A Cyclopropabenzenylidenethenone (Propadienone) via a New Route to Alkylidenecycloproparenes

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Cyclopropabenzenylidenethenone (Propadienone) via a New Route to Alkylidenecycloproparenes

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ABSTRACT
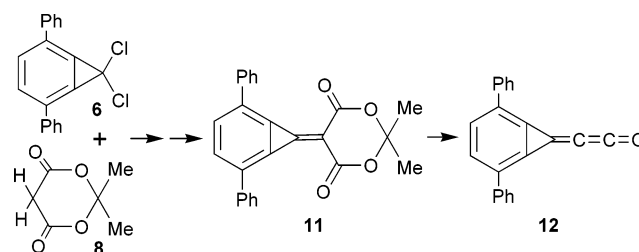
Reaction of 1,1-dichloro-2,5-diphenylcyclopropabenzene 6 with Meldrum's acid 8 in the presence of pyridine leads to coupling of the cycloproparenyl cation 7 with the stabilized diketo anion 9. Subsequent, spontaneous, base-induced dehydrochlorination gives the alkylidenecyclopropabenzene 11 in a one-pot reaction. Flash vacuum thermolysis of 11 at 650 °C ejects acetone and carbon dioxide, giving cyclopropabenzenylidenethenone 12 that is isolated in an Ar matrix at 20 K and characterized by a strong ketene band at 2107 cm^{-1} in the IR spectrum.

The class of strained aromatic hydrocarbons known as the cycloproparenes and illustrated by parent 1*H*-cyclopropabenzene **1** has provided much fascinating chemistry[1] in its 40-year history.[2] The pK_a of **1**, estimated[3] as ca. 36, has meant that C1 cycloproparenyl anions can be generated with comparative ease and used in synthesis to give, among others,[4] exocyclic alkenes, e.g., **2**, via Peterson olefination.[1,5,6] In contrast, 1-oxocycloproparenes, e.g., **3** (cycloproparenones),
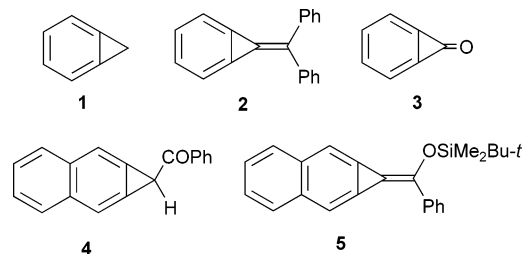
are unstable in solution[7] and either decarbonylate or ring-open above −50 °C, so their use in such olefinations with more readily available carbanions is precluded. Thus, until very recently, this one pathway has restricted the range of

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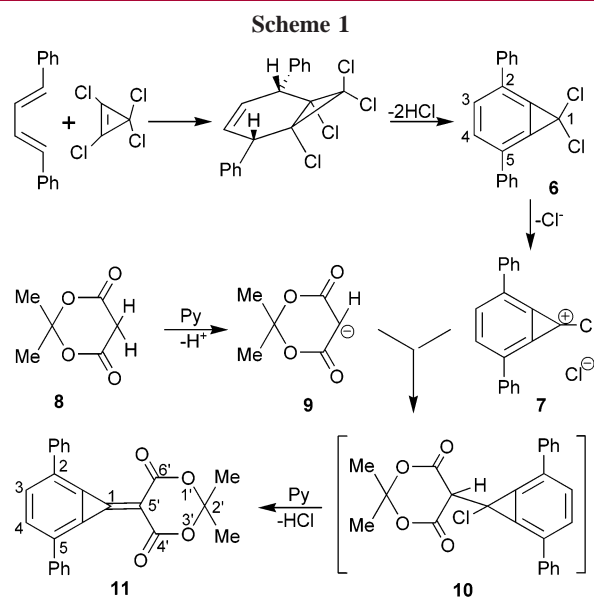(4) Halton, B.; Jones, C. S.; Northcote, P. T.; Boese, R. *Aust. J. Chem.* **1999**, *52*, 285−290.
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available cycloproparenes carrying an exocyclic C1 substituent. A second route via enolization of 1-acylcycloproparenes allowed the formation of a limited number of derivatives[8] through enolate capture at oxygen, e.g., **4 → 5**. We now report a new synthesis of alkylidene-substituted cycloproparenes that reverses the electron requirements of the Peterson protocol by coupling a cycloproparenyl cation with the anion derived from an active methylene compound. Furthermore, the target alkylidenecycloproparene **11** was chosen so as to provide easy entry to cyclopropabenzen-1-ylidenethenone **12**, the first propadienone to be formed directly from a preformed cycloproparene skeleton.

Many years ago, one of us recorded[9] what remains the highest yielding synthesis of a cycloproparene, namely, that of the 1,1-dichloro derivative **6**, from double dehydrochlorination of the Diels−Alder adduct between 1,4-diphenylbuta-1,3-diene and tetrachlorocyclopropene (Scheme 1). Subsequently, we[10] and others[11] demonstrated the ioniza-

reagents to give new cycloproparenes[13] functionalized at C1, there has been no other report of use of the cycloproparenyl cation in coupling reactions.[1]

Meldrum's acid[14] **8** is deprotonated easily at the active methylene site[15] often by use of pyridine in an appropriate solvent.[16] Since the *gem*-dichloride **6** undergoes easy ionization, it occurred to us that the interaction of cation **7** with a stabilized secondary carbanion should give the corresponding exocyclic alkene from coupling and subsequent dehydrochlorination. Such a sequence would provide an alternative synthesis of alkylidenecycloproparenes from more commonly available anions. In the event, reaction of **6** with **8** in pyridine leads to coupling of cation **7** with anion **9** to give the novel alkylidenecycloproparene **11**. Although the yield of product is not high (22%), the olefin is formed directly from a one-pot operation in dichloromethane, with the base inducing spontaneous dehydrochlorination of initial adduct **10** (not detected) under the reaction conditions. Alkene **11** is a stable yellow microcrystalline solid that cocrystallizes with water as a hemihydrate and displays spectroscopic data that are fully consistent with its formulation.

The ^{1}H NMR spectrum of **11** shows distinct singlets for the pair of equivalent cycloproparenyl H3/H4 protons and the methyl groups (δ 8.42 and 1.82, respectively) in a 1:3 ratio. The aromatic singlet is significantly deshielded in comparison to its position in precursor **6** [δ 7.935], and the protons of the pendant phenyl rings provide coupled signals as expected by analogy with substrate **6**. The ^{13}C NMR spectrum of **11** has C3/C4 at a somewhat higher chemical shift (δ 137.5) than might be expected for the incorporation of ortho (and meta) phenyl groups when compared with the 133.2 datum[17] for the same carbons of **2**. The typically[1] shielded C2/C5 carbons adjacent to the three-membered ring fusion that appear at δ 110.7 in **2** are at δ 129.9 in **11**. This marked downfield shift is substantially larger than the ca. 13 ppm expected[18] from incorporation of an adjacent phenyl substituent and reflects the enhanced cationic character present in the cross-conjugated six-membered ring. Support comes from the appearance of C1 at δ 136.5 and C5′ at δ 85.9 in **11**, markedly downfield and upfield shifted, respec-

Scheme 1

tion of **6** and related compounds and characterized the derived cations, e.g., **7**, spectroscopically; cation **7** was also isolated as its hexachloroantimonate.[10] Despite the ionization and dimerization[12] of **7** and its reactions with organometallic

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tively, compared to their positions in **2** (δ 113.3 and 111.3, respectively) and other simple analogues.[1,5] This is completely in agreement with the polarized enedione substructure of **11** and the significant polarity that it imbues. The dipole moment of **11** has been measured, and at 5.08 D it is notably higher than those of simpler diarylmethylidene compounds (μ 1.0−3.5 D).[19] Moreover, the ca. 0.5 ppm deshielding experienced by H3/H4 (δ 8.42) compared with **6** (δ 7.94) is nicely consistent with this polarity in which the cyclopropanenyl moiety is the electron donor (Scheme 2).[19]

Scheme 2
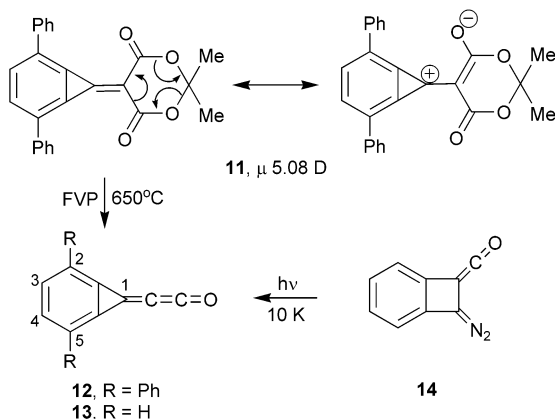
Subjection of **11** to flash vacuum thermolysis at 650 °C and 10^{-5} Torr leads to facile loss of CO_2 and Me_2CO (Scheme 2). As expected, the sought after propadienone, cyclopropabenzen-1-ylidenethenone **12** is formed and has been isolated in an Ar matrix at 20 K. The IR spectrum of **12** (Figure 1) shows a strong ketene stretch at 2107 cm^{-1}
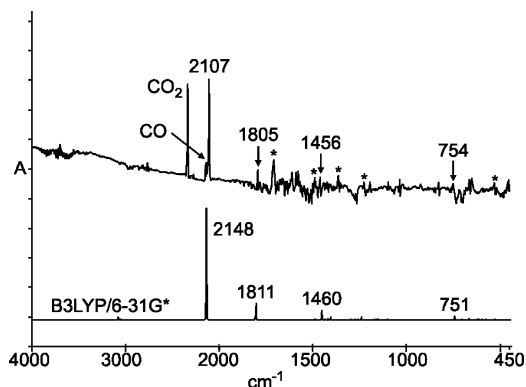

Figure 1. Measured and calculated (B3LYP/6-31G*) IR spectra of cyclopropabenzenylidenethenone **12**; * = peaks due to acetone [Supporting Information contains computational coordinates, energies, and a full-scale IR spectrum].

that matches well the 2148 value predicted from a B3LYP/6-31G* simulation. The ketene stretch is by far the most intense calculated band. Nevertheless, all the weaker bands

predicted computationally can be matched by weak bands in the experimental spectrum. The ketene stretch at 2107 cm^{-1} is nicely consistent with a band recorded at 2106 cm^{-1} that has been tentatively assigned to the parent **13** upon deazetation of **14**.

The intervention of **13** in photochemical decompositions of the bisdiazoketones **15** and **16** (Scheme 3) at cryogenic

Scheme 3
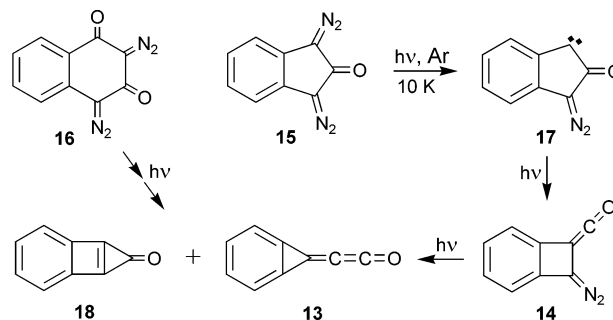
temperatures has been proposed by Tomioka and his group[20] and parallels some of the routes to cyclopropabenzenone.[7] Thus, initial nitrogen loss from **15** and Wolf-type rearrangement of the ensuing carbene **17** (characterized from its IR spectrum) provides diazo ketene **14**, which in turn loses N_2 in what is likely a second Wolf rearrangement to provide **13**; bis(diaza)dione **16** behaves similarly, and cyclopropenone **18** is the other product from both **14** and **15**. Although there can be little doubt in the validity of the mechanistic arguments advanced by the Tomioka group, the formation of propadienone **12** directly in a single-step cycloreversion reaction from the preformed and characterized alkylidenecyclopropaene **11** provides the needed definitive evidence for the existence of this class of novel reactive compounds.

At the B3LPY/6-31G*, B3LPY/6-311G**, and MP2/6-31G* levels of theory, **12** and **13** are very similar, with the propadienone moiety held in a zigzag molecular structure as expected[21] (Figure 2). Only slight differences in **12** and
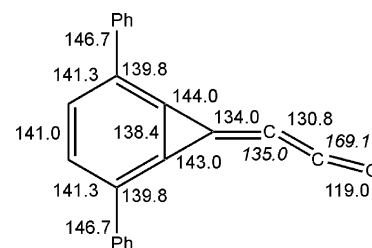

Figure 2. MP2/6-31G*-generated structure of propadienone **12** showing the zigzag dienone (bond lengths in pm, angles in deg).

13 are found within each set of calculations. The MP2/6-31G* data have C=C=C 135.0°/135.4° and C=C=O 169.1°/169.1° for **12** and **13**. Optimization of propadienone

(methyleneketene, H_2CCCO) at MP2/aug-cc-pCVQZ// MP2/cc-pVTZ[21e] gave 140.7°/168.7°. In **12**, both phenyl groups are rotated by about the same amount (24°) from the plane containing the cycloproparene ring system (see full data in Supporting Information).

The ease by which alkene **11** is available and subsequently transforms into **12** augurs well for alternative uses of the new synthetic procedure to provide other interesting and novel alkylidenecycloproparenes for chemical and physical study. We encourage others to explore such possibilities.

Supporting Information Available: Experimental procedures for synthesis and FVT of **11**, ^{1}H and ^{13}C spectra of **11**, Cartesian coordinates, structures, and energies for **12** and **13** at B3LYP/ 6-31G*, B3LPY/6-311G**, and MP2/6-31G* levels, vibrational data for **12**, and a full-page expansion of Figure 1. This material is available free of charge via the Internet at http://pubs.acs.org.

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