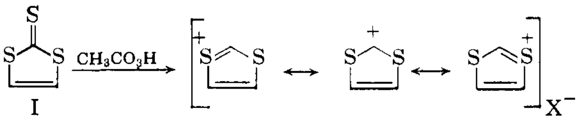
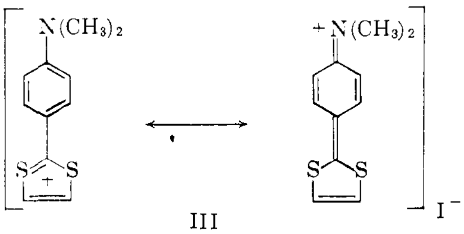


IIa, X = SO_4H; b, I; c, $(NO_2)_3C_6H_2O$

The bright yellow iodide (IIb), m.p. 134–135° dec. (AcOH), was prepared from IIa in propanol, (*anal.* Calcd. for $C_3H_3IS_2$: C, 15.7; H, 1.3; I, 55.2; S, 27.9. Found: C, 15.9; H, 1.3; I, 55.3; S, 28.1). The water-insoluble picrate (IIc) melted at 113–115° (MeCN).

Like 1,2-dithiolium[6] and benzo-1,3-dithiolium[2] derivatives, II is electrophilic. Condensation with dimethylaniline gives a violet dye (λ_{max} 515) isolated as the iodide, m. 220° dec. (AcOH), believed to be III.



III

Future communications will describe further properties of II and the synthesis of I, hitherto obtainable only in minute amounts from the reaction products of sulfur and acetylene at 450°.[7,8]

[6] E. Klingsberg and A. Schreiber, *J. Am. Chem. Soc.*, **84**, 2941 (1962).

[7] F. Challenger, E. A. Mason, E. C. Holdsworth and R. Emmott, *J. Chem. Soc.*, 292 (1953).

[8] D. Leaver, W. A. H. Robertson, and D. M. McKinnon have obtained the perchlorates of the 1,2- and 1,3-dithiolium cations by hydrogen peroxide treatment of the corresponding dithiolethione (*J. Chem. Soc.*, in press). We are exceedingly grateful to Dr. Leaver for informing us of his results in advance of publication.

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RECEIVED JULY 16, 1962

STERIC INHIBITION OF RESONANCE IN THE FORMATION OF RADICALS IN GAS PHASE. THE ALLYL RADICAL[1]

Sir:

Recent work on the interpretation of the reactions of cyclopropane,[1a,2,3a] cyclobutane[2] and their derivatives show that it is possible to account for most of the available kinetic data in terms of a common biradical precursor to all chemical changes. It is the purpose of the present note to call attention to two new studies which not only lend further support to this biradical mechanism but also yield information on the resonance energy of allyl radicals. They also provide the first example for the steric inhibition of resonance in the production of gas phase free radicals.

The general mechanism which we have proposed for the pyrolysis of small ring compounds[1,2] is

$$\text{Ring} \underset{2}{\overset{1}{\rightleftarrows}} \text{Biradical} \xrightarrow{3} \text{Olefin (one or more)}$$

For suitably chosen compounds, the recyclization step 2 can lead to geometrical isomerization[3,4] so that in these cases it is possible to obtain the ratio of the rate constants k_2/k_3. For all processes, the biradical lifetimes are of the order of 10^{-10} to 10^{-11} sec. so that collision processes do not intervene significantly. The steady state rate of olefin formation is given by $d(\text{olefin})/dt = K_{1.2}k_3(\text{Ring})/(1 + k_3/k_2) \approx K_{1.2}k_3(\text{Ring})$ since usually $k_3 \leqslant k_2$.

For cyclopropane and simple alkyl cyclopropanes, the over-all activation energies are of the order of 65 kcal./mole. In these cases it appears that $E_2 \approx E_3$ so that this value of 65 kcal. is approximately E_1. Similar values (62 kcal.) seem to be characteristic of cyclobutane and its alkyl derivatives.[4,5] However, the pyrolysis of vinylcyclopropane[6] which yields cyclopentene or allene + C_2H_4 as final products has an activation energy of 49.6 kcal./mole. This is about 15 to 16 kcal. less than the expected activation energy. It can be accounted for only if we assume that in this case the transition state for step 1 involves a species in which we have developed the nearly complete resonance energy of the allylic type radical, 3,5 biradical, pentene-1. To account for the geometrical isomerization of 1,2-dideuteriocyclopropane it has also been necessary to assume a transition state very close in structure and properties to the biradical.[1]

The structure of vinylcyclopropane will permit full allylic resonance in the transition state and the value of 15 kcal./mole is very close to the value estimated by us independently from considerations of bond energies. In this particular case, the back reaction is estimated to be negligible compared to the rate of cyclopentene formation, or cleavage to olefins.

In striking contrasts to these results, the pyrolysis of the isomeric methylenecyclobutane[7,8] yields allene + C_2H_4 with the usual activation energy of 62.5 ± 1.5 kcal./mole. The isomeric biradical precursor in this case is 1,4 biradical, 2-methylenebutane and the intermediate transition state cannot have the allylic resonance because the H atoms in the CH_2 radical of the opening ring are not in the same plane as the vinyl group but at almost right angles to it. Alternative explanations for the value of 62.5 kcal./mole which involve a low E_1 and a high E_3 may be shown to be inconsistent with thermal data as well as with the vinylcyclopropane system.

The pyrolysis of acetylcyclobutane[9] to give C_2H_4 + vinyl methyl ketone with an E_{act} of 54.5 kcal./

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[1] This work has been supported by Grants from the United States Atomic Energy Commission and the National Science Foundation.

[1a] S. W. Benson, *J. Chem. Phys.*, **34**, 521 (1961).

[2] S. W. Benson and P. Nangia, *ibid.*, in press. See also H. Frey, *J. Am. Chem. Soc.*, **82**, 5947 (1960), and earlier papers.

[3] B. S. Rabinovitch, E. W. Schlag and K. B. Wiberg, *J. Chem. Phys.*, **28**, 504 (1958); (a) B. S. R. and E. W. S., *J. Am. Chem. Soc.*, **82**, 5996 (1960).

[4] H. R. Gerberich and W. D. Walters, *ibid.*, **83**, 3935 (1961); **83**, 4884 (1961).

[5] S. M. E. Kellner and W. D. Walters, *J. Phys. Chem.*, **65**, 466 (1961).

[6] M. C. Flowers and H. Frey, *J. Chem. Soc.* (London), 3547 (1961).

[7] J. P. Chesick, *J. Phys. Chem.*, **65**, 2170 (1961).

[8] R. L. Brandaur, *et al.*, *ibid.*, **65**, 2269 (1961).

[9] L. G. Daignault and W. D. Walters, *J. Am. Chem. Soc.*, **80**, 541 (1958).

mole is consistent with the above discussion if the resonance energy in R—CO—$CH_2\cdot$ radicals is assigned a value of about 7 kcal. This is a few kcal. higher than we would expect from bond energy considerations but not outside the limits of error of the available data. On the other hand, the very low E_{act} of 32.5 kcal. observed[10] for the first order isomerization of cyclobutene to butadiene cannot be reconciled with the present discussion unless one assumes that the strain energy in cyclobutene exceeds that in cyclobutane by about 15 to 20 kcal. This seems rather unreasonable.

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[10] W. Cooper and W. D. Walters, *J. Am. Chem. Soc.*, **80**, 4220 (1958).

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RECEIVED MAY 31, 1962

CESIUM SALTS CONTAINING THE $ClHCl^-$ SPECIES

Sir:

The report of West[1] on the preparation of CsClHCl has stimulated much interest and some further study of this compound (including this work). Our work indicates that the compound prepared by West is not an anhydrous salt but contains an amount of water equivalent to the amount of HCl contained. This explains the failure of Sharp[2] to find the stretching frequency characteristic of the $ClHCl^-$ species. We wish to report the preparation of anhydrous CsClHCl.

On exposure of anhydrous CsCl to anhydrous HCl at −78.5°, rapid absorption of HCl initially takes place and then slow absorption for several days to form the stoichiometric compounds. Pressure–composition diagrams indicate the presence of CsCl·0.75HCl and CsCl·1HCl, the product being determined by the final pressure of HCl. No interaction of CsCl with HCl gas at one atmosphere could be detected at 0°. From pressure measurements at two temperatures the indicated pressures at 30°, the temperature of West's work, would be *ca.* 4.4 atmospheres and >400 atmospheres for the CsCl·0.75HCl and CsCl·1HCl compounds, respectively. Both of these anhydrous compounds were colorless.

Since these compounds appeared to be different from the compound reported by West, his preparative scheme was followed to obtain a sample for comparison. Four grams of Fisher purified grade CsCl were dissolved in 3 cc. of water, and the solution alternately treated with HCl gas and cooled. Approximately 2 g. of very pale yellow crystals were recovered and dried. Analysis for water using a Karl Fischer titration, HCl by titration with NaOH and total chloride by gravimetric determination as AgCl are all consistent with the compound CsCl·0.74HCl·0.74HOH. The compound prepared by West thus appears to be the hydrated CsCl·0.75HCl or the hydrated CsCl·1HCl or a mixture of the two.

Acknowledgment.—We are grateful to the National Science Foundation for a grant which supported this work.

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RECEIVED JULY 16, 1962

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[1] R. West, *J. Am. Chem. Soc.*, **79**, 4568 (1957).

[2] D. W. A. Sharp, *J. Chem. Soc.*, 2558 (1958).

TRICYCLO[4.4.0.0^{3,8}]DECANE

Sir:

Consideration of the structure and reactivity of the highly symmetrical molecule adamantane has prompted us to synthesize its twist[1] boat isomer tricyclo[4.4.0.0^{3,8}]decane (Fig. 1), a convenient trivial name for which is "twistane." Inspection of models reveals that twistane, in contrast to adamantane, is dissymmetric and composed exclusively of twist boat cyclohexane rings, but is

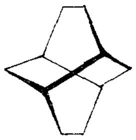

Fig. 1.

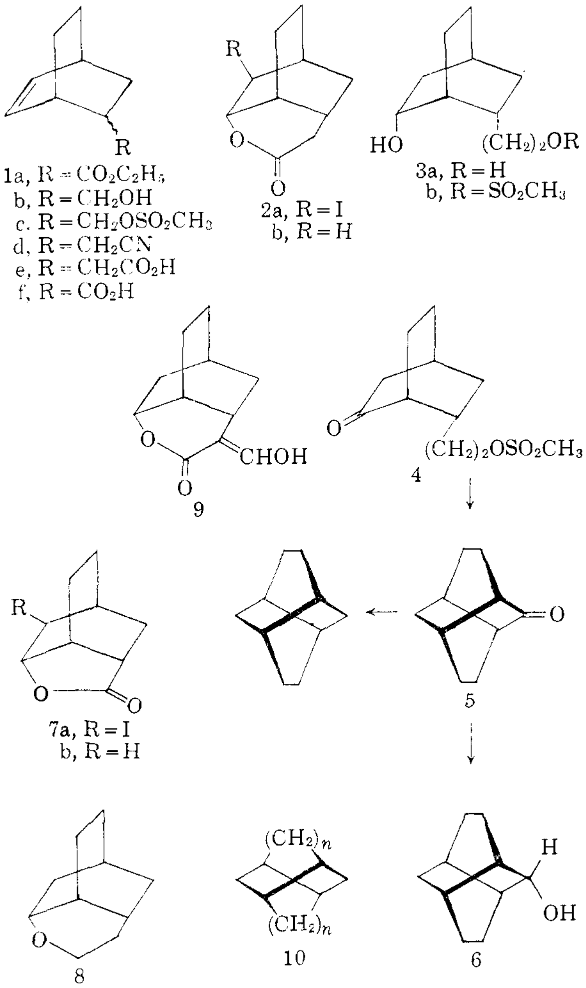

Fig. 2.

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[1] W. S. Johnson, V. J. Bauer, J. L. Margrave, M. A. Frisch, L. H. Dreger and W. N. Hubbard, *J. Am. Chem. Soc.*, **83**, 606 (1961).