

SYNTHESIS AND PROPERTIES OF METHYL 7-TRICYCLO[4.2.2.0^{1,6}]DECA-2,4,7,9-
TETRAENECARBOXYLATE

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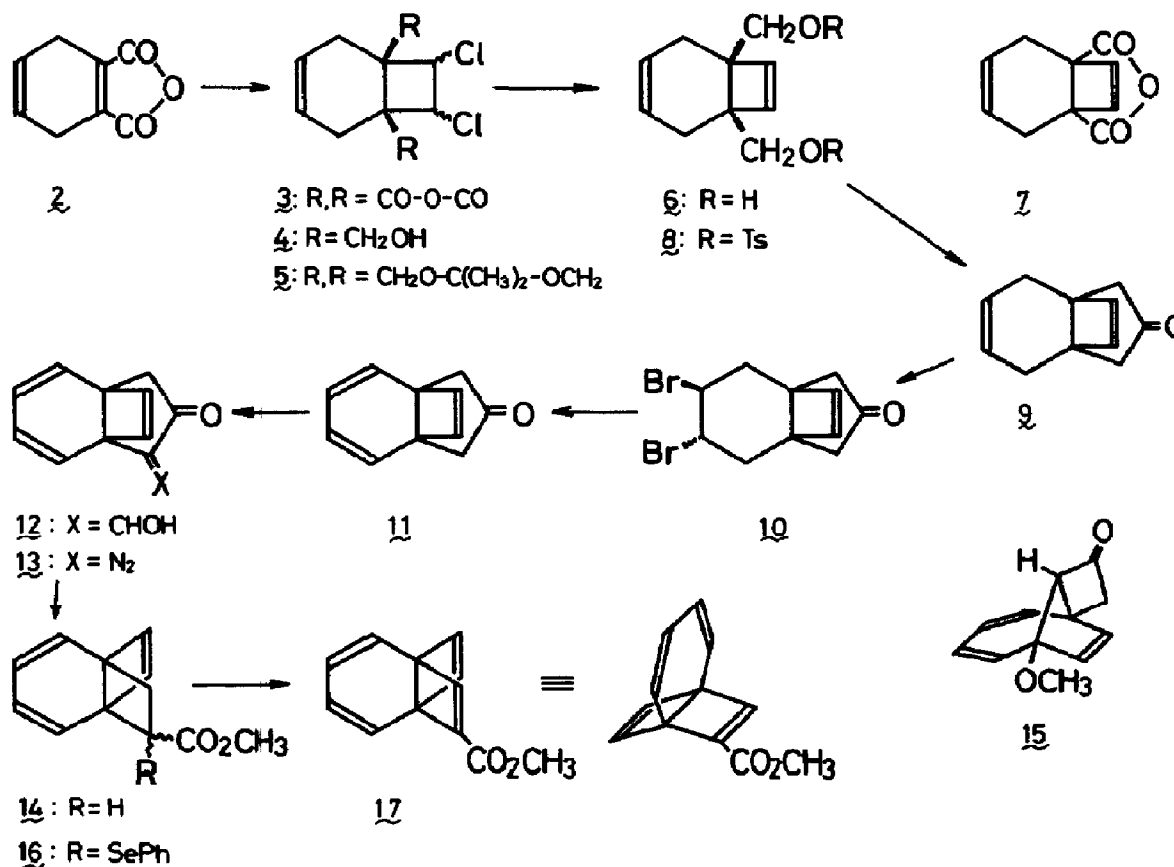
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Summary: Synthesis of methyl 7-tricyclo[4.2.2.0^{1,6}]deca-2,4,7,9-tetraenecarboxylate which possesses a novel carbon framework, a Dewar benzene bridged at C-1 and C-4 with 1,3-butadienylene, and its chemical properties have been reported.

Polycyclic unsaturated compounds have been extensively investigated in recent years and have provided important informations on the hydrocarbon chemistry. We report here preparation and characterization of methyl 7-tricyclo[4.2.2.0^{1,6}]deca-2,4,7,9-tetraenecarboxylate, **1**, which possesses a hitherto unknown carbon framework, i.e. a Dewar benzene bridged at C-1 and C-4 with 1,3-butadienylene, **1**.

Although some synthetic methods of Dewar benzene derivatives were known¹ when we undertook the preparation, a novel route was developed since they were not suited or not applicable for the synthesis of the present compound. Photocycloaddition of 1,2-dichloroethylene² to readily accessible 3,6-dihydrophthalic anhydride,³ **2**, with benzophenone as sensitizer afforded three isomeric products, a trans- and two cis-dichloro adducts, **3**, irrespective of the geometry of the dichloroethylene employed. Subsequent reactions (LiAlH₄ reduction of **3**, acetalization of **4** with (CH₃)₂C(OCH₃)₂/TsOH as elimination of chlorine from **5**), however, could be carried out without separating those isomers since reductive eliminations of chlorine with Na/liq NH₃⁴ from both the cis- and trans-dichloro derivatives of **5** cleanly afforded **6**, mp 103-104 °C, in almost quantitative yields after hydrolysis of the acetal. The diol, **6**, could also be obtained through photocycloaddition of acetylene to **2**⁵ followed by LiAlH₄ reduction of the resulting adduct, **7**. The former procedure was somewhat more laborious than the latter, but was superior in the over-all yield. The diol was treated with 5 mol equiv of tosyl chloride⁶ in pyridine to give the bistosylate, **8**, mp 101-102 °C, in 92% yield. Reaction of **8** with methylthiomethyl methyl sulfoxide (FAMSO)-ⁿBuLi in THF⁷ and treatment of the resulting cyclization product with acidic aq EtOH furnished **9** in 70% yield: **9**, mp 46.5-47.5 °C; nmr (CCl₄), δ 1.9-2.5 (m, 8H), 5.7-5.9 (m, s at δ 5.83, 4H); uv(EtOH), λ_{max} 283 nm (ε=21); ir(KBr), 1730 cm⁻¹. Bromination of **9** with a mol. equiv of pyridinium





bromide perbromide in CH_2Cl_2 in the presence of a small amount of pyridine produced **10** in 95% yield. Apparently, bromine addition to the cyclobutene ring in **2** was not important under the above reaction conditions.⁸ Dehydrobromination of the bromide with $Li_2CO_3-LiCl/HMPA$ at 80 °C proceeded smoothly giving **11** as a colorless oil in 91% yield: **11**, bp 66-68 °C/2 mmHg; nmr(CCl_4), δ 2.40 (AB q, $J=17$ Hz, 4H), 5.7-6.0 (m, 4H), 6.04 (s, 2H); uv(EtOH), λ_{max} 215 ($\epsilon=2490$), 220 (2550), 226^{sh} (2070), 267 (2700); ir(neat), 1740 cm^{-1} ; 2,4-dinitrophenylhydrazone mp 224-225 °C (dec). Successive treatment of **11** with HCO_2Et/CH_3ONa in benzene and then with tosyl azide in ether⁹ gave the α -diazoketone, **13**, in 64% yield as pale yellow oil, which could be purified by chromatography on Florisil: **13**, ir(CCl_4), 2075, 1680 cm^{-1} . Photolysis of **13** with a high-pressure Hg lump in dry methanol containing a small amount of triethylamine led to the formation of the Wolff rearrangement products, **14** (11%), together with a minor side product, to which the structure represented by **15** (6%) was ascribed on the basis of its spectroscopic property: **15**, nmr(CCl_4), δ 2.8-3.3 (m, 3H), 3.36 (s, 3H), 5.02 (d, $J=5.2$ Hz, 1H), 5.42 (d, $J=5.2$ Hz, 1H), 5.8-6.3 (m, 4H); ir(CCl_4), 1790 cm^{-1} .

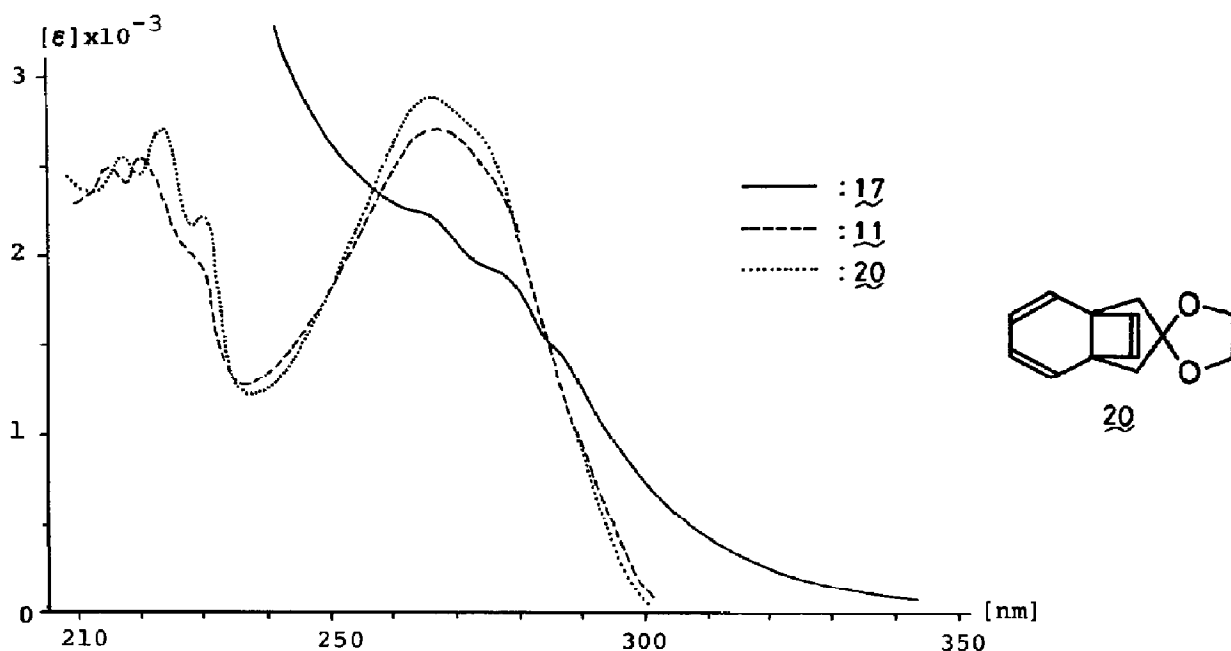
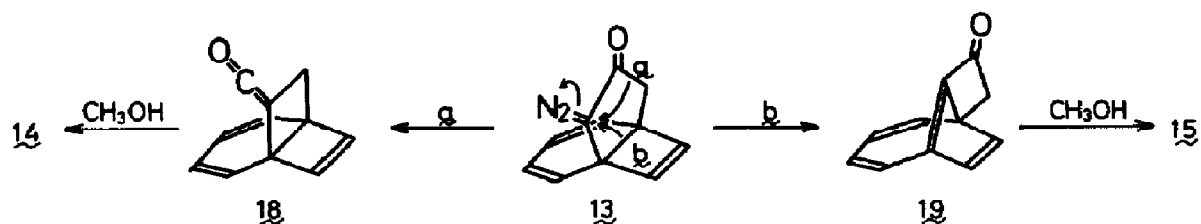


Fig. 1. The uv absorption spectra of 11, 17 and 20 in EtOH.

Formation of 15 may be rationalized, formally at least, in terms of the migration of the strained central bond, b, which competes with the Wolff rearrangement (rearrangement of bond, a) and the subsequent addition of methanol to the resulting presumably highly strained anti-Bredt enone, 19.

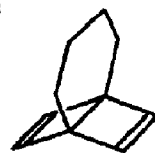


Treatment of 14 with lithium diisopropylamide in THF and reaction of the lithiated compound with diphenyldiselenide¹⁰ yielded 81% of the α -phenylseleno 16. Oxidation of 16 in CH_2Cl_2 with aq H_2O_2 and fragmentation of the selenoxide led to 69% of methyl 7-tricyclo[4.2.2.0^{1,6}]deca-2,4,7,9-tetraenecarboxylate, 1 bp $\sim 85^\circ\text{C}/1.5\text{ mmHg}$; ^{13}C -nmr(CDCl_3), δ 51.4, 53.1, 55.0, 121.6, 122.4, 122.5, 123.7, 142.2, 143.0, 145.7, 150.7, 162.2; ^1H -nmr(CCl_4), δ 3.65 (s, 3H), 5.5-6. (m, 4H), 6.32 (d, $J=2.2\text{ Hz}$, 1H), 6.49 (d, $J=2.2\text{ Hz}$, 1H), 6.91 (s, 1H); uv(EtOH) λ_{max} 212 ($\epsilon=6640$), 264^{sh} (2250), 274^{sh} nm (2040); ir(CCl_4), 1720 cm^{-1} .

The uv spectra of 17 and the related compounds, 11 and 20, are shown in Fig. 1. In contrast to the spectra of 11 and 20 which show absorption maxima at 260 to 267 nm and following steep drops in intensity at 280 to 300 nm, the absorption of 17 extends to 350 nm. Since Dewar benzene does not show an absorption at such a long wavelength,¹¹ the above observation suggests the presence of electronic

interaction through the three π -bond systems in **17**.

The thermal stability of **17** in which the aromatization of the Dewar benzen skeleton is blocked by the bridge substituted at the 1,6-positions is remarkably high and **17** decomposes only at 200 °C in dimethoxyethane¹⁴ with a measurable rate ($t_{1/2} \approx 10$ h). The thermolysis of **17** under the above conditions led to 21% of methyl 1- and 2-naphthalenecarboxylate (1-/2- =9) as the major products, together with a few minor unidentified products.



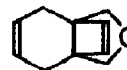
21

It is noteworthy that **17** is thermally far more stable than **21**, an analogue possessing a saturated side chain, the half-life of which has been reported to 26 min at 140 °C.¹⁵ This might be attributable to the electronic stabilization of **17** due to the longicyclic interaction among the three π -electron systems¹⁶ or to the increased rigidity of the framework of **17** compared to that of **21**, which might render the skeletal rearrangement in **17** more difficult.

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REFERENCES AND NOTES

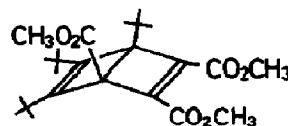
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- (11)



22



$\lambda_{\max}(\text{vapor})$ 205 nm.¹²



$\lambda_{\max}(\text{EtOH})$ 238^{sh} nm
($\epsilon=2800$).¹³

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