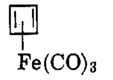
organic products produced in this reaction, Skell and Peterson deduce that cyclobutadiene possesses a triplet ground state.[3] However, this conclusion can be questioned on the grounds of the nature of the experimental conditions employed in the reaction; for example, if free tetramethylcyclobutadiene is indeed involved, then reaction *via* thermally produced triplet excited species is readily conceivable.

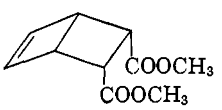
We have previously presented evidence that degradation of cyclobutadieneiron tricarbonyl (III) with ceric ion at 0° occurs with liberation of cyclobutadiene.[4]



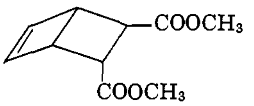
III

We now wish to report that the liberated cyclobutadiene reacts both as a diene and as a dienophile in a stereospecific manner; this supports the theory that cyclobutadiene possesses a singlet electronic ground state and, by implication, therefore has the structure II.

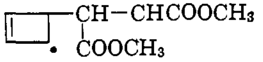
Degradation of the complex III at 0° in the presence of dimethyl maleate produced the *endo,cis*-dicarbomethoxybicyclohexene IV. On the other hand reaction of cyclobutadiene with dimethyl fumarate gave the *trans*-dicarbomethoxybicyclohexene V. In both experiments vapor phase chromatography indicated the absence of the adduct produced in the other reaction. The stereochemistry of the adducts IV and V were proved through ozonolysis followed by esterification, whereupon there was produced *cis,cis,cis*-1,2,3,4-tetracarbomethoxycyclobutane and *cis,cis,-trans*-1,2,3,4-tetracarbomethoxycyclobutane, respectively.[5]



IV



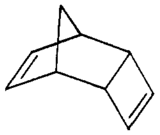
V



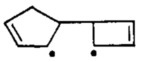
VI

The products IV and V are just those one would expect if cyclobutadiene were to act as a singlet diene in the normal Diels–Alder reaction. On the other hand, employing arguments analogous to those used by Skell and Woodworth in the determination of the spin multiplicities of carbenes,[6] one would not expect stereospecific addition to occur if cyclobutadiene were to be a triplet. In such an event the addition to both dimethyl maleate and dimethyl fumarate should be a two-step process involving the common triplet species VI; assuming electron spin inversion and ring closure to be slow with respect to rotation about single bonds,[7] then the same two adducts IV and V, as well as the *exo,cis* isomer, should be produced in both reactions. This is not observed.[8]

In common with other highly strained olefins,[9] cyclobutadiene also reacts as a dienophile and in a stereospecific manner. The reaction with cyclopentadiene at 0° produces a single C_9H_{10} adduct, the nmr spectrum of which is consistent with the structural formula VII;[10] this is the product to be expected if cyclopentadiene were to be the diene partner in the addition. Again, if cyclobutadiene were to be a triplet, the reaction with cyclopentadiene would be expected to proceed *via* the bisallyl radical species VIII, in which case a mixture of four C_9H_{10} hydrocarbons would reasonably be expected.

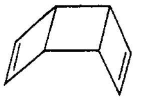


VII

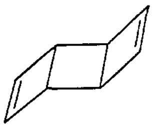


VIII

The only reaction of cyclobutadiene thus far shown to be nonstereospecific is its dimerization. When conducted in the absence of trapping agents, the degradation of complex III leads to the formation of the two dimers of cyclobutadiene, IX and X. Even in this case the *syn* isomer IX is formed preferentially (~5:1), as would be expected from both the normal "*endo,cis*" rule in Diels–Alder additions and the related arguments recently proposed by Hoffmann and Woodward.[11] Since cyclobutadiene is both a very reactive diene and dienophile it is not surprising that in the dimerization the stereochemical selectively is diminished.



IX



X

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[3] P. S. Skell and R. J. Peterson, *J. Am. Chem Soc.*, 86, 2531 (1964).

[4] L. Watts, J. D. Fitzpatrick, and R. Pettit, *ibid.*, **87**, 3253 (1965).

[5] We thank Professors R. Criegee and G. Griffin for providing spectral data of authentic specimens of these tetracarboxylic esters.

[6] P. S. Skell and R. C. Woodworth, *J. Am. Chem. Soc.*, **78**, 4496 (1956).

[7] The basic assumption in this paper, *viz.*, that a triplet species should undergo addition reactions nonstereospecifically and reactions of singlet species should be stereospecific, while apparently widely accepted, nevertheless lacks unequivocal proof. See P. P. Gaspar and G. S. Hammond in "Carbene Chemistry," W. Kirmse, Ed., Academic Press Inc., New York, N. Y., 1964.

[8] The products IV and V could conceivably result from 1,2-cycloadditions rather than 1,4-cycloadditions; however, this would not affect the argument pertaining to the spin multiplicity.

[9] K. B. Wiberg and W. J. Bartley, *J. Am. Chem. Soc.*, **82**, 6375 (1960).

[10] The nmr spectrum showed absorptions at τ 4.13, 4.22, 7.06, 7.43, 8.12, and 8.50 (areas 2:2:2:2:1:1); a coupling constant of 3.4 cps between the bridgehead and the allylic protons indicated an *endo* configuration.

[11] R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 4388 (1965).

[12] The authors thank the National Science Foundation, The Army Research Office (Durham), and the Robert A. Welch Foundation for financial support. We also gratefully acknowledge a generous gift of cyclooctatetraene from Badische Anilin und Soda Fabrik.

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Biogenetic-Type Synthesis of Phenolic Compounds

Sir:

As an extension of our previous studies[1] we have continued our investigations into the construction of pyrone structures which may be visualized as "protected" polyketide chains. In this way naturally occurring phenolic compounds can be synthesized by routes

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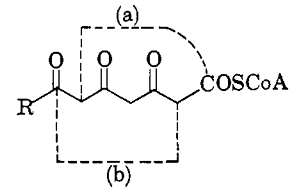
[1] T. Money, I. H. Qureshi, G. B. Webster, and A. I. Scott, *J. Am. Chem. Soc.*, **87**, 3004 (1965).

which may be considered analogous to that followed in nature.

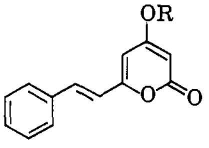
In this communication we report the synthesis and chemical behavior of the polypyrone compounds, III and IV. The former compound is potentially equivalent to the polyketide chain (see III, heavy lines) postulated by Birch[2] as the precursor of the stilbenes and flavonoids. These two groups of natural products often cooccur, and their structures provide excellent examples of the two basic types of ring closure processes (Ia and Ib) proposed for the biosynthesis of the majority of naturally occurring phenolic compounds.[2] It has been our primary purpose to simulate these processes in the laboratory.

The benzylidenebispyrone III was prepared in the following way. Condensation of triacetic acid methyl ether[3] with benzaldehyde in the presence of magnesium methoxide gave the benzylidene monopyrone methyl ether II (R = Me) which, on treatment with hydrobromic acid,[4] yielded the desmethyl compound II (R = H) [λ_{max}^{EtOH} 232, 240, 300, and 348 mμ (log ϵ 4.20, 4.18, 4.08 and 4.30)]. The benzylidene bispyrone III [λ_{max}^{EtOH} 232, 272, and 392 mμ (log ϵ 4.10, 4.01, and 4.35)] was obtained from II (R = H) by reaction with malonyl dichloride in a manner completely analogous to that used for the synthesis of the parent bispyrone IX.[1] Catalytic hydrogenation of III yielded the dihydro derivative IV [λ_{max}^{EtOH} 270 and 331 mμ (log ϵ 4.10 and 3.94)].

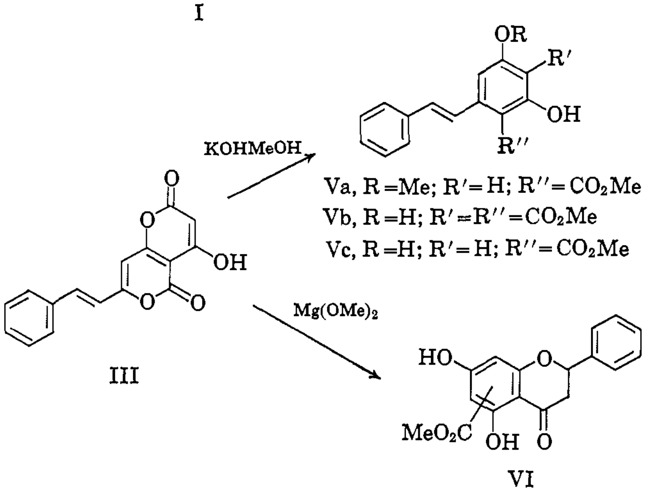
Several sets of basic conditions were used on III and IV to produce ring opening and subsequent intramolecular condensation. The results obtained show that the type of ring closure which occurs is dependent on the choice of reaction conditions. Thus aqueous or alcoholic potassium hydroxide produced the orcinol type of phenolic compound (see Ib), while methanolic magnesium methoxide yielded compounds with acylphloroglucinol skeletons (see Ia). In the specific cases we have chosen to study, III and IV, this has resulted in the formation of compounds having carbon skeletons representative of the stilbenes (Va–c), dihydrostilbenes (VIIa-e), dihydrochalcones (VIII), and flavanones (VI).[5] It is interesting to note that treatment of IV with aqueous potassium hydroxide yielded VIId and dihydropinosylvin (VIIe).



I



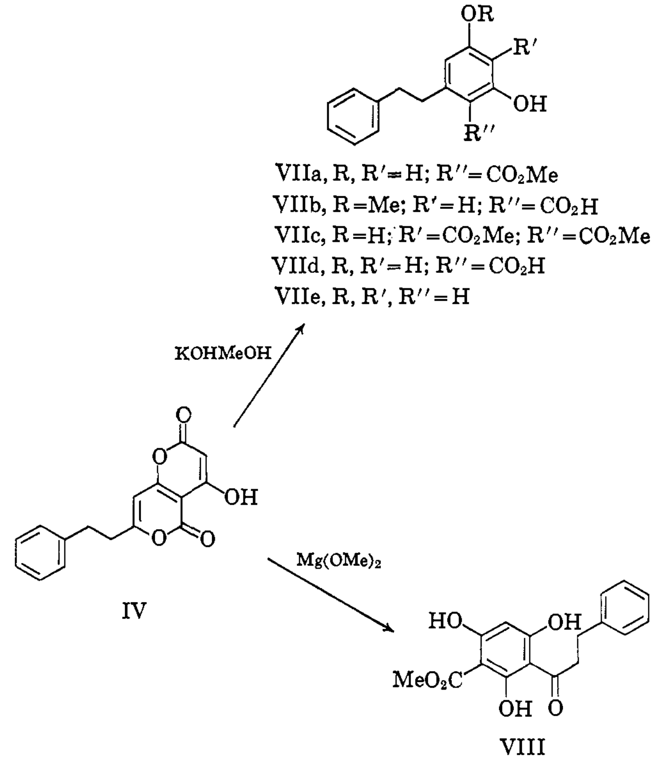
II



Va, R = Me; R' = H; R'' = CO_2Me
Vb, R = H; R' = R'' = CO_2Me
Vc, R = H; R' = H; R'' = CO_2Me

III

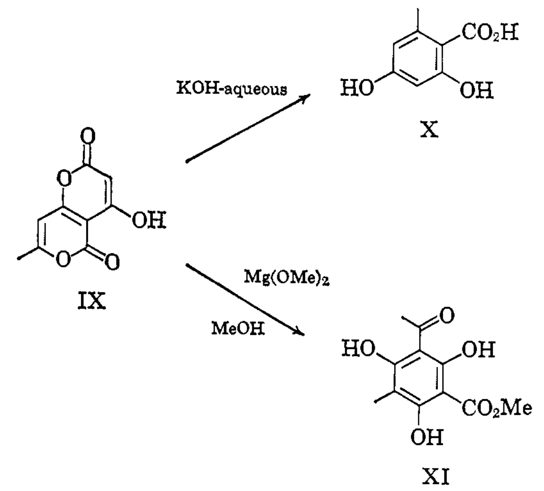
VI



VIIa, R, R' = H; R'' = CO_2Me
VIIb, R = Me; R' = H; R'' = CO_2H
VIIc, R = H; R' = CO_2Me; R'' = CO_2Me
VIId, R, R' = H; R'' = CO_2H
VIIe, R, R', R'' = H

IV

VIII



X

IX

XI

That the choice of basic conditions employed determines the mode of ring closure was further demonstrated with the bispyrone IX. Thus aqueous potassium hydroxide produced orsellinic acid (X)[1] while magnesium methoxide treatment yielded the acylphloroglucinol (XI).[5]

Variations and extensions of the theme expressed above are being actively investigated, and the epoxide of the benzylidene bispyrone is being studied as a possible synthetic precursor of the dihydroflavonols, flavones, aurones, and isoflavones.

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(2) A. J. Birch, *Proc. Chem. Soc.*, 3 (1962).
(3) J. D. Bu'Lock and H. G. Smith, *J. Chem. Soc.*, 502 (1960).
(4) H. Stetter and C. Schellhammer, *Ann.*, **605**, 58 (1957).

(5) Satisfactory analytical data and mass, nmr, ultraviolet, and infrared spectra have been obtained for the new compounds described.

Acknowledgment. We are grateful to the National Research Council of Canada for financial support of this research (Grant No. N.R.C. A2267).

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Thermodynamic Properties of Cubane

Sir:

The heat of formation of solid cubane (C_8H_8) has been determined by combustion with oxygen in a conventional bomb calorimeter.[1] Five determinations yielded an average value for $\Delta E_c°$ of -1156.0 kcal/mole, and, after allowance for a small amount of carbon adhering to the bomb wall, one calculates $\Delta H_f°_{298} = 129.5 \pm 0.8$ kcal/mole. The vapor pressure has been determined over the range 239 to 262°K by the Knudsen effusion method and is given by the equation

$$\log P_{\text{mm}} = (-4.19 \pm 0.097)(10^3/T) + (14.0 \pm 0.8)$$

Thus, at 298°K $\Delta H°_{\text{sub}} = 19.2 \pm 0.4$ kcal/mole and $\Delta H_f°_{[\text{cubane(gas)}]} = 148.7 \pm 1.0$ kcal/mole. By comparison, the heat of formation of an isomeric gas C_8H_8 (cyclooctatetraene) is $+71.1 \pm 0.1$ kcal/mole at 298°K.[2]

Franklin's[3] method of group equivalents assigns a value of -8.7 kcal/mole to eight $\gt$CH groups. This combined with the measured heat of formation gives a total strain energy of 157 kcal/mole for cubane. This strain energy distributed over the six cyclobutane faces of the cube gives 26.2 kcal/mole of strain energy per cube face, in close agreement with the value of 26.0 kcal/mole for the strain energy in cyclobutane.[4] Weltner[5] predicted that cubane (tricyclooctane) should be 80 kcal less stable than cyclooctatetraene which is almost exactly the case.

Mass spectra of cubane have been obtained with 50-v electrons at 100 and 25° on a Consolidated Electrodynamics Corporation Type 21-701 mass spectrometer.[6] The spectra at the two temperatures were in good agreement and thus showed that no significant amount of decomposition occurred in the instrument. Appearance potentials were determined for the principal ions, and these together with relative abundances are given in Table I. The ionization potential agrees quite well with the value computed by the group orbital method[7] employing parameters obtained from paraffin and cycloparaffin hydrocarbons.

Table I. Relative Abundances and Appearance Potentials of Principal Ions from Cubane

Mass no.	Formula	Rel abundance[a]	Appearance potential, ev
39	$C_3H_3^+$	75.6	11.14 ± 0.18
50	$C_4H_2^+$	30.9	16.85 ± 0.08
51	$C_4H_3^+$	48.0	16.74 ± 0.21
52	$C_4H_4^+$	43.8	13.78 ± 0.08
63	$C_5H_3^+$	13.2	14.59 ± 0.24
77	$C_6H_5^+$	32.1	12.21 ± 0.10
78	$C_6H_6^+$	89.1	9.15 ± 0.10
102	$C_8H_6^+$	9.0	10.26 ± 0.21
103	$C_8H_7^+$	100.0	9.50 ± 0.11
104	$C_8H_8^+$	16.5	8.74 ± 0.15

[a] At 25° (% of base peak; electron energy 50 v).

The appearance potentials of the fragment ions suggest that in all cases the ion has probably rearranged to an open-chain structure. The appearance potential for $C_6H_6^+$ agrees very closely with the ionization potential of benzene; nevertheless, we think this is fortuitous. The agreement of the 25 and 100° spectra shows little decomposition, and the relative intensities of the 78 and 77 ions and the appearance potential of $C_6H_5^+$ are quite different from those in benzene. Thus the 78 peak is probably a fragment ion of cubane.

A more detailed paper will be published in the near future.

Acknowledgments. Professor Philip E. Eaton of the University of Chicago generously furnished the cubane sample. The authors gratefully acknowledge the support of the Robert A. Welch Foundation, the National Aeronautical Space Administration, and the Petroleum Research Foundation of the American Chemical Society.

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(1) B. D. Kybett, G. K. Johnson, C. K. Barker, and J. L. Margrave, *J. Phys. Chem.*, 69, 3603 (1965).

(2) E. J. Prosen, W. H. Johnson, and F. D. Rossini, *J. Am. Chem. Soc.*, 72, 626 (1950).

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

(4) A. S. Pell and G. Pilcher, *Trans. Faraday Soc.*, 61, 71 (1965).

(5) W. Weltner, *J. Am. Chem. Soc.*, 75, 4224 (1953).

(6) H. G. Voorhies, C. F. Robinson, T. G. Hall, W. M. Brubaker, and C. E. Berry, "Advances in Mass Spectrometry," Vol. 1, J. D. Waldron, Ed., Pergamon Press, London, 1959, p. 44.

(7) J. L. Franklin, *J. Chem. Phys.*, 22, 1304 (1954).

(8) Chercheur qualifie of the Belgium Fonds National de la Recherce Scientifique. On leave of absence from the University of Liege, Belgium.

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Received November 23, 1965

The Formation of Monofluorocarbene by the Gas-Phase Decomposition of Dihalomethane Molecules Excited during Atomic Exchange Reactions[1]

Sir:

We have formed monofluorocarbene in the gas phase through dehydrohalogenation of excited dihalomethane molecules, in analogy with earlier experiments producing monochlorocarbene,[2] and have detected it through the observation of cyclopropyl fluoride in the presence of ethylene. The reactions have been carried out in the presence of substantial concentrations of O_2 and therefore presumably involve monofluorocarbene in the singlet electronic state.[3]

The excited dihalomethane molecules have been formed through these substitution reactions

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(1) This research was supported by AEC Contract No. AT-(11-1)-34, Agreement No. 126, with the University of California, Irvine.

(2) Y.-N. Tang and F. S. Rowland, *J. Am. Chem. Soc.*, 87, 1625 (1965).

(3) See, however, P. O. Gaspar and G. Hammond, Chapter 12 in "Carbene Chemistry," W. Kirmse, Ed., Academic Press Inc., New York, N. Y., 1964, for an analysis of the validity of these presumptions for CH_2.