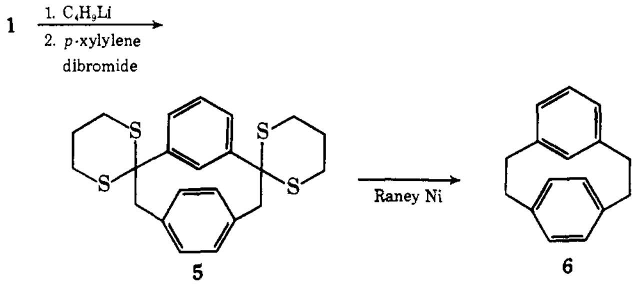
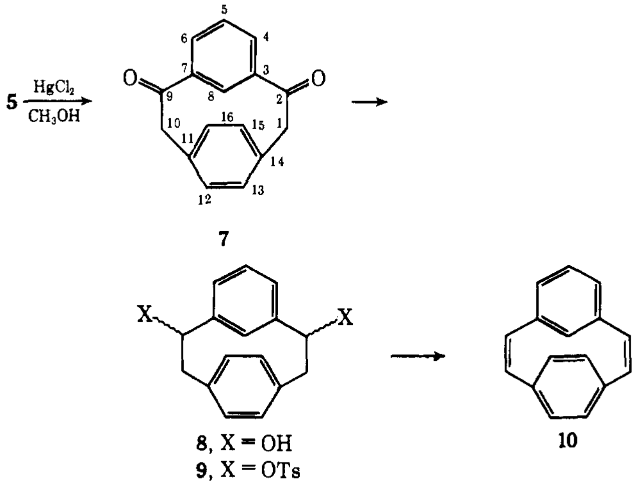
8 and 16 positions in the nmr spectrum appear as broad singlets at τ 5.79 and 4.10.

The alkylation of **1** was then investigated using *p*-xylylene dibromide. When the reaction was carried out as before, the yield of the desired [2.2]metaparacyclophane (**5**) was only 1.9%. However, when solutions of the dianion of **1** and of *p*-xylylene dibromide in tetrahydrofuran were added separately, but simultaneously, to a large volume of boiling tetrahydrofuran stirred vigorously in a Morton flask, **5** was isolated, after recrystallization from a benzene–hexane mixture, as white rhombic crystals, mp 244–246°, in 36% yield. Desulfurization with Raney nickel was carried out to give [2.2]metaparacyclophane (**6**), whose melting point (79–81°) and other physical properties are in accord with those described by Cram, *et al.*[13]



Dewhirst and Cram have described a synthesis of [2.2]paracyclophane-1,9-diene, an extreme example of inhibition of resonance resulting from the geometry of the molecule.[14] It was of interest, therefore, to see whether we could utilize the dithiane functions of **5** to introduce unsaturation and prepare the analogous diene **10**. Treatment of **5** with mercuric chloride and methanol, as before, led to the diketone **7** as white crystals, mp 129.5–129.8°, in 91% yield. As with **4**, the carbonyl frequency in the infrared was not unusual, appearing at 5.90 μ, and the signal in the nmr spectrum for the internal proton at the 8 position was at τ 4.36. Reduction of **7** with sodium borohydride gave a mixture of diastereoisomers (**8**) as fine white needles, mp 186–191°, in 97% yield. This was converted to the corresponding ditosylate **9**, isolated as white needles, mp 178–184°, in 95% yield. Treatment of **9** with potassium *t*-butoxide in *t*-butyl alcohol then gave [2.2]-metaparacyclophane-1,9-diene (**10**) as white crystals, mp 58–59°, in 68% yield.



As proof of structure, **10** readily absorbed 2 mol of hydrogen on reduction over palladium to give **6**, identical in all respects with the sample prepared previously. The mass spectrum of **10** showed the parent molecular ion at *m/e* 204, as expected. The ultraviolet absorption spectrum of **10** in hexane showed a maximum at 232.5 mμ (log ϵ 4.40) with a shoulder at 260 mμ (log ϵ 4.02) but with no absorption above 300 mμ. In the nmr (CCl_4), **10** showed doublets at τ 2.83 (2 H, J = 10.0 cps) and 3.40 (2 H, J = 10.0), a multiplet at τ 3.00–3.40 (7 H), and a broad singlet at τ 5.71 (1 H). Although the ultraviolet absorption bands of **10** are of high intensity, they occur at shorter wavelength than for either [2.2]paracyclophane-1,9-diene[14] or 8,16-dimethyl-[2.2]metacyclophane-1,9-diene.[15] A detailed interpretation of the nmr spectrum of **10** is best made when the precise geometry of **10** is known from a single-crystal X-ray analysis.

The synthesis of cyclophanes by this method appears to proceed in equal or better yields than the Wurtz reaction and has the advantage of allowing the synthesis of unsymmetrical cyclophanes containing functionality for later transformations. The use of this procedure for the synthesis of a variety of interesting molecules seems possible, and exploratory work along these lines is being continued.

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(13) D. J. Cram, R. C. Helgeson, D. Lock, and L. A. Singer, *J. Am. Chem. Soc.*, **88**, 1324 (1966).

(14) K. C Dewhirst and D. J. Cram, *ibid.*, **80**, 3115 (1958).

(15) H.-R. Blattmann, Ph.D. Dissertation, Federal Institute of Technology, Zurich, Switzerland, 1967.

(16) We express our gratitude to the National Science Foundation for their support of this investigation.

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Received September 23, 1968

Strain Energy in Bicyclo[3.3.1]non-1-ene[1]

Sir:

Recent syntheses of bicyclo[3.3.1]non-1-ene (**1**),[2,3] of interest in connection with limitations in the applicability of Bredt's rule, have prompted us to measure the strain energy present in this molecule. A sample of the substance was prepared by Wiseman's procedure,[4] purified by vapor chromatography on a Carbowax on Chromosorb P column, and flash distilled under vacuum prior to use. The material showed all of the spectral properties that have been reported for this compound.[2,3]

Bicyclo[3.3.1]non-1-ene (**1**) reacts rapidly with acetic acid in the absence of catalysts to furnish 1-acetoxybicyclo[3.3.1]nonane (**2**).[5] The quantitative nature of the reaction was demonstrated by comparison of the vapor chromatographic behavior and the infrared and

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(1) Support of this work through National Science Foundation Grant GP 203 is gratefully acknowledged.

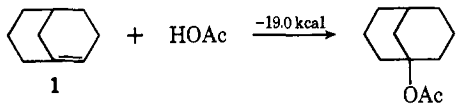
(2) J. A. Marshall and H. Faubl, *J. Amer. Chem. Soc.*, **89**, 5965 (1967).

(3) J. R. Wiseman, *ibid.*, **89**, 5966 (1967).

(4) We are indebted to Dr. Wiseman for supplying details of his experimental work in advance of publication.

(5) Product recovered from calorimetric runs by distillation of the acetic acid solvent and vapor chromatography of the resulting residue showed infrared and nmr absorption identical with that of an authentic sample. It is a pleasure to acknowledge the assistance of Professor W. G. Dauben in furnishing reference spectra.

nmr spectral properties of a mixture of pure **2** and acetic acid with those of a solution of 195 mg of **1** in 264 mg

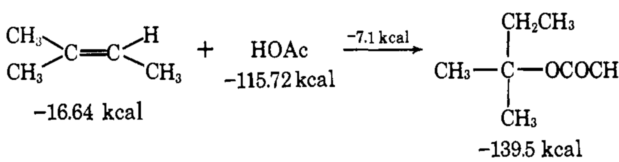


1 **2**

of acetic acid which had been allowed to stand over night at room temperature in an evacuated ampoule.

The enthalpy change for the transformation olefin (liquid) + acetic acid (liquid) → acetate (solution) is −18.51 ± 0.35 kcal/mol at 25°.[6] Correction of this figure for the heat of solution[6] of **2** in acetic acid (0.48 kcal/mol) gives a value of −19.0 kcal/mol for the heat of reaction with all components in the liquid state.

For purposes of comparison we have estimated the heat of reaction for the model transformation



$$(CH_3)_2C{=}CHCH_3 + HOAc \xrightarrow{-7.1\ \mathrm{kcal}} CH_3-\underset{CH_3}{\overset{CH_2CH_3}{C}}-OCOCH_3$$

under the same conditions of state. Unfortunately, reliable modern data on the heats of formation of acetate esters are not extensive, and in no case of which we are aware has the heat of formation of a tertiary acetate been determined. The calculation was therefore carried out as follows.

The heat of formation of 2-methylbutene-2 in the liquid phase at 25° (−16.64 kcal/mol) was obtained from the gas-phase value (−10.17 kcal/mol)[7] and the known heat of vaporization (6.47 kcal/mol).[7] The figure of −115.72 kcal/mol employed for the heat of formation of liquid acetic acid (25°) is that of Evans and Skinner.[8]

A value of −1000.4 kcal/mol has been reported for the heat of combustion of liquid isoamyl acetate at 20° by Schjanberg.[9] The heat of formation of liquid isoamyl acetate is thus −136.19 kcal/mol. This figure is corrected to one for *t*-amyl acetate by application of Franklin's gas-phase group equivalents[10] with the proviso that the heats of vaporization of isoamyl acetate and of *t*-amyl acetate do not differ materially (*cf.* Trouton's rule). Thus the Franklin gas-phase heats of formation (25°) of the isoamyl and *t*-amyl groups are, respectively, −31.18 and −34.49 kcal, the difference being −3.31 kcal. The heat of formation of liquid *t*-amyl acetate is thus calculated to be approximately −139.5 kcal/mol and is to be regarded as an essentially strain-free value.[11]

The heat change for the model reaction derived from this result is −7.1 kcal/mol. If the validity of this figure is assumed, then the strain associated with the double bond in bicyclo[3.3.1]non-1-ene (**1**) is about 12 kcal/mol.[12] Although this is the lowest of the values that can be calculated from currently available data,[11] we believe that it is based upon the most reliable experimental source. This degree of strain is of the same order of magnitude as that found in *trans*-cyclooctene (9.2 kcal/mol)[13] and in *cis*-di-*t*-butylethylene (9.3 kcal/mol)[14] and is substantially less than the double bond strain of about 20 kcal/mol found in dimethylcyclopropene.[15] The result is surprisingly low in view of the extreme reactivity of bicyclo[3.3.1]non-1-ene toward addition of acetic acid.

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(6) The colorimeter employed in this work has been described previously [R. B. Turner, W. R. Meador, and R. E. Winkler, *J. Am. Chem. Soc.*, **79**, 4116 (1957)]. Acetic acid (225 ml) was employed as solvent with olefin samples in the range 225–400 mg.

(7) "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons," American Petroleum Institute Research Project 44, Carnegie Press, Pittsburgh, Pa., 1954.

(8) F. W. Evans and H. A. Skinner, *Trans. Faraday Soc.*, **55**, 260 (1959).

(9) E. Schjanberg, *Z. Physik. Chem.*, **A172**, 197 (1935).

(10) J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949).

(11) Alternatively the heat of formation of *t*-amyl acetate can be calculated as the sum of Franklin group equivalents (4 CH_3, −40.48 kcal; CH_2, −4.926 kcal; C, +0.8 kcal; ester carboxylate, −79.8 kcal) and is −124.41 kcal/mol for the gas phase at 25°. Correction for the heat of vaporization, for which the isoamyl acetate value of 9.0 kcal/mol[9] is the only experimental one available (the Trouton rule figure for *t*-amyl acetate is 8.74 kcal/mol), gives a final liquid phase heat of formation of −133.41 kcal/mol. It should be noted that the Franklin ester carboxylate group equivalent is based upon a 1928 International Critical Tables heat of formation of ethyl acetate. The value of −133.41 kcal/mol can be revised upward to −131.88 or downward to −135.02 kcal/mol if more recent data for ethyl acetate are employed [ref 9 and A. A. Vvedenskii, P. Ya. Ivannikov, and V. A. Nekrasova, *Zh. Obshch. Khim.*, **19**, 1094 (1949)].

(12) Implicit in this argument is the assumption that residual strains in **1** and in **2**, if significant, are at least comparable. This assumption is supported in some degree by the fact that the heat of hydrogenation of bicyclo[3.2.1]oct-2-ene (−26.8 kcal/mol) is normal and close to that of cyclohexene (−27.1 kcal/mol) (unpublished results of B. J. Mallon and R. B. Turner).

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(14) R. B. Turner, D. E. Nettleton, and M. Perelman, *ibid.*, **80**, 1430 (1958).

(15) R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, and M. Pomerantz, *ibid.*, **90**, 4315 (1968).

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Received September 24, 1968

Oxidation and Isomerization of Phenylcyclopropane by Aqueous Palladium(II) Chloride[1]

Sir:

While the literature is replete with accounts of the addition of platinum(II) to olefins, the analogous reaction of the transition metal ion with cyclopropanes is almost without precedent. Cyclopropane is reported to cleave in the presence of platinum(II) to yield a complex with an incorporated trimethylene bridge as a bidentate ligand.[2] Recently cyclopropane–platinum chloride complexes, formed by ligand exchange with olefin–platinum chloride complexes, have been reported.[3]

Palladium(II) is postulated to provide a transient complex ion in aqueous solutions of olefins, which then undergoes an internal redox reaction, involving a 1,2-hydride shift, to produce carbonyl products.[4] There are no reports of a corresponding reaction of palladium(II) with cyclopropanes. While the cleavage reaction certainly would be expected to occur, the products are not predictable *a priori*. An intermediate

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(1) This research was supported by Grant GP3873 from the National Science Foundation.

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