September, 1982] © *1982 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, *55*, *3035—3036 (1982)* 3035

Oxidizing Action of Complex of *N*,*N*-Dimethylbenzylamine Oxide with $SbCl_5$

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(Received January 25, 1982)

Synopsis. A 1:1 complex of *N*,*N*-dimethylbenzylamine oxide–$SbCl_5$ (**1**) was prepared in carbon tetrachloride quantitatively. Complex **1** was found to be a better reagent for oxidation of benzoin, furoin, benzyl alchols and pinacols than the complexes pyridine *N*-oxide–$SbCl_5$ and trimethylamine oxide–$SbCl_5$. The reaction path in oxidation of benzhydrol with **1** is described.

In the previous paper,[1] we reported that 1:1 complexes of pyridine *N*-oxide (**2**) and trimethyamine oxide (**3**) with $SbCl_5$ behave as an oxidizing agent for some compounds. In this paper, we describe the oxidation of benzoin, furoin, benzhydrol and *o*- and *p*-nitrobenzyl alcohols using the complex formed *N*,*N*-dimethylbenzylamine oxide (**4**) with $SbCl_5$ [$PhCH_2(CH_3)_2N–OSbCl_5$, **1**].

Experimental

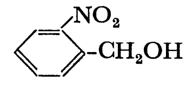
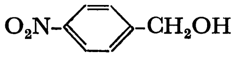
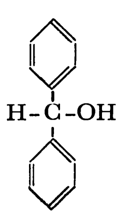
1:1 Complex of N,N-*Dimethylbenzylamine Oxide with* $SbCl_5$ *(1).* When a solution of **4** (9.50 g, 6.29 mmol) in CCl_4 (90 ml) was added to a solution of $SbCl_5$ (20.9 g, 62.9 mmol) in CCl_4, yellow crystalline complex **1** immediately deposited. The reaction mixture was filtered and washed with CCl_4 and then with petrolium ether. 30.1 g (99.0%), mp 206—208 °C (in a sealed capillary tube). ν_{max}^{KBr}; 1580 cm^{-1}, 1405 cm^{-1}, 1220 cm^{-1}, 1180 cm^{-1}, 1145 cm^{-1}, 975 cm^{-1}, 880 cm^{-1}, $\lambda_{max}^{CHCl_3}$; 268 nm (ε: 7120). Found: Cl, 39.40%. Calcd for $C_9H_{13}NOSbCl_5$: Cl, 40.10%.

Oxidation of Benzoin with 1. A mixture of benzoin (0.50 g, 2.35 mmol) in nitromethane was kept for 5 h at 60 °C. The reaction mixture was poured into water and filtered. After filtrates were extracted with ether, the ether solution was washed with dil. HCl. The solution was dried, filtered and evaporated, and then benzil (0.48 g, 95%) was separated from the residue by column chromatography (benzene–silica gel). The same procedure was also applied in the oxidation of furoin, except that chloroform was used as a eluent in column chromatography.

Results and Discussion

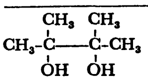
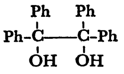
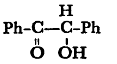
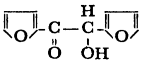
The oxidation of *o*- and *p*-nitrobenzyl alcohols with **1** gave the corresponding aldehydes in low yield (Table 1). In the equimolar reaction of benzhydrol with **1** in nitromethane at room temperature, bis(diphenylmethyl)ether was obtained in a 58% yield. The yield of benzophenone and bis(biphenylmethyl)ether increased when the reaction was carried out at 40 °C (Table 1). On the other hand, the yield of benzophenone increased at high temperature (Fig. 1). These results indicate that bis(diphenylmethyl)ether changes to benzophenone promptly, but benzophenone does not. After treatment of bis(diphenylmethyl)ether with equimolar **1** in nitromethane, benzhydrol and benzophenone were obtained (Fig. 2). Therefore, it should be concluded that both benzhydrol and bis(diphenylmethyl)ether are in equilibrium in the presence of **1**. The

TABLE 1. OXIDATION OF BENZHYDROL AND *o*- AND *p*-NITROBENZYL ALCOHOLS WITH *N*,*N*-DIMETHYLBENZYL AMINE OXIDE–$SbCl_5$ (1:1) COMPLEX

Substrates[a)] (mmol)		Reaction condition[b)]			Reaction products[c),d)] Yield/%		Recovered starting materials (%)
	Oxidant	Molar[e)] ratio	Temp °C	Time h	[A]	[B]	
 (3.3)	1	1.0	Reflux	1	9.3[f)]	6.2[g)]	68
		2.0	Reflux	10	17	5.8	58
		1.0	Reflux	1	15[h)]	6.3	74
 (3.3)		2.0	Reflux	2	32	17	37
		1.0	r.t.	110	2.4[i)]	58[j)]	26
		1.0	40	1	1.0	61	21
		1.0	40	2	2.4	65	16
		1.0	40	3	2.8	73	12
		2.0	40	1	14	33	24
(2.7)	4	20	40	3	2.4	4	77

a) Starting materials(0.5 g) were used in each run. b) Nitromethane (10 ml) was used as a solvent in each run. c) Tarry products were formed. d) All products were separated by TLC (benzene-silica gel). e) Substrates/Oxidants. f) *o*-Nitrobenzaldehyde; mp 46—47 °C (lit,[2)] 48 °C). g) They seem to be the corresponding bis(nitrobenzyl)ethers. h) *p*-Nitrobenzaldehyde; mp 104—105 °C (lit,[3)] 106—107 °C). i) Benzophenone; mp 47—48 °C (lit,[4)] 48 °C). j) Bis(diphenylmethyl)ether; mp 109 °C (lit,[5)] 109 °C).

TABLE 2. OXIDATION OF BENZOINS AND PINACOHOLS WITH N,N-DIMETHYLBENZYLAMINE OXIDE–$SbCl_5$ (1: 1) COMPLEX

Substrates[a] (mmol)	Reaction conditions[b]				Products yield/%	Recovered starting materials (%)
	Oxidant	Molar[c] ratio	Temp °C	Time h		
 $(CH_3)_2C(OH)-C(OH)(CH_3)_2$	1	1.0	r.t.	30	60[d]	63
		1.0	40	1	62[e]	14
		2.0	40	1	43	7
(4.2)		1.0	80	1	36	8
 $Ph_2C(OH)-C(OH)Ph_2$	1	1.0	r.t.	20	92	—
		1.0	50	5	81	—
		1.0	Reflux	5	80	—
(1.4)						
 $PhC(=O)-CH(OH)Ph$	1	1.0	r.t.	24	92[f]	5.0
		1.0	40	5	91	3.4
		1.0	60	5	95	—
(2.5)	4	2.0	60	5	16	73
	1	1.0	0	1	29[e],[g]	4.8
		1.0	5	1	30	4.6
		1.0	r.t.	1/6	38	10
(2.6)	4	2.0	30	20	—	87

a) Starting material (0.5 g) was used in each run. b) Nitromethane (10 ml) was used as a solvent in each run. c) Oxidants/substrates. d) The yield was determined as 2,4-dinitrophenylhydrazone. e) A lot of tarry products were formed. f) Benzil; 94—95 °C (lit,[6] 95 °C). g) Furil; 164—165 °C (lit,[7] 165 °C).

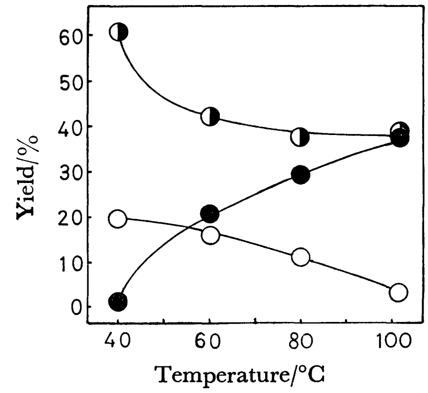
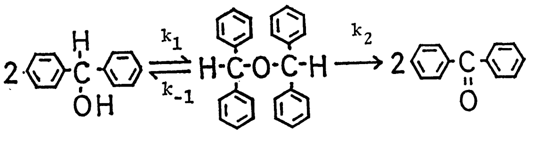


Fig. 1. The dependence of reaction temperature on the oxidation of benzhydrol with N,N-dimethylbenzylamine oxide–$SbCl_5$ (1:1) complex.
Reaction conditions: benzhydrol; 0.5 g (2.71 mmol), complex; 1.22 g (2.71 mmol), solvent; 10 ml of nitromethane, reaction time; 1 h. ●: Benzophenone, ◑: bis(diphenylmethyl)ether, ○: benbhydrol.

rate constants of each in the following equation depend



upon the reaction temperature, *i.e.* $k_2>k_1>k_{-1}$ near 40 °C, $k_1>k_2>k_{-1}$ from 60 °C to 70 °C and $K_2>k_1>k_{-1}\simeq 0$ near 100 °C (Fig. 1 and Fig. 2). In the first step of the reaction, a proton of benzhydrol is abstracted, as in the reaction of pyridine N-oxide with thiophenol.[8] After bis(diphenylmethyl)ether accumulates in the reaction system, it changes into both benzhydrol and benzophenone in accordance with the reaction temperature (Fig. 2). Compounds **4** seems to be less reactive than **1** in the reaction with benzhydrol (Table 1).

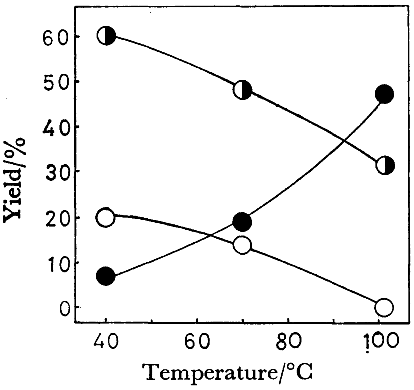


Fig. 2. The treatment of bis(diphenylmethyl)ether with N,N-dimethylbenzylamine oxide–$SbCl_5$ (1:1) complex. Reaction conditions: bis(diphenylmethyl)ether; 0.5 g (1.43 mmol), complex; 0.64 g (1.43 mmol), solvent; 10 ml of nitromethane, reaction time: 1 h. ●: Benzophenone, ◑: bis(diphenylmethyl)ether, ○: benzhydrol.

Although oxidation of benzoin with **1** under mild condition gave benzil in 95% that with **4** gave only 16.4%. A higher yield of benzoin was obtained in comparison with the case of using $SbCl_5$ as done for **2** and **3** reported before.[1] In the oxidation with furoin with **1**, moderate yields of furil were obtained (Table 2). Pinacolones were obtained in good yield in the oxidation of pinacols with **1** may be considered to be an effective catalyst for pinacol–pinacolone rearrangement.

The authors are grateful to Professors M. Tanaka and J. Kiji of Tottori University for their valuable advice.

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