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COMPETITION BETWEEN PHOTODIMERIZATION AND PHOTOCYCLOADDITION OF DIMETHYL 3-DEHYDROGIBBERELLENATE TO ETHYLENE, 1, 1-DICHLOROETHYLENE AND TRICHLOROETHYLENE

H. K. AL-EKABI and G. A. W. DERWISH*
Department of Chemistry, College of Science, University of Baghdad, Adamyia, Baghdad, Iraq

and

G. ADAM and K. SCHREIBER
Institute of Plant Biochemistry of the Academy of Sciences of GDR, 402 Halle (Saale), German Democratic Republic

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Abstract—Photocycloadditions of dimethyl 3-dehydrogibberellenate **1** to ethylene, 1, 1-dichloroethylene and trichloro-ethylene were investigated. The results exhibited markedly the competition between photodimerization and photocycloaddition of **1**, and showed that the yields of cycloaddition products increased with increasing polarity of the olefins. Strangely, photocycloaddition of **1** to olefins was found to proceed through the singlet excited state.

While photocycloaddition of α, β-unsaturated ketones (enones) to olefins has been extensively investigated, little is known about such reaction with α, β, γ, δ-unsaturated ketones (dienones),[1–4] except for steroidal systems. A thorough search of the literature revealed no information on this reaction with α, β, γ, δ-unsaturated gibberellin ketones.

In a previous communication we presented that photolysis of 2.7×10^{-2} M solution of dimethyl 3-dehydrogibberellenate **1**, as a heteroannular dienone, in *t*-butanol at $\lambda > 300$ nm for 3 hr gave three photodimers designated as **A**, **B** and **C** in 65, 12 and 7% yields, respectively.[5]

In this communication, we should like to present our results on the competition between photodimerization and photo-cycloaddition of **1** to ethylene, 1, 1-dichloroethylene and trichloroethylene.

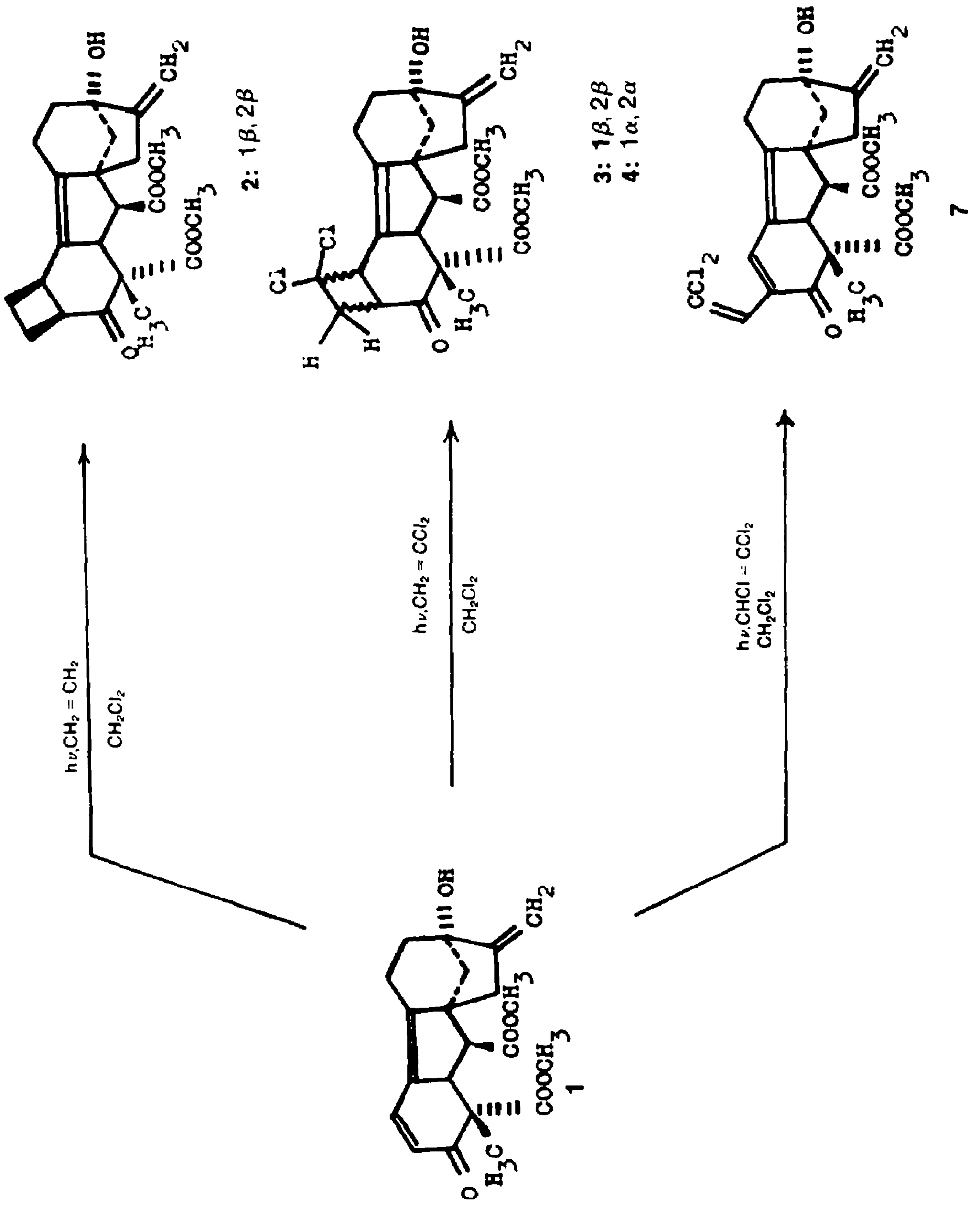
Irradiation of **1** in the presence of an excess of ethylene in methylene chloride gave three photoproducts, as indicated by tlc, which were separated by column chromatography on silica gel. The first photoproduct was eluted by benzene–ether (9:1) in 6% yield, and was identified as a cyclobutane adduct **2** (Scheme 1) on the basis of physical measurements. Its IR spectrum indicated the presence of unconjugated CO band at 1696 cm^{-1}, only $n \rightarrow \pi^*$ absorption band was shown in the UV spectrum and mass spectrum gave a molecular ion peak at *m/e* 400 (M$^+$). The *cis*-1β, 2β-stereochemistry was assigned on the basis of ORD measurements coupled with model construction and stability towards alumina. The ORD spectrum of **2** showed a weak positive Cotton effect with a molecular amplitude of +26 in agreement with the octant rule application.

The second and third photoproducts were separated in 66 and 8% yield, respectively. These two photoproducts were also identified on the basis of physical measurements (UV, IR, NMR and MS data), as the previously reported photodimers **A** and **B**, respectively.

Irradiation of **1** in the presence of excess 1, 1-dichloroethylene in methylene chloride gave large amount of a polymeric material derived from the olefin,[6] together with the formation of one major and one minor photoproducts as indicated by tlc. The products were separated by column chromatography on silica gel. The major photoproduct (95%) was identified as a cyclobutane adduct **3** by the following facts: the presence in the IR spectrum of the band at 1693 cm^{-1}, typical for unconjugated CO group; only $n \rightarrow \pi^*$ absorption band was found in the UV spectrum, a parent molecular ion peak at *m/e* 468 (M$^+$) was shown by mass spectrum; and absence of olefinic protons in ring A as NMR spectrum showed. The *cis*-1 β, 2β-stereochemistry was assigned on the basis of ORD measurements coupled with model construction and stability towards alumina. The ORD spectrum of **3** showed a positive Cotton effect with a molecular amplitude of +56, in agreement with the octant rule application. The observed molecular amplitude (a = +56), which is larger than that of ethylene adduct **2** (a = +26) may result from the replacement of the small H atom by the larger Cl atom.

The minor photoproduct (5%) was identified as a cyclobutane adduct **4**. The *cis*-1α, 2α-stereochemistry was assigned on the basis of ORD measurements, model construction and stability towards alumina. The ORD spectrum of **4** showed a weak negative Cotton effect with a molecular amplitude of −29, in agreement with octant rule application.

Irradiation of **1** in the presence of excess trichloroethylene in methylene chloride gave, as in the case of ethylene, three photoproducts as indicated by tlc. These three photoproducts were clearly separated by column chromatography on silica gel. A product of 43% yield of presumbly one rather unstable photocycloadduct assumed to have structure **5**, which was then immediately transformed to the stable highly conjugated compound **7**, was firstly eluted. Compound **7** was identified on the basis of physical measurements. Thus, UV spectrum showed an intense absorption band at 342



Scheme 1. Photocycloaddition of dimethyl 3-dehydrogibberellenate 1 to ethylene 1, 1-dichloroethylene and trichloroethylene

(ϵ = 13240); IR spectrum showed bands for conjugated CO group at 1680 cm^{-1} and conjugated C=C at 1650 cm^{-1}; mass spectrum gave a peak of highest mass number at *m/e* 466, indicating the elimination of HCl from the assumed adduct **5**; and finally NMR spectrum gave signals at 7.8 (s) and 6.75 (s) ppm for olefinic protons of **7** which were surely different from those of olefinic protons of the starting material which appeared as doublets at 7.5 and 6.05 ppm.

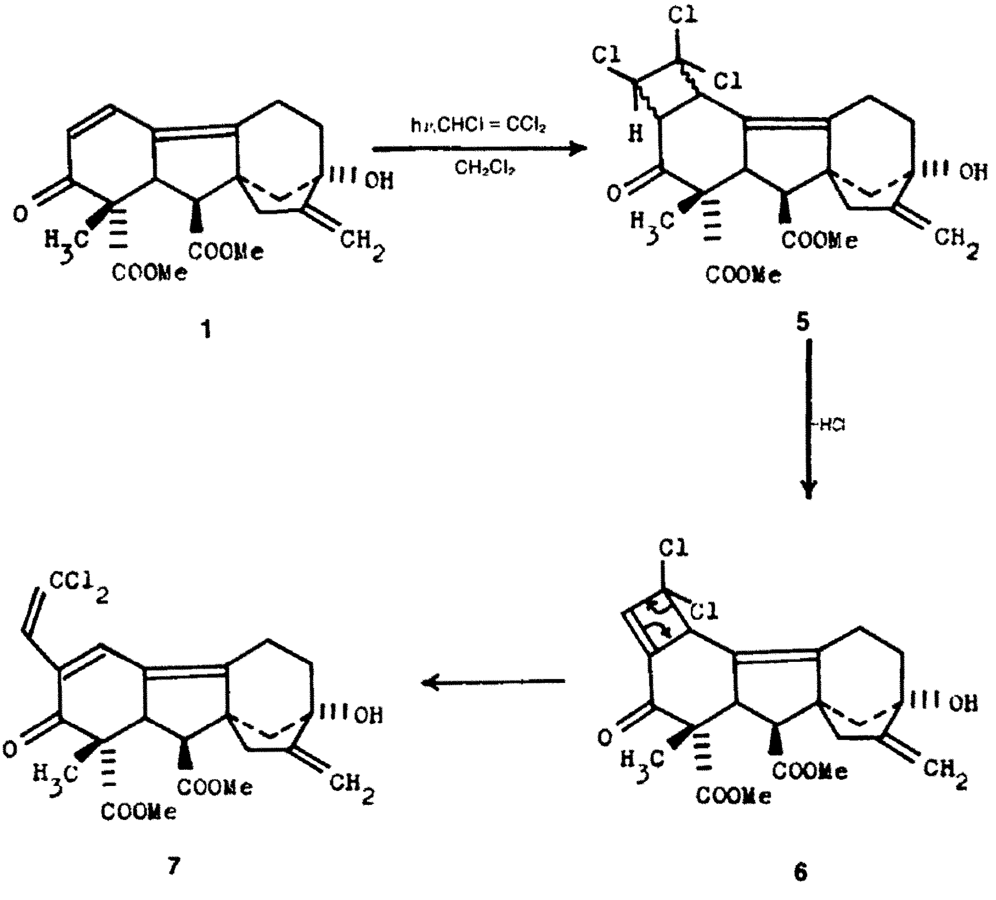
The presence of Cl atom at β-position to the CO group possibly facilitates the elimination of HCl[6] giving a highly strained cyclobutene derivative **6** which would undergo further transformation leading to the highly conjugated compound **7** (Scheme 2).

The second and third photoproducts were separated in 45 and 5% yields, respectively, and were identified on the basis of physical measurements (UV, IR, NMR and MS data) as the previously reported photodimers **A** and **B**, respectively.

Ethylene was found to be the least reactive olefin studied in the present work, and it was found that only one photoadduct was formed in 6% yield, together with the formation of the previously reported photodimers **A** and **B** in 66 and 8% yields, respectively. However, the dienone added nearly quantitatively to the 1, 1-dichloroethylene giving two photo-cycloadducts in 95 and 5% yields. On the other hand, the reactivity of trichloroethylne occupied an intermediate position between ethylene and 1, 1-dichloroethylene, giving one highly unstable photocycloadduct in 43% yield together with photodimers **A** and **B** in 45 and 5% yields, respectively.

The photocycloaddition reaction seems to be sensitive to the degree of polarity of the ethylenic double bond caused by the presence of strongly polarizing substituents. Thus, the results presented in Table 1 showed that the yield of cyclo-addition products increased with increasing polarity of olefins, while the yield of dimerization decreased with increasing polarity of the olefins. The results exhibited markedly the competition between photodimerization and photocycloaddition reaction of **1**.

The most interesting aspects of the photocycloaddition of the dienone **1** to olefins is the stereochemical specificity, giving only one photocycloadduct, with the exception of a minor product (5%) of the adduct **4** in case of 1, 1-dichloroethylene system. Irradiation of **1** in the presence of butadiene gave a rapid reaction with the diene to generate, in about equal yields, two adducts of [2+2]-cyclobutane type.† The stereo-specificity of addition, coupled with the addition of **1** to the diene indicated that the dienone **1** reacts exclusively from its singlet state.[4] The photocycloaddition proceeding from the singlet state is very rare, since photocycloaddition reactions are generally triplet state reactions.[7] Photodimerization of **1**, on the other hand, was found to proceed through triplet state.[8]



Scheme 2. Photocycloaddition of dimethyl 3-dehydrogibberellenate to trichloroethylene followed by subsequent chemical transformation.

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†The addition of **1** to dienes will be detailed in a forthcoming communication.

Table 1. Photodimerization and photocycloaddition of dimethyl 3-dehydro-gibberellenate 1 to ethylene, 1, 1-dichloroethylene and trichloroethylene

		Yields* of photodimerisation and photoaddition products %			
Olefin	Dipole moment(a)	Adduct(s)	Dimer A	Dimer B	Dimer C
-	-	-	65(b)	12(b)	7(b)
CH_2=CH_2	0	6	66	8	trace
CH_2=CCl_2	1.3	100	0	0	0
CHCl=CCl_2	0.9	43	45	5	trace

(*) Yields were based on the starting material

(a) See ref. 9,

(b) See ref. 5.

EXPERIMENTAL

UV Spectra were run in MeOH and IR spectra were taken in nujol. Varian Associate A-60 was used to record NMR spectra. All spectra were run in CD_3COCD_3 soln, HMDS as an internal standard. Electron-attachment mass spectrograph of the Research Institute Manfred Von Ardenne, Dresden was used to record MS spectra. ORD curves were run in MeOH on a JASCO ORD/UV-5 spectrometer. Tlc silica gel G(Merck) developed with benzene–AcOH 70:30; detection with 85% H_2SO_4, heating for 15 mins at 120°. Column chromatography: silica gel Woelm for partition chromatography.

Irradiation procedure. An external 500 W high-pressure mercury arc lamp THU 500 (VEB Thelta Electro-apparate Zella-Mehlis) was used as the source of UV light. All irradiations were run in pyrex flask, under argon, or, if a gaseous olefin was used the olefin served to exclude oxygen. All irradiations were followed by tlc, and were run until the disappearance of starting material was essentially complete.

Photocycloaddition of dimethyl 3-*dehydrogibberellenate* (1) *to ethylene.* A soln of 250 mg of 1[10] in 75 ml CH_2Cl_2 was irradiated for 4 hr while a slow stream of ethylene was passed through the soln. After this time the tlc showed, besides some starting 1, three new spots. The residue, after evaporation of the solvent under reduced pressure, was adsorbed on celite (500 mg) with acetone and chromatographed on 12.5 gm of silica gel. Elution (5 ml fractions) with benzene–ether 9:1 afforded 15 mg (6% yield based on recovered starting material) photo-cycloadduct 2, as a morphous substance. UV: $\lambda_{max}(\epsilon)$ 214 (4680), 240 (2900) and 315 nm (265). IR: ν_{max} 910 ($\rangle C{=}CH_2$), 1170 ($COOCH_3$), 1695 (unconj. C=O), 1730 ($COOCH_3$) and 3500 cm^{-1} (OH). ORD (C = 1.2130): $[M]_{315} = +198$, $[M]_{308} = 0$ and $[M]_{268} = -2440$.

Further elution with benzene–ether 8:2 gave 20 mg starting dienone 1.

Further elution with benzene–ether 6:4 gave 165 mg (66% yield) of photoproduct had the same physical properties (M.p., UV, IR, NMR and MS data) of the previously reported photodimer A.

Further elution with benzene–ether 4:6 yielded 20 mg (8% yield) of photoproduct had the same physical properties (M.p., UV, IR and MS data) of the previously reported photo-dimer B.

Photocycloaddition of 1 *to* 1, 1-*dichloroethylene.* A soln of 250 mg of 1 and 1, 1-dichloroethylene (10 ml) in 75 ml CH_2Cl_2 was irradiated for 1 hr. The mixture was filtered to remove polymeric materials and the reaction flask was cleaned. More 1, 1-dichloroethylene (5 ml) was added and irradiation was continued. After a total irradiation period of 3 hr, tlc showed that the starting material had been consumed and one major and one minor photo-products were formed. The soln then filtered off to remove the polymeric materials and the solvent was evaporated under reduced pressure. The residue was then adsorbed on celite (500 mg) with acetone and chromatographed on 12.5 gm silica gel. Elution with benzene–ether 9.5:0.5 gave 12.5 mg (5% yield) photocycloadduct 4 as amorphous substance. UV: λ_{max} (ϵ) 215 (4500), 242 (3120) and 305 nm (88). IR: ν_{max} 895 ($\rangle C{=}CH_2$), 1175 ($COOCH_3$), 1657 (C=C), 1693 (unconj. C=O), 1730 ($COOCH_3$), 3075 ($\rangle C{=}CH_2$) and 3510 cm^{-1} (OH). ORD (C = 1.6167): $[M]_{315} = +4053$, $[M]_{294} = 0$ and $[M]_{272} = -810$.

Further elution with benzene–ether 9.5:0.5 gave 237 mg (95% yield) photocycloadduct 3 as amorphous substance. UV: λ_{max} (ϵ) 216 (4980), 240 (3230) and 305 (72). IR: ν_{max} 900 ($\rangle C{=}CH_2$), 1170 ($COOCH_3$), 1660 (C=C), 1690 (unconj. C=O), 1725 and 1735 ($COOCH_3$), 3080 ($\rangle C{=}CH_2$), and 3495 cm^{-1} (OH). 60-MHz-NMR: $\delta_{HMDS}^{Acetone-D_6}$ 1.15 (s, 18–CH_3), 3.23 (q, 9.7 Hz, 6 – H), 3.50 (d, 5.4 Hz, 5–H), 3.65 and 3.68 (s, 7- and 19-methylesters–H_3) and 4.90 and 5.15 ppm (17-H_2). MS (positive ionization, $T_v = 75°C$): *m/e* 468 (M^+), 432, 409, 372, 357, 340 and 322. MS (negative ionization, $T_v = 60°C$): *m/e* 468 (M^-), 432, 409, 396 and 374. ORD (C = 1.1300): $[M]_{316} = +2816$, $[M]_{291} = 0$ and $[M]_{272} = -2816$.

Photocycloaddition of 1 *to trichloroethylene.* A soln of 250 mg of 1 and trichloroethylene (10 ml) in 75 ml CH_2Cl_2 was irradiated for 2 hr. After this time, tlc showed that the starting material had been consumed and three new products were formed. The residue, after evaporation of the solvent under reduced pressure, was adsorbed on celite (500 mg) with acetone and chromatographed on 12.5 gm silica gel. Elution with benzene gave 108 mg (43% yield) of presumbly one rather unstable photocycloadduct assumed to have structure 5, which was immediately transformed to the stable highly conjugated compound 6. UV: $\lambda_{max}(\epsilon)$ 211 (10000), 257 (8800) and 342 nm (13240). IR: ν_{max} 910 ($\rangle C{=}CH_2$), 1175 ($COOCH_3$), 1650 (s, C=C, streching), 1680 (s, conj. C=O), 1735 ($COOCH_3$), 3080 ($\rangle C{=}CH_2$) and 3500 cm^{-1} (OH). 60-MHz-NMR: $\delta_{HMDS}^{Acetone-D_6}$ 1.20 (s, 18–CH_3), 3.58 and 3.70 (s, 7- and 19-methylester–H_3), 5.00 and 5.24 (17-H_2), 6.78 (s, 1-H) and 7.75 ppm (s, β-H). MS (positive ionization, $T_v = 75°$): *m/e* 466 (M^+–HCl), 431, 407, and 371.

Further elution with benzene–ether 6:4 gave 112 mg (45% yield) of photoproduct, again, had the same physical properties (m.p., UV, IR, NMR and MS data) of the previously reported photodimer A.

Further elution with benzene–ether 4:6 gave 12.5 mg (5% yield) of photoproduct had the same physical properties (m.p., UV, IR and MS data) of the previously reported photodimer B.

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