Tetrahedron. Vol. 30, pp. 2301 to 2305. Pergamon Press 1974. Printed in Great Britain

PHOTO-REIMER–TIEMANN REACTION OF PHENOLS, ANILINES AND INDOLINES[a]

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(*Received in Japan* 25 *February* 1974; *Received in the UK* 1 *March* 1974)

Abstract—The photo-reaction of phenol (1) with chloroform in the presence of diethylamine gave salicylaldehyde (2) and 4-hydroxybenzaldehyde (3) in fair yield. Dihydroxybenzenes, sensitive to alkali, under similar conditions without the base gave corresponding aldehydes and a cyclohexa-2,5-dienone (15). The photo-reaction was also applied to diethylaniline (18), indoline (21) and N-methylindoline (24). In carbon tetrachloride instead of chloroform in an alcohol solution the same type of reaction took place to give esters. The mechanism involving the coupling of a phenoxy radical or a radical cation with dichloromethyl radical and not involving dichlorocarbene is proposed.

There are many reactions in which chloroform acts as a reactant, and the reacting species derived from chloroform are usually dichlorocarbene, trichloromethyl radical and dichloromethyl radical, whose formation is illustrated in the following four equations.

$$\mathrm{CHCl_3} \xrightarrow{\text{base}} \mathrm{:CCl_2 + HCl} \text{ ——— } (1)^{1,2}$$

$$\xrightarrow{h\nu \text{ or radical}} \mathrm{\cdot CCl_3 + \cdot H} \text{ ——— } (2)^{3,4}$$

$$\xrightarrow{\text{carbene}} \mathrm{\cdot CHCl_2 + \cdot Cl} \text{ ——— } (3)^{5}$$

$$\xrightarrow{e^-} \mathrm{\cdot CHCl_2 + Cl^-} \text{ ——— } (4)^{6,7}$$

The Reimer–Tiemann reaction[1] involves the process shown in the first equation, while the last reaction (Eq 4) resembles very closely an important step in the proposed mechanism[8] for the cyclization of N-chloroacetylphenethylamines, which afforded many novel heterocycles.[9] On irradiation, electron-rich aromatic compounds such as phenol, aniline, anisol, indole and so on are known to eject an electron to form the corresponding radical cations or radicals (e.g., phenoxy radical).[10] If an electron ejected from an electron-rich aromatic nucleus cleaves chloroform as Eq 4, the resultant dichloromethyl radical must easily couple with the aromatic radical cation to result in the formation of aromatic substitution products. In the present paper, we report on the photo-reaction of electron-rich aromatics with chloroform and also with carbon tetrachloride."[11]†

RESULTS

Phenol. Phenol is a typical compound to eject an electron by irradiation. When an aqueous methanol solution of phenol (1) and chloroform was irradiated, salicylaldehyde (2) and 4-hydroxybenzaldehyde (3) were mainly isolated. The results under various conditions are summarized in Table 1. The yields of 2 and 3 under the condition (a) are similar to those in the usual Reimer–Tiemann reaction.[1] The addition of large excess of diethylamine (b, c) for removal of liberated hydrogen chloride improved significantly the yield of the products, especially 3, whereas more strong bases, potassium hydroxide (e) and tetraethylammonium hydroxide (f) reduced the yield of both products. The use of bromoform (h) instead of chloroform changed the yield for the worse.

Similarly, irradiation of 1 and carbon tetrachloride in aqueous methanol gave methyl salicylate (4, 20·7%), methyl 4-hydroxybenzoate (5, 32·6%) and methyl 4-hydroxyisophthalate (6, 9·1%).

Dihydroxybenzenes. Since dihydoxybenzenes are sensitive to air, especially in an alkaline solution, the Reimer–Tiemann reaction is not applicable to these compounds.[1] However, the photo-reaction is expected to take place, because it does not necessarily need a base.

Irradiation of dihydroxybenzenes and 5 equivalents of chloroform in 90% aqueous methanol gave dihydroxybenzaldehydes and a dienone (15). A reaction with carbon tetrachloride gave a similar result. The results are summarized in Table 2.

The structure of dienone 15 was determined by its elemental analysis and spectral data. Compound 15 has the composition $C_7H_6O_2Cl_2$ [192] and the base peak at *m/e* 109 in the mass spectrum results from loss of the dichloromethyl group of 15. The characteristic IR absorption bands for cyclohexa-2,5-

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[a] Part of this work has been reported as a preliminary communication.[11]

†Similar photochemical reaction of ferrocene with haloalkanes has been reported by Sugimori *et al.*[12]

Table 1. Photo-reaction of phenol (1, 5 mM) and chloroform (55 mM) with a 10 W low pressure mecury lamp

Conditions	Yield (%) 1	2	3
(a) 50% MeOH, 3 h	6·2	18·6	11·9
(b) Et_2NH (125 mM), 50% MeOH, 2 h	13·9	22·2	30·9
(c) Et_2NH (125 mM), 50% MeCN, 2 h	4·8	19·1	46·0
(d) K_2CO_3 (155 mM), 50% MeOH, 2 h	8·0	15·5	16·5
(e) KOH (150 mM), 50% MeOH, 2 h	16·8	8·9	6·5
(f) $Et_4N^+OH^-$ (100 mM), 50% MeOH, 3 h	4·8	6·7	4·0
(g) 17% HCl, 50% MeOH, 2 h	1·3	—	—
(h) Et_2NH (125 mM), 50% MeOH, 2 h[a]	4·5	4·8	7·0
(i) Et_2NH (225 mM), 50% MeCN, 8 h[b]	21·4	12·3	39·2

[a] Bromoform was used instead of chloroform. [b] Preparative experiment; a solution of 1 (7·5 mM) and chloroform (75 mM) was irradiated with a 100 W high pressure mercury lamp.

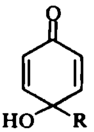
Table 2. Photoreaction of dihydroxybenzenes with chloroform or carbon tetrachloride

Dihydroxybenzene	mM	hr	Dihydroxybenzaldehyde	Yield (%)
Pyrocatechol (7)[a]	10	9	3,4- (**10**)	29·2
			2,3- (**11**)	3·4
Resorcinol (8)[a]	10	5	2,4- (**12**)	38·5
			2,6- (**13**)	10·6
Hydroquinone (9)[a]	100	5	2,5- (**14**)	37·1
			(**15**)[c]	24·3
Hydroquinone (9)[b]	80	3	(**16**)[d]	21·0
			(**17**)[e]	22·4

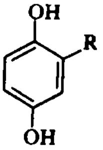
[a] Reaction with chloroform. [b] Reaction with carbon tetrachloride. [c] 4-Dichloromethyl-4-hydroxycyclohexa-2,5-dienone. [d] Methyl 2,5-dihydroxybenzoate. [e] 4-Hydroxy-4-trichloromethylcyclohexa-2,5-dienone.

dienones[13] appear at 1665 and 1620 cm^{-1}. Vinyl protons in the NMR spectrum are well-separated two-doublets at 6·30 and 6·88 ppm, and the dichloromethyl proton appears as a singlet at 5·70 ppm. The structure of **17** was determined in the same way.

Irradiation of hydroquinone (**9**) and chloroform-d in 90% aqueous methanol gave **14a** (42·8%) and **15a** (28·8%) deuterated completely at the expected positions. Compounds **14a** and **15a** have no signals of an aldehyde proton for **14** and a dichloromethyl proton for **15**, respectively, in their NMR spectra.



15: R = $CHCl_2$
15a: R = $CDCl_2$
17: R = CCl_3

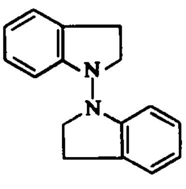


14: R = CHO
14a: R = CDO

Although the yields of dihydroxybenzaldehydes still remain unsatisfactory, the photo-reaction may be useful, because there are no good simple methods for preparation of dihydroxybenzaldehydes, except Vilsmeier reaction of resorcinol (**8**). The dienones (**15**, **17**), also difficult to synthesize by usual other methods, are rather unstable and decompose with the evolution of hydrogen chloride in a couple of weeks when allowed to stand at room temperature, and their chemical and photochemical behavior is under investigation.

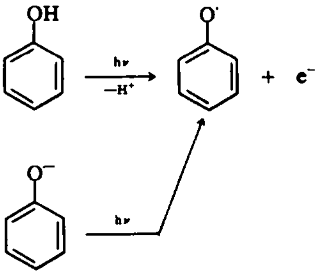
Anilines. Since anilines act usually more effectively as electron-donors than phenols, the photoreaction is expected to take place more efficiently. Although aniline, sensitive to light, gave a complex mixture of undefined compounds, irradiation of diethylaniline (**18**) and chloroform yielded 2- (**19**) and 4-diethylaminobenzaldehydes (**20**) in 36·5% and 56·4% yields respectively.

Indolines. When the reaction was applied to indole, a complex mixture of formylindoles was obtained.[14] For the purpose of the selective formylation at 5 and 7 positions of indole nucleus, indoline (**21**) and chloroform in the presence of diethylamine was irradiated. However, main products were N-formylindoline (**22**, 24·4%) and indole (13·7%), accompanied by indoline dimer (**23**) and small amounts of 5- and 7-formylindolines.



23

The structural assignment of 23 rests on its spectral data. It has the composition $C_{16}H_{16}N_2$ (high resolution mass) and no NH (IR). The NMR spectrum in carbon tetrachloride at 70° is almost superimposable to that of indoline. At room temperature, the signals of N-methylene protons centered at δ3·40 ppm is broadened showing the hindered rotation around the N–N bond. Compound 23 was also obtained by irradiation of 21 without chloroform. This type of indoline dimer was recently obtained by oxidation of 3,3-diarylindolines.[15]



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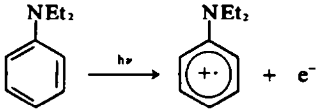
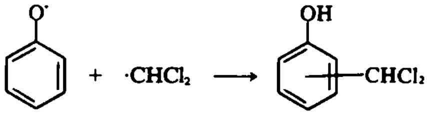


(6)

$$CHCl_3 + e^- \longrightarrow \cdot CHCl_2 + Cl^- \quad (4)$$



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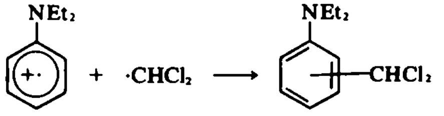

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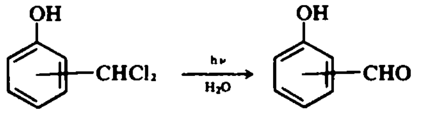
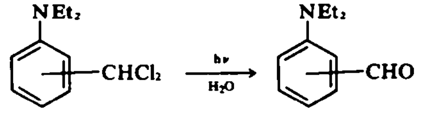
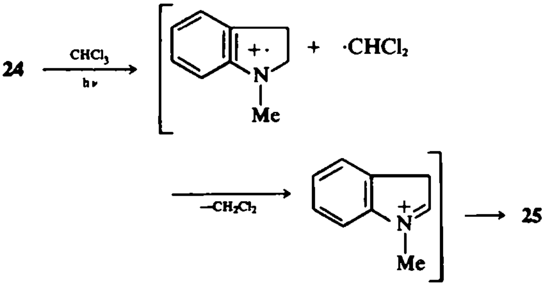


(9)



(10)

In order to avoid N-formylation, N-methylindoline (24) was next irradiated under the similar conditions to give N-methylindole (25, 23·1%), 5-formyl-N-methylindoline (26, 27·4%)[16] and 7-formyl-N-methylindoline (27, 14·4%). Although the concomitant dehydrogenation to 25 was unavoidable that may be shown in the following scheme,[17] the expected formylation on the indoline nucleus proceeded in moderate yield.



DISCUSSION

With regard to the results obtained, the mechanism of the photo-Reimer–Tiemann reactions of phenol (1) and diethylaniline (18), as representative examples, with chloroform may be described as shown in the following Eqs (5)–(10).

The mechanism involves dichloromethyl radical as a key intermediate, different from the usual Reimer–Teimann reaction, which involves the dichlorocarbene. The following discussion favors the mechanism.

In photochemical[4] and radical reactions,[3] chloroform cleaves usually at the C–H bond to form trichloromethyl radical as shown in Eq 2. However the formation of benzaldehydes and the dienone 15 in fairly good yields indicates that this is not the mechanism.

On irradiation, electron-rich aromatics are known to eject an electron (Eqs 5, 6), which can cleave chloroform at the C–Cl bond to form dichloromethyl radical probably according to Eq 4. The facts that irradiation of 1 and chloroform without a base [condition (a) in Table 1] gave benzaldehydes (2, 3) in poor yield and under the acidic conditions (g) neither 2 nor 3 were formed may be explained on the basis of that proton is an effective quencher for a solvated electron.[18]

The next step (Eqs 7 or 8), coupling of a phenoxy radical or an aromatic radical cation with dichloromethyl radical, may determine the proportion of products. The results are in good agreement with those expected from the calculated electron-spin densities in the phenoxy radicals derived from phenol[19] and dihydroxybenzenes[20] and in the radical cations of aniline derivatives,[21] and support the proposed mechanism; e.g., different from the Reimer–Tiemann reaction the photo-reaction of 1 gave mainly *para*-substituted compound 3, hydroquinone gave rather unstable dienone **15** in fair yield, and indoline (**21**) gave mainly N-formylindoline (**22**).

The final step (Eqs 9 or 10) proceeds only photochemically at least at room temperature. Although dichloro-compounds as intermediates have not been isolated, benzal chloride (**28**) in aqueous acetonitrile on irradiation converted easily to benzaldehyde (**29**). However **28** was recovered unchanged after allowed to stand at room temperature in 90% aqueous acetonitrile containing diethylamine or hydrochloric acid without light. Similar photo-hydrolysis of benzylic halogens has been reported.[22]

Finally the possibility of a carbene mechanism is discussed. The photo-reaction of hydroquinone (**9**) with chloroform-d in 90% aqueous methanol gave deuterium containing products, **14a** and **15a**, without no traces of **14** and **15**. This indicates clearly that the photo-reaction does not proceed through the carbene mechanism, which must result in a loss of deuterium.[1,23,*] The photo-reaction with chloroform-d provide one of potential methods for the preparation of completely deuterium exchanged benzaldehydes at the formyl position.

EXPERIMENTAL

Photo-reaction of phenol (1) *and chloroform*

(a) A soln of **1** (5 mM) and CHCl$_3$ (55 mM) in 10 ml of 50% aqueous MeOH or 50% aqueous MeCN in the presence of a base was irradiated with 10 W low pressure mercury lamp under N$_2$. After dilution by the addition of water (10 ml), the mixture was brought to *ca* pH 3 and extracted with CH$_2$Cl$_2$ (*ca* 30 ml). The solvent was evaporated *in vacuo*, and to the residue were added 1 ml of pyridine and an acetone soln of methyl benzoate (1 mg in 1 ml, an internal standard for GLC analysis). The soln was dried over molecular sieves for 30 min, and two drops of the soln was silylated by the addition of two drops each of TMCS and HMDS, and analyzed with Shimazu gas chromatograph 4APF using a column packed with 3% SE-52 on 60–80 mesh chromosorb W. The results are summarized in Table 1.

(b) A soln of **1** (290 mg), CHCl$_3$ (3·6 g) and diethylamine (6·6 g) in 50% aqueous MeCN (400 ml) was irradiated with 100 W high pressure mercury lamp under N$_2$ for 8 h. The soln was brought to pH *ca* 3 and extracted with CH$_2$Cl$_2$. The extract was dried over Na$_2$SO$_4$ and subjected to preparative TLC (silica-gel, CH$_2$Cl$_2$) to yield the recovered **1** (62·2 mg, 21·4%), *salicyl aldehyde* (**2**, 46·3 mg 12·3%) and 4-*hydroxybenzaldehyde* (**3**, 147·4 mg, 39·2%). The products were identical with the authentic samples, respectively, with regard to TLC and IR and NRM spectra.

Photo-reaction of **1** *and chloroform-d.* A 50% aqueous MeCN soln (400 ml) of **1** (290 mg), CDCl$_3$ (3·6 g) and diethylamine (6·6 g) was irradiated with 100 W lamp under N$_2$ for 7 h. Separation as described above partially deuterated **2** (39·1 mg, 10·7%) and **3** (154·5 mg, 42·3%), whose deuterium contents determined by NMR spectrometry in CDCl$_3$ are both *ca* 20%.

Photo-reaction of **1** *and carbon tetrachloride.* A 90% aqueous MeOH soln (250 ml) of **1** (470 mg) and CCl$_4$ (8 g) was irradiated with 100 W lamp under N$_2$ for 15 h. Work-up as described above gave *methyl salicylate* (**4**, 125·7 mg, 20·7%), *methyl 4-hydroxybenzoate* (**5**, 198 mg, 32·6%) and *methyl 4-hydroxyisophthalate* (**6**, 78·2 mg, 9·1%).

Photo-reaction of dihydroxybenzenes and chloroform. A 90% aqueous MeOH soln (40–300 ml) of dihydroxybenzene [pyrocatechol **7**, resorcinol **8** or hydroquinone **9**, 330 mg] and CHCl$_3$ (2 g) was irradiated with 200 W high pressure lamp for 5–9 h. The soln was concentrated *in vacuo* and extracted with AcOEt. The extract was separated on preparative TLC (silica-gel, CH$_2$Cl$_2$–MeOH). The results are summarized in Table 2.

4-*Dichloromethyl-4-hydroxycyclohexa-2-5dienone* (**15**), fine needles (from benzene), m.p. 118–119° (dp). (Found: C, 43·47; H, 3·21; Cl, 36·52. C$_7$H$_6$O$_2$Cl$_2$ requires. C, 43·55; H, 3·13; Cl, 36·74%). m/e 192 (M^+), 109 (M^+–CHCl$_2$, base peak); ν_{max} (Nujol) 3250, 1665, 1620 cm^{-1}; δ(CDCl$_3$) 5·70 (s, 1H), 6·30 (d, 2H, J = 10 Hz), 6·88 (d, 2H, J = 10 Hz).

Photo-reaction of **9** *and chloroform-d.* A 90% aqueous MeOH soln (400 ml) of **9** (330 mg) and CDCl$_3$ (2 g) was irradiated with 100 W lamp for 7 h. The soln was concentrated and extracted with AcOEt. The extract was separated on preparative silica-gel TLC (CH$_2$Cl$_2$, AcOEt) to give recovered **9** (138·2 mg), 2,5-*dihydroxybenzaldehyde-7-d* (**14a**, 103·5 mg 42·8%) and a dienone (**15a**, 97·5 mg 28·8%). **14a**; needles (from benzene), m.p. 96–99°; m/e 139 (M^+); NMR (CDCl$_3$) no signal of CHO. **15a**; fine needles (from benzene), m.p. 113–114° (dp); m/e 193 (M^+), 158 (M^+–Cl), 109 (M^+–CDCl$_2$, base peak); ν_{max} (Nujol) 3250, 2230 (C–D), 1665, 1625 cm^{-1}; NMR (CDCl$_3$) no signal of CHCl$_2$.

Photo-reaction of **9** *and carbon tetrachloride.* An 85% aqueous MeOH soln (40 ml) of **9** (330 mg) and CCl$_4$ (2·1 g) was irradiated with 100 W lamp for 2·5 h. Work-up as described above gave a result shown in Table 2. 4-*Hydroxy-4-trichloromethyl-cyclohexa-2,5-dienone* (**17**), fine needles (from benzene-n-hexane), m.p. 126–127° (dp). (Found: C, 36·87; H, 2·26. C$_7$H$_5$O$_2$Cl$_3$ requires: C, 36·96; H, 2·22%), m/e no M^+, 109 (M^+–CCl$_3$, base peak); ν_{max} (Nujol) 3200, 1670, 1620 cm^{-1}; δ(CDCl$_3$) 6·40 (d, 2H, J = 10 Hz), 7·09 (d, 2H, J = 10 Hz).

Photo-reaction of N,N-diethylaniline (18) *and chloroform*

(a) *In the presence of diethylamine.* An 80% aqueous MeCN soln (20 ml) of **18** (150 mg), CHCl$_3$ (1·3 g) and diethylamine (1·6 g) was irradiated with 10 W lamp under N$_2$ for 3 h. Pr^parative TLC (silica-gel, CH$_2$Cl$_2$–benzene) gave 2-*diethylaminobenzaldehyde* (**19**, 63·1 mg, 36·5%) as a pale yellow liquid [m/e 177 (M^+); ν_{max} (neat) 1680 cm^{-1}; δ (CCl$_4$) 1·02 (t, 6H, J = 7 Hz), 3·15 (q, 4H, J = 7 Hz), 7·4 (m, 4H), 10·36 (s, 1H)] and 4-*diethylaminobenzaldehyde* (**20**, 99·2 mg, 56·4%) as a yellow liquid [m/e 177 (M^+); ν_{max} (neat) 1670 cm^{-1}; δ(CCl$_4$) 1·14 (t, 6H, J = 7 Hz), 3·38 (q, 4H, J = 7 Hz), 6·58 (d, 2H, J = 9 Hz), 7·55 (d, 2H, J = 9 Hz), 9·62 (s, 1H)].

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[*] In the presence of diethylamine the photo-reaction of **1** and **18** with chloroform-d gave benzaldehydes, whose deuterium content is *ca* 20%. However this does not necessarily mean the presence of dichlorocarbene, because a deuterium-exchange reaction of chloroform in deuterium oxide in the presence of diethylamine occurs easily without light.[24] So far the mechanism under the basic conditions still remains a little uncertainty.

(b) *In the presence of* K_2CO_3. An 80% aqueous MeOH soln (20 ml) of **18** (150 mg), $CHCl_3$ (1·3 g) and K_2CO_3 (414 mg) was irradiated with 10 W lamp under N_2 for 3 h. Work up as described above gave 36·8 mg (20·7%) of **19** and 98·1 mg (55·4%) of **20**.

Photo-reaction of **18** *and chloroform-d.* An 80% aqueous MeCN soln (30 ml) of **18** (150 mg), $CDCl_3$ (0·8 ml, 8 eq.) and diethylamine (2·3 ml, 16 eq) was irradiated with 100 W lamp for 6 h under N_2. Work-up as described above gave partially deuterated **19** (27 mg) and **20** (44 mg), whose deuterium contents determined by NMR spectrometry in CCl_4 are both *ca* 20%.

Photolysis of indoline (**21**)

(a) *With chloroform.* A 90% aqueous MeOH soln (250 ml) of **21** (595 mg), $CHCl_3$ (3·2 g) and diethylamine (5·2 g) was irradiated with 200 W lamp for 7 h. Work-up as usual and silica-gel (40 g) chromatography hexane-AcOEt) gave the recovered **21** (81·5 mg, 13·7%), *N-formylindoline* (**22**, 175·8 mg, 24·4%), m.p. 61–63°, and *indoline-N,N'-dimer* (**23**, 11·3 mg, 1·9%) as needles, m.p. 110–111° [(m^+/e 236. 1293. $C_{16}H_{16}N_2$ requires: 236.1314); ν_{max} (Nujol 1600, 760 cm^{-1}; $\delta(CCl_4)$ 3·03 (d, 4H, J = 8 Hz), 3·40 (m, 4H), 6·75 (m, 8H); δ at 70° 3·03 (d, 4H, J = 8 Hz), 3·40(d, 4H, J = 8 Hz), 6·75(m, 8 H)].

(b) *Without chloroform.* Compound **21** (593 mg) in 90% aqueous MeOH was irradiated with 200 W lamp (pyrex filtered) for 10 h. Work-up as described above gave **23** (4·7 mg).

Photo-reaction of N-methylindoline (**24**) *and chloroform.* N-Methylindoline (**24**, 230 mg), $CHCl_3$ (1·3 g) and diethylamine (2·1 g) in 90% aqueous MeOH (35 ml) was irradiated with 100 W lamp (pyrex filtered) for 7 h. Preparative TLC (silica-gel, CH_2Cl_2–benzene) gave the recovered **24** (27·6 mg), *N-methylindole* (**25**, 48·3 mg, 23·1%), *5-formyl-N-methylindoline* (**26**, oil, 70·3 mg, 27·4%; semicarbazone m.p. 212–214°)[16] and *7-formyl-N-methylindoline* (**27**, oil, 48·3 mg, 14·4%). (m^+/e 161·0843. $C_{10}H_{11}NO$ requires: 161·0841), ν_{max} (neat 1660 cm^{-1}; $\delta(CCl_4)$ 2·87 (d, 2H, J = 8 Hz), ph-CH_2), 3·08 (s, 3 H), N–CH_3), 3·42 (d, 2H, J = 8 Hz), N–CH_2), 9·90 (s, 1H $C\underline{H}O$).

Photo-hydrolysis of benzal chloride (**28**) *to benzaldehyde* (**29**). A soln of **28** (21 mg) in MeCN (4 ml) and H_2O (2 ml) was irradiated with 100 W lamp externally for 3 h. The yield of **29** was determined by GLC; 56·4% or 80·9% based on the consumed **28** (3% SE-52 on chromosorb W; internal standard, naphthalene).

Acknowledgements—The authors thank Drs. A. Tahara and Y. Ohtsuka for the high resolution mass spectrometric measurements and the Takeda Science Foundation for financial support.

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