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PHOTOCHEMISTRY OF BRIDGED CYCLOHEPTADIENONES

DI-π-METHANE PHOTOREARRANGEMENT OF 6,7-BENZOBICYCLO[3.2.1]OCTADIENONE AND RELATED DIENES

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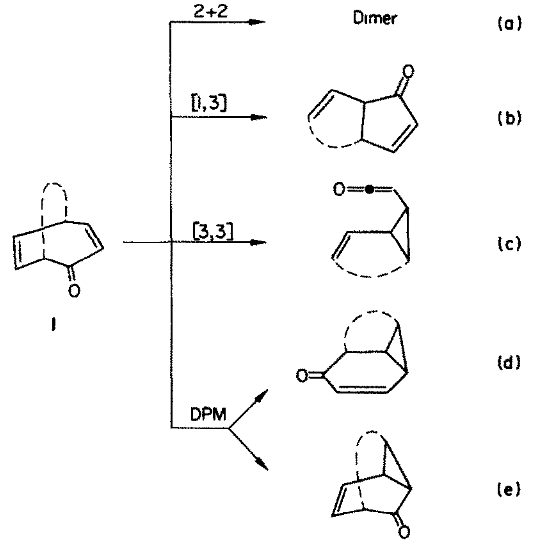
Abstract—A series of 6,7-Benzobicyclo[3.2.1]octadienes (**10–13**) have been prepared. Direct and sensitized irradiation of the dienes gave di-π-methane rearrangement products (**14–17**). Quantum yields for the direct and sensitized rearrangements were recorded and compared. Substituent effect and structure-multiplicity relationships are discussed.

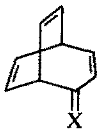
Bridged cycloheptadienones (**1**)[1] represent an interesting group of compounds which exhibit multiple photochemical reactivity. Thus, depending on the nature of the excited state (e.g. n,π^* or π,π^*), multiplicity and structure, **1** may undergo photoinduced dimerization (a),[1,2] [1,3] sigmatropic shift (b),[3–6] [3,3] sigmatropic shift (c)[2,4,6–8] and di-π-methane (DPM) rearrangement (d, e).[9–11] (Scheme 1).

Generally, it has been shown that whenever there are no structural limitations for these processes to occur, the [1,3] and [3,3] sigmatropic shifts take place from a singlet excited state,[4,6] whereas the triplet undergoes a di-π-methane rearrangement.[9] Regiospecificity has been observed for the latter process leading preferentially to the product which retains the enone function (route d).[9,12]

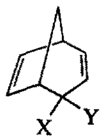


Scheme 1. Photochemical transformations of bridged cycloheptadienones.

Previously, we have focussed our attention on the role of the di-π-methane rearrangement in bridged cycloheptadienones (**2a**) and their related methylene counterparts (**2b**), derived from the bicyclo[3.2.2]nonatriene system (**2**).[9,13,14] We wish to report our results on the photochemistry of the closely related bicyclo[3.2.1]octadiene system (**3**). The 6,7-benzobicyclo[3.2.1]octa-3,6-diene system (**4**) was chosen as the test system for the di-π-methane rearrangement since the presence of a condensed benzo ring was expected to eliminate other favorable transformations. This assumption is supported by two previously reported communications by Hahn and Rothman for the parent hydrocarbon **11**,[15] and by Hart and Love for the hexamethyl ketone **5**,[10] both of which gave only di-π-methane photorearrangement products.



2a: X = O
b: X = CH$_2$



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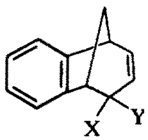

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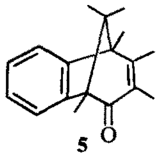

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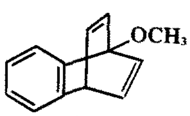

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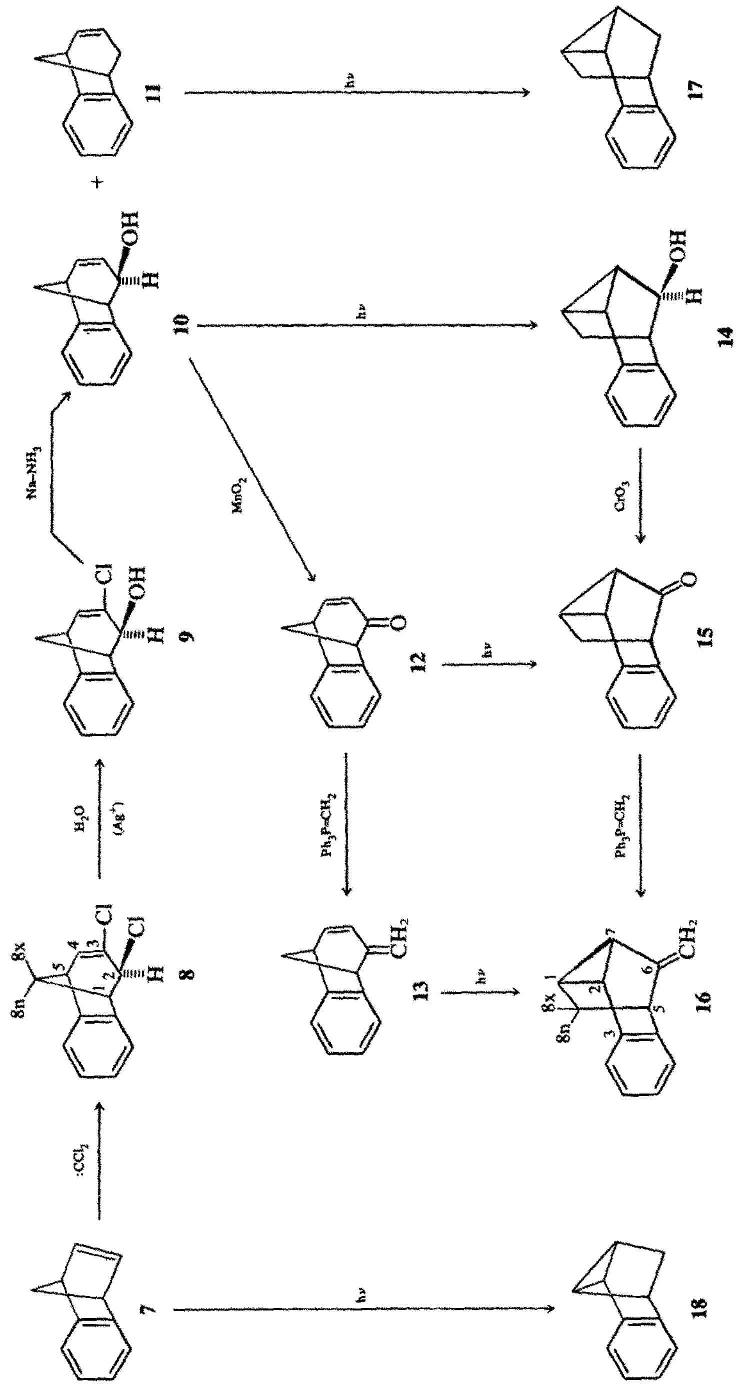
Synthetic aspects (Scheme 2).

Although benzobicyclo[3.2.1]octadien-2-one (**12** has been previously recorded in the literature[16] as



SCHEME 2. Synthesis and photochemistry of benzobicyclo[3.2.1]octadienes.

hydrolysis product of methoxybarrelene **6**, the low yield in which it was obtained required the development of a new and improved preparation. This was accomplished starting with a modification of Tanida's synthesis of dichlorodiene **8**,[17] by dichlorocarbene addition to benzonorbornadiene (**7**) using the recently reported phase transfer catalysis method.[18] Crystalline *exo*-dichlorodiene **8** was thus obtained in 65% yield. Silver ion catalysed hydrolysis of **8** in refluxing aqueous acetone[19] gave a quantitative yield of *exo*-chloroalcohol **9**,[17] which was reduced with sodium in liquid ammonia to the *exo*-alcohol **10**. The reduction was accompanied by a small amount of the parent hydrocarbon **11**,[15] which could be also prepared directly by Li-THF-t-BuOH reduction of **8**. Active MnO_2 oxidation[20] of alcohol **10** smoothly afforded ketone **12**.

Finally, a Wittig reaction of ketone **12**, with methylenetriphenylphosphorane resulted in the formation of methylene hydrocarbon **13**.

Structural assignments of the new compounds were based on elemental analyses and spectroscopic data. They are given in the Experimental.

Photochemistry

Direct irradiation of dilute cyclohexane, acetonitrile or ether solutions of alcohol **10** using a Rayonet RPR-100 Photochemical Reactor equipped with 2537Å lamps, in quartz vessels, resulted in rapid formation of a single photoproduct in high yield. The reaction was best monitored by vapor phase chromatography. The photoproduct was assigned structure **14** on the basis of its mass and NMR spectra. The NMR spectrum of **14** in $CDCl_3$ exhibits absorptions at δ 1·01 (H_{8n}, d, $J_{8,8}$ = 11 Hz), 1·7 (H_1, H_7, m), 2·2 (H_2, H_{8x}, m), 2·87 (H_5, dm, $J_{5,8}$ = 5), 3·6 (H_6, s), 7·06 ($4H_{Ar}$, m). This structural assignment was secured by decoupling experiments and by acetylation (acetic anhydride-pyridine) which led to *exo*-14-acetate reported previously by Tanida.[17]

Similarly, the direct irradiation of ketone **12** and its methylene analog **13** gave only photoproducts **15**† and **16** respectively. Their NMR spectra display essentially the characteristic features of this series (Experimental). For further structural confirmation, **14** was oxidized with CrO_3-pyrdine to give **15** which in turn was converted to **16** by a Wittig reaction.

Acetone sensitized (E_T = 80 kcal/mole) photolysis of compounds **10**, **12** and **13**, using a 3000 Å light source (Rayonet Reactor) with pyrex filter also afforded as sole products photoisomers **14**, **15** and **16** respectively.

In order to gain more insight into structure—multiplicity relationships, quantum yields of the direct and sensitized reactions were determined. Measurements of the direct irradiations were conducted in cyclohexane solutions at 2537 Å. For the sensitized runs 20% acetone-hexane solutions were used with 3000 Å light. The cyclopentanone–4-pentenal actinometer[22] was employed in the direct and sensitized reactions. Results are summarized in Table I, which includes also quantum yields for transformation of the parent hydrocarbon **11** to **17**,[15] and the previously recorded quantum yield for triplet benzonorbornadiene (**7**) rearrangement.[23]

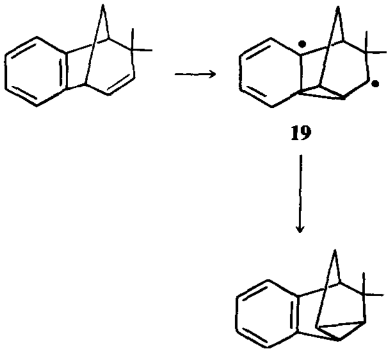
Table I. Quantum yields of direct and sensitized photolyses of benzobicyclo[3.2.1]heptadienes

	Reaction	Quantum yield Direct	Quantum yield Sensitized
Alcohol	**10**→**14**	0·06	0·06
Ketone	**12**→**15**	0·02	0·3
Methylene	**13**→**16**	0·11	0·02
Hydrocarbon	**11**→**17**	0·11	0·014
Hydrocarbon	**7**→**18**	—	0·5[a]

[a] No product could be isolated in the direct photolysis.[23]

DISCUSSION

A most striking aspect of the photochemistry of benzobicyclo[3.2.1]octadienes (**10**–**13**) is their capability to undergo a "benzo-vinyl" di-π-methane rearrangement (Eq. 1),[11] as the only phototransformation observed, from both the singlet and triplet excited states. Moreover, we note (Table I) that the efficiency of an excited state in undergoing rearrangement strongly depends on substituents conjugated to the di-π-methane system. Looking first at the quantum yields of ketone **12** we find that its triplet is highly reactive, being at least one order of magnitude higher than the triplets of the other non-carbonyl derivatives (**10**, **11** and **13**). This points to the n,π* triplet of **12** as the reactive excited state of the transformation, in contrast to the relative unreactiveness exhibited by the π,π* triplet of the other derivatives.



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(Eq. 1)

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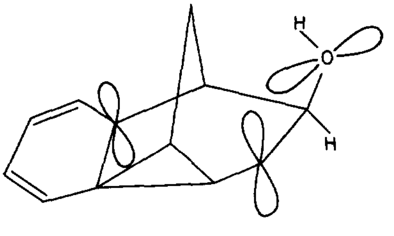
†Alcohol **14** and ketone **15** have been previously reported by Itô *et al*;[21] we are grateful to Prof. Itô for providing us with his spectroscopic data.

Turning to alcohol **10**, we note a relatively higher π,π^* triplet reactivity compared to hydrocarbons **11** and **13**. In view of the recent observation by Hart *et al*,[24] that OH groups can stabilize the intermediate diradical (**19**) in the di-π-methane rearrangement, it appears that this stabilization promotes intersystem crossing to the triplet, increasing its contribution in the rearrangement.



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Yet another striking result regarding structure—multiplicity relationships is found by comparing the quantum yields of the two hydrocarbons **11** and **13**. The practically identical efficiencies of the triplet states is surprising and points against the significance of a "free rotor" energy dissipation process in **13** which competes with the di-π-methane rearrangement.[11] Thus, as has been pointed out previously,[13,14] deactivation of the triplet excited state of bicyclic systems by free rotation of an exocyclic methylene group is probably slower than triplet di-π-methane rearrangement. Moreover, the higher quantum yields for singlet over triplet rearrangement of hydrocarbons **11** and **13** indicate that in the absence of competing bond relocation processes from the singlet (such as the intramolecular 2+2 cycloaddition in the related bicyclo[2.2.2]system[25]), di-π-methane systems may prefer a singlet state rearrangement.

Finally, however, we should note that structure-multiplicity relationship in di-π-methane rearrangement of bicyclic systems is affected by system rigidity in the excited state. This is particularly emphasized by the highly efficient triplet rearrangement of benzonorbornadience (**7**) compared to its homolog, hydrocarbon **11**. Inspection of Dreiding models of the two systems, using a "free rotating double bond" shows a considerable flexibility of the excited bicyclic[3.2.1]system which enable it to perform an out-of-plane twist of *ca* 30°. This will account for the low triplet efficiency of the di-π-methane rearrangement in this system as compared to the high triplet efficiency in the completely rigid excited bicyclic[2.2.1]system (**7**).

EXPERIMENTAL

All b.ps and m.ps are uncorrected. IR Spectra were recorded using a Perkin–Elmer Model 257 grating Spectrophotometer. NMR Spectra were determined on a Varian HA-100 Spectrophotometer and chemical shifts are reported in δ units from internal TMS. Mass spectra were recorded on a Hitachi-Perkin Elmer RMU-6E mass spectrometer. UV spectra were recorded on Perkin-Elmer Model 402 Spectrophotometer.

GLPC analyses and separations were performed on Varian Model 90-P and Packard Model 7300 gas chromatographs using columns of Carbowax 20M, SE-30 and OV-101 on Chromosorb W. Interpretation of GLPC results was accomplished using Hewlet-Packard 3370B integrator. Product yields were corrected for variance in detector response.

2-exo-3-*Dichloro*-6,7-*benzobicyclo*[3.2.1]*octa*-3,6-*diene* (**8**)[17]

To an ice cooled, stirred soln of **7**[26] (15 g; 116 mmole) in 120 g $CHCl_3$, was added 50% NaOHaq (250 ml) and benzyltriethylammonium chloride (1·1 g). The mixture was allowed to warm to room temp, stirred for 12 h, diluted with H_2O and the aqueous phase extracted with $CHCl_3$. The combined organic phase was washed with H_2O and dried over Na_2SO_4. Removal of solvent and fractionation gave 16·6 g (65%), b.p. 92°/0·04 mm (Lit.[17] 124–5°/2 mm), which crystallized on standing; m.p. 68–69° (pentane). (Found: C, 64·24; H, 4·29; Cl, 31·34 Calc. for $C_{12}H_{10}Cl_2$: C, 64·29; H, 4·02; Cl, 31·7%). The NMR spectrum was identical to that reported by Tanida.

2-exo-*Hydroxy*-3-*chloro*-6,7-*benzobicyclo*[3.2.1] *octa*-3,6-*diene* (**9**)[17]

To a refluxing soln of **8** (14·25 g; 63·5 mmole) in 80% aqueous acetone was added $AgClO_4$ (20·7 g) in 60 ml H_2O. The mixture was refluxed for 6 h, cooled and AgCl removed by filtration. The clear acetone soln diluted with H_2O and extracted with ether, then washed with sat NaCl aq and dried (Na_2SO_4). Removal of ether and crystallization from hexane gave 12·5 g (95%), m.p. 123–124° (Lit.[17] 119–120°). The NMR spectrum was identical to that reported.[17]

2-exo-*Hydroxy*-6,7-*benzobicyclo*[3.2.1]*octa*-3,6-*diene* (**10**)

A soln of **7** (2·06 g; 10 mmole) in 200 ml dry ether was added dropwise during 40 min to a a stirred soln of sodium (7·3 g) in liquid ammonia (200 ml). The ammonia was allowed to evaporate while 200 ml ether was added. Excess sodium and sodium amide were decomposed by cautious addition of MeOH (20 ml) and the mixture diluted with water. The aqueous soln was extracted with ether and the combined organic phase washed with sat NaClaq and dried over Na_2SO_4. Removal of ether and distillation gave 1·2 g (70%), b.p. 110–112°/0·07 mm. (Found: C, 83·46; H, 7·19; Calc. for $C_{12}H_{12}O$: C, 83·73; H, 6·98%), *m/e* 172, $\nu_{\max}^{CHCl_3}$ 3400 cm^{-1}; $\lambda_{\max}^{C_6H_{12}}$ 270 nm ($\epsilon = 510$), 277 (516); NMR ($CDCl_3$): δ 2·2 ($2H_8$, m), 3·2 (H_1, H_5, bs), 3·93: (H_2, bs); 5·2 (H_3, dm, $J_{3,4} = 10$); 6·23 (H_4, dd, $J_{4,5} = 8$ Hz); 6·94 ($4H_{Ar}$, m).

6,7-*Benzobicyclo*[3.2.1]*octa*-3,6-*dien*-2-*one* (**12**)

Compound **10** (860 mg; 5 mmole) in 15 ml ether was added gradually to a suspension of activated MnO_2 in 150 ml pentane. The mixture was stirred for 4 h, filtered and the MnO_2 washed thoroughly with ether. The residue after removal of solvents was recrystallized from pentane to give **12** (570 mg; 67%) m.p. 76–77°. (Found: C, 84·50; H, 5·89 Calc. for $C_{12}H_{10}O$: C, 84·71; H, 5·88%); *m/e* 170; $\nu_{\max}^{CHCl_3}$ 1675 cm^{-1}; $\lambda_{\max}^{C_6H_{12}}$ 271 sh nm ($\epsilon = 780$), 280 (sh) (560), 343 (134), 357 (152), 373 (147), 391 sh (715); NMR ($CDCl_3$): δ 2·66 ($2H_8$, bs), 3·58 (H_5, m), 3·73 (H_1, bs), 5·28 (H_3, d, $J_{3,4} = 10$ Hz), 7·14 ($4H_{Ar}$, m).

2-*Methylene*-6,7-*benzobicyclo*[3.2.1]*octa*-3,6-*diene* (**13**)

To an ice cooled slurry of triphenylmethylphosphonium bromide (715 mg; 2 mmole) in dry THF (30 ml) was added, under N_2, one ml of BuLi (2M in hexane). The orange mixture was stirred for ½ h and a soln of **12** (204 mg; 1·2 mmol) in dry THF (10 ml) was added. The mixture was stirred for 12 h, decomposed with H_2O, extracted with pentane, dried ($MgSO_4$) and concentrated. Kugelrohr distillation at 80°/0·05 mm afforded 52 mg (26%); *m/e* 168; $\lambda_{max}^{C_6H_{12}}$ 239 nm (ϵ = 22000), 244 sh (21500). NMR ($CDCl_3$) δ 2·3 ($2H_8$, m), 3·42 (H_5, t, $J_{4,5} = 8$), 3·79 (H_1, d, $J_{1,8} = 4$), 4·58 (H-methylene, s), 4·99 (H-methylene, s), 5·70 (H_3, d, $J_{3,4} = 10$), 6·21 (H_4, brt), 7·12 ($4H_{Ar}$, m). (Found: C, 93·00; H, 7·31 Calcd. for $C_{13}H_{12}$: C, 92·86; H, 7·14%).

6,7-*Benzobicyclo*[3.2.1]*octa*-3,6-*diene* (**11**)[15,28]

To a vigorously stirred soln of **8** (1 g, 4·48 mmole) in THF (10 ml) containing 1·3 g t-BuOH, freshly cut Li metal (254 mg) was added under N_2 during 1 h. The mixture was stirred under reflux for 24 h. After dilution with H_2O (200 ml) and extraction with ether, the combined extracts were washed with NaClaq and dried over $MgSO_4$. Removal of solvent and Kugelrohr distillation at 110°/10 mm gave 528 mg (75%) of **11**, whose NMR spectrum was identical with that reported previously,[28] $\lambda_{max}^{C_6H_{12}}$ 263 sh nm (ϵ = 595), 270 (775), 276 (750).

General procedure for irradiations. Irradiations were conducted in a Rayonet RPR-100 Photochemical Reactor equipped with a merry-go-round apparatus for the quantum yield experiments. The reactions were monitored by GLPC.

Direct irradiation of dilute solutions (*ca* 0·1%) of the dienes in a variety of solvents (cyclohexane, acetonitrile, ether) were carried out in quartz vessels using 2537Å lamps.

Sensitized photolyses were carried out in 20% acetone–hexane solns using pyrex vessels and 3000 Å lamps.

Quantum yield measurements were run in NMR tubes (quartz and pyrex). Concentration was adjusted so that the sample absorbed more than 95% of available light. The acetone concentration in the sensitized experiments was adjusted so that it absorbed more than 95% of the incident light. Freshly distilled neat cyclopentanone was used as actinometer. Reactions were run to low conversion (less than 10%) and analysed by GLPC using a 5% Carbowax 20M on Chromosorb W column.

Photolysis of **10**. Irradiation of **10** (132 mg) in cyclohexane (150 ml) gave after 1 h **14** (110 mg); m.p. 87–88° (pentane) (Lit.[21] m.p. 86–89°); *m/e* 172; $\nu_{max}^{CHCl_3}$ 3400 cm^{-1}; NMR ($CDCl_3$) δ 1·01 (H_{8n}, d, $J_{8,8} = 11$ Hz), 1·7 (H_1, H_7, m) 2·2 (H_2, H_{8x}, m), 2·87 (H_5, dm, $J_{5\cdot8} = 5$), 3·6 (H_6, s), 7·06 ($4H_{Ar}$, m).

Photolysis of **12**. Irradiation of **12** (34 mg) in 20% acetone-hexane (18 ml) gave after 4 h **15** (25 mg); m.p. 67–68° (pentane), (Lit.[21] m.p. 70–71°); *m/e* 170; $\nu_{max}^{CHCl_3}$ 1720 cm^{-1}; NMR ($CDCl_3$) δ 1·42 (H_{8n}, d, $J_{8,8} = 11$ Hz), 1·72 (H_1, m) 2·41 (H_7, H_{8x}, m) 2·68 (H_2, t, $J_{1,2} = J_{2,7} = 7\cdot5$), 2·96 ($H_5$, d, $J_{5,8} = 5$), 7·1 ($4H_{Ar}$, m).

Oxidation of **14**. Alcohol **14** (50 mg; 0·29 mmole) was added to CrO_3-pyridine-CH_2Cl_2 reagent[27] (prepared from 200 mg CrO_3, 1 ml pyridine and 25 ml CH_2Cl_2). Usual workup gave **15** (30 mg; 61%), identical in all respects with the ketone obtained by photolysis.

Photolysis of **13**. Irradiation of **13** (50 mg) in 100 ml cyclohexane gave **16** (35 mg) after Kuglrohr distillation at 80°/0·05 mm; *m/e* 168; NMR ($CDCl_3$) δ 1·14 (H_{8n}, d, $J_{8,8} = 11$ Hz), 2·03 (H_1, H_7, H_{8x}, m), 2·45 (H_2, t, $J_{1,2} = J_{2,7} = 7\cdot5$), 3·33 ($H_5$, d, $J_{5,8} = 5$), 4·72 (H-methylene, s), 4·88 (H-methylene, s), 7·1 ($4H_{Ar}$, m).

6-*Methylene*-3,4-*benzotricyclo*[3.2.1.$0^{2,7}$]*oct*-3-*ene* (**16**)

From **15** *by Wittig reaction*. A soln of **15** (72 mg; 0·42 mmole) in 5 ml ether was added to methylenetriphenylphosphorane (prepared from 390 mg methyltriphenylphosphonium bromide and 0·4 ml 2M BuLi in hexane) in 15 ml ether. After 3 h at room temp the mixture was diluted with pentane (50 ml) and H_2O (50 ml). The organic phase washed with H_2O, dried ($MgSO_4$) and concentrated. Kuglrohr distillation (80°/0·05 mm) gave **16** (50 mg; 70%), identical in all respect with the hydrocarbon obtained by photolysis.

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