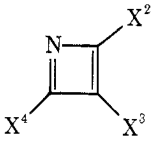
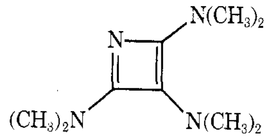
azacyclobutadiene (**3**) and several of its derivatives for which the "push–pull" effect has been proposed. The antiaromaticity of azacyclobutadiene (**3a**) is appreciably less than that of cyclobutadiene (**2a**); and electron-donating substituents in positions 2 and 4 stabilize the azacyclobutadienes, but destabilize in the 3 position. These results are in agreement with those of Wagner.[12] Only one substituted azacyclobutadiene (**4**) has been reported.[13] In Table I are several azacyclobutadienes that are predicted to be more stable than **4** and hence are good candidates for synthesis. However, possible reaction paths, here particularly those of dimerization, as well as inherent stability, determine whether or not a product can be isolated. The case of dimethylenecyclobutene, which can be isolated[14] in spite of its antiaromaticity,[15] illustrates this.



**3**



**4**

Very recently Aihara[16] has proposed an attractive alternative to our method of computing the reference polyene energy. The origin of his idea is a 1963 paper by Sachs[17] who showed how the characteristic polynomial of the adjacency matrix of a graph can be written down simply by counting certain of its subgraphs. This result was applied to molecular graphs (i.e., molecular structural formulas) by Gutman and Trinajstić with Wilcox, Mallion, and others.[18–21] Aihara then suggested that the energy of the polyene reference might be defined by summing the lower roots of a polynomial obtained from the Hückel matrix by Sachs' recipe, but neglecting all contributions of cyclic subgraphs. His results for hydrocarbons were similar to, but not identical with, ours and also to those of Herndon's[22,23] equally successful valence bond method.

We have applied Aihara's method to the substituted cyclobutadienes of Table I where these results are compared with ours. The numbers are parallel, but **2k, 2m, 2o,** and **3h,** which we predict to be olefin-like and hence relatively stable, are all calculated to have substantial antiaromatic character by Aihara's method. It must be admitted that few thermodynamic data were available for determining the heteroatom parameters used in both methods, and hence these predictions are not as sound as those for hydrocarbons, but still an experimental examination of these four molecules would be of considerable interest.

**Registry No.**—**2a,** 1120-53-2; **2b,** 59711-10-3; **2c,** 59711-11-4; **2f,** 59711-12-5; **2g,** 59711-13-6; **2j,** 59711-14-7; **2k,** 59711-15-8; **2n,** 59711-16-9; **2o,** 59711-17-0; **2p,** 59711-18-1; **2q,** 59711-19-2; **3a,** 287-24-1; **3b,** 59711-20-5; **3c,** 59711-21-6; **3d,** 59711-22-7; **3e,** 50870-40-1; **3f,** 59711-23-8; **3g,** 59711-24-9; **3h,** 59711-25-0.

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# Tricyclic Dimers from Cyclic α Diketones

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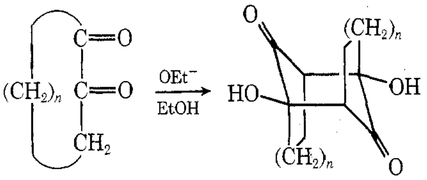
As a prelude to our syntheses of certain novel tricyclic macrolides, we prepared the known[1] cyclic diketones **1a–c** via acyloin condensation of the corresponding diesters or via oxidation of the corresponding cyclic α-bromo ketones.[2] During attempts to carry out base-catalyzed tetraalkylation of the α positions of these diketones, we repeatedly isolated varying amounts of highly insoluble, high-melting crystalline side products. These products were all colorless, in contrast to the bright yellow characteristic of the diketone precursors.

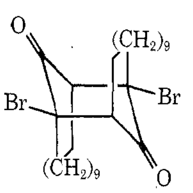
It was subsequently found that these side products could be directly prepared by simply treating the diketones with base. For example, when a solution of 1.96 g (10 mmol) of **1b** and 20 mmol of sodium ethoxide in 55 ml of absolute ethanol was stirred for 24 h at room temperature, 680 mg (after recrystallization from diglyme) of a colorless compound with mp 277–278 °C was isolated. The mass spectrum of this compound exhibited a parent ion at *m/e* 392 indicating a dimer of the starting diketone; the elemental analysis agreed with molecular formula $C_{24}H_{40}O_4$. Its infrared spectrum showed carbonyl (1702 $cm^{-1}$) and hydroxyl (3525 $cm^{-1}$) absorptions. NMR spectra for this compound could not be obtained owing to the extreme insolubility of the material (12 mg/ml diglyme at 161 °C). Attempts to increase its solubility by derivatizing the OH groups with acetic anhydride, acetyl chloride, methanesulfonyl chloride, and thionyl chloride all failed, indicating the extremely hindered nature of these groups. However, treatment with potassium *tert*-butoxide in glyme (70 °C, 2 h), or heating to 320 °C, regenerated yellow **1b.** These results, coupled with the observation that the reaction with ethoxide could not be pushed to completion, suggest that this product is reversibly formed bisaldol dimer **2b**. Further confirmation could be adduced from the observation that **2b** affords 1,2-cyclododecanediol[1b] upon treatment with sodium borohydride in diglyme.



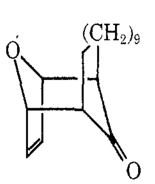
**1a**, *n* = 7
**b**, *n* = 9
**c**, *n* = 11

**2a**, *n* = 7
**b**, *n* = 9
**c**, *n* = 11

Compounds resembling **2** are known. Meier,[3] referencing unpublished work, reported that treatment of α,α′-dibromocyclododecanone (**3**) with potassium *tert*-butoxide led to tricyclic bromo ketone **4**. Similarly, treatment of **3** with zinc–copper couple in the presence of furan afforded **5** (ir 1703 cm$^{-1}$) along with several stereoisomers.[4]

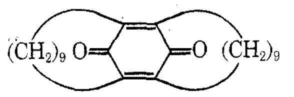


**4**



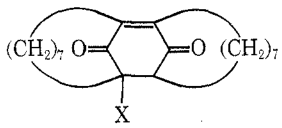
**5**

Although **4** apparently resists further base-catalyzed dehydrobromination, we attempted to prepare benzoquinone **6** from **2b**. However, treatment with dicyclohexylcarbodiimide (DCC), *p*-toluenesulfonic acid in refluxing diglyme, and potassium permanganate left **2b** unchanged, further indication of its low reactivity.



**6**

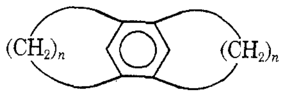
Diketone **1c** afforded dimer **2c** (mp 295–296 °C) in 38% yield, and its behavior matched that of **2b**. However, treatment of **1a** with ethoxide provided two products, the dimer **2a** (*m/e* 336, mp 247–248 °C) in 1% yield, and another product (*m/e* 318, mp 169–170 °C) in 35% yield. Absorptions for O–H (3450 cm$^{-1}$), C=O (1702), and C=C (1622) were apparent in its infrared spectrum, and its uv spectrum suggested conjugation with $\lambda_{max}$ (ethanol) 247 nm (log ε 3.9).[5] Elemental analysis corroborated molecular formula $C_{20}H_{30}O_3$, corresponding to dehydration of **2a**. These data, together with the observation that a mesylate derivative could be prepared, tentatively suggest this compound to be enedione **7a**, another violation of Bredt's rule.[6] Both **7**-OH and **7**-OMs proved soluble enough to allow $^1$H and $^{13}$C NMR spectra to be obtained (Experimental Section). Although complex, these spectra were consistent with the proposed structures. But as with **2b** and **2c** no conditions were found that could induce **7**-OH or **7**-OMs to undergo further elimination. Thus, **7**-OH could be reisolated after treatment with DCC, 9-BBN, $POCl_3$, or pyrolysis (passage through glass wool at 300 °C), and **7**-OMs could be recovered after heating in pyridine (100 °C, 12 h).



**7-X**

Space-filling molecular models of **2b** show that the nine-carbon bridges are best accommodated when they are axially disposed and static, as was suggested by the C=O stretch (vide supra and ref 4). This requires the O–H groups to occupy equatorial positions which are hindered by the cyclic methylene chains toward electrophilic attack.

Why the ten-membered rings in **2a** better accommodate the flattening attending formation of **7**-OH more than do the presumably[4] more flexible 12- and 14-membered rings in **2b** and **2c** is not clear. Models do suggest, however, that fully planar molecules such as **7** and **8** experience considerable buttressing of the one-carbon bridges with the *n*-carbon bridges, accounting for the low reactivity of the carbonyl groups. This type of dimerization may account for the fact that α diketones with α-methylene groups do not generally undergo the benzylic acid rearrangement in base.[7] Further work on the chemistry of these compounds is underway.[8,9]



**8**

## Experimental Section

The following instruments were employed: Beckman IR-12 (calibrated with polystyrene); Varian A-60 [δ, parts per million downfield from internal $(CH_3)_4Si$]; Varian CFT 20 ($^{13}$C data are in parts per million downfield from $Me_4Si$); Hitachi RMU-7 (70eV); Cary 14. All starting materials, reagents, and solvents were obtained from Aldrich Chemical Co. or Fisher Scientific Co. Diglyme was distilled from $LiAlH_4$. Melting points are not corrected. The elemental analyses were performed by Chemalytics, Inc., Tempe, Ariz.

**Dimerization of Cyclododecane-1,2-dione.** To a cool (0 °C) stirred solution of cyclododecane-1,2-dione[1b] (1.96 g, 10 mmol) in 5 ml of absolute ethanol was added a cool (0 °C) solution of sodium metal (0.46 g, 20 mg-atoms) in 50 ml of absolute ethanol. After stirring for 24 h at room temperature, the reaction mixture was poured over ice, then neutralized with 1 N HCl. The yellowish solid was filtered and washed with 50 ml of diethyl ether. The remaining white solid was recrystallized from dry diglyme to yield 680 mg (35%) of **2b:** mp 277–278 °C; ir (Nujol) 3525, 1702, 1250, 1090, 1047, 1028, 741 cm$^{-1}$; mass spectrum *m/e* (rel abundance) 392 ($M^+$, 75), 374 (16), 364 (28), 346 (73), 197 (100).

Anal. Calcd for $C_{24}H_{40}O_4$: C, 73.43; H, 10.27. Found: C, 73.58; H, 10.38.

**Reaction of Compound 2b with Sodium Borohydride.** Compound **2b** (392 mg, 1.0 mmol), sodium borohydride (75.6 mg, 2.0 mmol), water (1.0 ml), and 20 ml of diglyme were combined in a 50-ml round-bottom flask, then heated to 140 °C for 20 h. After cooling to room temperature, the reaction mixture was cautiously poured into 100 g of ice–water; then 10 ml of 10% NaOH was added to the solution. The white precipitate was filtered and recrystallized from ether-pentane to yield 360 mg (91%) of *cis*-cyclododecane-1,2-diol: mp 158–159 °C (lit.[1b] mp 159–160 °C); $R_f$ (EtOAc) 0.43; ir (KBr) 3312 cm$^{-1}$, no C=O; $^1$H NMR (pyridine-$d_5$) δ 1.31 (s, $\Delta\nu_{1/2}$ = 8 Hz, 16 H), 1.80 (br m, 4 H), 4.20 (t, *J* = 6 Hz, 2 H), 5.51 (s, 2 H); mass spectrum *m/e* (rel abundance) 200 ($M^+$, 2), 94 (100).

**Dimerization of Cyclotetradecane-1,2-dione.** Cyclotetradecane-1,2-dione[1c] (2.24 g, 10 mmol) in 5 ml of absolute ethanol and sodium metal (0.46 g, 20 mg-atoms) in 50 ml of absolute ethanol were allowed to react as described in the preparation of compound **2b**. After the usual aqueous workup and recrystallization from dry diglyme, compound **2c** was isolated in 38% yield (850 mg): mp 295–296 °C; ir (KBr) 3530, 2940, 2860, 1709, 1445, 1370, 1250, 1230, 1080, 1055, 1037, 1004 cm$^{-1}$; mass spectrum *m/e* (rel abundance) 448 ($M^+$, 28), 430 (20), 420 (16), 402 (34), 225 (100).

Anal. Calcd for $C_{28}H_{48}O_4$: C, 74.95; H, 10.78. Found: C, 74.89; H, 10.48.

**Dimerization of Cyclodecane-1,2-dione.** A 10-mmol sample of cyclodecane-1,2-dione[1a] in 5 ml of absolute ethanol was reacted with 20 mg-atoms of sodium metal in 50 ml of absolute ethanol. After the usual aqueous workup, the precipitate was filtered and washed with pentane. Fractional recrystallization from diethyl ether yielded 15 mg (1%) of compound **2a** at 15 °C and 620 mg (37%) of compound **7**-OH at −20 °C.

Compound **2a**: mp 247–248 °C; ir (KBr) 3535, 2950, 2865, 1699, 1468, 1450, 1258, 1229, 1141, 1000, 983, 965 cm$^{-1}$; mass spectrum *m/e* (rel abundance) 336 (M$^+$, 45), 318 (7), 308 (7), 290 (45), 169 (100). Compound **7**-OH: mp 169–170 °C; ir (KBr) 3450, 2950, 2870, 1702, 1622, 1470, 1220, 1191, 1140, 1080, 1043 cm$^{-1}$; $^1$H NMR (pyridine-$d_5$) δ 1.10–2.90 (m, 28 H), 3.22 (br m, 1 H) 7.05 (s, 1 H); uv (ethanol) $\lambda_{max}$ 247 nm (log ε 3.9); $^{13}$C NMR (CDCl$_3$) 20.4, 20.9, 21.8, 22.5, 23.2, 24.2, 24.7, 25.6, 25.8, 26.7, 37.4, 41.8, 51.1, 85.6, 138.2, 161.0, 164.8, 169.3 ppm; mass spectrum *m/e* (rel abundance) 318 (M$^+$, 100), 300 (12), 290 (18), 151 (16).

Anal. Calcd for $C_{20}H_{30}O_3$: C, 75.43; H, 9.50. Found: C, 75.29; H, 9.56.

**Preparation of 7-OMs.** To a frozen solution of compound **7**-OH (318 mg, 1.0 mmol) in pyridine (3.0 ml) was added a cool (−5 °C) solution of methanesulfonyl chloride (228 mg, 2.0 mmol) in pyridine (2.0 ml). The mixture was immediately frozen, then slowly allowed to warm to −20 °C. After storing at −20 °C for 2 days the reaction mixture was poured over 15 g of ice, then extracted with two 15-ml portions of diethyl ether. The ethereal layer was separated and washed with water, 1 N HCl, 5% NaHCO$_3$, and brine, then dried, filtered, and concentrated in vacuo. Preparative layer chromatography (benzene elution) of the white residue resulted in the isolation of 322 mg (81%) of compound **7**-OMs: mp 138–139 °C; $R_f$ (Bz) 0.46; ir (CHCl$_3$) 2940, 2879, 1719, 1700 (sh), 1620, 1470, 1350, 1330, 1173, 960, 932, 852 cm$^{-1}$; $^1$H NMR (CDCl$_3$) δ 1.00–2.30 (m, 24 H), 2.38 (m, 4 H), 3.30 (s, 3 H), 3.89 (m, 1 H); mass spectrum *m/e* (rel abundance) 396 (M$^+$, 0.4), 317 (25), 300 (100).

Anal. Calcd for $C_{21}H_{32}O_5S$: C, 63.60; H, 8.13. Found: C, 63.51; H, 8.14.

**Acknowledgment.** This work was generously supported by USPHS-NIH Grant 5 R01 AI 11690. The technical assistance of Rodney Erkes is also gratefully acknowledged. The $^{13}$C spectra were obtained with the help of Dr. David Behnke, U. C. School of Medicine.

**Registry No.**—**1a**, 96-01-5; **1b**, 3008-41-1; **1c**, 23427-68-1; **2a**, 59654-89-6; **2b**, 59654-90-9; **2c**, 59654-91-0; **7**-OH, 59654-92-1; **7**-OMs, 59654-93-2; *cis*-cyclododecane-1,2-diol, 4422-05-3; methanesulfonyl chloride, 124-63-0.

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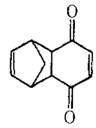
(2) D. P. Bauer and R. S. Macomber, *J. Org. Chem.*, **40**, 1990 (1975).

(3) H. Meier, *Synthesis*, 235 (1972).

(4) J. G. Vinter and H. M. R. Hoffmann, *J. Am. Chem. Soc.*, **95**, 3051 (1973). Compound **5** is stereochemically rigid, giving a single C═O ir stretch. Its cis,syn,cis isomer is fluxional and shows two C═O bands in solution.

(5) A. Wasserman [*J. Chem. Soc.*, 1511 (1935)] lists the $\lambda_{max}$ (ethanol) for the enedione below as 225 nm (log ε 4.11). Using Woodward's rules, two



i

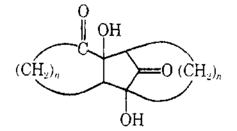
substituents (one α + one β) would add 22 nm: calcd 247 nm; observed 247 nm. The position and intensity of this band further argue for the near-planarity of the enedione moiety in **7-X**.

(6) For a leading reference, see H. O. Krabbenhoft, J. R. Wiseman, and C. B. Quinn, *J. Am. Chem. Soc.*, **96**, 258 (1974).

(7) W. Huckel, "Theoretical Principles of Organic Chemistry", Vol. I, American Elsevier, New York, N.Y., 1955, p 461.

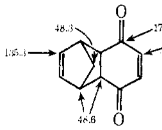
(8) The systematic names for these dimers follow: **2a**, 1,10-dihydroxytricyclo[9.7.1$^{2,10}$]eicos-19,20-dione; **2b**, 1,12-dihydroxytricyclo[11.9.1.1$^{2,12}$]-tetracos-23,24-dione; **2c**, 1,14-dihydroxytricyclo[13.11.1.1$^{2,14}$]octacos-27,28-dione; **7**-OH, 1-hydroxytricyclo[9.7.1.1$^{2,10}$]eicos-10-ene-19,20-dione.

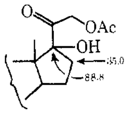
(9) One referee has suggested the structure below as an alternate of **2**. We

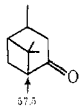


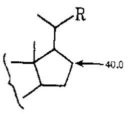
had considered this possibility, but eliminated it on the basis of the compounds' ir spectra. The structure below would show two carbonyl bands, one at ca. 1745 cm$^{-1}$. None of the compounds in this study exhibited a second C═O stretch, and none came above 1709 cm$^{-1}$.

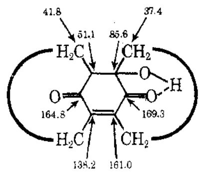
(10) Analogues for the $^{13}$C chemical shifts can be found in L. F. Johnson and W. C. Jankowski, "Carbon-13 NMR Spectra", Wiley, New York, N.Y., 1972, and the spectrum of i in footnote 5 (determined in this work). The substantial difference in chemical shift between the olefinic carbons in **7**-OH may be caused by internal hydrogen bonding in the neighboring carbonyl:











# Communications

## The Stereospecific Aluminum Chloride Catalyzed [2 + 2] Cycloaddition of Propiolate Esters with Unactivated Alkenes

*Summary:* The aluminum chloride catalyzed reaction of alkenes with propiolate esters at 25 °C produces either ene adducts and/or stereospecific [2 + 2] cycloadducts depending on the substitution pattern of the alkene.

*Sir:* We have previously shown that aluminum chloride catalyzes the reaction of methyl acrylate with 1,1-disubstituted olefins at 25 °C, giving good yields of ene adducts.[1,2] Since acetylenes are known to be more reactive than the corresponding alkene as enophiles,[1] we decided to examine Lewis acid catalyzed reactions of propiolate esters with alkenes. With 1,2-disubstituted olefins or monosubstituted double bonds an unexpected reaction occurs. With cyclohexene two products are obtained on treatment with ethyl propiolate and 0.5 equiv of aluminum chloride in benzene for 7 days at 25 °C. The expected ene adduct **17** is isolated in 15% yield.[3,4] The major product isolated in 72% yield is assigned structure **1** based on ir, NMR, and mass spectral considerations. The cis fusion is assigned based on steric considerations and the nature of the cycloaddition (vide infra). This type of cycloaddition has precedent in the cycloaddition of propiolate esters with enamines.[6] It has not been observed previously in nonphotochemical reactions of propiolates with unactivated olefins. In order to test the specificity of the addition, methyl propiolate was treated with excess *cis*- or *trans*-2 butene in the presence of 0.5 equiv of aluminum chloride for 2 days. In neither case is any ene adduct detected. The *cis*- and *trans*-3,4-dimethylcyclobutenecarboxylates, **2** and **3**, are obtained stereospe-