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Photo-Cycloaddition of 3-Methoxycyclohexenone and 3-Aminocyclohexenone to Ethoxyethylene: Stereochemistry of the Cycloadducts

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Irradiation of a methanolic solution of 3-methoxycyclohexenone and ethoxyethylene with 254 nm light gave four stereoisomeric head-to-tail [2+2] cycloadducts in the ratios indicated in Fig. 3. The structure and stereochemistry of all the isomers were determined by chemical correlations and spectroscopic means, respectively. The time-course product analysis suggested that, in this reaction, the *exo* and *endo* oriented π-complexes are equally formed, and both give the cycloadducts with a slight preference for antara-selectivity. The analogous cycloadduct of 3-aminocyclohexenone to ethoxyethylene decomposed into 2-ethoxycyclooctane-1,5-dione on silica gel chromatography.

Keywords——photo-cycloaddition; stereochemistry; 3-methoxycyclohexenone; 3-aminocyclohexenone; acyclic olefin; 2+2 adduct; bicyclo[4.2.0]octanone; cyclooctanedione; 2D NMR; time-course product analysis

The photo-cycloaddition of cyclic enones to cyclic and acyclic olefins has been a subject of much investigation, since the resultant cyclobutane products are useful intermediates in syntheses of complex natural products and unusual compounds.[1] Among these reactions, the cycloaddition of cyclohexenones to substituted acyclic olefins is particularly interesting from the mechanistic and stereochemical viewpoints. Based on a considerable amount of evidence on the reaction mechanism accumulated since Corey's elegant work,[2] the reaction is now believed to proceed through the formation of the oriented π-complex as an intermediate. The regio- and stereochemical features of this cycloaddition reaction can be summarized as follows: (1) the orientational mode of the addition is apparently governed by the electron demands of the substituents on the olefin: electron-rich olefins always give the head-to-tail (HT) products; (2) *trans*-bicyclo[4.2.0]octanes are usually obtained, sometimes as the major product.

However, despite many reports on this subject, the stereochemistry of the substituent on the cyclobutane ring originating from the acyclic olefin component is still uncetain; it has seldom been established rigidly. For example, Corey *et al.*[2] obtained three HT cycloadducts, two *cis* and one *trans* cyclobutanes, by the reaction of cyclohexenone with benzyloxyethylene, but the stereochemistry of the benzyloxy group was not established. The cycloaddition of 3-acetoxycyclohexenone to ethoxyethylene gave two *cis* adducts as the major products,[3] but again the stereochemistry of the ethoxy group was not determined. Atlhough some other examples are known,[4] the stereochemistry of the substituent in the products remains to be investigated.

In this paper we describe the photo-cycloaddition of 3-methoxycyclohexenone to ethoxyethylene together with a full stereochemical determination of all four theoretically possible cycloadducts. The results presented here, we believe, provide a rare example of the full stereochemical determination of photo-cycloadducts of cyclohexenone derivatives to mono-substituted acyclic olefins.

The photo-cycloaddition of 3-aminocyclohexenone to ethoxyethylene was also examined and the reaction was found to be particularly useful for the preparation of cyclooctanedione derivatives.

Photo-Cycloaddition of 3-Methoxycyclohexenone to Ethoxyethylene

When a methanol solution of 3-methoxycyclohex-2-en-1-one (**1**) and a large excess (15—20 eq) of ethoxyethylene was irradiated with a low-pressure mercury lamp (254 nm) for an appropriate time (see Experimental), four cycloadducts were produced (**a**, **b**, **c**, and **d**), which were separated in pure states by silica gel chromatography in combination with medium-pressure liquid chromatography (MPLC) on a Lobar Si-60 column. The homogeneity of each product was confirmed by thin-layer chromatography (TLC), gas liquid chromatography (GLC), high performance liquid chromatography (HPLC) (shown in Fig. 3), and also by their spectral patterns, which characterize each of them and differentiate them from one another. All products were liquids and had the same molecular formula, $C_{11}H_{18}O_3$, with an OMe group and an OEt group, as shown by the mass spectra (MS) and proton nuclear magnetic resonance (^{1}H-NMR) spectra (Table I).

The adduct **a** showed a carbonyl absorption at 1700 cm^{-1}. It was stable to alumina chromatography, but decomposed on heating with 5% HCl–MeOH to afford a cyclooctanedione **7** (for the structure determination, see below) in excellent yeild, showing that it is an HT cycloadduct with *cis*-fused stereochemistry; *i.e.*, **2** or **4**.

The adduct **b** showed a carbonyl absorption at 1722 cm^{-1}. On chromatography over neutral alumina,[2] it quantitatively isomerized into **a**. Therefore **b** is an HT cycloadduct with a *trans*-fused ring juncture, and has the same relative stereochemistry between the OMe group and the OEt group as in **a**; *i.e.*, **3** or **5**.

The adduct **c** showed a carbonyl absorption at 1700 cm^{-1} and was stable to alumina chromatography. On heating with 5% HCl–MeOH, it gave (though the reaction was slower

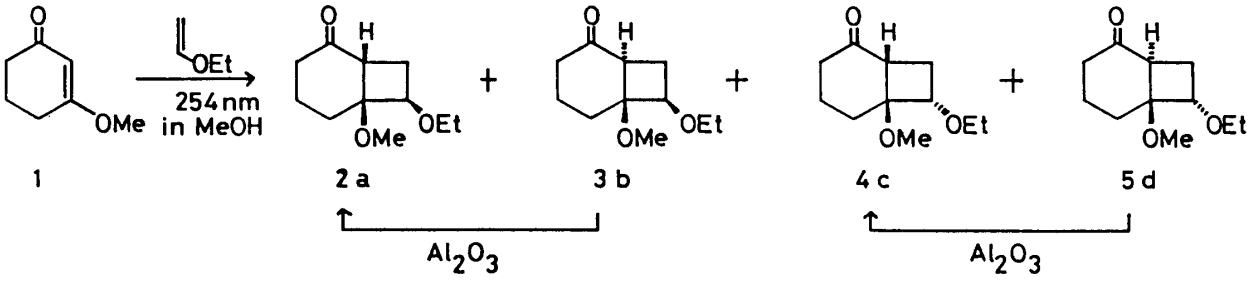


Chart 1

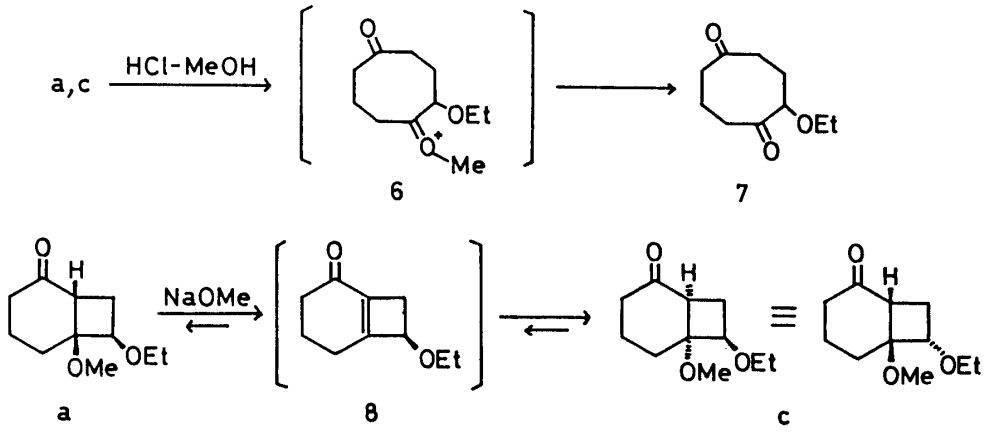


Chart 2

than that of **a**) the cyclooctanedione **7**, which was identical with the specimen obtained from **a**. Hence **c** is a *cis*-fused cyclobutane with HT regiochemistry and the stereochemistry of the OEt group is different from that of **a**.

The adduct **d** showed a carbonyl absorption at 1720 cm^{-1}, and quantitatively isomerized into **c** on alumina chromatography, thus showing that it is a *trans*-fused compound and isomeric to **b** only in the sterochemistry of the OEt group.

When **a** was treated with methanolic sodium methoxide, it isomerized exclusively to give **c**. Since this reaction obviously proceeded through the cyclobutene intermediate **8** as shown in Chart 2, the result indicates that **c** is the thermodynamically more stable *cis-anti* isomer **4** and **a** is the less stable *cis-syn* isomer **2**. This assignment is supported by the fact that, on acid treatment, **a** is more rapidly decomposed into **7** than **c** is, which implies that **a** is more strained than **c**. The same trend of greater stability of a *cis-anti* isomer than a *cis-syn* isomer has been reported in azabicyclo[3.2.0]heptane derivatives such as **9**.[5] Hence the stereochemistries of the cycloadducts, **a**, **b**, **c**, and **d**, are suggested to be as shown in **2**, **3**, **4**, and **5**, respectively.

The above stereochemical assignments were confirmed by the following spectral evidence. First, all proton signals of **a** (**2**) and **c** (**4**) were assigned by shift correlation two dimetional NMR (2D NMR) (COSY) at 400 MHz (Figs. 1-a, 1-b, and Table I). Remarkable differences between **a** and **c** are observed in the signals of H_1 and H_8. H_1 in **a** is more deshielded than that of **c**. The two H_8 protons in **c** appeared separately at δ 1.63 (H_{8b}) and 2.37—2.47 (H_{8a}), while those in **a** appeared with overlap at δ 2.25—2.44. These results suggest that the steric relationship between the above protons and the carbonyl group is different in these two compounds. Though the methylene protons of the OEt group appeared as a quartet in **c**, they appeared as a multiplet in **a**, indicating the presence of a restricted rotation of the O–CH_2 bond in the latter, which supported the *syn* OMe–OEt orientation in **a**. Carbon-13 nuclear magnetic resonance (^{13}C-NMR) (Table II) of the two compounds, assigned by selective proton decoupling experiments, again confirmed the above assignment. The carbon

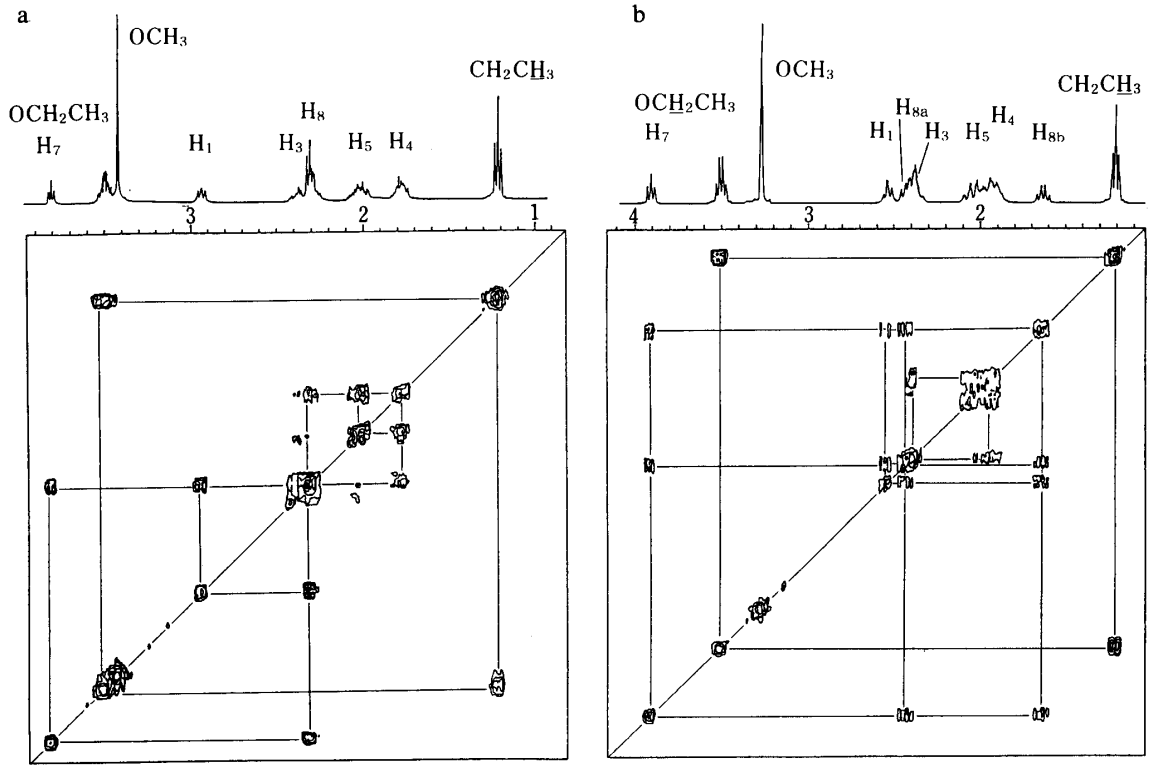
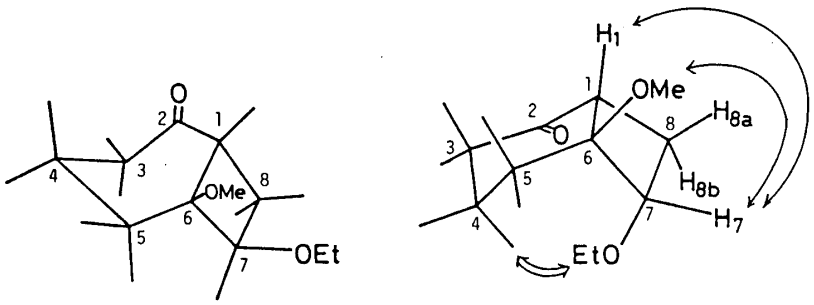


Fig. 1. Contour Plot of the COSY Map of **a** (a) and **c** (b)



2a **4c**

Fig. 2. Conformations of the Photo-Adducts **a** and **c**
↔, NOE observed; ⇔, steric compression.

TABLE I. ^{1}H-NMR Spectra of the Photo-Adducts **a**, **b**, **c**, and **d**, in Chloroform-*d* (Parenthetical Values Indicate the Coupling Constants (Hz))

Proton	**a** (400 MHz)	**b** (100 MHz)	**c** (400 MHz)	**d** (100 MHz)
1	2.94, t (8.2)	2.4—2.5 Overlapped with H_8	2.53, t (10.3)	3.54, dd (12, 8)
3	2.25—2.44, m		2.31—2.41, m	
4	1.74—1.83, m			
5	1.96—2.09, m			
7	3.81, t (6.5)	3.84, dd (8, 6.5)	3.90, t (8.5)	3.93, d (5)
8a	2.25—2.44, m		2.37—2.47, m	2.70, dt (12, 8)
8b			1.63, dt (10.3, 8.5)	1.86, dd (12, 8)
$-OCH_3$	3.42, s	3.13, s	3.26, s	3.13, s
$-OCH_2CH_3$	3.50, m	3.45, q (7.0)	3.49, q (7.3)	3.45, q (7.0)
$-OCH_2CH_3$	1.22, t (7.3)	1.20, t (7.0)	1.21, t (7.3)	1.23, t (7.0)

TABLE II. ^{13}C-NMR Chemical Shifts (δ) of the Adducts **a** and **c** in Chloroform-*d* (at 100 MHz)

Carbon	**a**	**c**	$\Delta_{\delta(a-c)}$
1	46.1 (d)	43.2 (d)	2.9
2	212.1 (s)	210.6 (s)	1.5
3	39.5 (t)	38.4 (t)	1.1
4	28.8 (t)	20.1 (t)	8.7
5	20.7 (t)	23.6 (t)	−2.9
6	83.8 (s)	85.0 (s)	−1.2
7	76.4 (d)	75.4 (d)	1.0
8	29.2 (t)	26.9 (t)	2.3
$-OCH_3$	51.6 (q)	50.9 (q)	0.7
$-OCH_2CH_3$	64.8 (t)	64.8 (t)	0
$-OCH_2CH_3$	15.3 (q)	15.3 (q)	0

signal of C_4 in **c** is shielded by *ca.* 9 ppm as compared with that of **a**, indicating the presence of a large steric compression between OEt and C_4 in the former. On the other hand, a shielding by *ca.* 3 ppm was observed for **a** at C_5. These spectral characteristics are well explained if we

consider the conformations depicted in Fig. 2 for these compounds, but can not be interpreted if other stereochemistries are assigned to **a** and **c**.

The nuclear Overhauser effect (NOE) correlation 2D NMR spectra (NOESY) in combination with NOE difference spectra showed the presence of appreciable NOE effects between H_1 and H_7, and H_7 and OMe in **c**, while no correlation was observed between these protons in **a**.

Time-Course Product Analysis and the Reaction Mechanism

The cycloaddition of 3-methoxycyclohexenone **1** to ethoxyethylene did not give a satisfactory result either in the other solvents such as acetone and hexane, or with >300 nm light. In either case, the reaction was too slow to allow practical isolation of the cycloadducts. This suggests that the reaction of **1** with ethoxyethylene in methanol with 254 nm light proceeds through a π–π^* excitation of the enone rather than an n–π^* excitation.

In order to obtain information on the reaction pathway, the time-course of the product ratios in methanol was analyzed by HPLC, by taking an aliquot from the reaction mixture every one hour (see Fig. 3). It was found that the four cycloadducts, **a**, **b**, **c**, and **d**, were formed at the initial stage of irradiation with a preference for the *trans* isomers, and the yield of each product increased with time. The relative ratio was constant until all the starting enone was consumed (*ca.* 8 h required when a 20 W pencil-type irradiator was used), then the relative ratio of **d** rapidly decreased with an increase of **c** and a new peak indicative of formation of an unknown compound **x** (see Fig. 3-b, c).

The above result demonstrates that the four adducts are formed independently with a preference for the *trans* isomers. They are photo-stable to 254 nm light as long as the enone consumes the photo-energy for cycloaddition, but they are photo-unstable when there is no other compound present that consumes photo-energy. Further photo-transformation of the cyclobutanes, for example of the *trans* isomer **d**, we consider, should be a disrotatory cycloreversion and suprafacial cycloaddition of the resulting bis-olefin **10** to **c** and probably to a bicyclo[4.1.1]octanone **11**,[6] although isolation and identification of the latter remain to be achieved.

Following the hitherto proposed 1,4-biradical mechanism,[7] the pathway of photo-cycloaddition of **1** to ethoxyethylene leading to the four cyclobutanes may be explained as shown in Chart 4-a: the twisted biradical is formed with a slight preference over the non-

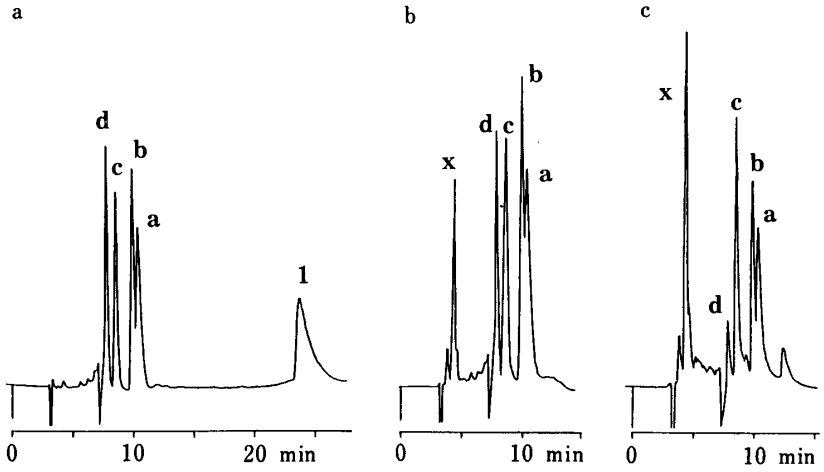


Fig. 3. HPLC of the Reaction Mixture

Column, TSKgel Silica-60 (4.61 i.d. × 250 mm); solvent, hexane : ethyl acetate = 2 : 1; flow rate, 1 ml/min.

a, 4 h, **a**:**b**:**c**:**d** = 1.0 : 1.3 : 1.2 : 1.4; b, 10 h, **a**:**b**:**c**:**d** = 1.0 : 1.5 : 1.2 : 1.2; c, 15 h, **a**:**b**:**c**:**d** = 1.0 : 1.3 : 1.8 : 0.3.

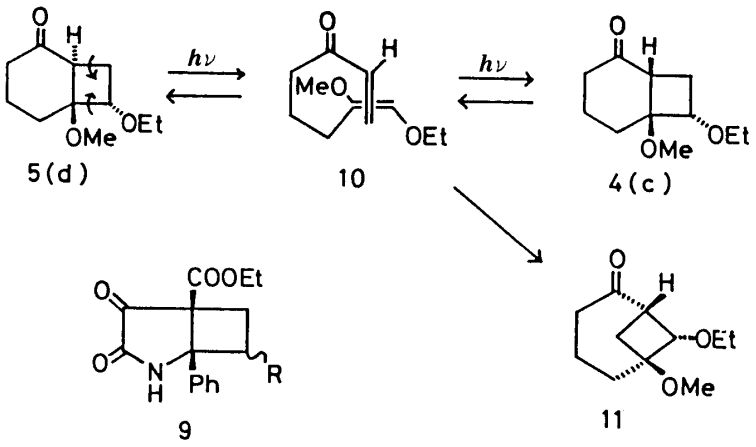


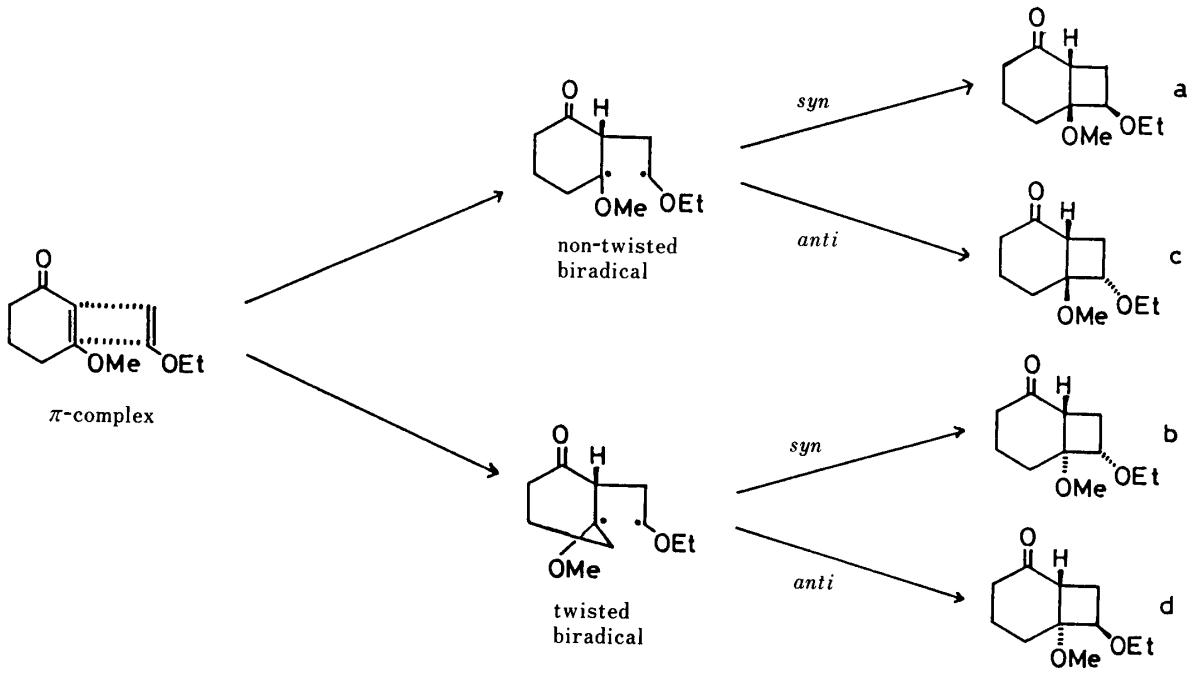
Chart 3

twisted species, as frequently observed in cycloaddition of cyclohexenones, and the *syn–anti* ratio of OMe and OEt is almost unity. However, this mechanism seems to be hardly acceptable, since the *syn* OMe–OEt orientation should have greater steric hindrance than the *anti* orientation, which would result in unbalanced formation of the *syn* and *anti* isomers.

We prefer an alternative explanation which assumes an equal formation of two stereoisomeric oriented π-complexes (Chart 4-b), both of which cycloadd with a preferred antarafacial mode in the triplet enone moiety (inversion of the configuration at the enone moiety), since $2s+2a$ cycloaddition in a polar enone–olefin pair has been predicted by Epiotis and Shaik.[8]

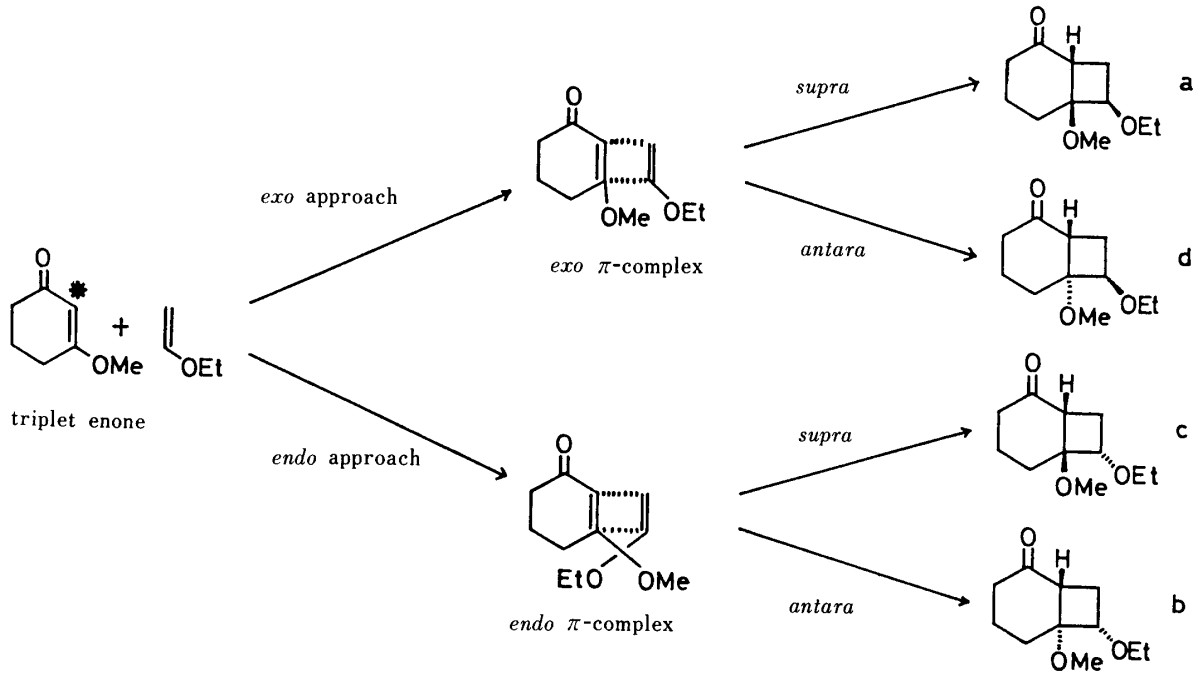
Photo-Cycloaddition of 3-Aminocyclohexenone to Ethoxyethylene

The photo-cycloaddition of 3-aminocyclohex-2-en-1-one (**12**) to ethoxyethylene in methanol was also examined. The adduct was smoothly produced by irradiation with 254 nm light, but light of >300 nm gave no addition product at an observable rate.



twist/non-twist>1, *syn*/*anti*≒1

Chart 4-a



endo/exo ≒ 1, *antara/supra* > 1

Chart 4-b

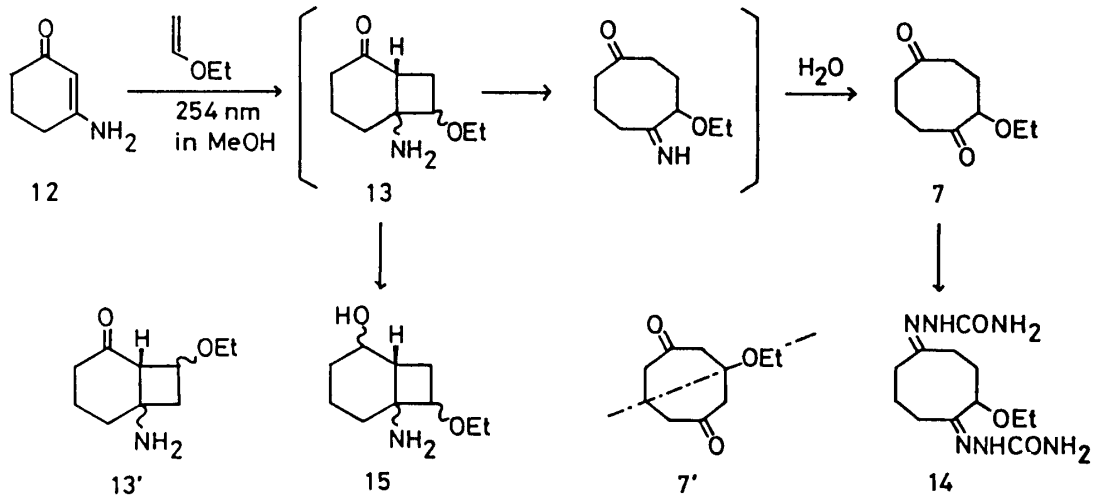


Chart 5

Upon chromatographic purification on silica gel, the reaction mixture gave an oily compound which was gas chromatographically homogeneous. The MS and ^{1}H-NMR indicated that it has the formula $C_{10}H_{16}O_3$ and possesses an OEt group. The presence of two carbonyl groups (corresponding to the infrared (IR) absorption at 1700 cm^{-1}) was confirmed by the formation of a bis-semicabazone, $C_{12}H_{22}N_6O_3$, mp 242 °C. These data indicate that this compound is an ethoxycyclooctane-1,5-dione (**7** or **7'**) which should have originated from the cycloadduct (**13** or **13'**). The ^{13}C-NMR exhibited ten carbon signals, unambiguously indicating that the compound has the asymmetric structure **7**, thus eliminating the possibility of the symmetric structure **7'** which might have originated from an HH adduct **13'**.

We thought that this was produced during the isolation from the real HT cycloadduct **13** upon silica gel chromatography. This view was supported by isolation of the basic compounds

15, though as a mixture of stereoisomers, when the photo-product was reduced with sodium borohydride prior to the chromatographic purification. The transformation of **13** to **7** must be very fast on silica gel, because TLC of the photo-product showed a single spot corresponding to **7**, other than that of the starting enone **12**. This transformation should proceed as shown in Chart 5.

Thus 3-aminocyclohexenone was shown to be a useful precursor for the preparation of cyclooctanedione derivatives.

Experimental

Melting points were taken on a Yanagimoto micro hot-stage melting point apparatus, and are uncorrected. IR spectra were taken in $CHCl_3$ solution on a JASCO IR-G spectrometer and are given in cm^{-1}. ^1H- and ^{13}C-NMR spectra were measured in $CDCl_3$ solution with tetramethylsilane as an internal standard on a JEOL FX-100 (100 MHz for ^1H and 25.0 MHz for ^{13}C) or a JEOL GX-400 spectrometer (400 MHz for ^1H and 100 MHz for ^{13}C). MS data were obtained at an ionizing voltage of 70 eV on a Hitachi M-80 machine. GLC analyses were performed on a Shimadzu GC4CM-PF instrument with an FID detector using 1.5% OV-1 (3 mm i.d. × 1 m, 100 °C, 60 ml/min N_2; column I) or 5% OV-17 (3 mm i.d. × 2 m, 180 °C, 60 ml/min N_2; column II). HPLC was carried out on a Toyo Soda apparatus (CCPD and CO-8000) equipped with an RI-8000 refractive index detector. Wakogel C-200 (silica gel) was used for column chromatography. For TLC, Merck precoated plates GF_{254} were used with solvent systems of benzene–acetone (9 : 1, solvent I), benzene–ethyl acetate (3 : 1, solvent II), and hexane–ethyl acetate (1 : 1, solvent III), and spots were observed by spraying 1% ceric sulfate in 10% H_2SO_4 followed by heating at 100 °C until coloration appeared.

Photo-Cycloaddition of 3-Methoxycyclohexenone 1 to Ethoxyethylene——i) 3-Methoxycyclohexenone (1.86 g) and ethoxyethylene (16 g, 15 eq) in methanol (400 ml) were irradiated with 254 nm light (100 W super-low-pressure mercury lamp with a quartz filter) at 5—10 °C for 10—15 h. The mixture was concentrated and the residue was chromatographed in benzene–ethyl acetate (1 : 1) to yield 7 fractions, each of which was subjected to MPLC in benzene–acetone (12 : 1) for further purification. The following compounds, each of which showed a single spot on TLC, and a single peak on GLC and HPLC, were obtained; **d** (18 mg), **c** (74 mg), **b** (18 mg), and **a** (614 mg). All of them were liquids. **a**, *Rf*: 0.35 (solvent I), 0.39 (solvent II), 0.50 (solvent III); t_R: 8.9 min (column I), 4.9 min (column II); MS *m/z* (%): 198 (M^+, 2), 128 (24), 127 (86), 126 (34), 98 (100), 72 (51), 68 (20), 55 (2). **b**, *Rf*: 0.38 (solvent I), 0.47 (solvent II), 0.50 (solvent III); t_R: 13.7 min (column I); MS *m/z* (%): 198 (M^+, 3), 128 (41), 127 (57), 126 (25), 98 (100), 72 (47), 68 (23), 55 (21). **c**, *Rf*: 0.40 (solvent I), 0.47 (solvent II), 0.62 (solvent III); t_R: 8.9 min (column I), 5.1 min (column II); MS *m/z* (%): 198 (M^+, 2), 128 (29), 127 (77), 126 (34), 98 (100), 72 (55), 68 (20), 55 (15). **d**, *Rf*: 0.42 (solvent I), 0.53 (solvent II), 0.62 (solvent III); t_R: 12.9 min (column I); MS *m/z* (%): 198 (M^+, 2), 128 (48), 127 (61), 126 (29), 98 (100), 72 (51), 68 (19), 55 (22). The other data are given in the text.

ii) The product from 1.1 g of 3-methoxycyclohexenone was dissolved in ether and passed through a column of Woelm neutral alumina (activity II). The pale yellow oily eluate showed two spots on TLC corresponding to **a** and **c**, which were separated by chromatography using benzene–ethyl acetate as an eluent to yield **a** (400 mg) and **c** (600 mg).

Isomerization of *trans-syn* Adduct 3 to *cis-syn* Adduct 2——The adduct **b** (2 mg) was dissolved in ether and passed through a column of Woelm netural alumina (activity II). Evaporation of the solvent from the eluate gave an oil (2 mg) whose TLC, ^1H-NMR, and GLC (column I) results were identical with those of **a**.

Isomerization of *trans-anti* Adduct 5 to *cis-anti* Adduct 4——The adduct **d** (9 mg) was dissolved in ether and passed through a column of Woelm netural alumina (activity II). Evaporation of the solvent from the eluate gave an oil (9 mg) whose TLC, ^1H-NMR, and GLC (column I) results were identical with those of **c**.

Isomerization of *cis-syn* Adduct 2 to *cis-anti* Adduct 4——The adduct **a** (10 mg) was dissolved in 2.5% NaOMe–MeOH (2 ml) and heated at 60 °C for 1 h. After neutralization with 2% HCl, the mixture was diluted with water, and extracted with $CHCl_3$. Concentration of the dried extract gave an oil whose TLC and ^1H-NMR results were identical with those of **c**.

Acid Treatment of *cis-syn* Adduct 2 and *cis-anti* Adduct 4——i) The adduct **a** (122 mg) in tetrahydrofuran (5 ml) and 2% HCl (1 ml) was refluxed for 0.5 h. The mixture was diluted with water, and extracted with CH_2Cl_2, then the extract was dried and concentrated to give an oily residue, which was chromatographed on silica gel. The benzene–ethyl acetate eluate gave a pale yellow oil (84 mg, 74%) which was identical with 2-ethoxycyclooctane-1,5-dione (**7**) in terms of ^1H-NMR, IR, and GLC behavior (column I).

ii) The adduct **c** (120 mg) in tetrahydrofuran (THF) (8 ml) and 2% HCl (2.5 ml) were heated under reflux for 8 h, then worked up as above. The product (50 mg, 54%) was identical with **7** in terms of ^1H-NMR, IR, GLC, and TLC behavior.

Time-Course Product Analysis——3-Methoxycyclohexenone (100 mg) and ethoxyethylene (860 mg) in methanol (15 ml) were irradiated by using a 20 W medium-pressure pencil-type mercury lamp at 5—10 °C and an aliquot of the

reaction mixture was collected every one hour. Each sample was concentrated to dryness, and the residue was dissolved in hexane–ethyl acetate (2:1), and analyzed by HPLC using a refractive index detector (see Fig. 3). The product ratio (**a**:**b**:**c**:**d**) was *ca.* 1.0:1.3:1.2:1.4 during 1—8 h, 1.0:1.5:1.2:1.2 after 10 h, and 1.0:1.3:1.8:0.3 after 15 h. The cyclohexenone disappeared after 8 h, when a new peak indicative of the formation of an unknown compound **x** began to appear.

Photo-Cycloaddition of 3-Aminocyclohexenone 12 to Ethoxyethylene——The enaminone **12** (0.88 g) and ethoxyethylene (5 g) in methanol (400 ml) were irradiated with 254 nm light for 4 h at 5—10 °C. After evaporation of the methanol below 40 °C, the residue was chromatographed on silica gel in CH_2Cl_2 to yield 2-ethoxycyclooctane-1,5-dione (**7**) (0.54 g, 37%) as a colorless oil, bp (1 mmHg) 120—140 °C (bath temp). IR: 1700 cm^{-1} UV (MeOH): no absorption at >210 nm. MS *m/z*: 183 (M^+). ^{1}H-NMR δ: 3.82 (1H, t, J=4 Hz, –CH–O), 3.47 (2H, q, J=7 Hz, OCH_2CH_3), 1.8—3.1 (10H, cyclooctane ring), 1.23 (3H, t, J=7 Hz, OCH_2CH_3). ^{13}C-NMR δ: 15.2 (q, OCH_2CH_3), 65.4 (t, OCH_2CH_3), 22.6, 28.9, 38.7, 42.3, 65.5 (each t, C-3, 4, 6, 7, 8), 84.1 (d, C-2), 212.9, 213.9 (each s, C-1, 5).

The oxime was prepared as follows. The octanedione **7** (54 mg), hydroxylamine hydrochloride (135 mg), and 10% NaOH (0.5 ml) were heated on a water-bath for 10 min. The resulting oxime was crystallized from H_2O–methanol as a white granular material, mp 85—88 °C. *Anal.* Calcd for $C_{10}H_{18}NO_3 \cdot 1/3H_2O$; C, 54.52; H, 8.54; N, 12.72. Found: C, 54.25; H, 8.72; N, 12.76.

The semicarbazone was prepared as follows. A mixture of the octanedione **7** (80 mg), semicarbazide hydrochloride (100 mg), and sodium acetate (150 mg) in water (1 ml) was heated on a water-bath for 30 min. The resulting semicarbazone was crystallized from water as colorless prisms, mp 242—242.5 °C. *Anal.* Calcd for $C_{12}H_{22}N_6O_3$: C, 48.31; H, 7.43; N, 28.17. Found: C, 48.33; H, 7.48; N, 28.15.

Reaction of the Photo-Product 13 with Picric Acid——The oily photo-product obtained from **12** after evaporation of the solvent was dissolved in ether and treated with an ethereal solution of picric acid. Addition of hexane to the mixture precipitated a yellow solid which, on crystallization from MeOH, gave yellow prisms, mp 252—260 °C (dec.). This was identified as ammonium picrate. The mother liquor was passed through a silica gel column to yeild **7**.

$NaBH_4$ Reduction of the Photo-Product 13——The reaction mixture from the photo-reaction of **12** and ethoxyethylene was treated with $NaBH_4$ at room temperature for 30 min. After evaporation of the solvent, the residue was dissolved in $CHCl_3$–EtOH and passed through a column of silica gel to remove inorganic materials. The product obtained from the eluate was again chromatographed to yield two fractions, each of which was treated with an ethereal solution of picric acid. One gave a gummy picrate and the other gave a crystalline picrate which formed yellow needles from methanol, mp 158—159 °C. *Anal.* Calcd for $C_{10}H_{19}NO_2 \cdot C_6H_3N_3O_7$: C, 46.37; H, 5.35; N, 13.52. Found: C, 46.16; H, 5.52; N, 13.36.

References and Notes

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