

## Valence Isomer Interconversion of Norbornadienes and Quadricyclanes having an Acyl Group

Ken-ichi Hirao\* and Asami Yamashita

Hokkaido Institute of Pharmaceutical Sciences, Katsuraoka, Otaru 047-02, Japan

Akira Ando, Tatsuo Hamada, and Osamu Yonemitsu

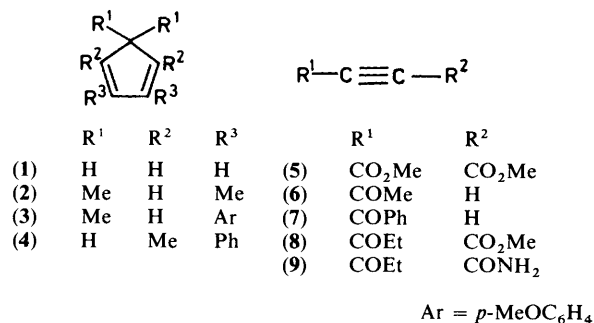
Faculty of Pharmaceutical Sciences, Hokkaido University, Sapporo 060, Japan

As a model for light energy conversion, various acylnorbornadienes and their corresponding valence isomers acylquadricyclanes have been prepared. Among these (19) and (31) were found to be the best pair for the purpose because of the visible light absorption of (19), a high quantum yield for its photocycloaddition and a rapid and complete reversion of (31) to (19) with an acid catalyst.

For the solar-energy storage cycle using organic molecules the norbornadiene-quadricyclane system is now accepted as one of the best possible models. However, because of practical and economical<sup>1</sup> considerations, various modifications are required to improve the overall efficiency and these have been the subject of numerous literature reports.<sup>2</sup>

As a preliminary model for a light-energy storage cycle we suggested pentacyclic cage compounds having a small strained ring system (bicyclo[2.2.0]hexane) conjugated with an acyl group.† Application of the valence isomerisation of this kind was extended to the fluoroalkyl norbornadiene-quadricyclane system.<sup>4</sup> The principle of this valence isomerisation has now been applied to the acylnorbornadiene-acylquadricyclane system, and the results will be described fully.<sup>5</sup>

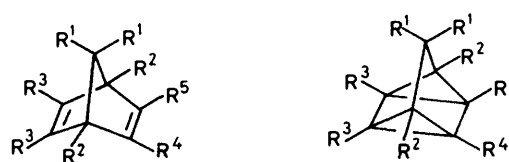
The acylnorbornadienes were synthesized by Diels-Alder reaction of cyclopentadiene having electron-donating groups (Me,<sup>3b</sup> Ph,<sup>4,6</sup> *p*-MeOC<sub>6</sub>H<sub>4</sub>,<sup>3b</sup>) with acetylenes having electron-withdrawing groups (CO<sub>2</sub>Me, COMe,<sup>7</sup> COEt,<sup>4,8</sup> COPh,<sup>7</sup> CONH<sub>2</sub>) and these were photochemically converted into their corresponding quadricyclanes.



**Acylnorbornadienes.**—Diels-Alder reaction between cyclopentadienes and acetylenes proceeded smoothly giving norbornadienes in good yields (see Table 1). All the adducts having both electron-withdrawing and electron-donating groups show a distinct red shift with an end of absorption (abbreviated as EA ‡) > 430 nm (visible light region) arising from intramolecular charge-transfer interaction between electron-rich and electron-deficient olefins (Table 2). In

† The principle of our model with acid-catalysed cycloreversion has appeared in ref. 3.

‡ Abbreviation of EA, see ref. 2b.



	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	R <sup>5</sup>	
(10)	Me	H	Me	CO <sub>2</sub> Me	CO <sub>2</sub> Me	(22)
(11)	H	Me	Ph	CO <sub>2</sub> Me	CO <sub>2</sub> Me	(23)
(12)	H	H	H	COMe	H	(24)
(13)	H	H	H	COPh	H	(25)
(14)	Me	H	Me	COPh	H	(26)
(15)	Me	H	Ar	COPh	H	(27)
(16)	H	H	H	COEt	CO <sub>2</sub> Me	(28)
(17)	Me	H	Me	COEt	CO <sub>2</sub> Me	(29)
(18)	Me	H	Ar	COEt	CO <sub>2</sub> Me	(30)
(19)	H	Me	Ph	COEt	CO <sub>2</sub> Me	(31)
(20)	H	Me	Ph	COEt	CONH <sub>2</sub>	
(21)	H	Me	Ph	COEt	CN	(32)

Ar = *p*-MeOC<sub>6</sub>H<sub>4</sub>

Table 1. Diels-Alder reaction between acetylenes and cyclopentadienes

Diene	Acetylene	Product	Conditions	Yield %
(2) <sup>a</sup>	(5)	(10)	Benzene, 50 °C, 15 h	32
(4)	(5)	(11)	Benzene, reflux, 15 h	92
(1)	(6)	(12) <sup>b</sup>	CH <sub>2</sub> Cl <sub>2</sub> , room temp., 6 h	57
(1)	(7)	(13) <sup>b</sup>	Benzene, room temp., 3 days	61
(2) <sup>a</sup>	(7)	(14)	Xylene, reflux, 4 h	54
(3)	(7)	(15)	Toluene, reflux, 25 days	54
(1)	(8)	(16)	Benzene, room temp., 5 h	85
(2) <sup>a</sup>	(8)	(17)	Benzene, room temp., 30 min	69
(3)	(8)	(18)	Benzene, reflux, 4 h	89
(4)	(8)	(19)	Benzene, reflux, 2.5 h	85
(4)	(9)	(20)	Benzene, reflux, 3 h	52

<sup>a</sup> *in situ* Generation of (2).<sup>3b</sup> <sup>b</sup> After purification these compounds decomposed slowly at ambient temperature.

particular, the EAs for compounds (15), (18), and (19) were > 500 nm. Among these the simplest acylnorbornadienes, (12) and (13), were moderately unstable and decomposed slowly at ambient temperature.

**Photochemical Reactions of Diels-Alder Adducts.**—Preparative photoreaction of the norbornadienes prepared in this article was performed in benzene or ethyl acetate with light of wavelength > 300 nm (Pyrex filter) using a high-pressure Hg arc

**Table 2.** End of absorption readings of norbornadienes

Norbornadiene	EA/nm	Norbornadiene	EA/nm
(10)	441	(17)	476
(11)	487	(18)	581
(15)	527	(19)	558
(16)	432		

**Table 3.** Quantum yields of the photocycloaddition of norbornadienes

Norbornadiene	$\Phi$	$\lambda/\text{nm}^a$
(10)	0.66 ± 0.06	383
(11)	0.56 ± 0.07	383
(16)	0.82 ± 0.08	356
(19)	0.75 ± 0.04	383

<sup>a</sup> Wavelength of the irradiated light (16 nm spectra band width).

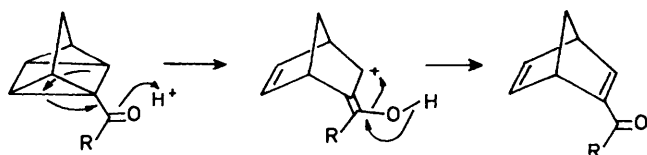
**Table 4.** Rates of cycloreversion of quadricyclanes

Quadricyclane	$k_{\text{m}}/\text{s}^{-1}[\text{CF}_3\text{CO}_2\text{H}]^{-1}$
(22)	$7.1 \times 10^{-3}$
(23)	$1.2 \times 10^{-3}$
(31)	1.3

lamp (200 W). On completion of the reaction, the reaction mixture [except for compounds (13), (14), (15), or (18)] contained only the corresponding quadricyclane without any detectable formation of by-products as judged by t.l.c. and/or n.m.r. Fairly high quantum yields for the photoreaction of the typical norbornadienes were observed at 383 nm [in the case of (16), light of wavelength 356 nm was used]. Table 3 shows a summary of the results.

Although it has been shown by George *et al.*<sup>9</sup> that 2,3-dibenzoylnorbornadiene photocyclizes effectively ( $\Phi = 0.17$ ) and similar transformations with high quantum efficiency have been reported for 2-aryloxy-3-arylnorbornadienes,<sup>10</sup> with only a small difference in the structure, our 2-arylnorbornadienes (13)–(15) failed to give quadricyclanes in detectable amounts under the conditions of the photolysis. 2-Propionylnorbornadiene (18) also failed to react photochemically under the conditions. Bearing in mind our observations<sup>5</sup> that introduction of 4-methoxyphenyl groups into the quadricyclane skeleton enhances the cycloreversion reaction to give the initial norbornadiene, the apparent lack of reactivity is probably attributable less to the inertness of (18) than the thermal instability of the quadricyclane (30).

**Acid Catalysed Reversion of Quadricyclanes.**—As shown earlier,<sup>3,11</sup> a small strained ring conjugated with a carbonyl group readily undergoes acid-catalysed cleavage. Thus, compound (31) instantly cycloreverts to (19) on treatment with trifluoroacetic acid. Since the reversion rates of (22) and (23) bearing ester groups were found to be  $10^3$  times smaller than that of (31) (Table 4), we suggest that the latter proceeds by the same mechanism as that presented by us for pentacyclic cage compounds<sup>3,11</sup> (see Scheme).

**Scheme 1.**

The n.m.r. spectra of the reaction mixtures show that although the quadricyclanes (24), (29), and (32) are formed by photolysis of the corresponding norbornadienes (12), (17), and (21), respectively, they undergo gradual cycloreversion to the original norbornadienes during purification.

Though incomplete, the (19)⇌(31) system is the most favourable of all the systems we have presented for the reversible storage of visible light energy. Its advantages are: (i) the absorption of a wide range of visible light; (ii) high quantum yield for the photolysis; (iii) clean and instant reversion by acid-catalysis. Finally, the photochemical reaction of (19) to (31) was shown to proceed readily and quantitatively with light of wavelength >400 nm (visible light) using a monochromatic irradiation or a halogen lamp with a filter.

## Experimental

N.m.r. spectra were recorded at 100 MHz unless otherwise stated with a JEOL JNM FX 100 spectrometer for solutions in  $\text{CDCl}_3$  or  $\text{C}_6\text{D}_6$  ( $\text{SiMe}_4$  as internal standard). I.r. spectra were measured with a JASCO IR-2 spectrometer, u.v. spectra with either a Shimadzu UV-3000 or Varian Cary 219 spectrophotometer, and mass spectra with either a JEOL JMS D-300 apparatus or a Shimadzu 9000 B machine. M.p.s were taken on a Yamato MP-1 apparatus and are uncorrected. Preparative photolysis was performed with a 200 W high-pressure Hg arc lamp (EIKOSHA, Osaka). Monochromatic irradiation was conducted with a JASCO CRM-FA Spectro Irradiator. After extraction, the organic layers were dried over anhydrous sodium sulphate.

### Diels–Alder Reactions of Cyclopentadienes with Acetylenes.

The conditions and the yields of the Diels–Alder reactions are shown in Table 1. But-3-yn-2-one (6),<sup>7a</sup> prepared by hydrolysis of methyl trimethylsilylethynyl ketone<sup>7b</sup> with sodium borate<sup>7c</sup> was distilled at 65–73 °C (lit.,<sup>7a</sup> 84.5–86 °C). 1-Phenylprop-2-yn-1-one (7), obtained by a literature process,<sup>7c</sup> was a solid. These acetylenes were of adequate purity as judged by n.m.r. for the Diels–Alder reaction without further purification.

**4-Oxohex-2-ynamide (9).**—A methanolic solution (13 ml) of methyl 4-hydroxyhex-2-ynoate<sup>4</sup> (1.99 g) was saturated with ammonia at 0 °C and stirred overnight at room temperature. It was then evaporated to dryness and the residue treated with ether to give the corresponding hydroxy amide (1.23 g, 69%);  $\nu_{\text{max}}$ (Nujol) 3 450–3 000, 2 230, 1 660, and 1 610  $\text{cm}^{-1}$ . The crude hydroxy amide (1.00 g) dissolved in acetone (25 ml) and cooled in ice was treated with Jones reagent: it was then kept in an ice-bath for 2 h. After a further 1 h the mixture was diluted with water and extracted with  $\text{CH}_2\text{Cl}_2$ . The extract was treated with solid sodium hydrogen carbonate, washed with brine, dried, and evaporated to dryness to give (9) as a solid (682 mg, 69% from hydroxy amide), m.p. 43 °C (from benzene–light petroleum) (Found: C, 57.6; H, 5.7; N, 11.1.  $\text{C}_6\text{H}_7\text{NO}_2$  requires C, 57.6; H, 5.6; N, 11.2%);  $\nu_{\text{max}}$ (Nujol) 3 350, 3 150, 1 680, 1 660, and 1 615  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ ( $\text{CDCl}_3$ ) 1.17 (3 H, t, *J* 7 Hz), 2.69 (2 H, q, *J* 7 Hz), and 5.90 (2 H, br s); *m/z* 125 ( $M^+$ , 4%), 96 (34), 81 (54), and 53 (100).

**Dimethyl 5,6,7,7-tetramethylbicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (10).** B.p. 111 °C/0.2 mmHg;  $\nu_{\text{max}}$ (neat) 1 725, 1 610, 1 430, and 1 270  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ ( $\text{CDCl}_3$ ) 1.15 (3 H, s), 1.16 (3 H, s), 1.78 (6 H, s), 3.16 (2 H, s), and 3.81 (6 H, s); *m/z* 264 ( $M^+$ , 23%) (Found:  $M^+$ , 264.136.  $\text{C}_{15}\text{H}_{20}\text{O}_4$  requires  $M$ , 264.136), 232 (19), 205 (30), 191 (84), and 173 (100).

**Dimethyl 1,4-dimethyl-5,6-diphenylbicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (11).** M.p. 85–87 °C (from hexane) (Found: C, 77.3; H, 6.2.  $\text{C}_{25}\text{H}_{24}\text{O}_4$  requires C, 77.3; H, 6.2%);  $\nu_{\text{max}}$ (Nujol) 1 720 and 1 610  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ ( $\text{CDCl}_3$ ) 1.46 (6 H, s), 2.40

(2 H, s), 3.79 (6 H, s), and 7.03—7.25 (10 H, m);  $m/z$  388 ( $M^+$ , 16%), 373 (6), and 178 (100).

2-Acetylbicyclo[2.2.1]hepta-2,5-diene (**12**).  $\delta_{\text{H}}(\text{C}_6\text{D}_6)$  1.81—1.86 (2 H, m), 1.91 (3 H, s), 3.22 (1 H, m), 4.66 (1 H, m), 6.46 (1 H, ddd,  $J$ , 5, 3, and 1 Hz), 6.72 (1 H, ddd,  $J$ , 5, 3, and 1 Hz), and 6.92 (1 H, d,  $J$  3 Hz).

2-Benzoylbicyclo[2.2.1]hepta-2,5-diene (**13**).  $\delta_{\text{H}}(\text{CDCl}_3)$  2.18 (2 H, dd,  $J$  2 and 2 Hz), 3.81 (1 H, br s), 4.10 (1 H, br s), 6.74 (1 H, m), 7.00 (1 H, m), 7.33—7.54 (5 H, m), and 7.64—7.72 (1 H, m).

2-Benzoyl-5,6,7,7-tetramethylbicyclo[2.2.1]hepta-2,5-diene (**14**). M.p. 72.5—74.5 °C (from hexane) (Found: C, 85.6; H, 8.0.  $\text{C}_{18}\text{H}_{20}\text{O}$  requires C, 85.7; H, 8.0%);  $\nu_{\text{max.}}$ (Nujol) 1 620, 1 590, and 1 560  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{CDCl}_3)$  1.14 (3 H, s), 1.17 (3 H, s), 1.71 (3 H, d,  $J$  1 Hz), 1.79 (3 H, d,  $J$  1 Hz), 2.96 (1 H, t,  $J$  3 Hz), 3.39 (1 H, dd,  $J$  3 and 1 Hz), 7.35—7.56 (4 H, m), and 7.72—7.78 (2 H, m);  $m/z$  252 ( $M^+$ , 30%), 237 (32), 196 (40), 179 (45), and 105 (100).

2-Benzoyl-5,6-bis(4-methoxyphenyl)-7,7-dimethylbicyclo[2.2.1]hepta-2,5-diene (**15**). Pale yellow semi-solid (Found: C, 82.6; H, 6.6.  $\text{C}_{30}\text{H}_{28}\text{O}_3$  requires C, 82.5; H, 6.5%);  $\nu_{\text{max.}}$ (Nujol) 1 630, 1 600, 1 570, 1 460, and 1 240  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{CDCl}_3)$  1.26 (3 H, s), 1.42 (3 H, s), 3.63 (1 H, t,  $J$  3 Hz), 3.78 (3 H, s), 3.79 (3 H, s), 4.00 (1 H, dd,  $J$  3 and 1 Hz), 6.80 (4 H, d,  $J$  9 Hz), 7.15 (2 H, d,  $J$  9 Hz), 7.38 (2 H, d,  $J$  9 Hz), and 7.26—7.82 (6 H, m);  $m/z$  436 ( $M^+$ , 100%), 378 (63), 363 (13), and 329 (57).

Methyl 3-propionylbicyclo[2.2.1]hepta-2,5-diene-2-carboxylate (**16**). Colourless liquid;  $\nu_{\text{max.}}$ (Neat) 1 710, 1 660, 1 606, and 1 550  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{C}_6\text{D}_6)$  1.05 (3 H, t,  $J$  7 Hz), 1.71 (1 H, d,  $J$  7 Hz), 1.87 (1 H, d,  $J$  7 Hz), 2.55 (1 H, q,  $J$  7 Hz), 2.56 (1 H, q,  $J$  7 Hz), 3.29 (3 H, s), 3.64 (1 H, m), 3.81 (1 H, m), and 6.64 (2 H, m);  $m/z$  206 ( $M^+$ , 35%) (Found:  $M^+$ , 206.095.  $\text{C}_{12}\text{H}_{14}\text{O}_3$  requires  $M$ , 206.094), 177 (100), 149 (94), and 66 (76).

Methyl 5,6,7,7-tetramethyl-3-propionylbicyclo[2.2.1]hepta-2,5-diene-2-carboxylate (**17**). Pale yellow liquid;  $\nu_{\text{max.}}$ (Neat) 1 710, 1 610, and 1 430  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{C}_6\text{D}_6)$  1.01 (3 H, s), 1.15 (3 H, s), 1.15 (3 H, t,  $J$  7 Hz), 1.70 (6 H, s), 2.69 (2 H, q,  $J$  7 Hz), 3.04 (1 H, d,  $J$  3 Hz), 3.21 (1 H, d,  $J$  3 Hz), and 3.38 (3 H, s);  $m/z$  262 ( $M^+$ , 30%) (Found:  $M^+$ , 262.156.  $\text{C}_{16}\text{H}_{22}\text{O}_3$  requires  $M$ , 262.157), 247 (23), 215 (39), 203 (63), and 189 (100).

Methyl 5,6-bis(4-methoxyphenyl)-7,7-dimethyl-3-propionylbicyclo[2.2.1]hepta-2,5-diene-2-carboxylate (**18**). M.p. 115—117 °C (from MeOH) (Found: C, 75.5; H, 6.8.  $\text{C}_{28}\text{H}_{30}\text{O}_5$  requires C, 75.3; H, 6.8%);  $\nu_{\text{max.}}$ (Nujol) 1 705, 1 670, 1 595, 1 505, and 1 495  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{C}_6\text{D}_6)$  1.02 (3 H, t,  $J$  7 Hz), 1.22 (3 H, s), 1.25 (3 H, s), 2.59 (1 H, q,  $J$  7 Hz), 2.61 (1 H, q,  $J$  7 Hz), 3.25 (3 H, s), 3.26 (3 H, s), 3.30 (3 H, s), 3.75 (1 H, d,  $J$  3 Hz), 3.92 (1 H, d,  $J$  3 Hz), 6.71 (4 H, d,  $J$  9 Hz), 7.38 (2 H, d,  $J$  9 Hz), and 7.48 (2 H, d,  $J$  9 Hz);  $m/z$  446 ( $M^+$ , 97%), 387 (100), 373 (31), and 357 (34).

Methyl 1,4-dimethyl-5,6-diphenyl-3-propionylbicyclo[2.2.1]hepta-2,5-diene-2-carboxylate (**19**). M.p. 95 °C (from hexane) (Found: C, 80.8; H, 6.9.  $\text{C}_{26}\text{H}_{26}\text{O}_3$  requires C, 80.8; H, 6.8%);  $\nu_{\text{max.}}$ (Nujol) 1 700, 1 685, and 1 600  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{C}_6\text{D}_6)$  1.04 (3 H, t,  $J$  7 Hz), 1.33 (3 H, s), 1.68 (3 H, s), 2.15 (2 H, s), 2.29—2.60 (2 H, m), 3.26 (3 H, s), and 6.89—7.32 (10 H, m);  $m/z$  386 ( $M^+$ , 35%), 371 (25), 329 (23), and 178 (100).

1,4-Dimethyl-5,6-diphenyl-3-propionylbicyclo[2.2.1]hepta-2,5-diene-2-carboxamide (**20**). Semi-solid. This compound was converted into (**21**) without further purification;  $\nu_{\text{max.}}$ ( $\text{CHCl}_3$ ) 3 470, 3 360, 1 670, 1 600, 1 450, and 1 380  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{CDCl}_3)$  0.98 (3 H, t,  $J$  7 Hz), 1.50 (3 H, s), 1.54 (3 H, s), 2.27—2.41 (4 H, m), 5.60 (1 H, br s), 6.10 (1 H, br s), and 7.08—7.26 (10 H, m);  $m/z$  371 ( $M^+$ , 40%), 356 (42), 314 (23), and 178 (100).

1,4-Dimethyl-5,6-diphenyl-3-propionylbicyclo[2.2.1]hepta-2,5-diene-2-carbonitrile (**21**). A solution of (**20**) (104.8 mg, 0.28 mmol) and toluene-*p*-sulphonyl chloride (119.8 mg, 0.63 mmol) in absolute pyridine (2 ml) was refluxed for 2.5 h. The mixture was poured onto ice, acidified with 10% HCl, and extracted with ether. The extract was washed with 10% HCl and brine, dried, and evaporated to dryness. Chromatography on silica gel with

hexane-ethyl acetate (10:1) as eluant yielded (**21**) (87.8 mg, 88%), m.p. 115 °C (from hexane) (Found: C, 85.1; H, 6.6; N, 4.1.  $\text{C}_{25}\text{H}_{23}\text{NO}$  requires C, 85.0; H, 6.6; N, 4.0%);  $\nu_{\text{max.}}$  2 170, 1 675, and 1 570  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{C}_6\text{D}_6)$  0.98 (3 H, t,  $J$  7 Hz), 1.38 (3 H, s), 1.50 (3 H, s), 1.80 (1 H, d,  $J$  7 Hz), 2.01 (1 H, d,  $J$  7 Hz), 2.32—3.14 (2 H, m), and 6.90—7.31 (10 H, m);  $m/z$  353 ( $M^+$ , 11%), 338 (14), and 178 (100).

*Photocycloaddition of Norbornadienes.*—Photolysis of the norbornadienes (**10**), (**11**), (**12**), (**16**), (**17**), and (**19**) was performed in [ $^2\text{H}_6$ ]benzene or AcOEt using a high pressure 200 W Hg arc lamp with a Pyrex filter. When the reaction was completed, the reaction mixture contained only the corresponding quadricyclanes (**22**), (**23**), (**24**), (**28**), (**29**), and (**31**), respectively without any detectable formation of by-products as judged by n.m.r. or t.l.c.

Dimethyl 3,3,6,7-tetramethyltetracyclo[3.2.0.0 $^{2,7}$ .0 $^{4,6}$ ]-heptane-1,5-dicarboxylate (**22**). M.p. 74—76 °C (from hexane) (Found: C, 68.3; H, 7.7.  $\text{C}_{15}\text{H}_{20}\text{O}_4$  requires C, 68.1; H, 7.6%);  $\nu_{\text{max.}}$ (Nujol) 1 700, 1 325, and 1 200  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{CDCl}_3)$  1.17 (3 H, s), 1.19 (3 H, s), 1.84 (2 H, s), and 3.68 (6 H, s);  $m/z$  264 ( $M^+$ , 7%), 232 (6), 205 (26), 191 (91), and 173 (100).

Dimethyl 2,4-dimethyl-6,7-diphenyltetracyclo[3.2.0.0 $^{2,7}$ .0 $^{4,6}$ ]-heptane-1,5-dicarboxylate (**23**). M.p. 92 °C (from hexane) (Found: C, 77.4; H, 6.1.  $\text{C}_{25}\text{H}_{24}\text{O}_4$  requires C, 77.3; H, 6.2%);  $\nu_{\text{max.}}$ (Nujol) 1 705, 1 600, and 1 320  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{C}_6\text{D}_6)$  1.21 (6 H, s), 1.82 (1 H, d,  $J$  8 Hz), 1.85 (1 H, d,  $J$  8 Hz), 3.06 (6 H, s), and 6.54—6.95 (10 H, m).

1-Acetyltetracyclo[3.2.0.0 $^{2,7}$ .0 $^{4,6}$ ]heptane (**24**).  $\delta_{\text{H}}(\text{C}_6\text{D}_6)$  1.07—1.38 (2 H, m), 1.50 (3 H, s), 1.78—1.84 (2 H, m), and 1.84—2.12 (3 H, m).

Methyl 5-propionyltetracyclo[3.2.0.0 $^{2,7}$ .0 $^{4,6}$ ]heptane-1-carboxylate (**28**). Colourless liquid (Found: C, 69.7; H, 6.9.  $\text{C}_{12}\text{H}_{14}\text{O}_3$  requires C, 69.9; H, 6.8%);  $\nu_{\text{max.}}$ (neat) 1 715 and 1 650  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{C}_6\text{D}_6)$  1.11 (3 H, t,  $J$  7 Hz), 1.59 (1 H, dt,  $J$  12 and 1 Hz), 1.81 (1 H, dt,  $J$  12 and 1 Hz), 1.96—2.21 (4 H, m), 2.38—3.04 (2 H, m), and 3.31 (3 H, s);  $m/z$  206 ( $M^+$ , 36%), 177 (100), 149 (96), and 66 (81).

Methyl 3,3,6,7-tetramethyl-5-propionyltetracyclo[3.2.0.0 $^{2,7}$ .0 $^{4,6}$ ]heptane-1-carboxylate (**29**).  $\delta_{\text{H}}(\text{C}_6\text{D}_6)$  0.92 (3 H, s), 1.04 (3 H, s), 1.17 (3 H, t,  $J$  7 Hz), 1.25 (3 H, s), 1.29 (3 H, s), 1.76 (1 H, d,  $J$  7 Hz), 1.88 (1 H, d,  $J$  7 Hz), 2.87 (1 H, q,  $J$  7 Hz), 2.90 (1 H, q,  $J$  7 Hz), and 3.34 (3 H, s).

Methyl 2,4-dimethyl-6,7-diphenyl-5-propionyltetracyclo[3.2.0.0 $^{2,7}$ .0 $^{4,6}$ ]heptane-1-carboxylate (**31**). M.p. 114—116 °C (from hexane) (Found: C, 80.9; H, 6.9.  $\text{C}_{26}\text{H}_{26}\text{O}_3$  requires C, 80.8; H, 6.8%);  $\nu_{\text{max.}}$ (Nujol) 1 720, 1 690, and 1 600  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{C}_6\text{D}_6)$  1.05 (3 H, s), 1.15 (3 H, t,  $J$  7 Hz), 1.51 (3 H, s), 2.21 (2 H, m), 2.42—2.83 (2 H, m), 3.30 (3 H, s), and 6.84—7.44 (10 H, m);  $m/z$  386 ( $M^+$ , 26%), 371 (21), 329 (21), and 178 (100).

*Quantum Yield Determinations.*—Nitrogen-purged MeCN solutions containing known concentrations (20—130 mmol  $\text{dm}^{-3}$ ) of norbornadienes in 10 mm quartz tubes were irradiated at 383 nm [for (**10**), (**11**), and (**19**)] of 356 nm [for (**16**)] from a monochromatic irradiator (JASCO CRM-FA Spectro Irradiator; 16 nm spectral band width). Irradiated samples were analysed using a u.v. spectrometer. Light intensity was measured by ferrioxalate actinometry.<sup>12</sup>

*Kinetics.*—Reversions of the norbornadienes (*ca.*  $10^{-3}$  mol  $\text{dm}^{-3}$ ) catalysed by trifluoroacetic acid ( $2 \times 10^{-2}$ — $8 \times 10^{-5}$  mol  $\text{dm}^{-3}$ ) in absolute benzene at  $32.0 \pm 0.1$  °C were followed by determination of the increase in the norbornadienes with time *via* a u.v. assay.

*Photochemical Reaction of (19) with Visible Light.*—A benzene solution of (**19**) ( $4$ — $9 \times 10^{-3}$  mol  $\text{dm}^{-3}$ ) was irradiated at 410 nm using a monochromatic irradiator (JASCO CRM-FA

Spectro Irradiator; 16 nm spectral band width) or with the light of a 650 W halogen lamp with a Toshiba L-42 filter. Both reactions were completed within 4 h giving only (31).

### References

- 1 C. Philippopoulos, D. Economou, C. Economou, and J. Marangozis, *Ind. Eng. Chem. Prod. Res. Dev.*, 1983, **22**, 627.
- 2 (a) Y. Havel, A. W. Adamson, C. Kutal, P. A. Grutch, and K. Yasufuku, *J. Phys. Chem.*, 1987, **91**, 901; (b) T. Kobayashi, Z. Yoshida, Y. Asako, S. Miki, and S. Kato, *J. Am. Chem. Soc.*, 1987, **109**, 5103; (c) K. Maruyama and H. Tamiaki, *J. Org. Chem.*, 1987, **52**, 3967; (d) P. G. Gassman and J. W. Hershberger, *ibid.*, 1987, **52**, 1337; (e) H. Nishino, S. Toki, and S. Takamuku, *J. Am. Chem. Soc.*, 1986, **108**, 5030; (f) Y. Yamashita, T. Hanaoka, Y. Takeda, and T. Mukai, *Chem. Lett.*, 1986, 1279; (g) D. J. File, W. M. Moore, and K. W. Morse, *J. Am. Chem. Soc.*, 1985, **107**, 7077.
- 3 (a) T. Hamada, H. Iijima, T. Yamamoto, N. Numao, K. Hirao, and O. Yonemitsu, *J. Chem. Soc., Chem. Commun.*, 1980, 696; (b) K. Hirao, A. Yamashita, A. Ando, H. Yamamoto, H. Iijima, T. Hamada, and O. Yonemitsu, *J. Chem. Res.*, 1987, (S), 164; (M), 1401.
- 4 K. Hirao, A. Yamashita, and O. Yonemitsu, *J. Fluorine Chem.*, 1987, **36**, 293.
- 5 K. Hirao, A. Ando, T. Hamada, and O. Yonemitsu, *J. Chem. Soc., Chem. Commun.*, 1984, 300.
- 6 P. Bladon, S. McVey, and P. L. Pauson, *J. Chem. Soc. C*, 1966, 306.
- 7 (a) A. Birkofer, A. Ritter, and H. Uhlenbrauck, *Chem. Ber.*, 1963, **96**, 3280; (b) D. R. M. Walton and F. Waugh, *J. Organomet. Chem.*, 1972, **31**, 45; (c) H. Newman, *J. Org. Chem.*, 1973, **38**, 2254.
- 8 cf. M. M. Midland, A. Tramonto, and J. R. Crable, *J. Org. Chem.*, 1980, **45**, 28.
- 9 S. Lahiri, V. Dabral, S. M. S. Chauhan, E. Chakachery, C. V. Kumar, J. C. Scaiano, and M. V. George, *J. Org. Chem.*, 1980, **45**, 3782.
- 10 T. Toda, E. Hasegawa, T. Mukai, H. Tsuruta, T. Hagiwara, and T. Yoshida, *Chem. Lett.*, 1982, 1551.
- 11 T. Iwakuma, K. Hirao, and O. Yonemitsu, *J. Am. Chem. Soc.*, 1974, **96**, 2570.
- 12 C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, A*, 1956, **235**, 518.

Received 7th December 1987; Paper 7/2141