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PHOTO-ADDITION REACTIONS OF DIMETHYL MALEATE AND DIMETHYL ACETYLENE DICARBOXYLATE WITH NORBORNENE

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Abstract—Photo-induced addition reaction of norbornene and dimethyl maleate afforded *exo*-3,4-dicarbomethoxy-*cis*, *trans*, *cis*-tricyclo[4,2,1,$0^{2,5}$]nonane (I) exclusively. In a similar way, the photochemical reaction of dimethyl acetylene dicarboxylate and norbornene gave rise to the 1:1 photo-adduct having the similar configuration, *exo*-3,4-dicarbomethoxy-tricyclo[4,2,1,$0^{2,5}$]nona-3-ene. Moreover, it was confirmed that the above reactions did not proceed through the charge-transfer complex.

Increasing interest has been shown in the study on the photo-addition of olefins from the viewpoint of synthesis of a variety of interesting cyclic compounds and the cross-cycloadditions between various olefins have been extensively investigated by Schenk *et al.*[1] And, much attention has been paid to the stereochemistry of the photo-adducts, and it has been reported that the photo-induced cyclodimerizations of mono-olefins, such as cyclopentene,[2] cyclopentenone[3] and norbornene,[4] gave rise to the formation of *exo*-adducts mainly. In order to gain further insight into the stereospecificity of the photo-addition, the present authors carried out the photochemical reaction of norbornene and dimethyl maleate or dimethyl acetylene dicarboxylate and made an attempt at the precise determination of the structure of the photo-adduct.

Irradiation of a solution of norbornene in dimethyl maleate, with a 450-watt high pressure mercury arc lamp, under nitrogen for 110 hr at room temperature afforded colourless crystals, m.p. 82°, in almost quantitative yield based on the reacted norbornene.

Since the molecular formula of the photo-adduct is $C_{13}H_{18}O_4$, and its IR spectrum exhibits carbonyl band at 1740 cm^{-1} and then the absence of unsaturation is shown in both its IR and NMR spectra, it may be assumed that the crystals is the tricyclic 1:1 photo-adduct. The results analyzed by gas chromatography and NMR measurement clearly pointed out that the above photo-adduct was composed of the sole component without any stereoisomers.

The NMR spectrum of the photo-adduct in carbon tetrachloride (20 mg/0·2 ml) showed 6 types protons in the ratio of 6:2:2:2:2:4 with the peaks at τ 6·36, 6·51, 7·05 7·81, 8·88 and ca. 9·0, respectively. The peak at τ 6·36 is a singlet and consistent with that of the —OCH_3 protons of carbomethoxy group. In rigid *trans*-fused tricyclononane system, the ester groups are in different environments, and so the —OCH_3 protons should show a doublet, whereas those of *cis*-fused isomer are held in virtually

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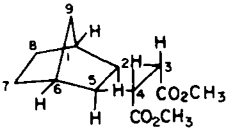
[1] G. O. Schenk, W. Hartmann and R. Steinmetz, *Chem. Ber.* **96**, 498 (1963).

[2] D. Scharf and F. Korte, *Chem. Ber.* **97**, 2425 (1964).

[3] P. Eaton, *J. Amer. Chem. Soc.* **84**, 2344, 2454 (1962).

[4] D. Scharf and F. Korte, *Tetrahedron Letters* 821 (1963).

identical environments, and so they show a singlet. Perhaps, this means that the photo-adduct has a *cis*-fused cyclobutane ring. The peak at τ 6·51 seems to be a quartet, which suggests that the C-4(C-3) proton is coupled with the C-5(C-2) proton and the C-3 proton is coupled with the C-4 proton ($J_{5-4} = J_{4-3} = 8{\cdot}0$ c/s). Then the peak at τ 7·05 is a quartet with a coupling constant of 8·0 c/s and indicates distinctly that the C-5 proton coupled with the C-2 proton and C-2(C-5) with C-3(C-4). High value of $J_{2-3} = J_{5-4} = 8{\cdot}0$ c/s. described above suggests that the protons attached to cyclobutane ring are arranged to *cis*, *trans*, *cis*-configuration, because it has been pointed out by P. Eaton *et al.* that, in the case of *cis*, *trans*, *cis*-tetracarbomethoxy cyclobutane, the coupling constant of the protons attached to cyclobutane ring is 8·0 c/s and of all *cis*-isomer, 4·0 c/s.[3] Furthermore, the peak at the C-3 proton in *endo*-chloro camphor is a doublet because of the coupling between the C-3 proton and the C-4 one, whereas, in the *exo*-epimer, a singlet (shown in Fig. 2).[5] From the above data, it seems to be more reasonable to consider that the photo-adduct has an *endo*-proton and an *exo*-cyclobutane ring at C-5(C-2).



I

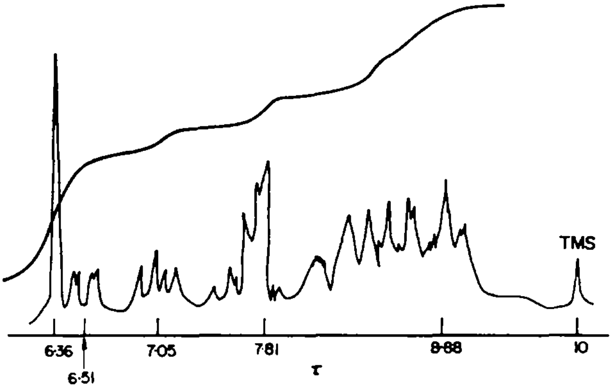
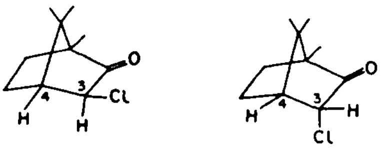


Fig. 1. The NMR spectrum of the photo-adduct (I) in CCl_4



exo-Chloro-camphor *endo*-Chloro-camphor

Fig. 2 α-Chloro-camphors

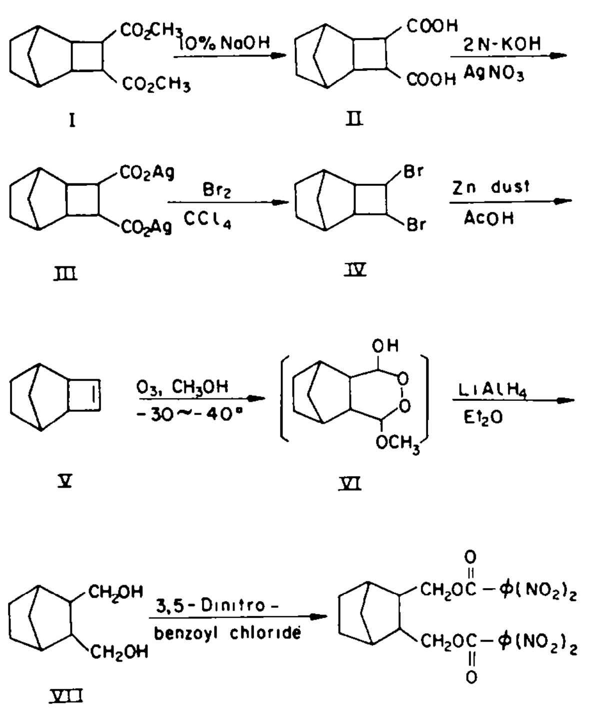
Moreover, the peaks at τ 7·81, 8·88 and ca, 9·0 are multiplets and suggest the bridge head, bridge methylene and ring protons, respectively.

[5] W. D. Kumler, J. N. Shoolery and F. Brutcher, Jr., *J. Amer. Chem. Soc.* **80**, 2533 (1958).

Therefore, it is probable that the more reasonable structure for the photo-adduct might be considered as 3,4-dicarbomethoxy-*cis*, *trans*, *cis*-tricyclo[4,2,1,$0^{2,5}$]nonane (I).

Chemical confirmation of the conclusion, especially the *exo*-configuration, based on the NMR experiment is provided by the process shown hereunder.

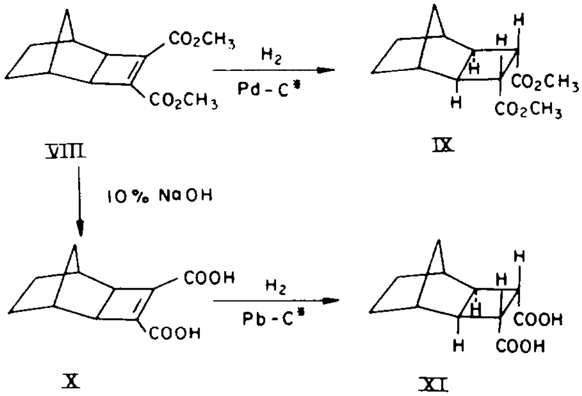
Firstly the photo-adduct was hydrolyzed by 10% sodium hydroxide solution to the dicarboxylic acid (II), which was decarboxylated to 3,4-dibromo-tricyclo[4,2,1,$0^{2,5}$]-nonane (IV) by the Hunsdiecker reaction. And then IV was debrominated to tricyclo-[4,2,1,$0^{2,5}$]nona-3-ene (V), which was ozonized, followed by reduction with LAH to 2,3-bis-hydroxymethyl-norbornane (VII). VII was confirmed to be *exo*-2,3-bis-hydroxymethyl norbornane by the mixing m.p. test of the 3,5-dinitro-benzoate with the authentic 3,5-dinitro-benzoate of *exo*-2,3-bis-hydroxymethyl norbornane[6] and by the comparison of the IR spectrum.



Consequently, the absolute structure of the photo-adduct was confirmed as *exo*-3,4-dicarbomethoxy-*cis*, *trans*, *cis*-tricyclo[4,2,1,$0^{2,5}$]nonane (I). Moreover, in this photochemical reaction, the formation of the respective homodimers of norbornene and dimethyl maleate was not detected by gas chromatography.

In a similar way, the photochemical reaction of dimethyl acetylene dicarboxylate and norbornene gave rise to the 1:1 photo-adduct having the similar but more highly strained configuration, *exo*-3,4-dicarbomethoxy-tricyclo[4,2,1,$0^{2,5}$]nona-3-ene, whose structure was decided by the comparison of the hydrogenated photo-adducts (IX) and (XI) with NMR spectra and mixed melting point of I and II, respectively.

[6] K. Alder and W. Roth, *Chem. Ber.* **87**, 161 (1954).



Concerning the formation of a bicyclo[4,2,0]octadiene dicarboxylic anhydride from maleic anhydride with benzene, D. Bryce-Smith[7] suggested that the above photo-addition proceeds through the charge-transfer complex intermediate. Moreover, Barltrop[8] has recently reported that in a series of photo-additions of cyclohexene with maleic anhydride, maleonitrile and fumaronitrile, the respective absorptions of charge-transfer complexes were shown of λ_{max} 270, 255 and 258 mμ.

In order to clarify the possibility of the mechanism *via* charge-transfer complexes, more precise UV measurements under our reaction conditions were undertaken, but a solution of norbornene and dimethyl maleate (or dimethyl acetylene dicarboxylate) did not show the charge-transfer absorption.

EXPERIMENTAL

All m.ps and b.ps are uncorrected. IR and UV spectra were determined in Shimadzu IR-27C spectrometer and Hitachi EPS-3 spectrophotometer, respectively. The NMR spectra were obtained on Varian Model A-60.

Norbornene,[9] dimethyl maleate and dimethyl acetylene dicarboxylate[10] used were prepared by the usual methods, and distilled before use.

Irradiation apparatus. All irradiations were conducted in a photochemical reactor of 200 ml capacity made from a wide-diameter glass tube, fitted with a 450-watt Eikosha high pressure mercury arc lamp.

Irradiation of a solution of norbornene in dimethyl maleate

In a typical irradiation, norbornene (0·64 mole, 60.3 g) was dissolved in dimethyl maleate (0·60 mole, 86·0 g) and the solution was irradiated under N_2 with 450-watt Hg arc lamp for 110 hr. After distilling off unreacted norbornene, the residual viscous red-yellow oil (101·2 g) was fractionally distilled. Two fractions were collected; (1) (21·2 g), b.p. 80 ~ 110°/2 mm, (2) (11·2 g), b.p. 110 ~ 135°/2 mm. Preparative GLC was run at 202° using a column 4 mm × 2·5 m of Silicone-DC 550 with a H_2 flow rate of 64 ml/min and the result was obtained as follows;

Fraction 1: dimethyl maleate (Rt* = 1·5 min) and dimethyl fumarate (Rt = 1·6 min). Fraction 2: photo-adduct (Rt = 13 min). The respective cyclic homodimers of dimethyl maleate (1,2,3,4-tetracarbomethoxy cyclobutane, Rt = 19·3 min) and norbornene (Rt = 4 and 6 min) were not detected by gas chromatography. Fraction 1 contained some crystals, and so was cooled to −20° and filtered off. IR spectrum of the collected crystals (12·5 g) was identical with that of authentic

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* Rt means retention time.

[7] D. Bryce-Smith and J. E. Lodge, *J. Chem. Soc.* 2675 (1962).

[8] R. Robson, P. W. Grubb and J. A. Barltrop, *J. Chem. Soc.* 2153 (1964).

[9] J. Meinwald and N. J. Hudak, *Organic syntheses* 37, 65 (1956).

[10] H. S. Rhinesmith, *Organic Syntheses* Coll. Vol. 2, 177: T. W. Abbott, R. T. Arnold and R. B. Thompson, *Ibid.* Coll. Vol 2, 10.

dimethyl fumarate (purified by sublimation and recrystallization from pet. ether, m.p. and mixed m.p. 104°). The filtrate was determined to unreacted dimethyl maleate by gas chromatography. Fraction 2 solidified when it was left overnight at room temp. IR spectrum of the above crystals showed both characteristic peaks of norbornene and dimethyl maleate (no C═C absorption). The crystals were purified by recrystallization from pet. ether and sublimation (100°/25 mm); m.p. 82°. (Found: C, 65·55; H, 7·55. $C_{13}H_{18}O_4$ requires: C, 65·53; H, 7·61%); ν_{max} 2995 s, 2900 m, 1740 s, 1200 s, 1080 w, 1030 w, 970 w, 910 w and 830 w cm^{-1} M.W. 236 (cryoscopically) Calc. for $C_{13}H_{18}O_4$: 238. The NMR spectrum (in CCl_4) showed a singlet at τ 6·36, a doublet at τ 6·51, a quartet at τ 7·05 and multiplets at τ 7·81, 8·88 and ca. 9·0.

Reduction of photo-adduct (I) *by LAH.* To an ethereal solution (20 ml) of LAH (0·013 mole, 0·5 g), an ethereal solution (20 ml) containing photo-adduct (0·0042 mole, 0·1 g) was added dropwise under stirring at 0 ~ 5°. Excess LAH was decomposed with water (5 ml) and the ethereal layer was collected, dried over $MgSO_4$ overnight. Evaporation of ether afforded a diol derivative (0·08 g), which was recrystallized from pet. ether, m.p. 80·5°. (Found: C, 72·57; H, 10·04. $C_{11}H_{18}O_2$ requires: C, 72·49; H, 9·96%); ν_{max} 3280 s, 1260 s and 1030 s cm^{-1}, no C═O band. The NMR spectrum (in CCl_4) showed a singlet at τ 5·78, a triplet at τ 6·54, multiplets at τ 7·89 and 8·76.

Hydrolysis of I. I (0·021 mole, 5·0 g.) was refluxed under 10% NaOH for 10 hr and then, neutralized with dil. HCl. The aqueous solution was extracted successively with a small quantity of ether. The combined ethereal extracts were dried over $CaCl_2$. Evaporation of ether gave II (0·021 mole, 4·5 g); m.p. 202·5°. (Found: C, 62·63; H, 6·57. $C_{11}H_{14}O_4$ requires: C, 62·84; H, 6·71%.) Treatment of the acid with diazomethane in ether afforded the original photo-adduct. No epimerization during hydrolysis was detected by treating a small portion of the acid with diazomethane.

Di-silver salt of tricyclo[4,2,1,$0^{2,5}$]*nonane* 3,4-*dicarboxylic acid* (III). A mixture of II (0·020 mole, 4·4 g) and 10 ml water was titrated to a phenolphthalein end point with 2N KOH. This solution was stirred vigorously while a solution of $AgNO_3$ (0·042 mole, 7·1 g) in 20 ml water was added during 10 to 15 min. The thick mixture was stirred for an additional 15 min, then the silver tricyclo[4,2,1,$0^{2,5}$]-nonane 3,4-dicarboxylate was collected by suction filtration. The Ag salt was stirred well 100 ml water, collected again, and washed with MeOH. After drying overnight at 100°, the salt was ground, dried overnight in a vacuum oven at 95 ~ 100° (7·5 g, 90% yield). (Found: C, 30·97; H, 2·66. $C_{11}H_{12}O_4Ag_2$ requires: C, 31·16; H, 2·85%); ν_{max} 1570 s and 1400 s cm^{-1}.

3,4-*Dibromo-tricyclo*[4,2,1,$0^{2,5}$]*nonane* (IV). A solution of Br_2 (0·04 mole, 6·4 g) in CCl_4 (50 ml) was cooled to −25° with stirring. The Ag salt (0·018 mole, 7·5 g) was added during about 1 hr. After an induction period of 30 to 50 min, vigorous evolution of CO_2 set in, and the remainder of the Ag salt was added continuously. When gas evolution had ceased, the AgBr was removed and washed with CCl_4. The filtrate was washed with 2N KOH and water, then dried over $CaCl_2$. Evaporation of CCl_4 afforded an oily residue, which was chromatographed on activated alumina. Elution with pet. ether gave a clear oil (1·1 g), which was recrystallized from pet. ether, m.p. 74 ~ 76°. (Found: C, 38·98; H, 4·44. $C_9H_{12}Br_2$ requires: C, 38·75; H, 4·36%.) τ 5·72, 7·29 and 7·70 (CCl_4). It showed positive result for the Beilstein test.

Tricyclo[4,2,1,$0^{2,5}$]*nona-3-ene* (V). A mixture of IV (1·1 g) and Zn dust was kept in acetic acid for 10 hr at 50 ~ 80°. Filtration of Zn dust and removal of acetic acid afforded an oily residue, which was chromatographed on activated alumina. Elution with pet. ether gave a clear oil (0·2 g). (Found: C, 89·95; H, 9·98. C_9H_{12} requires: C, 89·94; H, 10·06%); ν_{max} 1575 w cm^{-1}, τ 4·13, 7·13 and 7·78 (CCl_4).

2,3-*Bis-hydroxymethyl norbornane* (VII). Ozone (3% in air) was bubbled through a solution of V (0·15 g) in MeOH (100 ml) at −30 ~ −40° until KI solution was changed to red. After removal of MeOH under red. press., the obtainable peroxide (VI) was dissolved in ether and reduced with LAH at 0 ~ 5°. Evaporation of ether afforded *exo*-2,3-bis-hydroxymethyl norbornane b.p. 130 ~ 132°/1 mm, $n_D^{20.5}$ 1·4982, ν_{max} 3450 s, 1780 w and 1030 s cm^{-1}. The 3,5-dinitro-benzoate: m.p. 168 ~ 169°.

Synthesis of 2,3-*bis-hydroxymethyl norbornane* (endo-, exo- and trans-)

(1) endo-2,3-*Bis-hydroxymethyl norbornane.* Cyclopentadiene (0·1 mole, 6·6 g) and maleic anhydride (0·1 mole, 9·8 g) were dissolved in 50 ml benzene and left overnight at room temp. The mixture was diluted with 100 ml pet. ether (30 ~ 60°) and the crystalline product collected. The yield of colourless crystalline product, *endo*-bicyclo[2,2,1]nona-5-ene 2,3-dicarboxylic anhydride,

melting at 161 ~ 162°, was 13·2 g. *endo*-Bicyclo[2,2,1]nona-5-ene 2,3-dicarboxylic anhydride (5 g) was dissolved in absolute ether (20 ml) and a solution of LAH (1 g) in ether (40 ml) was added dropwise for 1 hr at 0°. Excess LAH was decomposed carefully with water, and ethereal layer was collected and dried over $MgSO_4$. Evaporation of ether afforded an oily residue (3·0 g): b.p. 180 ~ 183°/30 mm, m.p. 86°. The 3,5-dinitro-benzoate: m.p. 137°. And this was then hydrogenated on Pd-black to *endo*-2,3-bis-hydroxymethyl norbornane (2·8 g): b.p. 146 ~ 8°/1·5 mm, m.p. 62°. The 3,5-dinitro-benzoate: m.p. 180°.

(2). exo-2,3-*Bis-hydroxymethyl norbornane*. *endo*-Bicyclo-[2,2,1]nona-5-ene 2,3-dicarboxylic anhydride placed in an open flask was heated at 190 ~ 200° for 1·5 hr. The recrystallization of the crude product (m.p. 105°) from benzene gave the *exo*-anhydride, m.p. 140 ~ 142°, and this was converted to *exo*-2,3-bis-hydroxymethyl norbornane by reduction with LAH and successive hydrogenation on Pd-black. *exo*-2,3-Bis-hydroxymethyl norbornane, b.p. 110 ~ 116°/0·5 mm. The 3,5-dinitro-benzoate: m.p. 169 ~ 170°.

(3). trans-2,3-*Bis-hydroxymethyl norbornane*. *trans*-2,3-Dicarbomethoxy bicyclo[2,2,1]nona-5-ene was prepared from dimethyl fumarate and cyclopentadiene, converted to *trans*-2,3-bis-hydroxymethyl norbornane in a similar manner to that described above. *trans*-2,3-Bis-hydroxymethyl norbornane: b.p. 119 ~ 120°/0·3 mm. The 3,5-dinitro-benzoate: m.p. 120°.

Irradiation of solution of norbornene in dimethyl acetylene dicarboxylate

In a typical irradiation, norbornene (0·7 mole, 65·8 g) was dissolved in dimethyl acetylene dicarboxylate (0·56 mole, 79·5 g) and the solution was irradiated under N_2 with 450-watt Hg arc lamp for 75 hr. After distilling off unreacted norbornene and dimethyl acetylene dicarboxylate, the residual viscous red-yellow oil (60·0 g) was fractionally distilled. Two fractions were collected; (1) 5·5 g, b.p. 58 ~ 110°/2 mm, (2) 6·0 g, b.p. 110 ~ 120°/1 mm and residue 45·0 g. The fraction (2) was hydrolyzed by 10% NaOH and neutralized with dil. HCl. The aqueous solution was extracted successively with a small quantity of ether. The ethereal extracts were dried over $CaCl_2$. Evaporation of ether gave X (1·3 g), m.p. 185·5°. (Found: C, 63·55; H, 6·02. $C_{11}H_{12}O_4$ requires: C, 63·45; H, 5·81%.) Hydrogenation of the acid gave XI, m.p. 202·5°. There was no depression of mixed m.p. with II derived from the photo-adduct I.

Acknowledgments—We wish to thank the Research Laboratory of Shionogi Pharmaceutical Co., Ltd. for measurement of NMR.