	CCl_3	$C_6H_5CH_2$	*cis*	needles (54—55)	293.9601 ($C_{11}H_9Cl_3O_3$=293.9617)	1820[a]	0.55
			trans	plates (54—55)	—	1823[b]	0.61
8	CBr_3	C_6H_5	*cis*	powder (112—113)	411.7969 ($C_{10}H_7Br_3O_3$=411.7947)	1800[b]	0.61
			trans	needles (95—96)	—	1810[b]	0.68
9	CH_3	*p*-Cl·C_6H_4	*cis*	112/2	—	1807[a]	0.37
			trans	needles (60—61)	212.0242 ($C_{10}H_9ClO_3$=212.0240)	1812[a]	0.24
10	CH_3	*p*-$CH_3OC_6H_4$	*cis*	plates (40)	208.0763 $C_{11}H_{12}O_4$=208.0735)	1807[a]	0.22
			trans	plates (58—59)	—	1815[a], 1804	0.17
11	CH_3	C_6H_5	*cis*	98—99/1	—	1805[a]	0.35
			trans	plates (46—47)	178.0632 ($C_{10}H_{10}O_3$=178.0629)	1813[a]	0.26
12	C_2H_5	C_6H_5	*cis*	105—107/1	192.0800 ($C_{11}H_{12}O_3$=192.0786)	1800[a]	0.40
			trans	125—126/2	—	1803[a]	0.32

a) In CCl_4. b) KBr disc. c) R_f values were determined on a silica gel plate, which was coated with silica gel HF_{254} (Merck) at 0.25 mm thickness and activated at 110 °C, 40 min. (developer: benzene; detection: UV light at 254 nm).

shifts (δ) of the phenyl protons in $(CD_3)_2CO$ shift toward a lower-field side than those in CCl_4 or $CDCl_3$. Accordingly, the isomers with lower R_f's, whose phenyl protons show larger $|\Delta\delta_{AB}|$ values, can be assigned to a *cis*-configuration, because the protons should be subject to the larger magnetic anisotropy of the *cis* 2-trichloromethyl group;[4] this assignement is in accordance with those previously reported.[1] In the case of compounds without any highly anisotropic substituent, such as the 2-methyl-5-*p*-methoxyphenyl derivative (Compound **10**), however, the $|\Delta\delta_{AB}|$ values are not useful for assigning the configuration because of an ambiguous difference between the *cis* and the *trans* isomer. Therefore, the $J_{2,5}$ values can be a more significant measure for this purpose, as will be discussed later. In all the compounds, no significant solvent effect on the coupling constants of the phenyl protons is observed.

Table 3 lists the PMR spectral data of the 5-substituted- and 2,5-disubstituted-1,3-dioxolan-4-ones used in this study. The $J_{2,5}$ values of the *trans* forms of Compounds **5** and **6** ($|J|$=1.4—1.6 Hz) are larger than those ($|J|$=1.0—1.2 Hz) of the *cis* forms. These J values are barely affected by the *p*-substituent on the 5-phenyl group or by the solvents. Although the $J_{2,5}$ values of the 5-substituted derivatives (Compounds **1**—**4**) are smaller than those of the 2,5-disubstituted ones, there is a distinguishable difference between the $J_{2,5}$(*trans*) and the $J_{2,5}$(*cis*) values. The assignment based on the $J_{2,5}$ values for the methylene protons of Compounds **1**—**4** are in agreement with that made on the basis of the deshielding effects of their phenyl group. The same relationship between $J_{2,5}$ values has been found in the corresponding compound, with the 2- and the 5-substituents being exchanged for one another,[1] and also in the 2-phenyl[1] and 2-trichloromethyl derivatives. In general, therefore, the isomers with larger $J_{2,5}$ values can be assigned to the *trans*-configuration.

Table 2. PMR Spectral data for phenyl protons of 5-*p*-substituted phenyl derivatives

Compound (2-R, 5-R′)			Chemical shifts (δ) A Protons	Chemical shifts (δ) B Protons	$\lvert\Delta\delta_{AB}\rvert$[a]	Coupling constants (Hz)[b] $\lvert J_{ortho}\rvert$	$\lvert J_{meta}\rvert$	$\lvert J_{para}\rvert$
2 (H, *p*-Cl·C_6H_4)		*a*	7.33		*ca.* 0			
		b	7.38		*ca.* 0			
		c	7.49		*ca.* 0			
5 (CCl_3, *p*-Cl·C_6H_4)	higher[c]	*a*	7.36		*ca.* 0			
		b	7.40		*ca.* 0			
		c	7.52	7.60	7.6	8.8	2.5	0.4
	lower[c]	*a*	7.32	7.50	8.0	8.6	2.5	0.4
		b	7.40	7.49	9.3	8.9	2.5	0.3
		c	7.48	7.63	11.4	9.0	2.5	0.4
3 (H, *p*-$CH_3OC_6H_4$)		*a*	6.83	7.24	41.3	9.0	2.5	0.4
		b	6.93	7.34	40.9	9.0	2.5	0.4
		c	6.98	7.37	39.4	9.0	2.5	0.4
6 (CCl_3 *p*-$CH_3OC_6H_4$)	higher[c]	*a*	6.86	7.26	40.0	8.8	2.5	0.3
		b	6.95	7.32	37.6	8.8	2.5	0.3
		c	7.01	7.46	45.0	8.8	2.5	0.2
	lower[c]	*b*	6.91	7.41	50.1	8.9	2.5	0.3
		c	7.00	7.49	48.8	8.8	2.5	0.2
10 (CH_3, *p*-$CH_3OC_6H_4$)	higher[c]	*a*	6.82	7.26	43.9	8.8	2.5	0.2
		b	6.91	7.34	42.6	8.9	2.5	0.2
		c	6.96	7.36	40.1	8.9	2.4	0.3
	lower[c]	*a*	6.82	7.24	42.0	8.8	2.5	0.3
		b	6.91	7.34	40.1	8.8	2.5	0.3
		c	6.97	7.36	39.2	8.8	2.5	0.3

a) Hz at 100 MHz b) J_{ortho}: $J_{AB}=J_{A'B'}$, J_{meta}: $J_{AA'}=J_{BB'}$, J_{para}: $J_{AB'}=J_{A'B}$ c) higher: isomer of higher R_f value, lower: isomer of lower R_f value *a*: in CCl_4, *b*: in $CDCl_3$, *c*: in $(CD_3)_2CO$.

Table 3. PMR Spectral data of 5-substituted- and 2,5-disubstituted-1,3-dioxolan-4-ones

Compound		Chemical shifts (δ) 2–H *cis*[a]	2–H *trans*[b]	5–H *cis*[c]	5–H *trans*[d]	Phenyl protons	Others	Coupling constant (Hz) $\lvert J_{2,5}\rvert$	$\lvert J_{gem}\rvert$	$\lvert J_{vic}\rvert$
										(2-CH_2)
1	*a*	5.46(dd)	5.53(t)	5.07(s)		*ca.* 7.32(s)		0.7	0.4	0.4
	b	5.56(t)	5.63(t)	5.15(s)		*ca.* 7.38(c)		0.8	0.5	0.5
	c	5.63(dd)	5.71(t)	5.32(s)		*ca.* 7.42(c)		0.8	0.4	0.5
2	*a*	5.49(dd)	5.56(s)	5.05(s)		7.33(s)		0.9	0.4	0.5
	b	5.58(t)	5.65(t)	5.17(s)		7.38(s)		0.9	0.5	0.4
	c	5.68(dd)	5.80(t)	5.41(s)		7.49(s)		1.1	0.4	0.4
							(OCH_3)			(2-CH_2)
3	*a*	5.43(dd)	5.51(s)	4.99(s)		6.83 7.24	3.73	0.9	0.4	0.5
	b	5.54(t)	5.62(t)	5.14(s)		6.93 7.34	3.79	0.9	0.5	0.4
	c	5.62(dd)	5.72(t)	5.29(s)		6.98 7.37	3.79	1.0	0.5	0.5
							(5-CH_2)			(5-CH_2) (5H-CH_2)
4	*a*	5.21(d)	5.12(d)	4.29(m)		7.19(s)	2.95 3.10	1.0	0.5	14.7 6.9 4.0
	b	5.30(d)	5.12(t)	4.43(m)		7.27(s)	3.02 3.19	1.1	0.5	14.7 6.7 3.9
	c	5.39(s)		4.55(m)		7.29(c)	3.00 3.17	—	—	14.7 7.7 3.5
5 *cis*	*a*		5.89(d)		5.44(s)	7.32 7.50		1.0		
	b		5.97(d)		5.53(s)	7.40 7.49		1.0		
	c		6.33(d)		5.93(s)	7.48 7.63		1.0		
5 *trans*	*a*	5.97(d)		5.56(d)		7.36(s)		1.4		
	b	6.06(d)		5.66(d)		7.40(s)		1.6		
	c	6.58(d)		6.00(d)		7.52 7.60		1.4		
							(OCH_3)			
6 *cis*	*b*		5.89(d)		5.44(s)	6.91 7.41	3.80	1.1		
	c		6.24(d)		5.79(s)	7.00 7.49	3.81	1.2		
6 *trans*	*a*	5.92(d)		5.49(s)		6.86 7.26	3.75	1.5		
	b	6.03(d)		5.62(d)		6.95 7.32	3.81	1.6		
	c	6.49(d)		5.86(d)		7.01 7.46	3.82	1.5		

Compound			Chemical shifts (δ) 2-H *cis*[a]	2-H *trans*[b]	5-H *cis*[c]	5-H *trans*[d]	Phenyl protons	Others	Coupling constants (Hz) $\lvert J_{2,5}\rvert$	$\lvert J_{gem}\rvert$	$\lvert J_{vic}\rvert$
								(5-CH_2)		(5-CH_2)	(5H-CH_2)
7	*cis*	*a*		5.66(d)		4.55(m)	7.22(s)	3.13 3.17	1.0	14.6	7.2 5.8
		b		5.77(d)		4.68(m)	7.29(s)	3.20 3.24	1.1	14.6	7.9 5.0
		c		6.09(d)		5.00(m)	7.32(s)	3.20 3.26	1.0	14.6	9.7 3.3
	trans	*a*	5.35(d)		4.88(m)		7.24(s)	3.07 3.19	1.5	14.6	4.7 4.5
		b	5.45(d)		4.97(m)		7.30(s)	3.11 3.25	1.5	14.6	4.8 4.7
		c	5.90(d)		5.16(m)		7.33(s)	3.15 3.28	1.4	14.7	6.1 4.6
8	*cis*	*b*		5.77(d)		5.50(s)	*ca.* 7.41(c)		1.0		
		c		6.09(d)		5.87(s)	*ca.* 7.53(c)		1.0		
	trans	*b*	5.93(d)		5.71(d)		7.42(s)		1.5		
		c	6.40(d)		5.96(d)		*ca.* 7.52(c)		1.6		
								(CH_3)			(2H-CH_3)
9	*cis*	*a*		5.78(dq)		5.24(s)	7.35(s)	1.59(d)	0.8		5.1
		b		5.89(dq)		5.37(s)	7.39(s)	1.62(d)	0.9		5.0
		c		6.07(dq)		5.58(s)	7.49(s)	1.61(d)	0.9		5.0
	trans	*a*	5.70(dq)		5.06(d)		7.34(s)	1.62(d)	1.4		4.9
		b	5.80(dq)		5.19(d)		7.39(s)	1.66(d)	1.4		5.0
		c	5.93(dq)		5.46(d)		7.49(s)	1.64(d)	1.5		5.0
								(CH_3) (OCH_3)			(2H-CH_3)
10	*cis*	*a*		5.74(dq)		5.20(s)	6.82 7.26	1.55(d) 3.74	0.8		5.0
		b		5.87(dq)		5.34(s)	6.91 7.34	1.59(d) 3.78	0.9		5.0
		c		5.99(dq)		5.45(s)	6.96 7.36	1.56(d) 3.78	1.0		5.0
	trans	*a*	5.62(dq)		4.99(s)		6.82 7.24	1.57(d) 3.73	1.0		5.0
		b	5.76(dq)		5.17(s)		6.93 7.33	1.65(d) 3.79	1.3		5.0
		c	5.86(dq)		5.34(s)		6.97 7.36	1.61(s) 3.80	1.3		5.0
								(CH_3)			(2H-CH_3)
11	*cis*	*a*		5.76(dq)		5.26(s)	*ca.* 7.34(c)	1.56(d)	0.8		5.0
		b		5.88(dq)		5.39(s)	*ca.* 7.40(c)	1.60(d)	0.9		5.0
		c		6.04(dq)		5.54(s)	*ca.* 7.44(c)	1.59(d)	1.0		5.0
	trans	*a*	5.67(dq)		5.07(d)		7.35(s)	1.60(d)	1.2		4.9
		b	5.78(dq)		5.21(d)		7.41(s)	1.65(d)	1.4		5.0
		c	5.90(dq)		5.41(d)		7.44(s)	1.63(d)	1.5		5.0
								(CH_2) (CH_3)		(2H-CH_2)	(CH_2-CH_3)
12	*cis*	*a*		5.61(dt)		5.24(s)	7.34(s)	1.84(m) 1.04(t)	0.8	4.5	7.4
		b		5.74(dt)		5.37(s)	7.40(s)	1.89(m) 1.05(t)	1.0	4.6	7.3
		c		5.88(st)		5.52(d)	*ca.* 7.44(c)	1.93(m) 1.02(t)	1.0	4.8	7.4
	trans	*a*	5.51(dt)		5.07(d)		7.33(s)	1.88(m) 1.05(t)	1.2	4.6	7.3
		b	5.62(dt)		5.20(d)		7.40(s)	1.94(m) 1.07(t)	1.3	4.6	7.3
		c	5.75(dt)		5.41(d)		*ca.* 7.43(c)	1.97(m) 1.06(t)	1.3	4.7	7.5

a) *cis* to the 5-substituent group. b) *trans* to the 5-substituent group. c) *cis* to the 2-substituent group. d) *trans* to the 2-substituent group. *a*: in CCl_4, *b*: in $CDCl_3$, *c*: in $(CD_3)_2CO$. s: singlet or almost single peak, c: complicated singals, d: doublet, t: triplet, q: quartet, m: multiplet more than quartet, and for example, dd: doubly doublet.

On this basis, the configurations of the geometrical isomers of several 2,5-disubstituted derivatives (Compounds **7**—**12**) can be confirmed by the $J_{2,5}$ values.

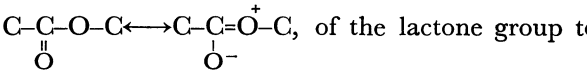
In 2-trichloromethyl (or 2-tribromomethyl)-5-phenyl (or benzyl) derivatives (Compounds **5**—**8**), all of the *trans* isomers show higher R_f values than the *cis* isomers on the tlc coated with silica gel, whereas in the corresponding 2-methyl (or 2-ethyl) derivatives (Compounds **9**—**12**) the isomers with smaller $J_{2,5}$ values appeared at the upper band on the tlc. Thus, in the latter the isomers assigned as *cis* isomers give higher R_f values than those of the *trans* isomers. The R_f values of the methyl (or ethyl) derivatives listed in Table 1 are shown to be lower than those of the corresponding trichloromethyl (or tribromomethyl) derivatives. A different behavior among the methyl (or ethyl) derivatives and the trichloromethyl (or tribromomethyl) derivatives was also observed on the chemical shifts of the 2-H and 5-H signals; the 2-H and 5-H signals in 2-trichloromethyl (or 2-tribromomethyl)-5-phenyl (or benzyl) derivatives (Compounds **5**—**8**) both appear at a slightly higher field in the *cis* than in the *trans* isomer, except for the 2-H signal of Compound **7**. However, in 2-methyl (or 2-ethyl) derivatives (Compounds **9**—**12**) the 2-H and 5-H signals both appear at a higher field in the *trans* than in the *cis* isomer.

Finally, since no report has been found on the signs of the $J_{2,5}$, we aimed at determining them by a partial

decoupling experiment. For this purpose, the 2-trichloromethyl derivative is the most suitable because a further complication due to additional couplings is eliminated; the PMR spectrum of this compound can be analyzed as an ABX system, in which only twelve transitions were observed. The analysis gave the following results by the usual procedure: $\nu_A-\nu_B=15.0$ Hz, $\nu_B-\nu_X=126.9$ Hz, $|J_{AB}|=15.1$ Hz, $|J_{AX}|=0.2$ Hz, $|J_{BX}|=1.4$ Hz (at 100 MHz), and J_{AX} and J_{BX} are of the same sign. Since the J_{AB} value corresponds to a normal J_{gem} value, it is possible to assume a negative sign for the J_{AB}. Thus, a partial decoupling experiment on this spectrum has been carried out according to the usual method.[10] The experiment showed that J_{AX} and J_{BX} are both positive.

Further, on the basis of the magnetic anisotropy of the 2-trichloromethyl group,[7] the signals at the lower field (B proton) were assigned to one of the 5-methylene protons *cis* to the 2-trichloromethyl group, while the signals at the higher field (A proton) were assigned to the *trans* proton. Those assignments are in agreement with those made on the basis of the $J_{2,5}$ values.

The facts that both of the $J_{2,5}$ values have the same positive sign, and that the *trans* coupling constant has a larger value than the *cis* one, are in accordance with the empirical generalization found in 2,5-dihydrofurans[11] and 2,5-dihydropyrroles,[12] which may be considered to be isoelectronic with 1,3-dioxolan-4-ones. Therefore, in view of a resonance contribution, such as



of the lactone group to the ring-planarity, as has been pointed out by Barfield *et al.*[13] the coupling mechanisms may be considered to be the same as those of 2,5-dihydrofurans.

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References

1) Part I: Y. Asabe, S. Takitani, and Y. Tsuzuki, This Bulletin, **46**, 661 (1973).
2) M. Barfield, *J. Chem. Phys.*, **41**, 3825 (1963).
3) K. Tori and M. Ohtsuru, *Chem. Commun.*, **1960**, 886.
4) L. A. Cort and R. A. Stewart, *J. Chem. Soc., C*, **1971**, 1386. They reported equal values for the $J_{2,5}$ (*cis*) and $J_{2,5}$ (*trans*) values of the 2-trichloromethyl-5-phenyl derivative. However, our result was different from theirs.
5) E. L. Salmi and A. Pohjolaninen, *Ber.*, **72**, 798 (1939).
6) M. Baron and D. P. Hollis, *Rec. Trav. Chim. Pays-Bas*, **84**, 1109 (1965).
7) M. Faiines and J. Soulier, *Bull. Soc. Chim. Fr.*, **1970**, 332.
8) R. Brettle, *J. Chem. Soc., Perkin I*, **1972**, 611.
9) O. Wallach, *Ann.*, **193**, 1 (1878).
10) R. Freeman and D. H. Whiffen, *Mol. Phys.*, **4**, 321 (1961).
11) C. Barbier, D. Gagnaire and P. Vottero, *Bull. Soc. Chim. Fr.*, **1968**, 2330; D. Gagnaire and P. Vottero, *ibid.*, **1970**, 164.
12) T. J. Batterham, N. V. Riggs, A. V. Robertson, and W. R. J. Simpson, *Aust. J. Chem.*, **22**, 725 (1969).
13) M. Barfield, R. J. Spear, and S. Sternhell, *J. Amer. Chem. Soc.*, **93**, 5322 (1971).