

PHOTOCYCLOADDITION REACTION OF HEXAKIS(TRIFLUOROMETHYL)BENZVALENE

Yoshiro Kobayashi, Itsumaro Kumadaki, Akio Ohsawa, Yuji Hanzawa,
and Masamitsu Honda

Tokyo College of Pharmacy, Horinouchi, Hachioji-shi, Tokyo 192-03, Japan

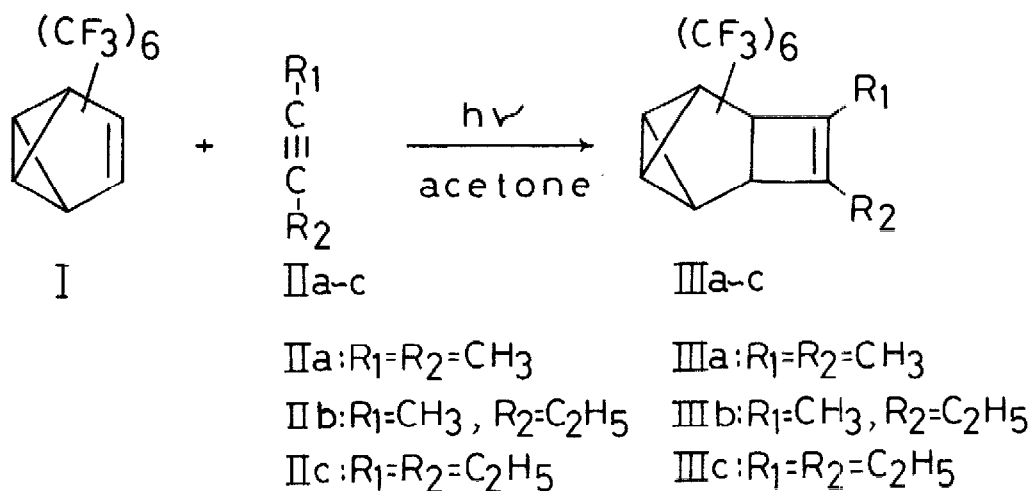
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Several reactions of hexakis(trifluoromethyl)benzvalene (I) are known,^{1,2,3,4,5,6)} but no photocycloaddition reaction of I has been reported. Furthermore, attempted photocycloaddition reaction of the unsubstituted benzvalene was unsuccessful.⁷⁾

In this paper, we report [2+2] photocycloaddition reaction of I with alkynes in the presence of acetone as a sensitizer. When an acetone solution of I in the presence of an excess of 2-butyne (IIa) was irradiated⁸⁾ for 40 hr, a cycloadduct (IIIa) was obtained in 60% yield, mp 168° (in a sealed tube, colorless needles from n-pentane); mass spectrum m/e 540 (M⁺); high mass spectrum calcd. for C₁₆H₆F₁₈: 540.018; found: 540.020; ir (CCl₄) 1560 cm⁻¹ (cyclopropane), 1205 cm⁻¹ (C-F); ¹H-nmr (CCl₄) δ 1.85 (6H, s); ¹⁹F-nmr (CCl₄) ppm⁹⁾ 1.0 (6F, m), -2.0 (6F, m), -7.2 (3F, m), -11.8 (3F, m). In a similar manner as above, 2-pentyne (IIb) (76 hr irradiation) and 3-hexyne (IIc) (116 hr irradiation) gave cycloadducts IIb and IIc, respectively; IIb was obtained in 46.3% yield, mp 141° (in a sealed tube, colorless solid from methanol); mass spectrum m/e 554 (M⁺); high mass spectrum calcd. for C₁₆H₈F₁₅ (M⁺-CF₃): 485.039; found: 485.040; ir (CCl₄) 1555 cm⁻¹ (cyclopropane), 1220 cm⁻¹ (C-F); ¹H-nmr (CCl₄) δ 1.17 (3H, t, J = 7.5 Hz), 1.83 (3H, s), 2.27 (2H, q, J = 7.5 Hz); ¹⁹F-nmr (CCl₄) ppm 1.6 (6F, m), -2.2 (6F, m), -7.2 (3F, m), -12.4 (3F, m). IIc was obtained in 34.0% yield, mp 101° (in a sealed tube, colorless needles from methanol); mass spectrum m/e 568 (M⁺); high mass spectrum calcd. for C₁₇H₁₀F₁₅ (M⁺-CF₃): 499.052; found: 499.054; ir (CCl₄) 1560 cm⁻¹ (cyclopropane), 1230 cm⁻¹ (C-F); ¹H-nmr (CCl₄) δ

1.17 (6H, t, $J = 7.5$ Hz), 2.30 (4H, q, $J = 7.5$ Hz); ^{19}F -nmr (CCl_4) ppm 1.2 (6F, m), -2.2 (6F, m), -7.4 (3F, m), -12.4 (3F, m).

As the size of substituent R increased, reaction rate and yield of cycloadduct decreased and those of the isomerization of I to hexakis(trifluoromethyl)benzene (IV) increased. The products having C_8 unit are very interesting compounds. Meinwald et al.⁷⁾ synthesized a similar C_8 unit compound starting from benzvalene through four steps. Our compounds are much easier to obtain and we are going to utilize these products synthetically.



References

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- 8) USIO UM-102 (100w) high pressure lamp in a pyrex tube.
- 9) Benzotrifluoride: +0 ppm as an internal standard.