

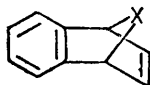
## Molecular Design by Cycloaddition Reactions. Part XIV.<sup>1</sup> Ready Chemical Transformation of the Bicyclo[3.2.2]nonadiene Skeleton

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The pentacyclo[7.6.1.0<sup>2,8</sup>.0<sup>3,5</sup>.0<sup>10,15</sup>]hexadecatetraen-4-ylacetamides (5b—d) and (6b—d) were easily prepared from the photoinduced reaction of compounds containing the bicyclo[3.2.2]nonadiene skeleton (enone- $\pi$ -methane system) in the presence of some amines in good yields. The dimethyl carboxamides (5d) and (6d) were converted into compounds containing the bicyclo[3.2.2]nona-2,6-diene skeleton, (10) and (11), by Hofmann degradation, followed by thermal [3,3] rearrangement (Cope rearrangement) probably *via* divinylcyclopropane intermediates.

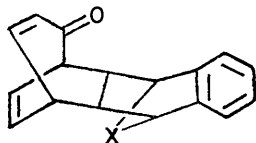
We have previously reported the cycloaddition of epoxy-bridged cyclic polyenes such as (1) with tropone and tropolone as the electron-deficient components,<sup>2</sup> and have also investigated substituent effects on the photochemical behaviour of the adducts.<sup>3</sup> However, attempted reaction of the bridged polyene (1) with cycloheptatriene to give a bicyclo[3.2.2]nonadiene skeleton is unsuccessful. This is probably because the bridged polyene is an electron-rich dienophile<sup>4</sup> and reacts preferentially with more electron-deficient dienes in inverse Diels-Alder reactions.

The present paper describes a ready chemical transformation of the bicyclo[3.2.2]nona-3,6-dien-2-one into the bicyclo[3.2.2]nona-2,6-diene skeleton *via* initial [3,3] photorearrangement of the tropone adduct followed by thermal [3,3] rearrangement possibly through a divinylcyclopropane intermediate.



- (1) X = O  
(2) X = C=CMe<sub>2</sub>

Adducts (3)<sup>2</sup> and (4) were prepared by reactions of the bridged polyenes (1) and (2)<sup>5</sup> with tropone in chlorobenzene at 130–140° in 90 and 74% yields, respectively. The n.m.r. spectrum of (4) was very similar to that of compound (3) except for the signals of the isopropylidene group. Thus, the product (4) was assigned as the [4 + 2] $\pi$  cycloadduct with *endo-exo* configuration. Attempted reactions of compounds (3) and (4) with cycloheptatriene were unsuccessful even under more drastic conditions.



- (3) X = O  
(4) X = C=CMe<sub>2</sub>

The photolyses of the adducts (3) and (4) in methanol resulted in the formation of the esters (5a) and (6a) by the nucleophilic trapping of the keten intermediates formed by the photochemical [3,3] rearrangements. Treatment of the ester (6a) with saturated ammonia-

<sup>1</sup> Part XIII, T. Sasaki, K. Kanematsu, and Y. Yukimoto, *Heterocycles*, in the press.

<sup>2</sup> T. Sasaki, K. Kanematsu, and K. Hayakawa, *J.C.S. Perkin I*, 1972, 1951.

<sup>3</sup> T. Sasaki, K. Kanematsu, K. Hayakawa, and A. Kondo, *J. Org. Chem.*, 1973, **38**, 4100.

methanol and/or 28%-ammonia water-acetonitrile (1 : 1) solution gave the carboxamide (6b) in low yields (Table 1).

TABLE 1

Preparations of cyclopropane esters and carboxamides with tropone adducts

Compound	Reaction conditions	Product	Yield (%)
(3)	$h\nu$ * in MeOH	(5a)	95—100
(4)	$h\nu$ * in MeOH	(6a)	90
(6a)	sat. NH <sub>3</sub> -MeOH, at 25° for 6 days	(6b)	58.5
(4)	$h\nu$ * MeCN-28%-NH <sub>4</sub> OH (1 : 1)	(6b) and (7)	56.5 and 14

\* High pressure 100 W mercury lamp through a Pyrex filter at room temperature.

On the other hand, irradiation of the adducts (3) and (4) in the presence of various amines gave the corresponding carboxamide derivatives (5b—d) and (6b—d) in almost quantitative yields. The i.r. spectra of these products showed a characteristic band at 1640—1655 cm<sup>-1</sup> due to carboxamide. Structural proofs of these carboxamides were based on elemental analyses and spectroscopic data, and the reactions are summarized in Table 2.

TABLE 2

Photolyses of tropone adducts in amines

Compound	Reaction conditions	Product	Yield (%)
(3)	sat. NH <sub>3</sub> -CHCl <sub>3</sub> , NH <sub>3</sub> gas	(5b)	90
(4)	sat. NH <sub>3</sub> -CHCl <sub>3</sub> , NH <sub>3</sub> gas	(6b)	93
(3)	sat. MeNH <sub>2</sub> -C <sub>6</sub> H <sub>6</sub>	(5c)	89
(4)	sat. MeNH <sub>2</sub> -C <sub>6</sub> H <sub>6</sub>	(6c)	91
(3)	sat. Me <sub>2</sub> NH-C <sub>6</sub> H <sub>6</sub>	(5d)	86.5
(4)	sat. Me <sub>2</sub> NH-C <sub>6</sub> H <sub>6</sub>	(6d)	87

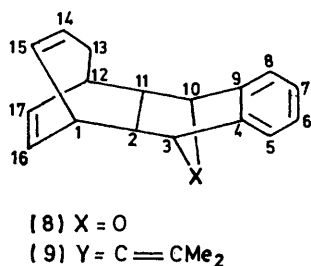
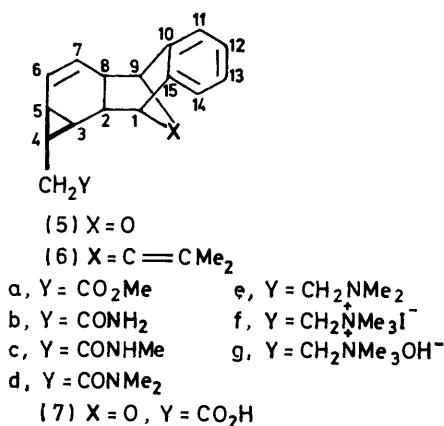
**Thermal [3,3] Sigmatropic Rearrangement (Cope Rearrangement).**—Treatments of the dimethyl carboxamides (5d) and (6d) with lithium aluminium hydride gave the corresponding amines (5e) and (6e) in almost quantitative yields. The structures of the amines (5e) and (6e) were determined by their n.m.r. spectra (see Experimental section).

The Hofmann degradation of the methiodides (5f) and (6f) at 130–150° under reduced pressure yielded the degradation products (8) and (9) in 75% overall yield. The n.m.r. spectrum of (9) exhibited signals at  $\delta$  1.9—2.8 (6H, complex-m, 1-, 2-, 11-, 12-, and 13-H), 3.26 (1H,

<sup>4</sup> T. Sasaki, K. Kanematsu, K. Hayakawa, and M. Uchide, *J.C.S. Perkin I*, 1972, 2750.

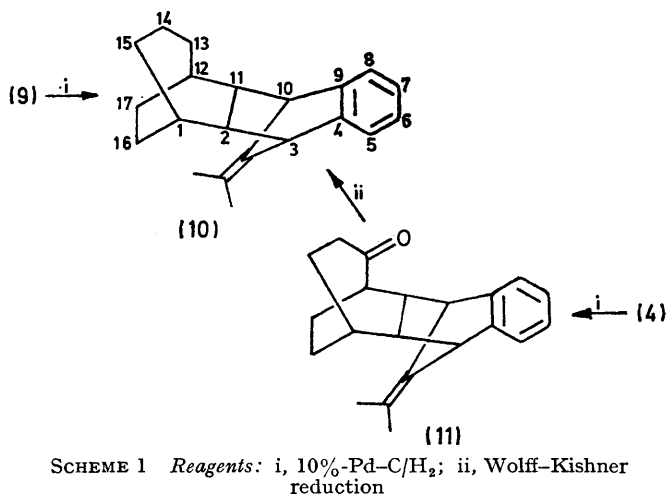
<sup>5</sup> P. L. Watson and R. N. Warrenner, *Austral. J. Chem.*, 1973, **26**, 1725.

d,  $J$  1.5 Hz, 10-H), 3.36 (1H, d,  $J$  1.5 Hz, 3-H), 5.15 (1H, dt,  $J$  11.0 and 3.0 Hz, 14-H), 5.82 (1H, t,  $J$  8.0 Hz, 17-H),



5.89 (1H, dd,  $J$  11.0 and 8.0 Hz, 15-H), and 6.09 (1H, t,  $J$  8.0 Hz, 16-H), and suggested the presence of the bicyclo[3.2.2]nona-2,6-diene system. The n.m.r. spectrum of (8) contained similar signals to compound (9) for the bicyclo[3.2.2]nona-2,6-diene system.

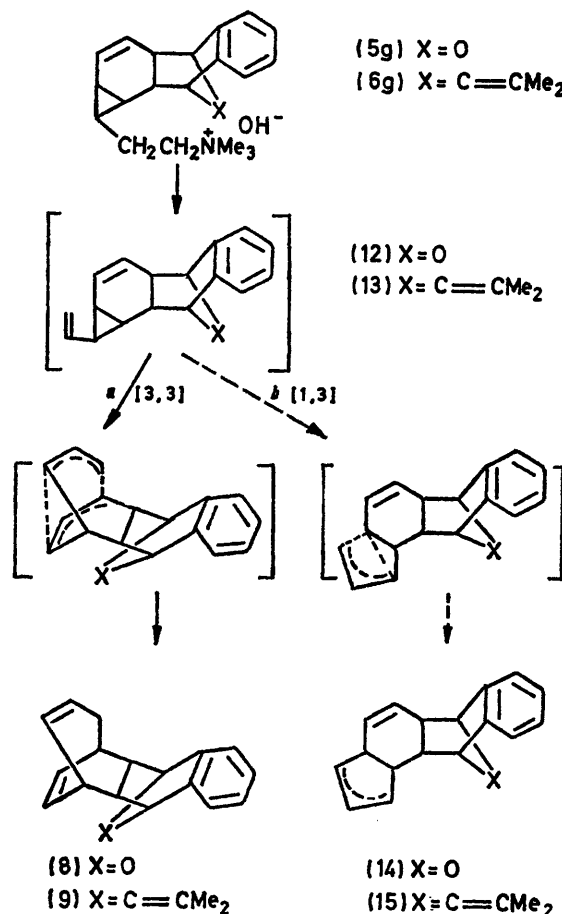
Catalytic hydrogenation of (9) over palladium on charcoal gave compound (10) in quantitative yield, which was also identical (mixed m.p., and i.r. and n.m.r.



spectra) with a sample prepared by hydrogenation of (4) followed by Wolff-Kishner reduction as shown in Scheme 1.

From these results, the structures of compounds (8) and (9) were assigned as shown.

The formation of compounds (8) and (9) might proceed preferentially *via* path *a* (Scheme 2), initially producing divinyl cyclopropane intermediates (12) and (13) followed by thermal [3,3] sigmatropic rearrangement, rather than path *b*.



#### EXPERIMENTAL

Microanalyses were performed with a Perkin-Elmer 240 elemental analyser. N.m.r. spectra were taken with a JEOL C-60-XL spectrometer with tetramethylsilane as internal standard. I.r. spectra were taken with a JASCO-IR-S spectrophotometer. Mass spectra were obtained with a Hitachi RMU-D double-focusing spectrometer operating at an ionization potential of 70 eV. The solid samples were ionized by electron bombardment after sublimation directly into the electron beam at 100–150 °C.

18-Isopropylidene-pentacyclo[10.3.2.1<sup>3,10</sup>.0<sup>2,11</sup>.0<sup>4,9</sup>]octadeca-4,6,8,14,16-pentaen-13-one (4).—A solution of tropone (1.82 g) and the isopropylidene-benzonorbornadiene (2)<sup>5</sup> in chlorobenzene (80 ml) was heated at 130–140° in a sealed tube for 60 h. Chromatography on silica gel using benzene, followed by recrystallization from chloroform–n-hexane gave the adduct (4) (3.23 g) as prisms; m.p. 188–190°;  $\nu_{\max}$  (KBr) 1655, 1630, 1460, 1450, 1380, and 1370 cm<sup>-1</sup>;  $\delta$  (CCl<sub>4</sub>) 1.48 (3H, s, Me), 1.53 (3H, s, Me), 2.18 (1H, d,  $J$

7.8 Hz, 11-H), 2.31 (1H, d,  $J$  7.8 Hz, 2-H), 3.21 (1H, t,  $J$  7.5 Hz, 1-H), 3.41 (1H, dd,  $J$  7.5 and 2.0 Hz, 12-H), 3.32 (1H, s, 10-H), 3.48 (1H, s, 3-H), 5.46 (1H, dd,  $J$  12.0 and 2.0 Hz, 14-H), 5.86 (1H, t,  $J$  7.5 Hz, 17-H), 6.18 (1H, t,  $J$  7.5 Hz, 16-H), 6.90 (1H, dd,  $J$  12.0 and 7.5 Hz, 15-H), and 6.85—7.10 (4H, m, ArH);  $m/e$  288 ( $M^+$ ), 273, 156 (100%), 141, and 115 (Found: C, 87.4; H, 7.1.  $C_{21}H_{20}O$  requires C, 87.45; H, 7.0%), and recovered starting material (2) (340 mg).

**Photolysis of (4).**—A solution of (4) (450 mg) in methanol (100 ml) was irradiated by a high pressure 100 W mercury lamp through a Pyrex filter at room temperature for 1 h. After removal of the solvent, recrystallization from ethanol gave methyl 16-isopropylidenepentacyclo[7.6.1.0<sup>2,8</sup>.0<sup>3,5</sup>.0<sup>10,15</sup>]-hexadeca-6,10,12,14-tetraen-4-ylacetate (6a) (450 mg, 90%) as needles; m.p. 109—110°;  $\nu_{max}$  (KBr) 1740, 1460, 1435, 1370, and 1170  $cm^{-1}$ ;  $\delta$  ( $CDCl_3$ ) 1.28 (3H, m, cyclopropane

m, cyclopropane H), 1.59 (3H, s, Me), 1.67 (3H, s, Me), 1.83 (2H, s,  $CH_2CO_2H$ ), 1.92—2.30 (2H, m, 2- and 8-H), 3.39 (1H, s, 9-H), 3.60 (1H, s, 1-H), 5.75 (2H, m, olefinic H), 6.9—7.2 (4H, m, ArH), and 10.95br (1H, s,  $CO_2H$ ). The second fraction gave the carboxamide (6b) (60 mg, 57%).

**General Procedure for Photolysis.**—A solution of the tropone adduct in the corresponding dry saturated amine was irradiated by a high pressure 100 W mercury lamp through a Pyrex filter at room temperature. The photolyses were monitored by t.l.c. The solvent was removed under reduced pressure and the residue was purified by recrystallization and then analysed by n.m.r.

(a) **Photolysis of (3) in ammonia.** A solution of (3) (450 mg) in saturated dry ammonia-chloroform (100 ml) was irradiated for 2 h with dry ammonia gas bubbling through. Work-up gave 16-oxapentacyclo[7.6.1.0<sup>2,8</sup>.0<sup>3,5</sup>.0<sup>10,15</sup>]-hexadeca-6,10,12,14-tetraen-4-ylacetamide (5b) (430 mg) as needles;

TABLE 3

N.m.r. spectra of cyclopropane carboxamides ( $\delta$ values; $J$ in Hz; solutions in $CDCl_3$ )							
Compound	H-6, H-7	H-1, H-9	H-2, H-8, $CH_2Y$	H-3, H-4, H-5	Others	Aromatic H	=CMe <sub>2</sub>
(5b)	5.76 (m)	4.85 (s) 5.10 (s)	1.75—2.15 (m)	1.25—1.65 (m)	NH <sub>2</sub>	6.84—7.20 (m)	
(5c)	5.82 (m)	4.90 (s) 5.15 (s)	1.78—2.28 (m)	1.28—1.73 (m)	5.45—6.10 (br) * NHMe 5.28—5.81 (br) * 2.68 (d) $J$ 4.5	6.88—7.25 (m)	
(5d)	5.70 (dd) $J$ 10.0, 3.0 5.84 (dd) $J$ 10.0, 4.0	4.85 (s) 5.11 (s)	1.75—2.20 (m)	1.25—1.65 (m)	NMe <sub>2</sub> 2.80 (s)	6.85—7.20 (m)	
(6b)	5.70 (m)	3.40 (d) $J$ 1.5 3.60 (d) $J$ 1.5	1.70—2.10 (m)	1.03—1.52 (m)	NH <sub>2</sub> 5.30—5.90 (br) *	6.80—7.10 (m)	1.56 (s) 1.65 (s)
(6c)	5.70 (m)	3.40 (d) $J$ 1.5 3.61 (d) $J$ 1.5	1.73—2.06 (m)	1.00—1.50 (m)	NHMe 5.10—5.95 (br) * 2.70 (d) $J$ 4.6	6.85—7.25 (m)	1.56 (s) 1.63 (s)
(6d)	5.62 (m)	3.37 (d) $J$ 1.5 3.59 (d) $J$ 1.5	1.70—2.10 (m)	1.20—1.60 (m)	NMe <sub>2</sub> 2.77 (s) 2.80 (s)	6.80—7.10 (m)	1.55 (s) 1.63 (s)

\* Exchangeable by D<sub>2</sub>O.

H), 1.56 (3H, s, Me), 1.64 (3H, s, Me), 1.82 (2H, s,  $CH_2CO_2$ -Me), 2.0—2.15 (2H, m, 2- and 8-H), 3.55 (3H, s, OMe), 3.41 (1H, s, 9-H), 3.64 (1H, s, 1-H), 5.70 (2H, m, olefinic-H), and 6.9—7.2 (4H, m, ArH) (Found: C, 82.75; H, 7.55.  $C_{22}H_{24}O_2$  requires C, 82.45; H, 7.55%).

**Ammonolysis of (6a).**—A solution of (6a) (450 mg) in saturated ammonia-methanol (200 ml) was left at room temperature for 6 days. After removal of the solvent, chromatography on silica gel using chloroform followed by recrystallization from ether-n-hexane gave 16-isopropylidene-pentacyclo[7.6.1.0<sup>2,8</sup>.0<sup>3,5</sup>.0<sup>10,15</sup>]-hexadeca-6,10,12,14-tetraen-4-ylacetamide (6b) (250 mg, 59%) as needles; m.p. 102—108° (decomp.);  $\nu_{max}$  (KBr) 3400, 3200, and 1655  $cm^{-1}$ ; n.m.r. (see Table 3) (Found: C, 81.55; H, 7.95; N, 4.6.  $C_{21}H_{23}NO_2$  requires C, 81.4; H, 7.65; N, 4.5%).

**Photolysis of (4) in Ammonia-Water.**—A solution of (4) (100 mg) in 28% aqueous ammonia-acetonitrile (1:1) (80 ml) was irradiated for 1 h. After removal of the solvent, the residue was subjected to silica gel chromatography using benzene-chloroform. The first fraction gave the carboxylic acid (7) (15 mg);  $\nu_{max}$  ( $CHCl_3$ ) 1705  $cm^{-1}$ ;  $\delta$  ( $CCl_4$ ) 1.37 (3H,

m.p. 161—162° (chloroform-ether);  $\nu_{max}$  (KBr) 3420, 3175, and 1655  $cm^{-1}$  (Found: C, 76.15; H, 6.6; N, 5.1.  $C_{17}H_{17}NO_2$  requires C, 76.4; H, 6.4%).

(b) **Photolysis of (3) in methylamine.** A solution of (3) (100 mg) in saturated dry methylamine-benzene (50 ml) was irradiated for 20 min. *N*-methyl-(16-oxopentacyclo[7.6.1.0<sup>2,8</sup>.0<sup>3,5</sup>.0<sup>10,15</sup>]-hexadeca-6,10,12,14-tetraen-4-yl)acetamide (5c) (100 mg) as prisms; m.p. 156—158° (benzene-n-hexane);  $\nu_{max}$  (KBr) 3280, 1640, and 1570  $cm^{-1}$  (Found: C, 76.95; H, 6.85; N, 4.9.  $C_{18}H_{19}NO_2$  requires C, 76.85; H, 6.8; N, 5.0%).

(c) **Photolysis of (3) in dimethylamine.** A solution of (3) (500 mg) in saturated dry dimethylamine-benzene (100 ml) was irradiated for 1.5 h. Work-up gave *NN*-dimethyl-(16-oxapentacyclo[7.6.1.0<sup>2,8</sup>.0<sup>3,5</sup>.0<sup>10,15</sup>]-hexadeca-6,10,12,14-tetraen-4-yl)acetamide (5d) (510 mg) as needles; m.p. 70—73° (ether-n-hexane);  $\nu_{max}$  (KBr) 3500, 1640, and 1630  $cm^{-1}$  (Found: C, 75.65; H, 7.25; N, 4.5.  $C_{19}H_{21}NO_2$  requires C, 75.7; H, 7.24; N, 4.65%).

(d) **Photolysis of (4) in ammonia.** A solution of (4) (680 mg) in saturated dry ammonia-chloroform (150 ml) was

irradiated for 2 h with bubbling of dry ammonia gas. Work-up gave the carboxamide (6b) (670 mg) as needles; m.p. 102—108° (decomp.) (ether-n-hexane).

(e) *Photolysis of (4) in methylamine.* A solution of (4) (500 mg) in saturated dry methylamine-benzene (100 ml) was irradiated for 30 min. Work-up gave *N-methyl-(16-isopropylidene-pentacyclo[7.6.1.0<sup>2,8</sup>.0<sup>3,5</sup>.0<sup>10,15</sup>]hexadeca-6,10,12,14-tetraen-4-yl)acetamide* (6c) (500 mg) as needles; m.p. 155—156° (benzene-n-hexane);  $\nu_{\max}$  (KBr) 3280, 1640, and 1570  $\text{cm}^{-1}$  (Found: C, 82.65; H, 7.9; N, 4.1.  $\text{C}_{22}\text{H}_{26}\text{NO}$  requires C, 82.7; H, 7.9; N, 4.4%).

(f) *Photolysis of (4) in dimethylamine.* A solution of (4) (500 mg) in saturated dry dimethylamine-benzene (100 ml) was irradiated for 1.5 h. Work-up gave *NN-dimethyl-(16-isopropylidene-pentacyclo[7.6.1.0<sup>2,8</sup>.0<sup>3,5</sup>.0<sup>10,15</sup>]hexadeca-6,10,12,14-tetraen-4-yl)acetamide* (6d) (500 mg) as needles; m.p. 98—101° (n-hexane);  $\nu_{\max}$  (KBr) 3520, 1640, and 1625  $\text{cm}^{-1}$  (Found: C, 81.5; H, 8.1; N, 4.3.  $\text{C}_{23}\text{H}_{27}\text{NO}$ , 0.33 $\text{H}_2\text{O}$  requires C, 81.35; H, 8.2; N, 4.1%).

*18-Oxapentacyclo[10.3.2.1<sup>3,10</sup>.0<sup>2,11</sup>.0<sup>4,9</sup>]octadeca-4,6,8,14,16-pentaene* (8).—To a stirred suspension of lithium aluminium hydride (200 mg) in dry ether (50 ml) was added a solution of (5d) (200 mg) in dry ether (50 ml) at room temperature. After the mixture was refluxed for 12 h, the usual work-up gave *NN-dimethyl-2-(16-oxapentacyclo[7.6.1.0<sup>2,8</sup>.0<sup>3,5</sup>.0<sup>10,15</sup>]hexadeca-6,10,12,14-tetraen-4-yl)ethylamine* (5e) in about quantitative yield as an amorphous solid without purification;  $\delta$  ( $\text{CDCl}_3$ ) 0.85—1.50 (5H, m,  $\text{CH}_2\text{CH}_2\text{NMe}_2$  and cyclopropane H), 2.02 (6H, s,  $\text{NMe}_2$ ), 1.70—2.35 (4H, m, 2- and 8-H, and  $\text{CH}_2\text{NMe}_2$ ), 4.76 (1H, s, 9-H), 5.00 (1H, s, 1-H), 5.56 (1H, dd,  $J$  10.0 and 3.0 Hz, 7-H), 5.74 (1H, dd,  $J$  10.0 and 3.5 Hz, 6-H), and 6.70—7.06 (4H, m, ArH).

A solution of (5e) in ether (20 ml) and methyl iodide (2 ml) was stirred at room temperature for 2 h. Filtration gave the *methiodide* (5f) in quantitative yield; m.p. 184—185° (methanol), needles (Found: C, 54.7; H, 6.2; N, 3.05.  $\text{C}_{20}\text{H}_{26}\text{INO}$ ,  $\text{H}_2\text{O}$  requires C, 54.4; H, 6.4; N, 3.15%).

To a solution of *methiodide* (5f) (160 mg) in water (20 ml) was added silver oxide freshly prepared from silver nitrate (510 mg) and sodium hydroxide (125 mg). After the mixture was stirred at room temperature for 15 h, water was removed under reduced pressure to give a brownish residue, which was heated gradually in a flask fitted with a trap, under reduced pressure for 2—3 h. Decomposition occurred slowly at 130—150° to give the *pentaene* (8) as sublimed crystals.

Further purification by chromatography on silica gel using benzene gave (8) (70 mg) as prisms; m.p. 116—117° (ethanol) [total yield from (5d) ca. 75%];  $\nu_{\max}$  (KBr) 3030, 1630, and 1460  $\text{cm}^{-1}$ ;  $\delta$  ( $\text{CCl}_4$ ) 1.9—2.8 (6H, m, 1-, 2-, 11-, 12-, and 13-H), 4.62 (1H, s, 10-H), 4.71 (1H, s, 3-H), 4.95 (1H, dt,  $J$  11.0 and 3.0 Hz, 14-H), 5.59 (1H, tt,  $J$  7.5 and 2.0 Hz, 17-H), 5.75 (1H, dd,  $J$  11.0 and 7.5 Hz, 15-H), 5.97 (1H, t,  $J$  7.5 Hz, 16-H), and 6.60—7.0 (4H, m, ArH) (Found: C, 86.2; H, 7.0.  $\text{C}_{17}\text{H}_{16}\text{O}$  requires C, 86.4; H, 6.85%).

*18-Isopropylidene-pentacyclo[10.3.2.1<sup>3,10</sup>.0<sup>2,11</sup>.0<sup>4,9</sup>]octadeca-4,6,8,14,16-pentaene* (9).—To a suspension of lithium aluminium hydride (200 mg) in dry ether (50 ml) was added a

solution of (6d) (200 mg) in dry ether (50 ml) at room temperature. After the mixture was refluxed for 12 h, the usual work-up gave *NN-dimethyl-2-(16-isopropylidene-pentacyclo[7.6.1.0<sup>2,8</sup>.0<sup>3,5</sup>.0<sup>10,15</sup>]hexadeca-6,10,12,14-tetraen-4-yl)ethylamine* (6e) in about quantitative yield as crystals without purification; m.p. 103—104°;  $\delta$  ( $\text{CCl}_4$ ) 0.80—1.30 (5H, m,  $\text{CH}_2\text{CH}_2\text{NMe}_2$  and cyclopropane H), 1.57 (3H, s, Me), 1.64 (3H, s, Me), 1.83 (2H, s, 2- and 8-H), 2.02 (6H, s,  $\text{NMe}_2$ ), 1.86—2.15 (2H, m,  $\text{CH}_2\text{NMe}_2$ ), 3.30 (1H, d,  $J$  1.5 Hz, 9-H), 3.35 (1H, d,  $J$  1.5 Hz, 1-H), 5.70 (2H, m, 6- and 7-H), and 6.8—7.2 (4H, m, ArH).

Similar treatment of amine (6e) afforded a crystalline *methiodide* (6f) quantitatively; m.p. 193—194° (methanol), needles (Found: C, 61.45; H, 6.8; N, 2.9.  $\text{C}_{24}\text{H}_{33}\text{IN}$ , 0.5 $\text{H}_2\text{O}$  requires C, 61.25; H, 7.05; N, 3.0%).

To a solution of *methiodide* (6f) (180 mg) in water (30 ml) was added silver oxide freshly prepared from silver nitrate (510 mg) and sodium hydroxide (125 mg); similar work-up gave the *pentaene* (9) (85 mg) as prisms; m.p. 151—152° (ethanol) [total yield from (6d) ca. 75—80%];  $\nu_{\max}$  (KBr) 3035, 1630, 1450, 1370, and 1350  $\text{cm}^{-1}$ ;  $\delta$  ( $\text{CCl}_4$ ) 1.43 (3H, s, Me), 1.49 (3H, s, Me), 1.9—2.8 (6H, m, 1-, 2-, 11-, 12-, and 13-H), 3.26 (1H, d,  $J$  1.5 Hz, 10-H), 3.36 (1H, d,  $J$  1.5 Hz, 3-H), 5.15 (1H, dt,  $J$  11.0 and 3.0 Hz, 14-H), 5.82 (1H, t,  $J$  8.0 Hz, 17-H), 5.89 (1H, dd,  $J$  11.0 and 8.0 Hz, 15-H), 6.09 (1H, t,  $J$  8.0 Hz, 16-H), and 6.90 (4H, m, ArH) (Found: C, 91.85; H, 8.15.  $\text{C}_{21}\text{H}_{22}$  requires C, 91.9; H, 8.1%).

*Catalytic Hydrogenation of (9).*—A solution of (9) (35 mg) in ethanol (100 ml) was hydrogenated over 10% palladium on charcoal (50 mg) under atmospheric pressure to give *18-isopropylidene-pentacyclo[10.3.2.1<sup>3,10</sup>.0<sup>2,11</sup>.0<sup>4,9</sup>]octadeca-4,6,8-triene* (10) (35 mg) as needles; m.p. 164—166° (ethanol);  $\nu_{\max}$  (KBr) 1440, 1370, 750, and 695  $\text{cm}^{-1}$ ;  $\delta$  ( $\text{CCl}_4$ ) 1.15—1.7 (12H, m, 1-, 12-, 13-, 14-, 15-, 16-, and 17-H), 1.61 (6H, s, 2Me), 1.85—2.15 (2H, m, 2- and 11-H), 3.37 (2H, s, 3- and 10-H), and 6.93 (4H, m, ArH) (Found: C, 90.6; H, 9.4.  $\text{C}_{21}\text{H}_{26}$  requires C, 90.6; H, 9.4%).

*Catalytic Hydrogenation of Tropone Adduct (4).*—A solution of (4) (300 mg) in ethanol (150 mg) was hydrogenated over 10% palladium on charcoal (100 mg) under atmospheric pressure to give *18-isopropylidene-pentacyclo[10.3.2.1<sup>3,10</sup>.0<sup>2,11</sup>.0<sup>4,9</sup>]octadeca-4,6,8-trien-13-one* (11) (300 mg) as crystals; m.p. 165—166° (ethanol);  $\nu_{\max}$  (KBr) 1695, 1455, and 1375  $\text{cm}^{-1}$ ;  $\delta$  ( $\text{CDCl}_3$ ) 1.67 (6H, s, 2Me), 1.4—2.1 (8H, m, 1-, 11-, 15-, 16-, and 17-H), 2.2—2.8 (4H, m, 2-, 12-, and 14-H), 3.57 (2H, s, 3-, and 10-H), and 6.9—7.2 (4H, m, ArH) (Found: C, 86.4; H, 8.35.  $\text{C}_{21}\text{H}_{24}\text{O}$  requires C, 86.25; H, 8.25%).

*Wolff-Kishner Reduction of (11).*—A mixture of ketone (11) (200 mg), diethylene glycol (11.7 g), and hydrazine hydrate (100%) (3.7 g) was heated at 100—120° for 30 min, and then potassium hydroxide (1.0 g) was added and heated gradually at 200° for 4 h. After the nitrogen evolution had subsided, the mixture was cooled and poured into water (50 ml). After neutralization with 6*N*-hydrochloric acid, extraction with ether gave hydrocarbon (10) (170 mg, 90%) as needles, m.p. 164—166° (ethanol).