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METAL-CATALYZED ORGANIC PHOTOCHEMISTRY
PHOTOCHEMICAL REACTION OF α,β-UNSATURATED KETONES IN METHANOL IN THE PRESENCE OF TITANIUM(IV) CHLORIDE

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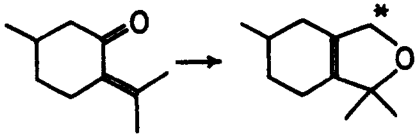
We reported that the photochemical reactions of dypnone and isoxazole were influenced extensively by the presence of copper(II) ion.[1)]

We now observed that $TiCl_4$ also exhibited a remarkable effect on the photochemical reaction of α,β-unsaturated ketone in methanol. Two types of reaction were observed under these conditions: (A) cyclization to form dihydrofuran, and (B) formation of dimethyl acetal. The reactions of pulegone 1[2a)] and dypnone 2 belong to the type A, which afforded 5 and 6, respectively, while the reactions of mesityl oxide 3 and 3-methyl-2-cyclohexenone 4 belong to the type B, affording 7 and 8, respectively. These reactions are notable in that one carbon increment (marked with asterisk) is introduced at the carbonyl carbon of the substrate while the carbonyl function is being lost. Yields and other by-products are summarized in the table. Each reaction is fairly clean and the amounts of other products not shown in the table are negligible, as revealed from the PMR and vpc analyses on the crude reaction mixture. The yields of 5, 6 and 8 shown in the table might be lower than the actual yields because of the loss during distillation.

The reaction medium was acidic due to the formation of HCl from $TiCl_4$ and methanol. Irradiation of these ketones in the presence of HCl or BF_3-etherate, or standing in the presence of $TiCl_4$ in dark resulted in either methanol addition to the double bond, or isomerization of double bond

Type A



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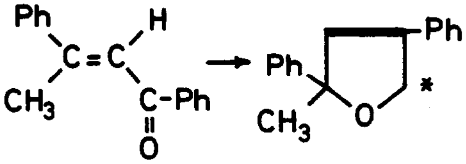

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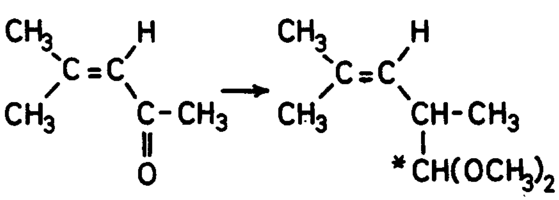

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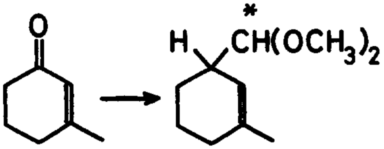

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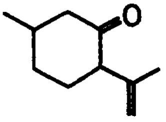
Table[a)]

ketones	products (isolated yields)			recovered ketones
1	5 (62%) bp 79-80°/10 mmHg	9 (1.8%)	10 (4.7%)	11%
2	6 (53%) bp 135-9°/0.05 mmHg	unknown-a (12%)	unknown-b (15%)	0%
3[b)]	7 (41%)	11 (41%)		18%
4	8 (33%) bp 64-7°/22 mmHg	unknown-c (1%)		3%

a) In experiments with ketones 1, 3 and 4, a solution containing 1.2 ml of ketone and 1.2 ml of $TiCl_4$ in 60 ml of methanol was irradiated for 6-8 hr at running water temperature. In case of ketone 2, a solution containing 2.5 ml of ketone and 2.0 ml of $TiCl_4$ in 40 ml of methanol was irradiated for 24 hr at the same temperature.

b) Yields were determined from PMR spectrum of the crude reaction mixture. Pure samples of 7 and 11 were collected on a preparative vpc.

(positional to β,γ, or *cis*-*trans*), and no traces of products 5-8 were detected. Thus, it is presumable that the by-products shown in the table arose from the thermal or photochemical reactions induced by the acid. When a solution of 1 containing $TiCl_4$ was refluxed for 4 hr, *retro*-aldol reaction resulted and 3-methylcyclohexanone was isolated. The acidic condition seems to be essential for the present reaction to proceed, because double bond migration to β,γ-position was the sole reaction pattern, in case of mesityl oxide, under the irradiation in *neutralized* medium which should contain only $Ti(OCH_3)_4$ as catalyst. The present reaction is characteristic of α,β-unsaturated ketone system, since ketone 12 was intact under these conditions.$^{2c)}$



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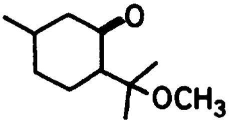

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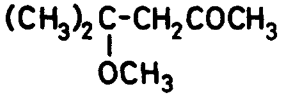

$(CH_3)_2\underset{\displaystyle OCH_3}{\underset{|}{C}}-CH_2COCH_3$

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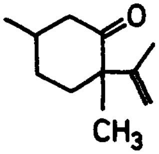

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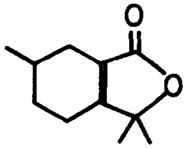
The structures of the main photoproducts 5-8 were deduced as follows. IR spectra revealed that all these products did not contain hydroxyl nor carbonyl groups. Satisfactory spectroscopic data were obtained for all other products.



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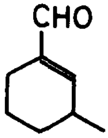
5 PMR (CCl_4): δ 1.05 (d, 8Hz, 3H), 1.20 (s, 6H), 1.5-2.2 (m, 7H) and 4.42 (bs, 2H). Signals at δ 1.20 and 4.42 underwent a remarkable downfield shift on adding $Eu(DPM)_3$. CMR (neat)$^{3)}$: δ 126.6 and 134.5 for C=C; 74.0 and 86.5 for C-O; 23.3, 23.7, 28.1, 28.5, 30.7, 31.9 and 33.0 for remaining carbons. MS: m/e 151 (M - CH_3, base peak), 109, 95 and 81. When the compound was kept at 125° for 2 hr in an open air, it was oxidized to a lactone 13.

6 PMR (CCl_4): δ 1.69 (s, 3H), 5.11 (t, 2Hz, 2H), 6.40 (t, 2Hz, 1H) and 7.2-7.6 (m, 10H). MS: m/e 236 (M), 221 (base peak), 115, 105, 91 and 77.

7 PMR (CCl_4): δ 0.89 (d, 8Hz, 3H), 1.62 (d, 1Hz, 3H), 1.72 (d, 1Hz, 3H),

2.4-2.8 (m, 1H), 3.24 (s, 3H), 3.32 (S, 3H), 4.0 (d, 8Hz, 1H) and 5.0 (bd, 10Hz, 1H). When the proton at δ 2.4-2.8 was irradiated, signals at δ 0.89, 4.0 and 5.0 became singlets. MS: m/e 127 (M - OCH_3), 95 and 75 (base peak).

8 PMR (CCl_4): δ 1.61 (s, 3H), 1.1-2.4 (m, 7H), 3.15 (s, 3H), 3.19 (s, 3H), 3.82 (d, 9Hz, 1H) and 5.21 (bs, 1H). CMR (neat)[3]: δ 124.7 and 137.9 for C=C, 111.5 for O-C-O, 53.8 and 54.0 for C-O, 24.8, 26.8, 27.3, 32.8 and 40.3 for remaining carbons. MS: m/e 139 (M - OCH_3), 107, 95 and 75 (base peak). When the compound was treated with dilute HCl, it gave an aldehyde 14.



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Although the mechanism of the present reaction is unknown, it might be evident that titanium plays an important role on effecting oxidation and reduction. In support of this postulation, no trace of 6 was detected when the reaction with 2 was carried out while bubbling with air. Investigations are now under way for extending these reactions to general procedures for obtaining dihydrofuran derivatives or unsaturated aldehydes.

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REFERENCES AND FOOTNOTES

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   b. T. Matsui, A. Komatsu and T. Moroe, Bull. Chem. Soc. Japan, 40, 2204 (1967).
   c. R. C. Cookson, J. Hudec, A. Szabo and G. E. Usher, Tetrahedron, 24, 4353 (1968).

3) The chemical shifts were determined from external chloroform signal, and have been expressed in terms of ppm from TMS.