material (except for optical rotation), and hence structure I for platycerine is confirmed.

### Experimental Section

**2-Benzyloxy-3-methoxybenzaldehyde (V)** was prepared by benzylation of *o*-vanillin according to the method of Uff.[6a] V was obtained in 80% yield as colorless needles (crystallized from ether), mp 44° (lit.[6b] mp 44.0–44.5°).

**7-Methoxy-8-benzyloxyisoquinoline (IX).**—An adaptation of the method of Jackson and Stewart[7] was used. Intermediates to IX were isolated but were not rigorously purified at each step. A mixture of V and 10% excess aminoacetaldehyde dimethyl acetal was heated in benzene at reflux with a Dean–Stark trap until the calculated amount of water was collected. Excess amino acetal was removed by washing, and distillation *in vacuo* left the product Schiff's base VI as a yellow oil. VI was quantitatively reduced to the amine in ethanol with 1% by weight $PtO_2$ in a Parr apparatus at 50 psi hydrogen. The amine was converted to the tosylate VII in good yield with *p*-toluenesulfonyl chloride in pyridine. VII (0.1 mol) was dissolved in a solution of 100 ml of peroxide-free dioxane and 15 ml of 6 *M* HCl and the solution was heated at reflux in the dark until tlc showed complete disappearance of VII. The reaction mixture was washed with water and the solvent was removed *in vacuo* to leave VIII as a brown oil. VIII was stirred for several hours in a solution of potassium *tert*-butoxide in *tert*-butyl alcohol under gentle heat. After the mixture had cooled, benzene and water were added and the benzene layer was washed several times with additional water. The benzene layer was dried and the solvent was evaporated to leave a red oil, which was purified by Florisil column chromatography to yield red needles of IX, mp 188° (lit.[6] mp 185–188°), in 60% yield from V.[8]

***N*-Benzoyl-8-benzyloxy-1,2-dihydro-7-methoxyisoquinoline-1-carbonitrile (X).**—To 75 ml (0.15 mol) of an aqueous solution of KCN in an ice-cold three-neck flask fitted with a mechanical stirrer, addition funnel, and condenser was added IX (13 g, 0.05 mol). The mixture was stirred until a fine suspension of IX in the solution was obtained. Benzoyl chloride (0.1 mol) was then added dropwise with stirring. Stirring was continued until the Reissert compound X separated as a tan solid. This was filtered off and recrystallized from ethanol to yield 65% X as a white solid, mp 135° (lit.[6a] mp 135°).

**1-(3,4-Dimethoxybenzyl)-7-methoxy-8-benzyloxyisoquinoline (XI).**—The nitrile X (12 g in 100 ml of DMF at 0°) was treated under nitrogen with a threefold excess of NaH, and then a twofold excess of 3,4-dimethoxybenzyl chloride in 50 ml of DMF was added. The mixture was stirred overnight and then ethanol was added to destroy the excess NaH. Benzene and water were added and the benzene layer was separated and washed again with water and finally with 6 *M* HCl. The acidic layer was made basic with NaOH and extracted with $CHCl_3$. The $CHCl_3$ layers were combined, dried over $K_2CO_3$, and evaporated to yield XI in 80% yield. Recrystallization from ethanol gave XI as a white solid: mp 117°; nmr ($CDCl_3$) $\delta$ 8.2 (d, 1, H on $C_3$), 7.7–6.6 (m, 6, aromatic H), 5.0 (s, 2, $OCH_2C_6H_5$), 4.88 (s, 2, $CH_2$), 3.93 (s, 3, $OCH_3$), 3.70 (s, 3, $OCH_3$), 3.60 (s, 3, $OCH_3$).

*Anal.* Calcd for $C_{26}H_{25}NO_4$: C, 75.08; H, 5.97; N, 3.29. Found: C, 75.16; H, 6.06; N, 3.37.

**(±)-Platycerine (I).**—The isoquinoline XI (3 g) was converted to the methiodide by heating in a mixture of 15 ml of $CH_3I$ and $CH_3OH$. The solvents were removed *in vacuo* and the yellow solid which was obtained was dried and then added to a slurry of $LiAlH_4$ (0.75 g) in dry ether. The slurry was stirred for 3 hr and the excess hydride was decomposed by the addition of wet ether and a saturated solution of sodium potassium tartrate. The ether layer was separated and evaporated to yield the 1,2-dihydroisoquinoline XII as a yellow oil. To XII was added 25 ml of 7:5 $HCOOH-H_3PO_4$ and the solution was heated at reflux until all XII had disappeared as evidenced by tlc. The solution was then diluted with water and washed with $CHCl_3$. The aqueous layer was made basic to pH 8 with NaOH solution and extracted with $CHCl_3$. The $CHCl_3$ layers were combined, dried over $K_2CO_3$, and evaporated to yield a crude oil shown by tlc and nmr to be the desired I in 60–70% yield. Preparative layer chromatography yielded a sample of pure (±)-platycerine (I) whose $CHCl_3$ ir, $CDCl_3$ nmr, cyclohexane uv, and tlc $R_f$ value (0.55 using silica gel G and 3:2 benzene–methanol) were identical with those of the natural alkaloid.[4]

**Registry No.**—I, 38863-79-5; V, 2011-06-5; VI, 38868-50-7; VII, 38868-51-8; VIII, 38868-52-9; IX, 36454-41-8; X, 38868-54-1; XI, 38868-55-2.

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[7] A. H. Jackson and G. W. Stewart, *Chem. Commun.*, 149 (1971).

[8] We are indebted to Mr. John Lawson for technical assistance in this preparation.

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## The Photocycloaddition of Diphenylacetylene to 1,5-Cyclooctadiene

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It is known that diphenylacetylene photoreacts with tetramethylethylene[1] and cyclic vinyl ethers[2] to give the cyclobutene derivatives. In an earlier paper[3] we reported the photocycloaddition of diphenylacetylene to norbornadiene, in which the products that were considered to be formed by the further reactions of the intermediate cyclobutene were obtained in contrast to the above reactions. In order to observe the behavior of diphenylacetylene in other dienes, we photolyzed a solution of diphenylacetylene in 1,5-cyclooctadiene. The reaction mixture was irradiated for 40 hr through a Pyrex filter with a high-pressure mercury lamp. Chromatography on silica gel gave only one product, 1 (72%).

Elemental analysis and the mass spectrum ($M^+$ 286) indicated that this product was a 1:1 adduct of diphenylacetylene and 1,5-cyclooctadiene. The nmr spectrum showed no signals in the vinyl region, and was very simple, indicating that this product has the symmetrical structure. The possible structure for this product is 1 or 2, whose type of structure was assigned to the photoadduct of acetylenedicarboxylic acid and 1,4-cyclohexadiene.[4,5]

This product was stable on heating for 1 hr at 47° in 2 *N* sulfuric acid, where norcarane completely decomposed,[6] and the signal at $\delta$ 3.04 is at too low field to be assigned to the ring protons of cyclopropanes.[7] Structure 1 is compatible with these properties, but structure 2 is not. Thus, this product was assigned the structure 9,10-diphenyltetracyclo[6.2.0.0$^{4,10}$.0$^{5,9}$]decane.

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[1] O. L. Chapman and W. R. Adams, *J. Amer. Chem. Soc.*, **90**, 2333 (1968).

[2] H. M. Rosenberg and P. Servé, *J. Org. Chem.*, **33**, 1653 (1968); M. P. Servé and H. M. Rosenberg, *ibid.*, **35**, 1237 (1970).

[3] T. Kubota, K. Shima, and H. Sakurai, *Chem. Commun.*, 360 (1971).

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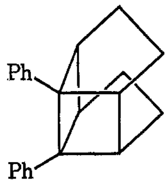
[5] The photoreaction of diphenylacetylene and 1,4-cyclohexadiene gave the complex mixtures, but a 1:1 adduct corresponding to that of diphenylacetylene and 1,5-cyclooctadiene could not be isolated.

[6] R. T. LaLonde and L. S. Forney, *J. Amer. Chem. Soc.*, **85**, 3767 (1963).

[7] L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, New York, N. Y., 1969, pp 196, 228.



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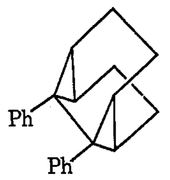

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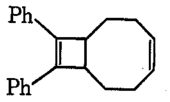

3

This reaction was neither sensitized by thioxanthone ($E_T$ = 65.5 kcal/mol)[8] and triphenylene ($E_T$ = 66.6 kcal/mol),[8] whose triplet energies are considered to be effectively transferred to diphenylacetylene ($E_T$ = 62.5 kcal/mol),[8] nor quenched by diacetyl ($E_T$ = 54.9 kcal/mol).[8] These results suggest that the addition involves singlet-excited diphenylacetylene; this is a contrast to the results that other photoreactions of diphenylacetylene proceeded *via* triplet diphenylacetylene.[2,9] This reaction is considered to involve the intramolecular photocycloaddition of the intermediate cyclobutene **3**. However, this intermediate was never observed when the photolysis was monitored by glc and uv. This can be well explained by the assumptions that the intermediate diphenylcyclobutene **3** is preferentially photoexcited on account of its large molar extinction coefficient[10] at the excitation wavelengths, and the quantum efficiency of the intramolecular reaction is greater than that of diphenylacetylene with 1,5-cyclooctadiene.

### Experimental Section

Melting points are uncorrected. Ir spectra were obtained on a Hitachi EPI-S2 spectrophotometer. Uv spectra were obtained on a Hitachi 124 spectrophotometer. Mass spectra were obtained on a Hitachi RMS-4 spectrometer. Nmr spectra were taken on a high Hitachi Perkin-Elmer R-20 spectrophotometer. Glc was performed on a Simadzu GC-3AF (2 m × 3 mm, 3% SE-30 on Chromosorb W column).

**Photoaddition of Diphenylacetylene and 1,5-Cyclooctadiene.**—In a Pyrex vessel, a solution of diphenylacetylene (0.8 g, 0.0045 mol) in 1,5-cyclooctadiene (48 g, 0.44 mol) was irradiated for 40 hr with a 350-W high-pressure mercury lamp. After removal of the unreacted diene under reduced pressure, the remaining liquid (1.4 g) was subjected to column chromatography on Merck silica gel, 50 g (70–230 mesh). Elution in 200-ml fractions gave fractions 1–3, *n*-hexane, nil; 4–5, 5% benzene in *n*-hexane, a crystalline material. Recrystallization of this crystalline material from ethanol gave 9,10-diphenyltetracyclo[6.2.0.$0^{4,10}$.$0^{5,9}$]-decane: 924 mg (72%); mp 105.5–106.5°; ir (KBr) 3040, 3010, 2930, 1595, 1487, 1440, 750, 721, and 695 $cm^{-1}$; nmr ($CCl_4$) $\delta$ 2.0 (m, 8 H, methylene), 3.04 (br s, 4 H, cyclobutane), and 7.0 (m, 10 H, aromatic); mass spectrum *m/e* (rel intensity) 286 (1), 144 (48), 143 (100), 142 (83), 128 (39), 115 (15), and 91 (11); uv (*n*-hexane) 223 nm ($\epsilon$ 10,700), 248 (1500), 253 (920), 262 (800), and 272 (490).

*Anal.* Calcd for $C_{22}H_{22}$: C, 92.26; H, 7.74. Found: C, 92.25; H, 7.56.

**Attempted Sensitization with Thioxanthone and Triphenylene.**—Diphenylacetylene (50 mg, 0.28 mmol), 1,5-cyclooctadiene (300 mg, 2.78 mmol), and thioxanthone (10 mg, 0.047 mmol) or triphenylene (10 mg, 0.044 mmol) in benzene (3 ml) were irradiated through a liquid filter (an aqueous solution of NaBr and $Pb(NO_3)_2$, >330 nm)[11] with the 350-W high-pressure mercury lamp for 20 hr. However, the product was not observed by glc.

**Attempted Quenching with Diacetyl.**—Each of two quartz tubes was charged with 3 ml of a solution of diphenylacetylene (0.0337 *M*) and 1,5-cyclooctadiene (0.926 *M*) in cyclohexane. Diacetyl (44 mg, 0.512 mmol) was added to one of the tubes. The tubes were irradiated for 2 hr at 254 nm in which most of the light was absorbed by diphenylacetylene. No quenching was observed by glc.

**Registry No.**—**1**, 38821-22-6; diphenylacetylene, 501-65-5; 1,5-cyclooctadiene, 111-78-4.

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[11] A. Schönberg, "Preparative Organic Photochemistry," 2nd ed, Springer-Verlag, New York, N. Y., 1968, p 492.

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## Sterol Metabolism. XXIII. Cholesterol Oxidation by Radiation-Induced Processes[1]

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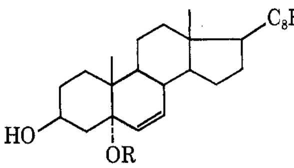
The common cholesterol oxidation products 3β-hydroxycholest-5-en-7-one (IV), cholesta-3,5-dien-7-one (V), and the epimeric cholest-5-ene-3β,7-diols (IIb, IIIb) derive by thermal decomposition of sterol hydroperoxides formed by two distinct mechanisms from cholesterol. Photosensitized oxidation of cholesterol in solution by excited-state (singlet) molecular oxygen gives 3β-hydroxy-5α-cholest-6-ene-5-hydroperoxide (Ia),[3] which may rearrange in solution to the 7α-hydroperoxide IIa,[3c,4] which in turn may epimerize to the 7β-hydroperoxide IIIa.[5] Alternatively,



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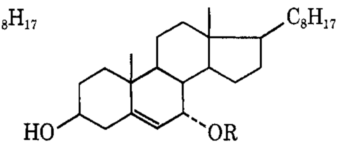
b, R = H



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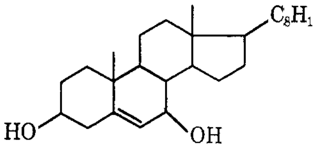
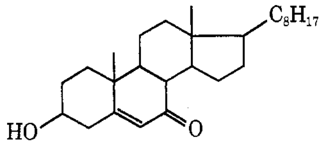
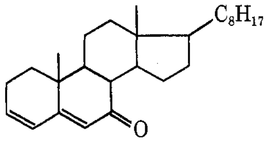


IIIa, R = OH
b, R = H



IV



V

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