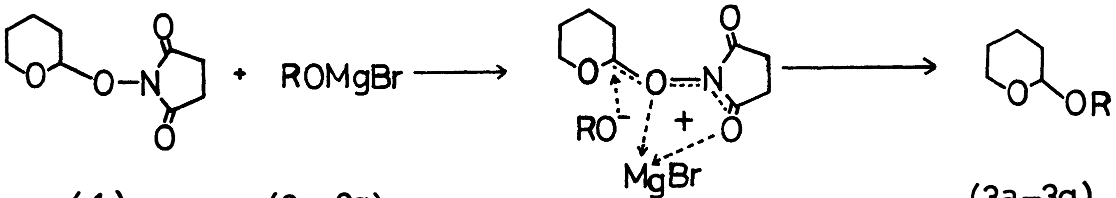
CHEMISTRY LETTERS, pp. 817-818, 1977. Published by the Chemical Society of Japan

A NEW OXANYLATION OF ALCOHOLS UNDER NEUTRAL CONDITIONS [1)]

Kyo ABE, Takanori SATO, Nobuo NAKAMURA, and Takeo SAKAN
Department of Chemistry, Faculty of Science, Osaka City University,
459 Sugimotocho, Sumiyoshiku, Osaka 558

N-(2-Oxanyloxy)succinimide transfered its oxanyl group to alkoxide anions and carbanions to give oxanylated products (3a - 3g and 5a - 5d) under almost neutral condition.

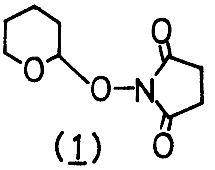
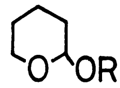
Oxanylation of alcohols under neutral or alkaline conditions has not been known. We wish to report that an activated oxanyl compound, N-(2-oxanyloxy)succinimide (1), is useful as an oxanylating agent for alcohols under neutral condition. N-(2-Oxanyloxy)succinimide (1) was synthesized from N-hydroxysuccinimide and 4H-2,3-dihydrooxin in a good yield according to the ordinary method.[2)] It was recrystallized from a mixture of benzene and n-hexane (2 : 1) to give white needles: mp 123°C; Anal. Calcd for $C_9H_{13}NO_4$: C, 54.26; H, 6.58; N, 7.03%. Found: C, 54.47; H, 6.61; N, 7.11%. ; ir ν_{max}^{nujiol} cm^{-1} 1740, 1720, 1220; nmr $\delta_{TMS}^{CDCl_3}$ ppm 1.42 - 2.20 (6H, m), 2.26 (4H, s), 3.40 - 3.68 (1H, m), 5.27 (1H, q, J = 4, 2 Hz).



(1) (2a-2g) (3a-3g)

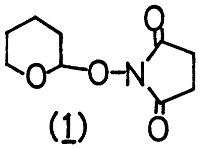
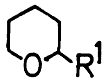
General oxanylation of O-anions in alkoxymagnesium bromides (2a - 2g) using N-(2-oxanyloxy)succinimide (1) was carried out as follows; to an ethereal solution of ethylmagnesium bromide, prepared from magnesium turnings (30 mg; 1.2 mg atom) and ethyl bromide (131 mg; 1.2 mmol) in ether (2 ml), was added alcohol (2) (1.2 mmol) in ether (2 ml) at 5°C. The white precipitate of alkoxymagnesium bromide was immediately formed. To this suspension was added a solution of N-(2-oxanyloxy)succinimide (1) (200 mg; 1 mmol) in dried benzene (10 ml) at room temperature. After the reaction mixture had been refluxed for 1 hr, the resulted solid was filtered off. The filtrate was washed with water and saturated brine, and dried over sodium sulfate. After evaporating the solvent, the residue was distilled under reduced pressure to give the 2-alkoxyoxane (3a - 3g). Its purity was examined by nmr. The yields of the products were summarized in table I.

Table I. The yields of the 2-alkoxyoxanes (3a - 3g)

Reactant (1)	R in ROMgBr (2)		product (3) (C°/ mmHg)		Yield (%)
 (1)	C_2H_5-	2a	3a	(75 - 80/ 103)	37
	$HC\equiv CCH_2$-	2b	3b	(76 - 79/ 25)	98
	C_4H_9-	2c	3c	(70 - 72/ 21)	72
	sec-C_4H_9-	2d	3d	(80 - 85/ 25)  (3)	65
	t-C_4H_9-	2e	3e	(54 -58 / 13)	95
	cyclo-C_6H_{11}-	2f	3f	(150 - 157/ 25)	72
	4-OH-cyclo-C_6H_{10}-	2g	3g	(128 - 136/ 1)	51

This procedure was not successful when it was applied to the syntheses of oxanylamines and β-oxanyloxyketones. Recently, the reaction of 2-(2,4-dichlorophenoxy)oxanes with the Grignard reagents has been reported.[3] We also tried the oxanylation of carbanions, generated from the Grignard reagents (4a - 4d), using the N-(2-oxanyloxy)succinimide (1) as follows; to an ethereal solution of the alkylmagnesium bromide (4), prepared from magnesium turnings (60 mg; 2.5 mg atom) and the alkyl bromide (2.4 mmol) in ether (6 ml), was added a solution of (1) (400 mg; 2 mmol) in dried benzene (30 ml). The reaction mixture was kept stirring for 1 hr at room temperature. The resulted precipitate was filtered off. The filtrate was washed with aqueous ammonium chloride solution and saturated brine, and dried over sodium sulfate. After evaporating the solvent, the residue was distilled under reduced pressure to give 2-alkyloxanes (5a -5d). The yields of the products were summarized in table II.

Table II. The yields of the 2-alkyloxanes (5a -5d)

Reactant (1)	R^1 in R^1MgBr (4)		Product (5) (C°/mmHg)		yield (%)
 (1)	n-C_6H_{13}-	4a	5a	(105 - 110/ 22)	66
	$C_6H_5CH_2$-	4b	5b	(94 - 103/ 5)  (5)	23
	$C_6H_5CH_2CH_2$-	4c	5c	(71 - 80/ 1)	79
	C_6H_5-	4d	5d	(97 - 102 / 20)	60

REFERENCES

1) The studies of the activated compound. part II. Part I of this series: K. Abe, T. Sato, N. Nakamura, and T. Sakan, Chem. Lett., 645(1977).

2) D. N. Robertson, J. Org. Chem., 25, 931 (1960).

3) H. Ishikawa, S. Ikeda, and T. Mukaiyama, Chem. Lett., 1051 (1975).

(Received May 12, 1977)