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FLUOROALKYLNORBORNADIENES AND THEIR CORRESPONDING VALENCE ISOMER QUADRICYCLANES --- A LIGHT ENERGY STORAGE SYSTEM

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SUMMARY

As a model for light energy conversion, some fluoroalkylnorbornadienes were prepared using the Diels-Alder reaction between fluoroalkylpropiolates and cyclopentadienes having electron donating substituents (H-, Me-, C_6H_5-). Trifluoromethylpropiolate (5) shows the highest reactivity as a dienophile. Esters were converted to ketones which show an intramolecular charge transfer absorption. Irradiation of trifluoromethylnorbornadienes which have a ketonic group using a high pressure Hg lamp quantitatively gave the corresponding quadricyclanes. The latter compounds are rather unstable in benzene at room temperature gradually reverting to the original norbornadienes.

INTRODUCTION

Recently, we reported an initial model for light energy conversion; on irradiation various Diels-Alder adducts (**A**) easily obtained from cyclic olefins gave strained pentacyclic cage ketones (**B**), which smoothly and cleanly reverted to the starting compounds (**A**) with the evolution of heat (∿20 kcal/mol) via an acid catalysed reaction [1]. As shown in Scheme 1,

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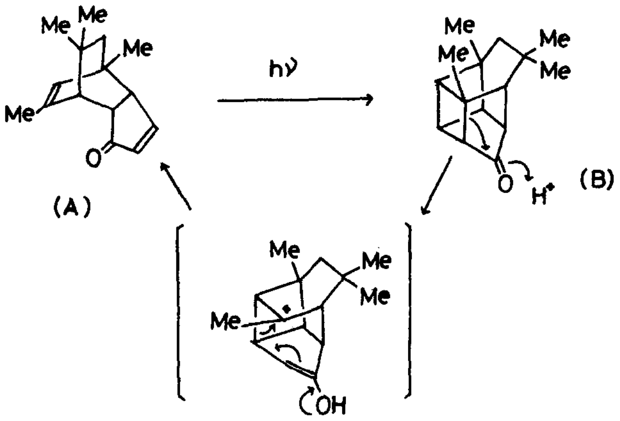
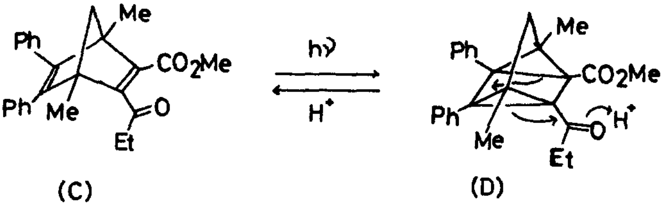
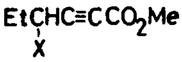


Scheme 1. A representative initial model

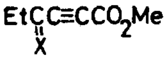


Scheme 2. Our donor-acceptor norbornadiene model



$EtCH(X)C\equiv CCO_2Me$

(1) X=OH
(2) X=F



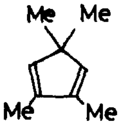
$EtC(=X)C\equiv CCO_2Me$

(3) X=O
(4) X=F$_2$

$CF_3C\equiv CCO_2Me$

(5)

(6)



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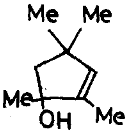

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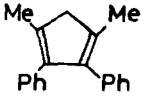

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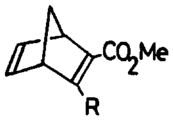
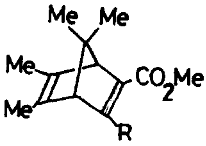
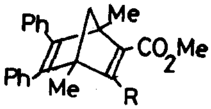


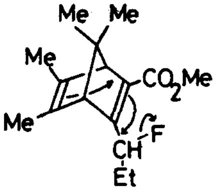
(10) R = CHFEt
(11) R = CF_2Et
(12) R = CF_3



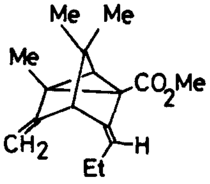
(13) R = CHFEt
(14) R = CF_2Et
(15) R = CF_3



(16) R = CHFEt
(17) R = CF_2Et
(18) R = CF_3



(13a)



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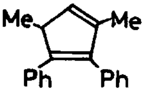

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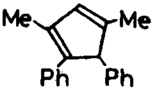

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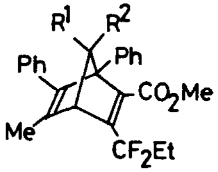
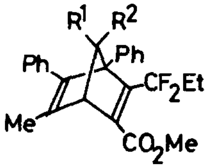
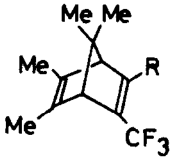


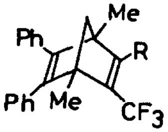
(22a) R^1 = H, R^2 = Me
(22b) R^1 = Me, R^2 = H



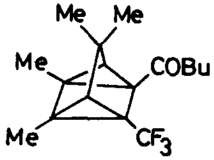
(23a) R^1 = H, R^2 = Me
(23b) R^1 = Me, R^2 = H



(24) R = CO_2H
(25) R = COBu



(26) R = CO_2H
(27) R = COBu
(28) R = COMe
(29) R = COCl



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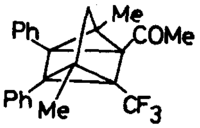

(31)

the presence of a carbonyl group conjugated with the four membered strained ring is essential. This acid-catalysed reversion is the striking characteristic of our model, and was extended to the interconversion between the valence isomers norbornadinene and quadricyclane, the best studied system among the photochemical energy storage cycles of organic compounds [2]. Thus, we prepared many donor-acceptor norbornadienes[A] having carbonyl groups, and among them the diphenyl ketoester (**C**) was found to be eminently suitable for the purpose in every respect [3]. We now present the synthesis of norbornadienes, having a fluoroalkylated olefin as an intramolecular electron-acceptor, by the Diels-Alder reaction between cyclopentadienes and fluorinated propiolates.

RESULTS AND DISCUSSION

Our attempts to prepare fluorinated derivatives directly from norbornadienes failed. Therefore, we turned our attention next to study the preparation of fluorinated acetylenic compounds and their reactivity as a dienophile toward cyclopentadienes.

(a) Dienophiles and dienes

The monofluoride (**2**) and the difluoride (**4**) were prepared from the corresponding alcohol (**1**)[B] and ketone (**3**), respectively, by treatment with diethylaminosulphur trifluoride (DAST) [5] in satisfactory yields. The trifluoride (**5**) was prepared from the stable phosphorane $Ph_3PCHCOOMe$ and $(CF_3CO)_2O$ using the intramolecular Wittig reaction [6].

Cyclopentadiene (**6**) was obtained by the standard procedure [7]. The tetramethylcyclopentadiene (**7**) was generated _in situ_ from the alcohol (**8**) by dehydration with _p_-toluenesulphonic acid [8]. The dimethyldiphenylcyclopentadiene (**9**) was prepared according to modified Bladon's method [9].

(b) Diels-Alder reaction

Intermolecular Diels-Alder reactions between the dienophiles and the dienes synthesized above were undertaken, and results were summarised in Table 1. Several comments concerning the results are in order. First, the dienophiles exhibit in principle the normal reactivity toward the dienes, thus the trifluoride (5) was most reactive (entry 3, 7, and 10) as

TABLE 1

Summary of Diels-Alder reaction of fluorinated acetylenes with cyclopentadienes

Entry	Diene	Dienophile	Conditions	Product(yield%)	
1	**(6)**	**(2)**	Toluene, 90°C, 12h	**(10)**	(16)
2	**(6)**	**(4)**	Benzene, room temp., 3 days	**(11)**	(41)
3	**(6)**	**(5)**	Benzene, reflux 1h	**(12)**	(78)
4	(7)[a]	**(2)**	Benzene, TsOH 110°C, 8h	no reaction	
5	(7)[a]	**(2)**	Benzene, TsOH 200°C, 4h	**(19)**	(30)
6	(7)[a]	**(4)**	Benzene, TsOH 110°C, 2.5h	**(14)**	(55)
7	(7)[a]	**(5)**	Benzene, TsOH reflux, 0.5h	**(15)**	(90)
8	**(9)**	**(2)**	Xylene, reflux, 2.5h	no reaction	
9	**(9)**	**(4)**	Benzene, 120°C, 3h	**(17)**	(5)[b]
10	**(9)**	**(5)**	Benzene, reflux 1h	**(18)**	(69)

[a] _in situ_ Generation of **(7)**.

[b] A mixture of **(22a,b)** and/or **(23a,b)** was obtained in 52% yield.

expected. The reaction of the least reactive monofluoride (**2**) actually proceeded under drastic conditions (entry 5) but was unfortunately accompanied by dehydrofluorination through the π-participation (cf. **13a**) to give a diene (**19**), whose structure was readily confirmed by analysis of its spectroscopic properties (see the experimental section). The three cyclopentadienes were proved to show practically the same order of reactivity toward dienophiles. The dimethyldiphenylcyclopentadiene (**9**) was somewhat unstable and changed to an isomer (**20**), which then reacted with a dienophile. This was easily proved by the n.m.r. spectrum of the crude product. Thus under the conditions of entry 9, the expected norbornadiene (**17**) was obtained only in 5% yield, whereas two isomeric norbornadienes[c] derived from (**20**) were obtained in 52% yield. Other isomeric norbornadienes arising from the third possible isomer (**21**) could not be detected by the n.m.r. spectroscopic analysis. Finally, even under milder conditions (entry 10), the expected norbornadiene (**18**) was contaminated by a small amount (1/8) of an undesired isomeric norbornadiene again derived from (**20**), but they could be easily removed by recrystallisation.

(c) Preparation of ketones

For the preparation of keto norbornadienes, ester groups were first hydrolysed to carboxylic acids under alkaline conditions. On account of the steric interaction between the methyl group on C-1 and the ester group on C-2, (**18**) was much less subject to the hydrolysis than (**15**). The easily obtainable acid (**24**) was then treated with n-BuLi at room temperature to give the desired butyl ketone (**25**) in 47% yield. On the contrary, the reaction of the less obtainable acid (**26**) with n-BuLi was retarded on account of the same steric reason, and the desired ketone (**27**) was obtained only in 3% yield. Conversion of (**26**) to the methyl ketone (**28**) was achieved by treatment of the corresponding acid chloride (**29**) with MeLi using a rhodium catalyst [10]. These two ketones (**25**) and (**28**) showed a pale yellow-colour attributable to the charge transfer interaction between the electron-rich and -deficient olefins [2g]. Thus (**25**) and (**28**) showed an end of absorption [8] at 460 and 510 nm, respectively.

(d) Photocycloaddition and reversion

Photolysis of the norbornadiene derivatives synthesized in this work was undertaken in benzene-d_6 using a high pressure Hg arc lamp with a Pyrex filter. When the reaction was completed, the reaction mixture contained only the corresponding quadricyclane without any detectable formation of by-products as judged by n.m.r. and t.l.c. criteria.

Perfluoroalkyl groups generally give stabilizing effects on highly strained frameworks [11], and these are designated as the 'perfluoroalkyl effect' [12]. Therefore, strained quadricyclane molecules were expected to be stabilized by the fluoroalkyl substituents. Contrary to expectation, however, fluorinated keto quadricyclanes (**30**) and (**31**) were rather unstable at room temperature, and the half-life times ($t_{1/2}$) in benzene-*d*$_6$ were determined to be 38 and 86 h, respectively. When a trace of trifluoroacetic acid was added to the benzene-*d*$_6$ solution of (**30**) and (**31**), these compounds were almost spontaneously reverted, of course, to the corresponding norbornadienes in quantitative yields (n.m.r. and t.l.c. vide ante) [8].

EXPERIMENTAL

N.m.r. spectra were recorded at 100 MHz unless otherwise stated with a JEOL JNMFX 100 spectrometer for solutions on chloroform-*d* or benzene-*d*$_6$ ($SiMe_4$ as internal standard). I.r. spectra were measured with a JASCO IR-2, and UV spectra with either a Shimadzu UV-300 or Varian Cary 219 spectrophotometer, and mass spectra with either a JEOL JMS-D 300 apparatus or a Shimadzu 9000 B machine. Melting points were taken on a Yazawa BY-1 apparatus and are uncorrected. Photolysis were performed with a 200 W high pressure Hg arc lamp (EIKOSHA, OSAKA). After extraction, the organic solutions were dried over anhydrous sodium sulphate.

Methyl 4-fluoro-2-hexynoate (2)

A solution of methyl 4-hydroxy-2-hexynoate (**1**) (75 mg, 0.6 mmol), prepared according to Midland's procedure [4] in 75% yield (b.p. 118-125°C/ 17 mmHg) and DAST (0.1 ml, 0.76 mmol) in CH_2Cl_2 (2.5 ml) was stirred overnight under Ar at room temperature. The solution was poured onto ice and extracted with CH_2Cl_2. The extract was washed with water, dried, and evaporated to dryness to give monofluoride (**2**) (nc) (68.7 mg, 90%) as an oil. Analysis: Found: C, 58.6; H, 6.3%. $C_7H_9FO_2$ requires C, 58.3; H, 6.3%; $\nu_{max.}$(neat) 1715 cm^{-1}; δ_H ($CDCl_3$) 1.07 (3H, t, *J* 7 Hz), 1.76-2.04 (2H, m), 3.80 (3H, s), and 5.12 (1H, dt, *J* 6 and 48 Hz).

Methyl 4,4-difluoro-2-hexynoate (4)

In a similar manner as above, keto ester (**3**) prepared by Jones oxidation of (**1**) gave difluoride (**4**)(nc)(85%) as an oil. Analysis: Found: C, 51.55; H, 5.4%. $C_7H_8F_2O_2$ requires C, 51.85; H, 5.0%; $\nu_{max.}$ (neat) 1720 cm^{-1};δ_H ($CDCl_3$) 1.12 (3H, t, *J* 7 Hz), 2.12 (2H, tq, *J* 7 and 7 Hz), and 3.84 (3H, s); m/z 162 (M^+, 27%)(Found: 162.048. $C_7H_8F_2O_2$ requires 162.049), and 130 (100).

Diels-Alder reactions of fluoroalkylacetylene derivatives with cyclopentadienes

Methyl 3-(1-fluoropropyl)bicyclo[2.2.1]hepta-2,5-diene-2-carboxylate (**10**)

Colourless liquid (nc) purified by chromatography on silica gel column. $\nu_{max.}$ (neat) 1700 and 1620 cm^{-1}: δ_H ($CDCl_3$) 0.92 (3H, dt, *J* 8 and 16 Hz), 1.60-2.16 (4H, m), 3.70 (3H, s), 3.80-4.00 (2H, m), 5.46-6.22 (1H, m), 6.68-6.96 (2H, m).

Methyl 3-(1,1-difluoropropyl)bicyclo[2.2.1]hepta-2,5-diene-2-carboxylate (**11**)

Colourless liquid (nc) purified by chromatography on silica gel column. $\nu_{max.}$ (neat) 1720, 1640 and 1560 cm^{-1}: δ_H ($CDCl_3$) 0.96 (3H, t, *J* 8 Hz),1.86-2.40 (4H, m), 3.76 (3H, s), 3.84 (1H, brs), 3.92 (1H, brs), 6.62 (1H, dd, *J* 4 and 6 Hz), and 6.92 (1H, dd, *J* 4 and 6 Hz); m/z 228 (M^+, 23%)(Found: 228.096. $C_{12}H_{14}F_2O_2$ requires 228.096) and 66 (100).

Methyl 3-trifluoromethylbicyclo[2.2.1]hepta-2,5-diene-2-carboxylate (**12**)

Colourless liquid (nc) purified by distillation, b.p. 50-60 ℃/10mmHg. $\nu_{max.}$ (neat) 1735 cm^{-1};δ_H ($CDCl_3$) 2.07 (1H, brd, *J* 7 Hz), 2.27 (1H, brd, *J* 7 Hz), 3.80 (3H, s), 3.95 (2H, d, *J* 8 Hz), and 6.92 (2H, brs); m/z 218 (M^+, 42%)(Found: 218.054. $C_{10}H_9F_3O_2$ requires 218.055) and 59 (100).

Methyl 6,7,7-trimethyl-3-ethylidene-5-methylenetricyclo[2.2.1.0^{2,6}]hepta-2-carboxylate (**19**)

A solution of trimethylcyclopentenol (**8**) (52 mg, 0.37 mmol), monofluoroacetylene (**2**) (48.4 mg, 0.34 mmol) and p-toluenesulphonic acid (1 mg) in benzene (1 ml) was heated at 200℃ in a sealed tube for 4 h. The mixture was then evaporated to dryness. The residue was purified by preparative t.l.c. to give the nortricyclane (**19**) (nc) as an oil (25.2 mg, 30%). $\nu_{max.}$ (neat) 1710 and 1670 cm^{-1}; δ_H ($CDCl_3$) 0.94 (6H, s), 0.98 (3H, t, *J* 7 Hz), 1.41 (3H, s), 2.04 (2H, dq, *J* 7 and 7 Hz), 2.12 (1H, s), 2.47 (1H, s), 3.73 (3H,s) 4.69 (1H, s), 4.84 (1H, s), and 5.83 (1H, t, *J* 7 Hz); δ_C (22.5 MHz, $CDCl_3$) 8.7 (q), 15.0 (q), 21.0 (q), 21.0 (q), 22.0 (t), 40.0 (s), 42.0 (s), 43.0 (s), 47.0 (d), 51.3 (q), 52.1 (d), 99.8 (t), 119.7 (d), 139.9 (s), 155.5 (s), and 170.6 (s); m/z 246 (M^+, 70%) (Found: 246.161. $C_{16}H_{22}O_2$ requires 246.162) and 199 (100); Diels-Alder adduct (**13**) was not available from monofluoro acetylene (**2**) under the conditions given in Table 1 (entry 4).

Methyl 3-(1,1-difluoropropyl)-5,6,7,7-tetramethylbicyclo[2.2.1]hepta-2,5-diene-2-carboxylate (**14**)

Colourless liquid (nc) purified by chromatography on silica gel column. δ_H ($CDCl_3$) 0.93 (3H, t, *J* 8 Hz), 1.08 (3H, s), 1.10 (3H, s), 1.76 (6H, s), 2.12 (2H, m), 3.00 (1H, d, *J* 3 Hz), 3.12 (1H, d, *J* 3 Hz) and 3.72 (3H, s); m/z 284 (M^+, 35%)(Found: 284.158. $C_{16}H_{22}F_2O_2$ requires 284.159) and 173 (100); $\lambda_{max.}$ (EtOH) 236 nm (log ε 3.5).

Methyl 3-trifluoromethyl -5,6,7,7-tetramethylbicyclo[2.2.1]hepta-2,5-diene-2-carboxylate (**15**)

Colourless liquid (nc) purified by chromatography on silica gel column. $\nu_{max.}$ (neat) 1730 cm^{-1}; δ_H ($CDCl_3$) 1.11 (6H, s), 1.75 (6H, s), 3.04 (1H, d, *J* 3 Hz), 3.16 (1H, brd, *J* 3 Hz), and 3.78 (3H, s); m/z 274 (M^+, 24%)(Found: 274.119. $C_{14}H_{17}F_3O_2$ requires 274.118) and 201 (100) ; $\lambda_{max.}$ (EtOH) 235 nm (log ε 3.5).

Methyl 3-(1,1-difluoropropyl)-1,4-dimethyl-5,6-diphenylbicyclo[2.2.1]-hepta-2,5-diene-2-carboxylate (**17**) and its stereoisomers (**22a,b**) and/or (**23a,b**)

After the reaction mixture was evaporated to dryness, the residue was purified by chromatography on silica gel to give the Diels-Alder adduct (**17**) (nc) (5%) and a mixture of its two stereoisomers (isomer A and B) (**22a,b**) and/or (**23a,b**) (52%) with unknown stereochemistry (Compound A : Compound B = 3:1 from n.m.r.). Colourless liquid (**17**). δ_H ($CDCl_3$) 1.08 (3H, t, *J* 7z), 1.34 (3H, s)1.57 (3H, s), 2.37(2H, s), 2.40-2.62 (2H, m), 3.78 (3H, s), 7.06-7.28 (10H, m); Colourless liquid, a mixture of (**22a,b**) and/or (**23a,b**). $\nu_{max.}$ (neat) 1720 cm^{-1}; δ_H ($CDCl_3$) from an isomer A 0.80 (3H, d, *J* 8 Hz), 1.08 (3H, t, *J* 8 Hz), 2.00 (3H, s), and 3.74 (3H, s); δ_H ($CDCl_3$) from an isomer B 0.76 (3H, d, *J* 8 Hz) 1.10 (3H, t, *J* 8 Hz), 2.06 (3H, s), and 3.81 (3H, s); m/z 408 (M^+, 38%) (Found: 408.190. $C_{26}H_{26}F_2O_2$ requires 408.190) and 292 (100).

Methyl 3-trifluoromethyl-1,4-dimethyl-5,6-diphenylbicyclo[2.2.1]hepta-2,5-diene-2-carboxylate (**18**)

Pale yellow prisms (nc) from hexane, m,p, 98-101°C. Analysis: Found: C, 72.4; H, 5.4%. $C_{24}H_{20}F_3O_2$ requires C, 72.4; H, 5.3%; $\nu_{max.}$ (Nujol) 1720 and 1650 cm^{-1}; δ_H ($CDCl_3$) 1.37 (3H, s), 1.47 (3H q, *J* 0.6 Hz), 2.40 (2H, s), 3.86 (3H, s), and 6.96-7.23 (10H, m);$\lambda_{max.}$ (EtOH) 234 nm (log ε 4.1).

After purification by chromatography on silica gel column, n.m.r. spectrum of (**18**) showed that the fraction was contaminated by a stereoisomer [δ_H ($CDCl_3$) 0.82 (d, *J* 7 Hz), 3.82 (s)] derived from the diene (**20**) in a ratio of one to eight. But the isomer was easily removed by recrystallisation.

3-Trifluoromethyl-5,6,7,7-tetramethylbicyclo[2.2.1]hepta-2,5-diene-2-carboxylic acid (24)

The ester (**15**)(300 mg, 1.1 mmol) in 3% NaOH aqueous methanol solution was stirred at 50°C for 30 min. The solution was concentrated to dryness and the residue was dissolved in water. The aqueous solution was washed with ether, acidified with 10% HCl, and extracted with ether. The extract was washed with brine, dried, and evaporated to dryness. The residue (257 mg, 97%) was recrystallised from hexane-ethyl acetate to give the acid (**24**) (nc), colourless powder, m.p. 99-103°C. Analysis: Found: C, 59.95; H, 5.8%. $C_{13}H_{15}F_3O_2$ requires C, 60.0; H, 5.8%; $\nu_{max.}$ (Nujol) 1690 cm^{-1}; δ_H ($CDCl_3$) 1.12 (6H, s), 1.77 (6H, s), 3.10 (1H, d, *J* 3 Hz) and 3.22 (1H, brd, *J* 3 Hz).

3-Trifluoromethyl-5,6,7,7-tetramethyl-2-valerylbicyclo[2.2.1]hepta-2,5-diene (25)

To the carboxylic acid (**24**) (100 mg, 0.42 mmol) in ether (2 ml) was added dropwise a hexane solution of n-butyllithium (0.57 ml, 0.91 mmol) at 0°C under Ar. This solution was stirred at room temperature for 1h, then diluted with ether, and poured onto ice. The mixture was acidified with 10% HCl and extracted with ether. The extract was washed with brine, dried, and evaporated to dryness. The residue was applied on a preparative t.l.c. to provide the ketone (**25**) (nc) as a pale yellow oil (53.4 mg, 46%); $\nu_{max.}$ (neat) 1690 and 1440 cm^{-1}; δ_H($CDCl_3$) 0.92(3H, t, *J* 6 Hz), 1.10 (3H, s), 1.14 (3H, s), 1.22-1.66(4H, m), 1.76 (6H, s), 2.62 (2H, t, *J* 6 Hz), 3.02 (1H, d, *J* 3 Hz), and 3.08 (1H, d, *J* 3 Hz); $\lambda_{max.}$ (EtOH) 240 nm (log ε 5.5). Semicarbazone, needles from aqueous ethanol, m.p. 95-99°C. Analysis: Found: C, 60.6; H, 7.35; N, 11.6%. $C_{18}H_{26}F_3N_3O$ requires C, 60.5; H, 7.3; N, 11.75%.

3-Trifluoromethyl-1,4-dimethyl-5,6-diphenylbicyclo[2.2.1]hepta-2,5-diene-2-carboxylic acid (26)

A mixture of the ester (**18**) (722 mg, 1.81 mmol) and KOH (200 mg) in dimethylsulphoxide (2 ml) - H_2O (1 drop) was refluxed for 30 min. The solution was washed with ether, acidified with 10% HCl and extracted with ether. The extract was washed with brine, dried and concentrated to dryness. Chromatography on silica gel gave a solid (592 mg, 83%), which on recrystallisation from benzene yielded the acid (**26**) (nc) as colourless prisms, m.p. 135-137 ℃. Analysis: Found: C, 72.0; H, 4.9%. $C_{23}H_{19}F_3O_2$ requires C, 71.9; H, 5.0%; $\nu_{max.}$ (Nujol) 1690 and 1635 cm^{-1}; δ_H ($CDCl_3$) 1.48 (3H, s), 1.50 (3H, brq, *J*, 1 Hz), 2.42 (2H, brs), and 6.92-7.28 (10H, m).

2-Acetyl-3-trifluoromethyl-1,4-dimethyl-5,6-diphenylbicyclo[2.2.1]hepta-2,5-diene (28)

A solution of the acid (**26**) (200 mg, 0.52 mmol) and thionyl chloride (2 ml) in benzene (4 ml) was refluxed for 2h. The mixture was concentrated to dryness. Chromatography on silica gel short column with benzene-hexane (1 : 3) as eluant yielded the acid chloride (**29**) (191.1 mg, 91%); $\nu_{max.}$ (neat) 1780 cm^{-1}. To a tetrahydrofuran solution (3.7 ml) of $RhCl(CO)(PPh_3)_2$ [10] (331 mg, 0.48 mmol) was added 1.6 M etheral solution of methyllithium (0.3 ml, o.48 mmol) at -80°C under Ar and the mixture was stirred for 1h. To this mixture was added dropwise the above acid chloride (**29**) in tetrahydrofuran (0.5 ml). After stirring for 2h the solution was diluted with hexane (5 ml) and stirred at 0 °C for 3h. The precipitate was filtered off, washed with hexane, and the filtrate was concentrated in vacuo. Chromatography on silica gel with hexane-ethyl acetate (30 : 1) as eluant yielded the ketone (**28**) (77 mg, 44%), m.p. 89-92 °C (Pale yellow prisms from hexane). Analysis: C, 75.2; H, 5.5%. $C_{24}H_{21}F_3O$ requires C, 75.4; H, 5.5%; $\nu_{max.}$ (Nujol) 1700 and 1620 cm^{-1}; δ_H ($CDCl_3$) 1.35 (3H, s), 1.48 (3H, q, *J*, 1 Hz), 2.31 (3H, q, *J* 1 Hz), 2.32 (2H, brs), and 7.26-7.14 (10H, m); $\lambda_{max.}$ (EtOH) 282 nm (log ε 5.8).

Photolysis of ketonorbornadienes

A benzene-d_6 (pre-treated with alumina Woelm B, Akt I) solution of a ketone having a 30 mmol/l concentration was prepared in a Pyrex tube and was irradiated with a 200 W high pressure Hg arc lamp for 1h. Judging from n.m.r. and t.l.c., the starting ketone was completely consumed and only the formation of the corresponding quadricyclane was observed.

5-Trifluoromethyl-3,3,6,7-tetramethyl-1-varelyltetracyclo[3.2.0.$0^{2,7}$.$0^{4,6}$]heptane **(30)** (nc)

δ_H (benzene-d_6) 0.84 (3H, s), 0.84(3H, t, *J* 6 Hz), 0.92 (3H, s), 1.04-1.36 (4H, m), 1.12 (3H, q, *J* 1 Hz), 1.20 (3H, s), 1.58 (1H, d, *J* 4 Hz), 1.66 (1H, d, *J* 4 Hz), and 2.22 (2H, t, *J* 8 Hz).

1-Acetyl-5-trifluoromethyl-2,4-dimethyl-6,7-diphenyltetracyclo[3.2.0.$0^{2,7}$.$0^{4,6}$]heptane **(31**) (nc)

δ_H (benzene-d_6) 0.49 (3H, brs), 1.03 (3H, s), 1.22 (2H, brs), 2.09 (3H, q, *J* 1 Hz) and 6.85-7.15 (10H, m).

Reversion of quadricyclanes

(i) Half-lives of the quadricyclanes **(30)** and **(31)** in benzene-d_6 were determined by n.m.r. at ambient temperature.

(ii) When trace amounts of trifluoroacetic acid was added to a solution of the quadricyclane in benzene-d_6, an acid-catalyzed reversion [1 ,3] spontaneously occured to give the original norbornadiene as a sole product.

FOOTNOTES

[A] The term 'donor-acceptor norbornadiene' was initially introduced by Yoshida [2g].

[B] The alcohol **(1)** was prepared according to Midland's procedure [4] and was used without further purification for the synthesis of **(2)** and **(3)**.

[C] Among four theoretically possible isomers **(22a,b)** and **(23a,b)**, two isomers were actually formed under the conditions of entry 9. These were not separated but the ratio of the amount of these isomers were determined by n.m.r. spectroscopy (see the experimental section).

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