isomeric alcohols 3 and 4 by a large excess of RuO_2 hydrate at room temperature gave, of course, the corresponding aldehydes 5 and 6 with high stereospecificity.

The dehydrogenation of the other alcohols were further studied. Thus, prenol (7) was converted to senecioaldehyde (8) in a 76% yield by O_2/RuO_2 (Scheme II). Secondary allylic alcohols such as carveol (9) and β-ionol (10) were also selectively oxidized to carvone (11) (O_2/RuO_2: 34% conversion, >95% selectivity) and β-ionone (12) (Ar/RuO_2: 98% conversion, 80% selectivity), respectively. However, the secondary alcohols were less reactive than the primary ones in the reaction system described here. This trend is also observed in the oxidations with MnO_2 and seems common to dehydrogenation of allylic alcohols by ruthenium irrespective of its valence state.[9]

Saturated alcohols were scarcely oxidized by RuO_2 or O_2/RuO_2. Activated alcohols such as α-keto alcohols and α-hydroxy lactones were dehydrogenated by using the present oxidation system, though they required the rigorous reaction conditions (>100 °C). Consequently, the reactivity order of the alcohols toward RuO_2 or O_2/RuO_2 was shown to be as follows: primary allylic alcohols > secondary allylic alcohols > α-keto alcohols and α-hydroxy lactones > saturated alcohols.

For the dehydrogenation of allylic alcohols, we used hydrated RuO_2. On the contrary, anhydrous RuO_2 was found to effect neither the stoichiometric nor catalytic oxidation of alcohols. Hydrated RuO_2 has been reported to be significantly different from the anhydrous form.[10] The former is formulated as $RuO_{2+x}\cdot yH_2O$ [values of x up to 0.12 (chemisorbed oxygen) have been found whereby y is often 1 to 1.3] and possesses a large surface area (200 m^2/g). On the other hand, anhydrous RuO_2 has little chemisorbed oxygen and a small surface area (4 m^2/g). These differences might decisively affect the activity of RuO_2 in the oxidation of allylic alcohols.

Registry No. 1, 104-54-1; 2, 14371-10-9; 3, 106-24-1; 4, 106-25-2; 5, 141-27-5; 6, 106-26-3; 7, 556-82-1; 8, 107-86-8; 9, 99-48-9; 10, 472-80-0; 11, 99-49-0; 12, 79-77-6; 2,6-di-*tert*-butyl-*p*-cresol, 128-37-0.

Supplementary Material Available: Representative experimental procedures of 1 (1 page). Ordering information is given on any current masthead page.

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Synthesis of Tris-Annelated Benzenes Incorporating a Three-Membered Ring

Summary: Tris-annelated benzenes incorporating a three-membered ring can be prepared by dehydrohalogenation of the Diels–Alder adducts of 1,1′-bicycloalkenes and 1-bromo-2-chlorocyclopropene (7).

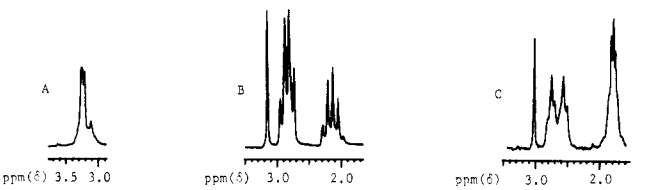
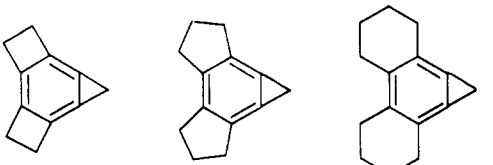


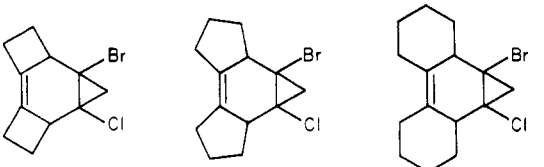
Figure 1. 90-MHz ^1H NMR spectra of 1 (A), 2 (B), and 3 (C) in $CDCl_3$.

Sir: Although tricyclobutabenzene has been reported,[2] tris-annelated aromatics incorporating a three-membered ring are unknown.[3] We report here the synthesis of dicyclobutacyclopropabenzene[4] (1) and the homologues 2 and 3.



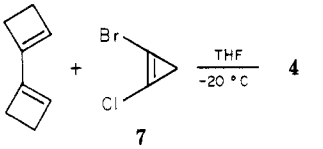
1 2 3

The synthesis of compounds 1–3 relies on the aromatization of the Diels–Alder adducts 4–6,



4 5 6

respectively, which can be prepared readily from 1-bromo-2-chlorocyclopropene (7)[5] and the appropriate diene. Thus cycloaddition of 1,1′-bicyclobutenyl (8)[6] and 7



8 7

in tetrahydrofuran at −20 °C for 48 h yielded 4 in 19% yield. Gas chromatography suggests that 4 is predominantly one isomer.

Dehydrohalogenation of 4 using potassium *tert*-butoxide in tetrahydrofuran at 25 °C for 1.5 h yielded 1 in 53% yield. The hydrocarbon was concentrated in vacuo and purified by sublimination from the reaction flask at 10-m torr and 25 °C. A solution of 1 in $CDCl_3$ could be stored at −20 °C for several days without decomposition, but it decomposed after ~36 h at 25 °C. The cyclopropenyl protons of 1 resonate at δ 3.1 and the cyclobutenyl methylenes at δ ~3.15–3.4 (Figure 1, spectrum A). The characteristic infrared band resulting from the combination of a three-membered ring skeletal vibration with the aromatic double bond stretch appears at 1664 cm^{-1}. The ultraviolet spectrum (pentane) has absorptions at λ_{max} 247 (ε 400), 268 (420), and 275 nm (400). It is interesting that the position of these absorption maxima are close to those reported [λ_{max} (hexane) 264, 270, 271.5 nm] for nonlinear

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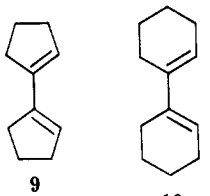
cyclobutacyclopropabenzene.[8] In contrast, a sizeable bathochromic shift is observed for the linear isomer [λ_{max} (cyclohexane) 284, 287.5, 294 nm]. Elemental analysis was provided by high-resolution mass spectrometry: calcd for $C_{11}H_{10}$ m/e 142.0783, found m/e 142.0785.

The dienes **9** and **10**, required for the synthesis of precursors **5** and **6**, can be prepared from the simple two-step



9 **10**

pinacol approach described by Greidinger and Ginsberg.[9] Dehydrohalogenation of **5** yielded **2** in 55% yield. The NMR spectrum is diplayed in Figure 1 (spectrum B). Other spectral properties are as follows: IR (CCl_4) 1651 cm^{-1}; UV (pentane) λ_{max} 270 (ϵ 920), and 279 nm (960); calcd for $C_{13}H_{14}$ m/e 170.1096, found m/e 170.1092.

Under similar conditions **6** yielded **3** in 83% yield; NMR (Figure 1, spectrum C); IR (CCl_4) 1660 cm^{-1}; UV (pentane) λ_{max} 273 (ϵ 908), 283 nm (915); calcd for $C_{15}H_{18}$ m/e 198.1408, found m/e 198.1406.

The results of studies on the chemical and physical properties of these cycloproparenes will be reported later.

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Registry No. **1**, 90968-12-0; **2**, 90968-13-1; **3**, 90968-14-2; **4**, 90968-15-3; **5**, 90968-16-4; **6**, 90968-17-5; **7**, 88180-95-4; **8**, 69573-29-1; **9**, 934-02-1; **10**, 1128-65-0.

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A Safe Facile Synthesis of Difluorophosphonoacetic Acid

Summary: Copper(I) halide catalyzed acylation of [(diethoxyphosphinyl)difluoromethyl]zinc bromide with ethyl chloroformate provides a safe, easily scaled up preparation of ethyl difluoro(diethoxyphosphinyl)acetate from readily available precursors. Silyation of this ester, followed by hydrolysis, gives difluorophosphonoacetic acid.

Sir: Pronounced biological effects are often observed when hydrogen atoms in a biologically active molecule are replaced by fluorine.[1,2] Recently, we,[3,4] as well as others,[5]

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Scheme I

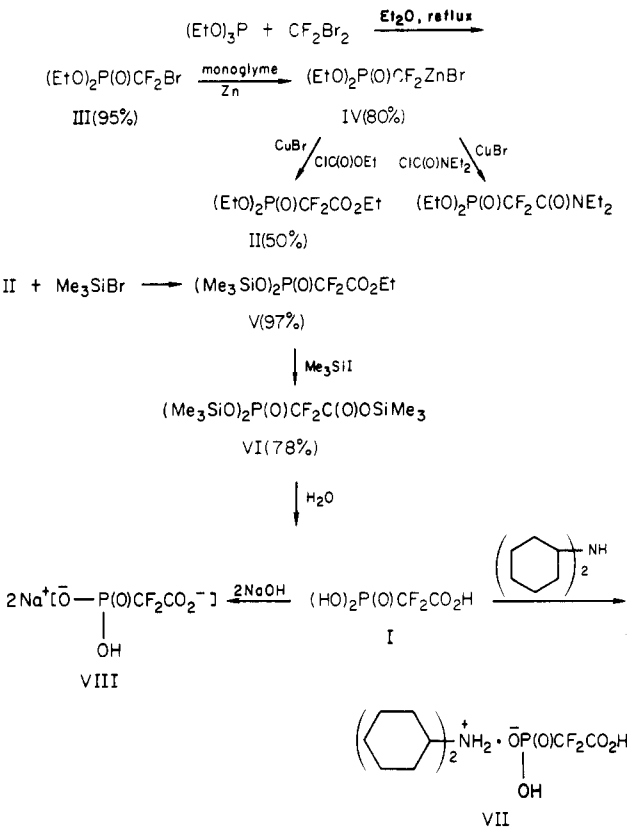

Table I. Ionization Constants

	$(HO)_2P(O)$-CF_2CO_2H	$(HO)_2P(O)$-CH_2CO_2H[22]	$(HO)_2P(O)$-$CF_2P(O)(OH)_2$[4]
pK_{a_1}	1.30 ± 0.10	2.0	1.46 ± 0.15
pK_{a_2}	1.95 ± 0.03	5.11 ± 0.04	2.14 ± 0.05
pK_{a_3}	6.16 ± 0.02	8.69 ± 0.05	5.78 ± 0.05
pK_{a_4}			8.16 ± 0.02

have been interested in fluorinated analogues of biologically important phosphonic acids. Thus, our attention was drawn to a comparison of the biological and chelation properties of phosphonoacetic acid[6-8] and difluorophosphonoacetic acid (I). Unfortunately, the preparation of I has not been described; only a poorly characterized ester of I has been reported[9] in low yield via the reaction of triethyl phosphite and tetrafluoroethylene oxide.[10]

We now report a safe, facile, easily scaled up preparation of ethyl difluoro(diethoxyphosphinyl)acetate (II) from readily available precursors (cf. Scheme I).

Diethyl (bromodifluoromethyl)phosphonate (III) is readily prepared from triethyl phosphite and dibromodifluoromethane.[11] Reaction of III with zinc dust gives the

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(9) Ginsburg, V. A.; Vasuk'eva, M. N. *Zh. Obshch. Khim.* **1967**, *37*, 2483 (English Translation, 2371).
(10) The ester was obtained in only 14% yield (impure). The major product of this route is the toxic diethyl fluorophosphate [$(EtO)_2P(O)F$]. Also, tetrafluoroethylene oxide is an explosive reagent and should be handled with caution.
(11) Burton, D. J.; Flynn, R. M. *J. Fluorine Chem.* **1977**, *10*, 329.

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