

1,2-Photoaromatization: Entry into the Tetracyclo[4,2,0,0^{2,4},0^{3,5}]oct-7-ene System

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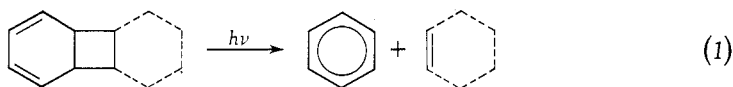
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Abstract

The synthesis of 1,2,3,4,5,6-hexakis(trifluoromethyl)tetracyclo[4,2,0,0^{2,4},0^{3,5}]oct-7-ene is described by a three-step sequence involving the application of a photofragmentation reaction in the final step.

It is well established that fluorine or trifluoromethyl substituents enhance the thermal stability of strained alicyclic systems. A number of recent syntheses attest to this fact,¹⁻³ especially in the C_nH_n carbocyclic framework, although some of the C₄H₄ network have yet to yield to this, or any other, synthetic stratagem.⁴

This communication deals with a member of the C₈H₈ series, namely 1,2,3,4,5,6-hexakis(trifluoromethyl)tetracyclo[4,2,0,0^{2,4},0^{3,5}]oct-7-ene (5; R = H). The present synthesis utilizes our 1,2-photoaromatization reaction, shown schematically in equation (1). Since our initial enunciation of the synthetic potential of this reaction,⁵ numerous examples of its application to synthesis have appeared. The present example joins a growing list⁶⁻¹⁸ of highly strained and/or reactive molecules which have yielded to this method. These include dihydrobarrelenes,⁷⁻⁹ barrelene,⁹ benzo-barrelenes,^{10,11} four-membered heterocycles¹³⁻¹⁵ and cyclobutadienes.¹⁶⁻¹⁸



¹ Barlow, M. G., Haszeldine, R. N., and Hubbard, R., *J. Chem. Soc. C*, 1970, 1232.

² Kobayashi, Y., Kumadaki, I., Ohsawa, A., Hanzawa, Y., and Honda, M., *Tetrahedron Lett.*, 1976, 2545.

³ Pelosi, L. F., and Miller, W. T., *J. Am. Chem. Soc.*, 1976, **98**, 4311.

⁴ Warrener, R. N., Nunn, E. E., and Paddon-Row, M. N., *Tetrahedron Lett.*, 1976, 2639.

⁵ Anderson, C. M., Bremner, J. B., Westberg, H. H., and Warrener, R. N., *Tetrahedron Lett.*, 1969, 1585.

⁶ Kobayashi, Y., Kumadaki, I., Ohsawa, A., Hanzawa, Y., and Honda, M., *Tetrahedron Lett.*, 1976, 2703.

⁷ Nunn, E. E., Wilson, W. S., and Warrener, R. N., *Tetrahedron Lett.*, 1972, 175.

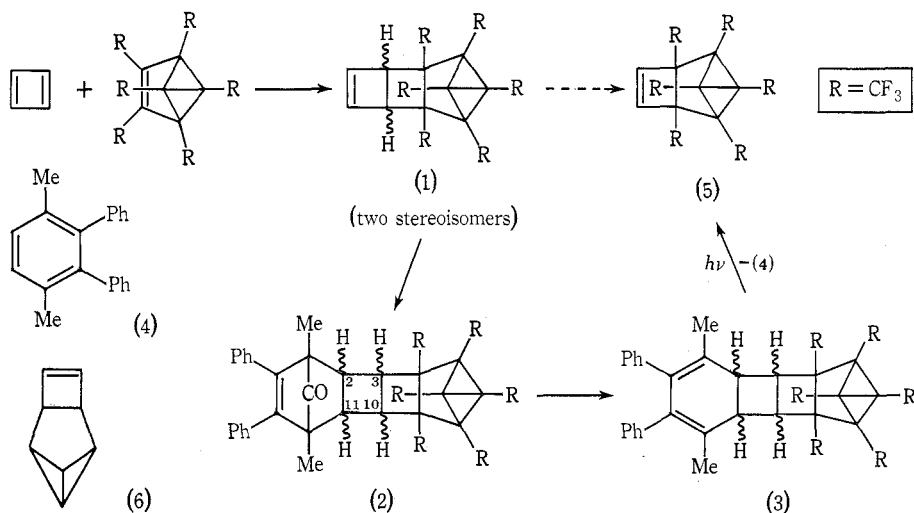
⁸ Butler, D. N., and Snow, R. A., *Can. J. Chem.*, 1974, **52**, 447.

⁹ Dauben, W. G., Rivers, G. T., Twig, R. J., and Zimmerman, W. T., *J. Org. Chem.*, 1976, **41**, 887.

¹⁰ Nunn, E. E., Ph.D. Thesis, Australian National University, 1972.

¹¹ Nunn, E. E., and Warrener, R. N., *Synth. Commun.*, 1972, **2**, 67.

Previously two routes to this ring system have appeared in the literature. The first was utilized in the synthesis of the parent member of this system (6).¹⁹ While this involved a multistep sequence it does appear a versatile route capable of extension to other examples. The second method used a sensitized photochemical [$\pi 2_s + \pi 2_s$] cycloaddition of dialkyl alkynes onto hexakis(trifluoromethyl)benzvalene to yield dialkyl derivatives (5; R = alkyl) of the present system,⁶ but it is significant that the reaction with acetylene was not reported.



Scheme 1

Pentacyclo[4.4.0.0^{2,4}.0^{3,5}.0^{7,10}]dec-8-ene (1) is available^{4*} as a mixture of stereoisomers from the cycloaddition of cyclobutadiene [generated by cerium(IV) oxidation of the cyclobutadiene tricarbonyl iron(II) complex] with hexakis(trifluoromethyl)benzvalene (Scheme 1). This mixture was used as the starting material for reaction with 2,5-dimethyl-3,4-diphenylcyclopenta-2,4-dienone which formed two 1 : 1 adducts (2) in excellent yield (92%). The stereochemistry of these adducts was not determined, since it was not critical to the subsequent steps. Photolysis was carried out in ether solution (Vycor filter) at 0°. Smooth conversion into the *o*-terphenyl (4) and tetracyclooctene (5) was achieved. The latter was purified by g.l.c., and obtained as a waxy solid. The structure of the product followed from the ¹H n.m.r. spectrum (singlet at δ 6.69) and the ¹⁹F n.m.r. spectrum [multiplets at δ 25.80, 20.20 (bicyclobutyl CF₃

* A recent X-ray analysis has shown²⁰ that our original stereochemical assignment was not correct.

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¹³ Nunn, E. E., and Warren, R. N., *J. Chem. Soc., Chem. Commun.*, 1972, 818.

¹⁴ Kretschmer, G., and Warren, R. N., *Tetrahedron Lett.*, 1975, 1335.

¹⁵ Kretschmer, G., Ph.D. Thesis, Australian National University, 1976.

¹⁶ Masamune, S., Nakamura, N., Suda, M., and Ona, H., *J. Am. Chem. Soc.*, 1973, **95**, 8481.

¹⁷ Maier, G., and Schneider, M., *Angew. Chem., Int. Ed. Engl.*, 1971, **10**, 809.

¹⁸ Maier, G., and Reisenauer, H. P., *Tetrahedron Lett.*, 1976, 3591.

¹⁹ Gream, G. E., Smith, L. R., and Meinwald, J., *J. Org. Chem.*, 1974, **39**, 3461.

²⁰ Kobayashi, Y., Kumadaki, I., Ohsawa, A., Hanzawa, Y., Honda, M., Miyashita, W., and Iitaka, Y., *Tetrahedron Lett.*, 1977, 1795.

groups), 14·90 (C 2,5-cyclopropyl CF₃), 11·18 (C 1,6-cyclobutyl CF₃)]. The lack of ultraviolet absorption ruled out the related valene structure.

Typical of poly(trifluoromethyl)-substituted alicyclics, this compound was particularly stable and could be recovered upon heating up to 300°C.

Experimental

1,12-Dimethyl-13,14-diphenyl-4,5,6,7,8,9-hexakis(trifluoromethyl)heptacyclo[10,2,1,0^{2,11},0^{3,10},0^{4,9},0^{5,7},0^{6,8}]pentadec-13-en-15-ones (2)

A mixture of the *syn* and *anti* cyclobutenes (1)⁴ (269 mg, 0·5 mmol), 2,5-dimethyl-3,4-diphenylcyclopenta-2,4-dienone dimer (130 mg, 0·25 mmol) and deuteriochloroform (0·4 ml) were sealed into a glass vial and heated in an oil bath at 100°. Reaction was complete after 8 h (p.m.r. analysis). The solution was evaporated to dryness, triturated with n-hexane to yield the *product* (367 mg, 92%) as colourless prisms. The mixture of isomers had m.p. 162–169° (Found: C, 52·5; H, 2·6; F, 42·9. C₃₅H₂₀F₁₈O requires C, 52·6; H, 2·5; F, 42·8%). P.m.r. (CDCl₃)—isomer A: δ 1·22 (s, 6H, C 1,12-Me), 2·64, 3·10 (br s, 2H, 2H, C 2,3,10,11-cyclobutyl); 6·9–7·4 (m, 10H, ArH); isomer B: δ 1·21 (s, 6H, C 1,12-Me), 2·75, 3·04 (br s, 2H, 2H, C 2,3,10,11 cyclobutyl), 6·9–7·4 (m, 10H, ArH).

I.r. (Nujol mull): ν_{max} 697ms, 767m, 1075ms, 1160–1390 (a series of unresolved absorption bands), 1768s, 1779s cm⁻¹. U.v. (EtOH): λ_{max} (ε) 260 nm (7700). Mass spectrum *m/e* 798 (M⁺, 7%), 779 (8), 770 (31), 258 (100).

1,2,3,4,5,6-Hexakis(trifluoromethyl)tetracyclo[4,2,0,0^{2,4},0^{3,5}]oct-7-ene (5)

A mixture of the abovementioned adducts (2) (200 mg, 0·25 mmol) was dissolved in dry ether (1·0 ml) under nitrogen in a thin quartz tube and irradiated at 0° with an American Hanovia (450 W) lamp and Vycor filter for 2 h. After this time c. 80% conversion into photoproducts had occurred. The ether was carefully removed at 0° by distillation under reduced pressure (12 mm), while sublimation of the residue at room temperature (0·05 mm) gave the colourless waxy crystalline *product* (5) (37 mg, 27%). An analytical sample was obtained by g.l.c. (Found: C, 32·6; H, 0·3. C₁₄H₂F₁₈ requires C, 32·8; H, 0·4%). P.m.r. (CDCl₃) δ 6·69 (s, C 7,8-vinyl H). ¹⁹F n.m.r. (ether) δ 11·18 (m, 6F, C 1,6-cyclobutyl CF₃), 14·90 (m, 6F, C 2,5-cyclopropyl CF₃), 20·20, 25·80 (m, m, 3F, 3F, C 3,4-bicyclobutyl CF₃). I.r. (CCl₄): ν_{max} 884m, 1073w, 1190m, 1209s, 1221ms, 1240s, 1316ms cm⁻¹. U.v.: no absorption above 225 nm. Mass spectrum *m/e* 511·9870 [M⁺, C₁₄H₂F₁₈ requires 511·9869] (12%), 493 (18), 443 (56), 424 (10), 405 (18), 374 (21), 355 (25), 305 (19), 69 (100).

Pyrolysis of 1,2,3,4,5,6-Hexakis(trifluoromethyl)tetracyclo[4,2,0,0^{2,4},0^{3,5}]oct-7-ene at 300°C

A small sample of the tetracyclooctene (c. 5 mg) was carefully sealed into a small glass tube (approximate volume 1 ml), and completely immersed in a Wood's metal bath at 300° for 2 min. G.l.c. (6 ft by 3/8 in column of 10% SE30 on Embacel, 75°) examination of the product showed that only one compound was present, whose retention time, infrared and ultraviolet spectra were identical to that of the starting material.