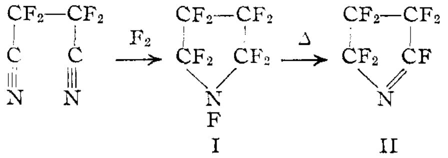


This transformation was accomplished by passing I on a stream of dry nitrogen through a stainless steel tube packed with steel gauze and maintained at 500°. After purification by preparative chromatography, II was a colorless liquid, b.p. 22° (extrapolated), and mol. wt. 198 ± 4 (calcd. 195). The infrared spectrum showed a sharp band at 5.81 μ which has been assigned to the C$=$N stretching vibration. When II reacted with an excess of 10% NaOH solution in a sealed tube for 24 hours at room temperature, it was hydrolyzed to ammonia, sodium carbonate and sodium tetrafluorosuccinate. The latter was identified by comparing its infrared spectrum with that of an authentic sample prepared by the oxidation of 1,2-dichlorotetrafluorocyclobut-1-ene.[3] The free acid, obtained by the acidification and ether extraction of the hydrolysis product, gave an anilinium salt, m.p. 223–225°. A mixture melting point with a sample of the dianilinium salt of tetrafluorosuccinic acid[4] showed no depression.

Subsequent to the submission of this communication, II has been claimed by Ulrich,[5] who presented only an unconvincing elemental analysis in support of this assignment. His reported boiling point for II of 56 to 58° is unreasonable in view of the close relationship between structure and boiling point which has been observed for highly fluorinated organic compounds.

[3] A. L. Henne and W. F. Zimmer, *J. Am. Chem. Soc.*, **73**, 1103 (1951).

[4] M. W. Buxton, *et al.*, *J. Chem. Soc.*, 3830 (1952).

[5] H. Ulrich, *et al.*, *J. Org. Chem.*, **27**, 2585 (1962).

DEPARTMENT OF CHEMISTRY B. C. BISHOP
DUKE UNIVERSITY J. B. HYNES
DURHAM, N. C. L. A. BIGELOW

RECEIVED JULY 5, 1962

THE BECKMANN REARRANGEMENT OF KETOXIMES: A NEW METHOD

Sir:

The Beckmann rearrangement has widespread synthetic applications.[1] Experimental procedures[1] frequently involve the use of strongly acidic reagents or of elevated temperatures, causing isomerization of the oximes prior to rearrangement. We now wish to report a facile and rapid general method of Beckmann rearrangement of immediate utility for the synthesis of amides and lactams.

A solution of the ketoxime in acetone was treated at 0° with successive equimolar quantities of 8% aqueous sodium hydroxide solution and of benzene(or *p*-toluene)-sulfonyl chloride, and the mixture shaken at 0° for ten minutes. Removal of acetone *in vacuo* at 25° gave a quantitative yield of the benzene(or *p*-toluene)-sulfonate ester (which may be isolated in the usual manner). The crude ester was taken up in benzene and the benzene solution, concentrated *in vacuo* at 25° to a small volume, was poured onto a column of alumina (Brockmann activity I or II, alkaline or acid-washed; *ca.* 25 g. of alumina per g. of ester) covered with hexane. Unreacted sulfonyl chloride was removed by washing with hexane, and elution with benzene containing an increasing proportion of chloroform then gave the pure amide or lactam, usually in almost quantitative yield.

In this manner methyl 2-thienyl ketoxime, m.p. 112–113°, gave first the oxime benzenesulfonate, m.p. 85–86°, and then 2-acetamidothiophene, m.p. 161°, in 90% yield. The isomeric unstable methyl 2-thienyl ketoxime, m.p. 81–84°, afforded an oxime benzenesulfonate, m.p. 83–84° (preparation to be described) and thence 66% N-methylthiophene-2-carboxamide, m.p. 112–114°. *tert*-Butyl 2-thienyl ketoxime, m.p. 142–144°, yielded a benzenesulfonate ester, m.p. 67–68°, converted to 40% pure N-*tert*-butylthiophene-2-carboxamide, m.p. 147–148°. Phenyl 2-thienyl ketoxime, m.p. 114–116°, gave 90% thiophene-2-carboxanilide, m.p. 143–144.5°; and benzophenone oxime afforded 90% benzanilide. Finally 5-α-cholestane-3-one oxime, m.p. 199–201°, gave (*via* the *p*-toluenesulfonate ester, prepared in pyridine instead of acetone) 85% of pure 3-aza-A-homo-5-α-cholestane-4-one,[2,3] m.p. 271–273°.

Satisfactory analytical and spectroscopic data were obtained for all new compounds reported herein, and identity of all products was confirmed by mixed melting points with authentic samples.

The only previous report of the Beckmann rearrangement of a ketoxime ester by chromatography on alumina appears to be the production of benzanilide on attempted purification of benzophenone oxime diphenylphosphate.[4]

[1] L. G. Donaruma and W. Z. Heldt, *Organic Reactions*, **11**, 1 (1960).

[2] C. W. Shoppee and J. C. P. Sly, *J. Chem. Soc.*, 3458 (1958).

[3] N. J. Doorenbos and H. Singh, *J. Pharm. Sci.*, **51**, 418 (1961).

[4] J. H. Turnbull, *Chem. and Ind.*, 350 (1956).

DEPARTMENT OF
PHARMACEUTICAL CHEMISTRY J. CYMERMAN CRAIG
UNIVERSITY OF CALIFORNIA A. R. NAIK
SAN FRANCISCO 22, CALIFORNIA

RECEIVED JUNE 21, 1962

1,3-DITHIOLIUM SALTS; A NEW PSEUDOAROMATIC CATION

Sir:

The 1,3-dithiolium system heretofore has been known only in the form of benzo[1,2] and aryl[3] derivatives, although LCAO-MO. calculations[4] suggested that the existence of the parent cation was "probable." We have obtained 1,3-dithiolium hydrogen sulfate (IIa) in 80% yield by peracetic acid oxidation of 1,3-dithiole-2-thione (I) in acetone solution; this reaction earlier proved valuable in the synthesis of 1,2-dithiolium salts.[5]

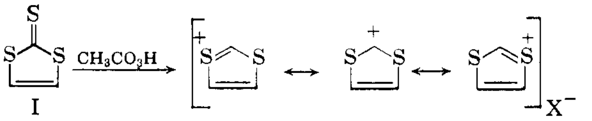
[1] W. R. H. Hurtley and S. Smiles, *J. Chem. Soc.*, 1821 (1926); 534 (1927).

[2] L. Soder and R. Wizinger, *Helv. Chim. Acta*, **42**, 1733, 1779 (1959).

[3] D. Leaver and W. A. H. Robertson, *Proc. Chem. Soc.*, 252 (1960).

[4] J. Koutecký, J. Paldus and R. Zahradník, *Coll. Czechoslov. Chem. Commun.*, **25**, 617 (1960), *cf.* R. Zahradník and J. Koutecký, *Tetrahedron Letters*, 632 (1961).

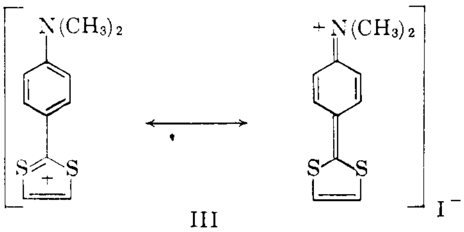
[5] E. Klingsberg, *J. Am. Chem. Soc.*, **83**, 2934 (1961).



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.

BOUND BROOK LABORATORIES
AMERICAN CYANAMID COMPANY
BOUND BROOK, N. J.
ERWIN KLINGSBERG

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./

---

(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).