SYNTHESES OF VINYLOGOUS 4H-PYRONES FROM 2,6-DIMETHYL-4H-PYRAN-4-THIONE AND ARENYL BROMOMETHYL KETONES

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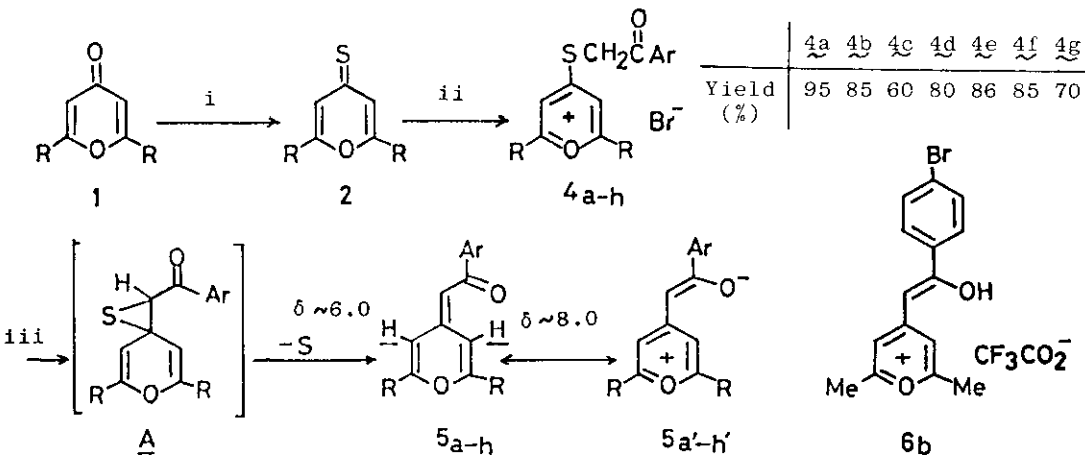
Abstract - 2,6-Dimethyl-4H-pyran-4-ylideneacetophenones (5) were prepared by desulfurization of mercaptopyrilium salts (4) with diazabicyclo[5.4.0]undecene (DBU) in moderate yield. The ^{1}H NMR spectra in $CDCl_3$ solution of 5 show the exclusive preference for s-cis conformation at the enone site.

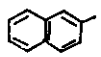
Although some synthetic methods for vinylogous 4H-pyrones have been devised,[1] there are inherent limitations in each methodology. In this report, we wish to describe the synthesis of 4H-pyran-4-ylideneacetophenone derivatives from easily available 2,6-dimethyl-4H-pyrone (1; R = Me). Thionation of 1 with phosphorus pentasulfide in the presence of $NaHCO_3$ in tetrahydrofuran solution afforded 4-thione derivative (2) in 70% yield. 4H-pyran-4-thione (2'; R = H) also was obtained in 70% yield by means of the same method. Treatment of 2 with arenyl bromomethyl ketones (3) in acetone solution under reflux gave the corresponding 4-mercaptopyrylium derivatives (4a-h) as precipitates in 60-95% yield, respectively.

Typical conditions for sulfide contraction and desulfurization by means of base and phosphine were applied to 4a according to the literature[2] but the desired product (5a) was obtained in just a low yield (20%). On the other hand, treatment of 4a with DBU without phosphine furnished 5a in 37% yield. In order to select a better reagent for preparation of vinylogous 4H-pyrones, various bases were examined. The best result was obtained when DBU was used as a base without any phosphine (Table I). It is considered that sulfide contraction with base results in the formation of spiro-episulfide derivative (A) and is followed by

desulfurization to give the product (5a-h), which is a zwitter-ionic species. A typical reaction utilizing DBU is described. To a stirred suspension of 4-(p-bromophenacyl)mercapto-2,6-dimethylpyrylium bromide (4b: 209 mg, 0.5 mmol) in acetonitrile (10 ml) was added dropwise at -15 °C a solution of DBU (80 mg, 0.5 mmol) in the same solvent (5 ml). The mixture was stirred at the same temperature for 1 h. The homogeneous solution was concentrated and the residue was purified by preparative TLC on silica gel (ethyl acetate-hexane; 1:3) to give 87 mg of 2,6-dimethyl-4-p-bromophenacylidene-4H-pyran (5b: 57%: mp 88-90 °C from hexane-ether).[3] Table II shows typical yields for the preparation of 5a-h. ^{1}H NMR spectral data are shown in Table III. In ^{1}H NMR spectra, one of β-protons of pyrone ring appears at very low field (δ ca. 8. 0) as compared with the counterpart (δ ca. 6.0). The downfield shift of one of β-protons in 5a-h is ascribed to deshielding anisotropies due to the exclusive existence of the s-cis conformation which minimizes the steric interactions between β-H and the benzoyl group, as has previously been described.[1b,4] The distinct two peaks at δ 5.92 and δ 7.95 for 5b coalesced into a single peak at δ 7.2 by addition of CF_3CO_2H to the solution, showing the formation of pyrylium salt (6b).



	4a	4b	4c	4d	4e	4f	4g	4h
Yield (%)	95	85	60	80	86	85	70	70

	a	b	c	d	e	f	g	h
R	Me	Me	Me	Me	Me	Me	Me	H
Ar	C_6H_5	4-BrC_6H_4	4-$MeOC_6H_4$	4-MeC_6H_4			C_6H_5CH=CH	4-BrC_6H_4

Reagents and conditions: (i) P_4S_{10}, $NaHCO_3$ in THF ; (ii) $BrCH_2COAr$ in Me_2CO ; (iii) DBU in CH_3CN.

Table I.
Reaction Conditions for Desulfurization of 4a,b in Acetonitrile at -15 °C

compd	Ar	reagents (1 equiv)	yield (%)
4a	C_6H_5	DBU/Ph_3P	22
		DBU/n-Bu_3P	20
		DBU	37
4b	4-BrC_6H_4	Et_3N	0
		Dabco[a]	0
		NaH	24
		PMP[b]	27
		DBU	57

[a], diazabicyclo[2.2.2]octane.
[b], 1,2,2,6,6-pentamethylpiperidine.

Table II.
Preparation of 4H-Pyrone Vinylogues (5a-h) by Desulfurization of 4a-h

compd	R	Ar	yield (%)
5a	Me	C_6H_5	37
5b	Me	4-BrC_6H_4	57
5c	Me	4-$MeOC_6H_4$	22
5d	Me	4-MeC_6H_4	36
5e	Me	2-$C_{10}H_7$[a]	51
5f	Me	2-C_4H_3S[b]	42
5g	Me	C_6H_5CH=CH	8
5h	H	4-BrC_6H_4	11

[a], 2-naphthyl. [b], 2-thiophenyl.

Table III. ^{1}H NMR and Mass Spectra of 4H-pyran-4-ylidene Derivatives (5a-h)

compd	Mass (m/z)	^{1}H NMR (δ, $CDCl_3$) methyl		vinyl		aromatic
5a	226(M^+)	2.11(d)[b]	2.16(d)[a]	5.91(q)[b]	6.09(s)	7.37-7.44(m,3H)
	149(base)			7.95(q)[a]		7.84-7.95(m,2H)
5b	305(M^+)	2.13(d)[a]	2.17(d)[b]	5.92(q)[a]	6.01(s)	7.51, 7.77(ABq,4H)[e]
	149(base)			7.95(q)[b]		
5c	256(M^+)	2.11(d)[a]	2.15(d)[b]	5.90(q)[a]	6.07(s)	6.90, 7.89(ABq,4H)[f]
	149(base)	3.84(s)		7.92(q)[b]		
5d	240(M^+)	2.10(d)[b]	2.15(d)[b]	5.89(q)[b]	6.08(s)	7.20, 7.81(ABq,4H)[d]
	149(base)	2.37(s)		7.95(q)[b]		
5e	276(M^+)	2.10(s)	2.15(s)	5.94(s)	6.24(s)	7.43-7.99(m,7H)
	149(base)			8.38(s)		
5f	232(M^+)	2.12(s)	2.19(s)	5.90(s)	5.97(s)	7.05(dd,1H)[k]
	149(base)			7.91(s)		7.46(dd,1H)[i]
						7.59(dd,1H)[h]
5g	252(M^+)	2.13(s)	2.16(s)	5.59(s)	5.86(s)	7.23-7.62(m,7H)
	140(base)			7.94(s)		
5h	277(M^+)	---	---	6.16(dd)[j]	6.15(s)	7.52,7.74(ABq,4H)[g]
	121(base)			8.07(dd)[j]	7.16(d,2H)[c]	

[a], J=0.7 Hz. [b], J=0.9 Hz. [c], J=6.2 Hz. [d], J=8.1 Hz. [e], J=8.8 Hz. [f], J=9.0 Hz. [g], J=13 Hz. [h], J=1.1 and 3.7 Hz. [i], 1.1 and 4.9 Hz. [j], J=2.3 and 5.4 Hz. [k], J=3.7 and 4.9 Hz.

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REFERENCES AND NOTES

1. (a) A. T. Balaban, P. T. Frangopol, A. R. Katritzky, and C. D. Nenitzescu, J. Chem. Soc., 3889 (1962). (b) E. T. Østensen and K. Undheim, Acta. Chem. Scand., 27, 2184 (1973). (c) J. A. VanAllan, G. A. Reynolds, and D. P. Maier, J. Org. Chem. 33, 4418 (1968). (d) I. Belsky, H. Dodiuk, and Y. Shvo, J. Org. Chem., 39, 989 (1974). (e) Y. Suzuki, T. Toda, and T. Mukai, Heterocycles, 4, 739 (1976). (f) A. T. Balaban, Tetrahedron Lett., 599 (1978).
2. M. R. P. Dubs, E. Götschi, and A. Eschenmoser, Helv. Chim. Acta, 54, 710 (1971).
3. Elemental analysis and spectral data for 5b were fully compatible with the given assignment.
4. A. T. Balaban, M. Fahmy, M. D. Gheorghiu, and V. Wray, Liebigs Ann. Chem., 1807 (1983). A. T. Balaban, V. Wray, N. G. Furmanova, V. I. Minkin, L. S. Minkina, Y. E. Czernysch, and G. S. Borodkin, Liebigs Ann. Chem., 1587 (1985).

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