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A NOVEL SYNTHESIS OF A CYCLOPENTANE RING FROM HOMOPYRONE DERIVATIVES

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2-Acylcyclopent-3-en-1-ol derivatives, 2, were synthesized by the reaction of homopyrones with phenyllithium. The intermediate may be a cyclopropylmethanol derivative, 3, which was isomerized into 2. Similar treatment with methyllithium, methylmagnesium iodide, or lithium aluminium hydride also gave 2.

In connection with our search for the reactivity of 2-oxabicyclo[4.1.0]hept-3-en-5-one (homopyrone) derivatives, 1, [1] we wish to report here preliminarily the formation of cyclopentenol derivatives, 2, starting from homopyrones. Treatment of homopyrones, 1a-c, with phenyllithium, methyllithium, methylmagnesium iodide, or lithium aluminium hydride in ether afforded cyclopentenes, 2a-c, as the major products in most cases. The structures of the products were assigned on the basis of their spectra and elemental analyses. Stereochemical assignments have not yet been made although one of the stereoisomers has been formed predominantly. The results are summarized in Table 1 and 2.

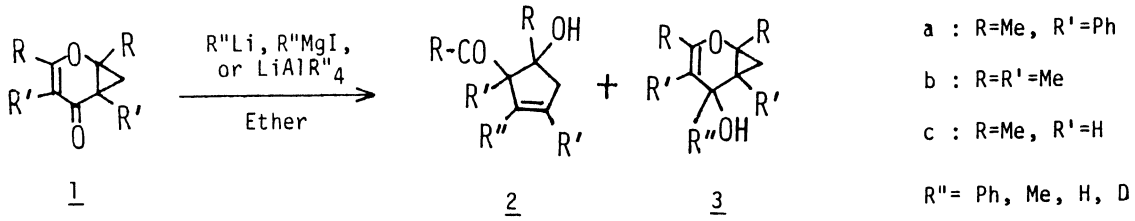

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Table 1. Reaction of Homopyrones, 1a-c, with PhLi, MeLi, MeMgI, or $LiAlH_4$ in Ether

Homopyrone	Reagent	Reaction Condition		Products (yields of purified ones)
1a (R=Me, R'=Ph)	PhLi	Room temp.	15 min.	2a(R"=Ph) (11%;oil)+3a(R"=Ph) (86%;mp 190-192°)[a]
	MeLi	0°C	15 min.	2a(R"=Me) (58%;mp 128-130°)
	MeMgI	reflux	4 h	2a(R"=Me) (37%;mp 128-130°)
	$LiAlH_4$ ($LiAlD_4$)	0°C	5.5 h	2a(R"=H or D) (11%;oil)
1b (R=R'=Me)	PhLi	Room temp.	5 min.	2b(R"=Ph) (46%;mp 109-111°)+3b(R"=Ph) (31%;mp 118-120°)[a]
1c (R=Me, R'=H)	PhLi	Room temp.	5 min.	2c(R"=Ph) (29%;mp 32-34°)

a) The product ratio varies with the experimental procedure.

In the reaction of tetrasubstituted homopyrone, 1a or 1b, with phenyllithium, 2-oxabicyclo-[4.1.0]hept-3-en-5-ol (cyclopropylmethanol) derivative, 3a or 3b,[2] could be isolated by careful, quick work-up of the reaction mixture, in addition to 2a or 2b, respectively. These compounds, 3a and 3b, have been easily transformed into 2a and 2b in aprotic solvents as shown in Table 3. Isolation of another cyclopropylmethanol derivative like 3a or 3b was unsuccessful in other cases, but it might be a reaction intermediate in all the reactions giving 2. In a protic solvent such as ethanol, 3a was converted into the seven-membered acetal, 5 (X=OEt).[3] Together with 2a, the diketone, 4a, was contaminated in 23% yield in the reduction of 1a with lithium aluminium hydride.[4]

Since homopyrone is accessible starting from a carboxylic acid and a ketone,[1] the present procedure may be useful as a novel synthesis of a cyclopentane ring.[5]

Table 2. Spectral Data of Cyclopentenes, 2

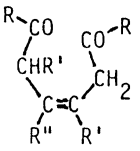
Compound	m/e (M^+)	ν_{max} (cm^{-1})	PMR (δ ppm in $CDCl_3$ using TMS as an internal standard) R	R'	R''	methylene	OH
2a (R''=Ph)*	368	3460, 1690	1.13(3H, s),	1.67(3H, s)	7.5-6.8(15H, m)	2.77, 2.93(2H, ABq, J=16Hz)	4.40
2a (R''=Me)	306	3480, 1675	0.88(3H, s),	2.12(3H, s)	7.5-6.9(10H, m) 2.12(3H, s)	2.72, 3.22(2H, ABq, J=16Hz)	5.15
2a (R''= H or D)	292	3500, 1690	0.77(3H, s),	1.92(3H, s)	7.25(10H, s) (6.28(1H, br s))	2.78, 3.08(2H, ABq, J=16Hz)	5.03
2b (R''=Ph)	244	3480, 1690	1.18(3H, s), 1.37(3H, s)	2.12(3H, s),	1.73(3H, br s) 7.4-6.9(5H, m)	2.43, 2.90(2H, ABq, J=17Hz)	2.75
2c (R''=Ph)	216	3480, 1700	1.53(3H, s),	2.10(3H, s)	3.70(1H, br s) 7.22(5H, s) 6.33-6.17(1H, m)	3.13-2.63(3H, m)	

* CMR δ : 213.3(s), 142.5(s), 138.3(s), 137.8(s), 137.5(s), 136.8(s), 129.7, 128.6, 128.1, 127.7, 127.4, 127.1, 83.4(s), 80.8(s), 49.8(t), 32.2(q), 25.6(q).

Table 3. Conversion of 3b(R''=Ph) into 2b(R''=Ph)

Solvent(conc. ca. 7%)	Reaction time[a]	Conversion[b]
chloroform	12 h	100%
benzene	72 h	100%
acetonitrile	72 h	ca. 80%

a) At room temperature. b) Monitored by PMR spectroscopy.



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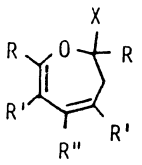

5 : X=alkoxy
5': X= OH

REFERENCES AND NOTES

1) Previous reports; H. Yamaoka, I. Mishima, M. Miyamoto, and T. Hanafusa, Bull. Chem. Soc. Jpn., 53, 469 (1980); H. Yamaoka, Y. Yamada, S. Ono, and T. Hanafusa, Chem. Lett., 523 (1979). 2) Properties: 3a(R''=Ph): m/e 368(M^+); PMR δ 0.95, 2.27(2H, ABq, J=6Hz), 1.42, 1.72(each 3H, s); CMR δ 146.3, 143.9, 138.2, 136.5, 116.8, 76.2, 63.3, 43.7(each s), 21.4, 18.0(each q), 18.0(t). 3b(R''=Ph): m/e 244(M^+); PMR δ 0.23, ca. 1.5(2H, ABq, J=7Hz), 0.80, 1.38, 1.50, 1.70(each 3H, s). 3) Properties: 5(R=Me, R'=R''=Ph, X=OEt): mp 116-117°C, m/e 396(M^+); PMR δ 1.20(3H, t), 3.78(2H, q, J=7Hz for Et), 1.37, 2.07(each 3H, s), 2.85, 3.17(2H, ABq, J=13Hz). 4) Diketone, 4, may be produced by the ketonization of the corresponding hemiacetal, 5', which is probably made from cyclopropylmethyl-allylmethyl rearrangement of 3; H. Yamaoka, K. Ohkata, and T. Hanafusa, Bull. Chem. Soc. Jpn., 49, 245 (1976). 5) Recent reviews; D. Tsunemoto and K. Kondo, Yuki Gosei Kagaku Kyokai Shi, 35, 1070 (1977); P. H. Bentley, Chem. Soc. Revs., 2, 29 (1973), and references cited therein.

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