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METAL-CATALYZED ORGANIC PHOTOREACTIONS.
TITANIUM(IV) CHLORIDE-CATALYZED PHOTOREACTIONS OF ALCOHOLS AND FORMIC ESTERS

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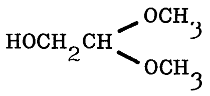
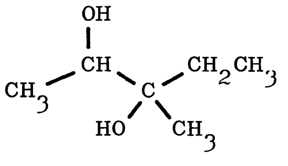
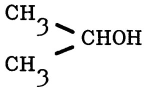
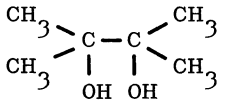
The UV-irradiation of some alcohols in the presence of titanium(IV) chloride gave products with a C-C bond formation between alcohol molecules. The titanium(IV) chloride-catalyzed photoreaction of formic esters in alcohols induced the formylation of alcohol at the α-position.

Previously we reported that when saturated[1] or unsaturated[2] ketones, Schiff's bases,[2] or nitriles[3] were irradiated in alcohols in the presence of titanium(IV) chloride, a C-C bond formation proceeded between the substrate and the alcohol molecules to produce 1,2-diol or its equivalents.

We have observed now that the irradiation of an alcohol solution of titanium(IV) chloride, not containing any other substrates than the metal compound, induced a C-C bond formation between the alcohol molecules. Actually the compound 1 - 3 were obtained quite selectively from methanol, ethanol, and 2-propanol, respectively (Table 1), although the reaction rates were slow as compared with those of the reactions involving appropriate substrates. The structures of the products were determined by spectroscopic data and/or by comparing with the authentic samples.[4]

All the reactions could be schemed as involving the initial electron transfer from the alcohol molecule to titanium followed by the proton elimination to produce a radical 4 (Scheme 1). The radicals from 2-propanol and ethanol (4b and 4c, respectively) would be stable enough to give the corresponding

Table 1. Photoreaction of Alcohols in the Presence of Titanium(IV) Chloride.[a]

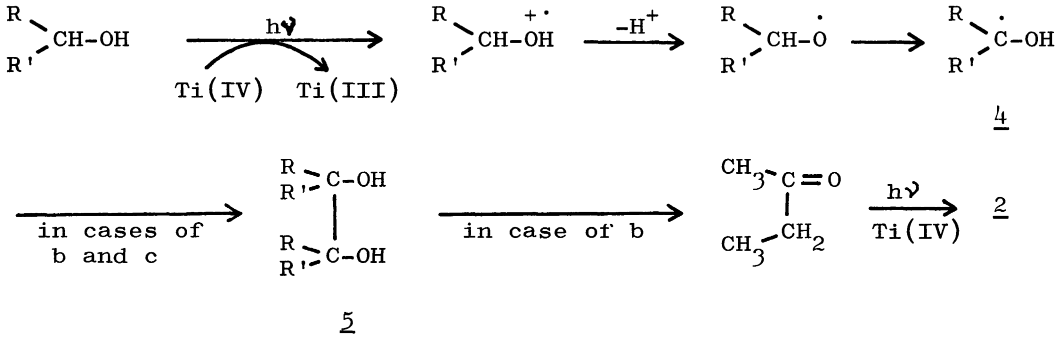
Alcohol	Product	Yield (%)[b]
CH_3OH	 $HOCH_2CH(OCH_3)_2$ 1	30
CH_3CH_2OH	 2[c]	50
 $(CH_3)_2CHOH$	 3	25

a) A solution of titanium(IV) chloride (0.1 ml) in alcohol (10 ml) was irradiated with UV-light from high-pressure mercury lamp (Ushio 452 (450 W)) for 15 h in a quartz tube.

b) Based on the molar amount of titanium(IV) chloride.

c) Threo and Erythro isomers were produced in a ratio of 1.7 : 1, and separated on a preparative VPC. The major component was tentatively assigned the structure of threo because of the more favorable transition state with less steric repulsion.

Scheme 1



a: $R = R' = H$ b: $R = CH_3$, $R' = H$ c: $R = R' = CH_3$

Scheme 2

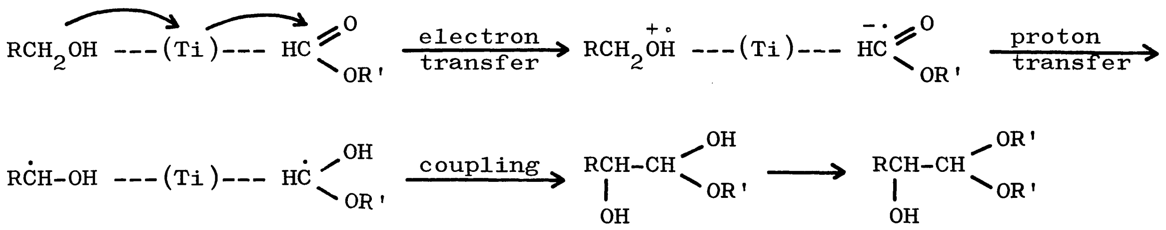
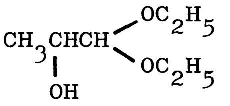
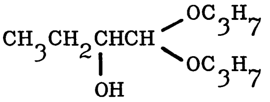


Table 2. Photoreaction of Formic Acid and Its Esters with Alcohols in the Presence of Titanium(IV) Chloride.[a)]

Formic acid or ester	Alcohol	Product	Yield(%)
HCOOH	CH_3OH	1	37
$HCOOCH_3$	CH_3OH	1	68
$HCOOC_2H_5$	C_2H_5OH	 $CH_3CH(OH)CH(OC_2H_5)_2$ 6	69
$HCOOC_2H_5$	$CH_3CH_2CH_2OH$	 $CH_3CH_2CH(OH)CH(OC_3H_7)_2$ 7	52

a) A solution of formic acid or ester (60 mg) and titanium(IV) chloride (0.1 ml) in alcohol (10 ml) was irradiated with UV-light from high pressure mercury lamp (Ushio 452 (450 W)) for 3 h in a quartz tube.

dimers 5. Although 2,3-dimethylbutanediol (5c = 3) from 2-propanol is stable under the reaction conditions and isolable as such, the diol 5b from ethanol is dehydrated to give 2-butanone, which in turn reacts with ethanol to give 2. The last step is a typical pattern of the titanium(IV) chloride-catalyzed photoreaction between ketone and alcohol which has been well characterized by our previous studies.[1] In support of this scheme, both of dl-2,3-butanediol and 2-butanone gave 2, when irradiated in ethanol in the presence of titanium(IV) chloride.

In contrast with the apparent dimerization of the radical 4 in cases of ethanol and 2-propanol, the reaction scheme for methanol seems to be slightly different. The following two schemes are conceivable as a possible route to the observed product in case of methanol: (i) 4a dimerizes to give ethylene glycol, which is oxidized to the product 1, or (ii) 4a eliminates a hydrogen atom to produce formaldehyde, which is further oxidized to formic acid, and the formic acid reacts with methanol to give the product 1 by the reaction scheme now generalized by our previous studies[1] (Scheme 2).

Although the reaction of formaldehyde with methanol under the present conditions was as slow as that of methanol alone, the reaction of formic acid with methanol proceeded much faster and afforded 1 as a sole product. On the other hand, however, the irradiation of ethylene glycol in ethanol did not give any amount of ethyl ester corresponding to 1. Thus we concluded that the scheme (ii) might be favorable for the present reaction. Presumably the radical 4a would be too unstable to dimerize, and would eliminate hydrogen atom to give formaldehyde instead. The slow step from formaldehyde to formic acid might be responsible for the slow formation of 1 from methanol.

Since the irradiation of formic acid in methanol gave an appreciable amount of 1, we carried out the reaction with some alcohols. It was found that formic acid, or more preferably formic esters, induced the formylation of alcohol at the α-position in reasonalbe yields and good selectivity (Table 2), when irradiated with UV-light in the presence of titanium(IV) chloride.

References
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2 T. Sato, S. Yoshiie, T. Imamura, K. Hasegawa, M. Miyahara, S. Yamamura, and O. Ito, Bull. Chem. Soc. Jpn, 50, 2714 (1977).
3 T. Sato and S. Yoshiie, Chem. Lett., 1976, 415.
4 1: IR(neat), 3400, 2940, and 1060 cm^{-1}; NMR(CCl_4), δ 2.80 (1H, bs), 3.43 (6H, s), 3.57 (2H, d, J = 6 Hz), and 4.43 (1H, t, J = 6 Hz). Threo-2: IR(CCl_4), 3400, 2970, 2930, 2880, 1460, 1380, and 1100 cm^{-1}; NMR(CCl_4), δ 0.91 (3H, t, J = 8 Hz), 1.05 (3H, s), 1.06 (3H, d, J = 8 Hz), 1.45 (2H, octet, J = 8 Hz), 3.28 (2H, b), and 3.58 (1H, q, J = 8 Hz). Erythro-2: IR(CCl_4), 3400, 2970, 2930, 2880, 1460, 1380, and 1110 cm^{-1}; NMR(CCl_4), δ 0.90 (3H, t, J = 8 Hz), 0.98 (3H, s), 1.06 (3H, d, J = 8 Hz), 1.42 (2H, quintet, J = 8 Hz), 3.50 (1H, q, J = 8 Hz), and 3.50 (2H, b). 3: Identical with the authentic sample. 6: IR(neat), 3450, 2980, 1120, and 1060 cm^{-1}; NMR(CCl_4), δ 1.0 - 1.4 (9H, m), 2.39 (1H, bs), 3.4 - 3.9 (5H, m), and 4.18 (1H, d, J = 7 Hz). 7: IR(neat), 3450, 2960, 2925, 2870, 1460, 1110, and 1060 cm^{-1}; NMR(CCl_4), δ 0.95 (3H, t, J = 7 Hz), 0.98 (6H, t, J = 7 Hz), 1.4 - 1.8 (6H, m), 2.01 (1H, bs), 3.4 - 3.9 (5H, m), and 4.26 (1H, d, J = 7 Hz).

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