The **monoadducts** have been prepared by the method of Price and Gillis.[21] Allyl methyl sulfide[21]: b.p. 93.5–95°; infrared,[22] 3.27 (=CH),[23a] 5.45 (overtone to =CH$_2$),[23b] 6.14 (C=C),[23c] 10.95 μ (=CH$_2$ deform.).[23d] Allyl acetyl sulfide: b.p. 48–49° (27 mm.) (*Anal.* Calcd. for C_5H_8OS: C, 51.69; H, 6.94. Found: C, 51.98; H, 6.97); infrared, 3.26 (=CH),[23a] 5.45 (overtone to =CH$_2$),[23b] 6.13 (C=C),[23c] 10.90 μ (=CH$_2$ deform.).[23d] Allyl phenyl sulfide[24]: b.p. 51–52° (0.4 mm.); infrared, 6.12 (C=C olefinic),[23c] 10.90 μ (=CH$_2$ deform.).[23d]

The **diadducts** have been prepared by the general method of Mann and Purdie.[25] 1,3-Bis(methylthio)propane[26]: b.p. 99–100° (27 mm.); infrared, 3.45, 7.0, 7.95, 8.04, 10.50 μ. 1,3-Bis(acetylthio)propane: b.p. 105–106° (2 mm.) (*Anal.* Calcd. for $C_7H_{12}O_2S_2$: C, 43.73; H, 6.29. Found: C, 43.53; H, 6.25); infrared, 3.40, 5.90, 6.97, 7.39, 8.07, 8.80 μ. 1,3-Bis(phenylthio)propane[25]: b.p. 170–171° (0.3 mm.). 1,2-Bis(methylthio)propane: b.p. 90.5–91° (27 mm.) (*Anal.* Calcd. for $C_5H_{12}S_2$: C, 44.06; H, 8.87; S, 47.06. Found: C, 44.45; H, 9.01; S, 47.1); infrared, 3.36 and 3.43, 6.99, 7.29, 7.60, 7.94, 8.17, 8.43, 9.05, 9.38, 9.83, 10.47, 14.82 μ. 1,2-Bis(acetylthio)propane: b.p. 70–72° (0.2 mm.) (*Anal.* Calcd. for $C_7H_{12}O_2S_2$: C, 43.72; H, 6.29. Found: C, 43.59; H, 6.15). 1,2-Bis(phenylthio)propane: b.p., 158–160° (0.3 mm.) (*Anal.* Calcd. for $C_{15}H_{16}S_2$: C, 69.18; H, 6.19; S, 24.63. Found: C, 69.50; H, 6.36; S, 24.75); infrared, 3.29, 3.40, 3.45, 6.34, 6.77, 6.97, 7.32, 8.50, 9.20, 9.77, 13.50, 14.50 μ.

Acknowledgment.—The authors wish to thank A. M. Palmer and G. F. Shea for technical help and Miss M. J. Doolan for the g.c. analyses.

---

[21] C. C. Price and R. G. Gillis, *J. Am. Chem. Soc.*, **75**, 4750 (1953).

[22] For the monoadducts the bands characteristic of the double bond are reported. For the diadducts the strongest bands of the spectrum are reported without correlating them to particular structural elements.

[23] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1959: (a) p. 43; (b) p. 50; (c) pp. 35–38; (d) pp. 49–51.

[24] C. D. Hurd and H. Greengard, *J. Am. Chem. Soc.*, **52**, 3356 (1930).

[25] F. G. Mann and D. Purdie, *J. Chem. Soc.*, 1557 (1935).

[26] See also S. Mathias, *Bol. Fac. Filosof., cienc. letras, Univ. São Paulo; Quim. No. 1*, **14**, 75 (1942).

Transannular Sulfoxide–Ketone Salt Formation across a Seven-Membered Ring[1]

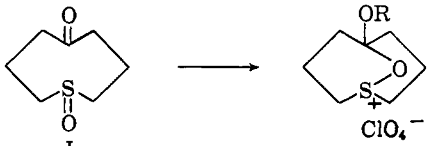
NELSON J. LEONARD AND WALLACE L. RIPPIE

Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois

Received March 1, 1963

This investigation has established for the first time the occurrence of a transannular reaction between sulfoxide and ketone groups, with protonation, across a seven-membered ring: 1-thiacycloheptan-4-one 1-oxide (III) with perchloric or fluoboric acid gave the corresponding 5-hydroxy-8-oxa-1-thioniabicyclo[3.2.1]octane salt (IVa,b), with an oxygen bridge between the sulfur and the carbonyl carbon. The bicyclic fluoborate was methylated with 2,2-dimethoxypropane to give 5-methoxy-8-oxa-1-thioniabicyclo[3.2.1]octane fluoborate (IVc). Hydrolysis of both the bridgehead hydroxy and methoxy salts occurred so readily that all operations had to be conducted in a dry box. We found it hazardous to work with the perchlorate salts in this bicyclic series.

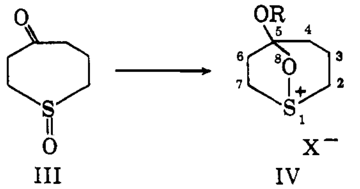
In an investigation of the occurrence of transannular interactions and reactions of diametric sulfoxide and ketone groups in medium rings (eight–eleven members), monocyclic 1-thiacyclooctan-5-one 1-oxide (I) was converted to a bicyclic perchlorate salt by transannular reaction involving protonation of the carbonyl oxygen.[2] The protonic salt and its methoxy and acetoxy derivatives were shown to have 1-thioniabicyclo[3.3.1]nonane structures (II), with an oxygen bridge between the sulfur and the carbonyl carbon.



I II

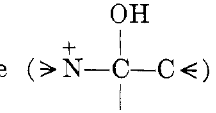
IIa, R=H
b, R=CH_3
c, R=$COCH_3$

This type of bridging generates two six-membered rings from an eight-membered ring rather than two five-membered rings, as would have been the case had sulfur acted as the donor. The action of oxygen of the sulfoxide as the donor suggested that in the seven-membered ring system, 1-thiacycloheptan-4-one 1-oxide (III), similar bridging could lead to a probable structure of the 1-thioniabicyclo[3.2.1]octane type (IV) consisting of a five- and a six-membered ring, whereas the result of direct sulfur–carbon bridging would be a structure consisting of four- and five-membered rings, thermodynamically unstable under the reversible conditions of salt formation.



III IV

IVa, R=H, X=ClO_4
b, R=H, X=BF_4
c, R=CH_3, X=BF_4

A test of the ability of III, and possibly of a six-membered-ring compound of the 1-thiacyclohexan-4-one 1-oxide type, to undergo transannular reaction is also of theoretical interest because it should provide information concerning the lower limits of ring size for this phenomenon to occur. The lower limit for transannular bond formation, accompanying protonation, between diametric tertiaryamine and ketone[3] or sulfide and ketone functions[4,5] is presently at the eight-membered ring. However, when an additional atom is introduced between amino nitrogen and the 4-carbon of a six-membered ring in configuration and conformation favorable for reaction, a bridge may be formed creating two five-membered rings in an azoniabicyclo[2.2.1]heptane system. Thus, Bell and Archer[6] have shown that the salt of 3α-phenyl-3β-tropanyl phenyl ketone exists mainly in a transannular bridged structure  $(>\overset{+}{N}-\overset{OH}{\underset{|}{\overset{|}{C}}}-C<)$ and Polonovski and Polonovski[7] reported that scopin-

---

[1] Support of this work by research grants (NSF-G6040 and NSF-G14121) from the National Science Foundation is gratefully acknowledged.

[2] N. J. Leonard and C. R. Johnson, *J. Am. Chem. Soc.*, **84**, 3701 (1962).

[3] N. J. Leonard, R. C. Fox, and M. Ōki, *ibid.*, **76**, 5708 (1954).

[4] N. J. Leonard, T. L. Brown, and T. W. Milligan, *ibid.*, **81**, 504 (1959); **82**, 4075 (1960).

[5] C. G. Overberger and A. Lusi, *ibid.*, **81**, 506 (1959).

[6] M. R. Bell and S. Archer, *ibid.*, **82**, 151 (1960).

ium tropate (containing $\geqslant\overset{+}{N}—O—C\leqslant$) is formed when *l*-scopolamine is treated with hydrogen peroxide. In carbocyclic systems, Cope, Liss, and Wood[8] have provided an example of a proximity effect operating across a seven-membered ring, by detection of 2.4% of transannular products in the solvolysis of cycloheptene oxide with dilute hydrochloric acid; further, by careful product isolation procedures evidence was found for transannular participation to the extent of 0.3% in a six-membered ring analog.

The synthesis of the required 1-thiacycloheptan-4-one 1-oxide (III), m.p. 75.5–76°, was accomplished by oxidation of 1-thiacycloheptan-4-one[9] with aqueous sodium metaperiodate.[10] The infrared spectrum of III, as in the case of the analogous eight-membered ring compound, showed no anomaly. The ultraviolet spectrum in cyclohexane solution exhibited a maximum corresponding to the low energy carbonyl transition at 287 mμ and a second maximum at 217 mμ, which is in the region of absorption of some model sulfoxides. The absorption curve did not show an intermediate maximum such as that observed for 1-thiacyclooctan-5-one 1-oxide (I), *i.e.*, at 235 mμ, responsive to solvent change.[2] The electron donor and basic characteristics of sulfoxides have been demonstrated by the obtainment of salts with perchloric acid.[11] Addition of 70% perchloric, 48% and 70% fluoboric, and 70% nitric acid to ether solutions of 1-thiacycloheptan-4-one 1-oxide uniformly failed to produce any separation of salt. We ascribe the failure to the presence of water, which has been shown to hydrolyze 5-hydroxy-9-oxa-1-thioniabicyclo[3.3.1]nonane perchlorate (IIa) very rapidly.[2] In order to reduce the water content of the acids a distribution of the strong acid between its concentrated aqueous solution and ether was utilized. Upon admixture of a saturated ethereal solution of the sulfoxide–ketone and the appropriate ethereal-distributed acid, only perchloric acid among the three cited before produced an ether-insoluble salt. The mixture resulting from the addition of ethereal-distributed perchloric acid to the sulfoxide ketone in ether was allowed to stand six hours in a nitrogen-filled dry box, or until the salt had separated completely and the supernatant was clear. The microcrystalline perchlorate was triturated with fresh anhydrous ether. The salt–ether suspension was filtered through a coarse glass fritted filter. It was advisable because of the electrostatic and explosive nature of the perchlorate to perform all transfers of the salt as an ether slush and to perform microanalytical and spectral analyses immediately when the salt reached constant weight. The salt underwent rapid decomposition when dry. An attempt to obtain a 180-mg. sample failed when the sample exploded *in vacuo*. A better acid—nonaqueous, nonoxidizing, strong,[12,13] and having an anion of low nucleophilicity—to employ in salt formation was anhydrous hydrogen tetrafluoborate.[14] A stoichiometric quantity of distilled boron trifluoride ethereate was brought into contact with freshly condensed dry hydrogen fluoride. To the fuming oil anhydrous ether was added in a drybox. After shaking and allowing the solution, in which some of the oil was suspended, to settle, dropwise addition of the ethereal hydrogen tetrafluoborate to 1-thiacycloheptan-4-one 1-oxide (III) dissolved in anhydrous ether produced a white milky mixture. The supernatant became clear after standing overnight and was decanted and replaced by fresh anhydrous ether. The microcrystalline residue was shaved from the sides of the flask with a spatula and triturated with ether. The hygroscopic ethereal slush was transferred and analyzed satisfactorily as described for the perchlorate salt.

Both the perchlorate and the fluoborate of III exhibited strong infrared absorption (in acetonitrile solution) at 3320 cm.$^{-1}$ indicative of O—H. Neither salt was transparent in the region of S=O stretch because of absorption by the anions, but neither salt showed a strong absorption band in the 1245 cm.$^{-1}$ region corresponding to S^+=O stretch as in trimethyloxosulfonium perchlorate (in acetonitrile).[2] The spectral observations require modification of both ketone and sulfoxide function in III on salt formation. The presence of strong O—H absorption and apparent absence of an $\geqslant S^+$=O function in the cationic species limit the structure to IV (a or b), 5-hydroxy-8-oxa-1-thioniabicyclo[3.2.1]octane perchlorate or fluoborate. The very weak absorption of these salts observed just above 1700 cm.$^{-1}$ is considered to arise from the formation of the original sulfoxide ketone ($\nu_{\max}^{CH_3CN}$ 1704 cm.$^{-1}$) as a result of very rapid hydrolysis of the salt. In support, when a Nujol mull of the hydroxy salt was exposed to a moist atmosphere the hydroxyl band disappeared and the carbonyl band became intense. The alternative possibility that the salts contain a mixture of $>\overset{+}{S}—O—\overset{|}{\underset{|}{C}}—OH$ and $>\overset{+}{S}—OH >C=O$ cations is less likely on the basis of n.m.r. spectra and the behavior of model compounds, such as methyl 4-ketopentyl sulfoxide and 1-thiacyclohexan-4-one 1-oxide,[2,10] on attempted salt formation.

Recovery of the original sulfoxide ketone (III) from the salt was possible by titration with base followed by continuous extraction with methylene chloride, thereby establishing the point that compound III had not undergone rearrangement during acid treatment and completing the assignment of the salt structure as IV (a or b). Chemical evidence for the transannular salt structure was obtained, as in the case of the eight-membered ring analog,[2] by the preparation of an O-methyl derivative. This was accomplished by addition of 2,2-dimethoxypropane to an acetone solution of 5-hydroxy-8-oxa-1-thioniabicyclo[3.2.1]octane fluoborate (IVb). A compound was obtained which had the correct analysis for IVb plus CH_2, consistent with the structure IVc. Any alternative alkylated structure appears less likely in view of the failure of C=O models to add CH_2 and of S=O models to form derivatives under the the reaction conditions specified. The crystals of 5-methoxy-8-oxa-1-thioniabicyclo[3.2.1]octane fluoborate (IVc) were electrostatic and hygroscopic, reverting

---

(7) M. Polonovski and M. Polonovski, *Bull. soc. chim.*, [IV] **43**, 79 (1928); *Compt. rend.*, **185**, 277 (1927).

(8) A. C. Cope, T. A. Liss, and G. W. Wood, *Chem. Ind.* (London), 823 (1956); *J. Am. Chem. Soc.*, **79**, 6287 (1957).

(9) C. G. Overberger and A. Katchman, *ibid.*, **78**, 1965 (1956).

(10) N. J. Leonard and C. R. Johnson, *J. Org. Chem.*, **27**, 282 (1962).

(11) J. de Pascual Teresa, *Anales soc. españ. fis. y quim.*, **45B**, 235 (1949); *Chem. Abstr.*, **44**, 3935 (1950).

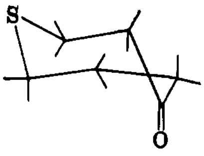
(12) E. L. Mackor, A. Hofstra, and J. H. van der Waals, *Trans. Faraday Soc.*, **54**, 66 (1958).

(13) E. Wilke-Dörfurt, *Z. angew. Chem.*, **37**, 712 (1924).

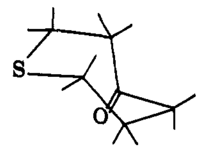
(14) E. Müller and H. Huber-Emden, *Ann.*, **649**, 70 (1961).

rapidly by hydrolysis to the sulfoxide ketone (III), as evidenced by the appearance of carbonyl absorption in the infrared spectrum. In comparison with the corresponding transannular hydroxy and methoxy salts of the eight-membered ring sulfoxide ketone (IIa and b),[2] compounds IVa, b, and c are much less stable and are more susceptible to hydrolysis.

The n.m.r. spectrum of 1-thiacycloheptan-4-one 1-oxide (III) in deuteriochloroform was complicated and consisted of overlapping sets of signals corresponding to the ten different C—H protons in the unsymmetrical molecule. Reading from high to low field, one encounters two proton signals with different chemical shifts and different splitting patterns corresponding to the C-6 hydrogens, signals corresponding to the four protons adjacent to C=O and signals for the four protons adjacent to S=O. There was no proton resonance at lower field than τ value 6.2.[15] Both the perchlorate and fluoborate salt, which were determined in trifluoroacetic acid solution, showed a shift of the low field group, due to the protons on the carbons adjacent to sulfur, terminating downfield at τ value 5.5, consistent with the introduction of a positive charge on the sulfur. The conformation of the $\mathrm{O_{CO}}$-protonated bicyclic salt structure IVa,b is relatively fixed, with a near-planar or envelope-conformed five-membered ring on one side and a six-membered ring, with probable preferred chair structure, on the other. Two postulated conformations of 1-thiacycloheptan-4-one may be constructed, V and VI, in which 1,2-interactions are at a minimum and the opposing H:H interactions have been balanced as much as possible.[16] The sulfoxide oxygen may then be introduced into V or VI on either side of the C—S—C plane to indicate the possible preferred conformations of 1-thiacycloheptan-4-one 1-oxide (III). The dynamic process of protonation and bridging has not been investigated.



V



VI

Experimental[17]

1-Thiacycloheptan-4-one 1-Oxide (III).—1-Thiacycloheptan-4-one[9] (6.78 g., 0.052 mole) was added to an ice-cold magnetically stirred solution of sodium metaperiodate (12.24 g., 0.057 mole) in 212 ml. of water. The mixture was stirred for 21 hr. in the ice bath. The precipitated sodium iodate was removed by filtration and the solution was extracted continuously with methylene chloride. The contents of the flask containing the methylene chloride was changed frequently to avoid pyrolysis of the accumulating sulfoxide.[18] The solvent was evaporated at reduced pressure. The crude product was twice sublimed at 50° (0.1 mm.) to give analytically pure 1-thiacycloheptan-4-one 1-oxide, m.p. 75.5–76°; $\nu_{\max}^{\mathrm{CH_3CN}(5\%)}$ 1704 cm.$^{-1}$ (C=O) and $\nu_{\max}^{\mathrm{CHCl_3}}$ 1705 (C=O) and 1017 cm.$^{-1}$ (S=O); $\lambda_{\max}^{\mathrm{CH_3CN}}$ 287 and 217 mμ, with the magnitude of the extinction coefficients in some doubt due to the hygroscopic nature of the compound.

Anal. Calcd. for $C_6H_{10}O_2S$: C, 49.30; H, 6.89. Found: C, 49.64; H, 6.68.

5-Hydroxy-8-oxa-1-thioniabicyclo[3.2.1]octane Perchlorate (IVa).—A mixture of 10 g. of 70% aqueous perchloric acid and 300 g. of anhydrous ether was shaken and allowed to stand in order to separate completely. A freshly prepared solution may be utilized if the upper layer is first centrifuged to separate suspended water. In a drybox under nitrogen the ethereal perchloric acid was added dropwise to an ether solution containing *ca.* 300 mg. of 1-thiacycloheptan-4-one 1-oxide until precipitation was complete and the presence of excess perchloric acid was indicated. The crystals which separated from the mixture after 6 hr. were scraped from the flask, washed onto a coarse fritted glass filter, and thoroughly washed with ether. The electrostatically charged crystals were easily transferred when wet with ether to the platinum combustion boat which was placed in an aluminum pig. The sample was dried under high vacuum and weighed at 3-min. intervals until a constant weight was obtained. It was then quickly transferred to the combustion train for analysis. It *explodes* at 77°. The infrared spectrum (15% in acetonitrile) had only slight absorption in the carbonyl region but exhibited a strong band at 3320 cm.$^{-1}$ (O–H). Special precautions were taken during combustion for microanalysis.

Anal. Calcd. for $C_6H_{11}ClO_6S$: C, 29.21; H, 4.50; neut. equiv., 246.6. Found: C, 29.17; H, 4.49; neut. equiv. (titration in cold ethanol), 247.6.

Upon attempted vacuum desiccation (complete ether removal), a 180-mg. sample exploded.

5-Hydroxy-8-oxa-1-thioniabicyclo[3.2.1]octane Fluoborate (IVb).—Anhydrous hydrogen tetrafluoborate in ether[14] was prepared in the following manner. Redistilled boron trifluoride etherate (14.379 g., 0.1014 mole) was contained in a tightly closed 30-ml. polyethylene bottle. The requisite amount (2.025 g., 0.1014 mole) of anhydrous hydrogen fluoride was condensed in a dry, nitrogen-filled 250-ml. side-siphon polyethylene wash bottle. The gas was passed from a cylinder of anhydrous hydrogen fluoride through polyethylene tubing and safety bottle to a 5-ft. coiled piece of 304 stainless steel tubing which had been immersed in a ice–salt bath. The first few milliliters of the liquefied gas were discarded. A slight excess of the liquid hydrogen fluoride was passed into the polyethylene bottle. The cap was secured, and the excess hydrogen fluoride was allowed to evaporate. Slight pressure was applied to the bottle while the exit tube was below the surface of the boron trifluoride etherate. Upon releasing the pressure, the liquid was drawn into the wash bottle containing hydrogen fluoride. In a drybox, anhydrous ether was added to the small polyethylene bottle containing the remaining boron trifluoride etherate and then drawn into the wash bottle. Additional anhydrous ether was added with shaking to the anhydrous hydrogen tetrafluoborate, bringing the volume to about 200 ml. After standing for 1 hr. a small amount of straw-colored liquid remained undissolved. The depth of the dispensing tube was adjusted to deliver only the colorless solution. To 200 ml. of anhydrous ether containing *ca.* 200 mg. of 1-thiacycloheptan-4-one 1-oxide which had been filtered in the dry box, ethereal acid was added until no further cloudiness appeared and the mixture was allowed to stand 6 hr. The ether was decanted from the deposited solid and replaced by fresh anhydrous ether. After the crystals were scraped from the flask onto a coarse fritted glass filter, a few milligrams were transferred to a preweighed analytical boat in an aluminum pig. These electrostatic crystals were dried to a constant weight and then analyzed immediately. The compound decomposes at 92°. The infrared spectrum (10% in acetonitrile) had only slight absorption in the carbonyl region but exhibited a strong band at 3320 cm.$^{-1}$ (O–H).

Anal. Calcd. for $C_6H_{11}BF_4O_2S$: C, 30.79; H, 4.74. Found: C, 31.02; H, 4.85.

5-Methoxy-8-oxa-1-thioniabicyclo[3.2.1]octane Fluoborate (IVc).—To 100 mg. of 5-hydroxy-8-oxa-1-thioniabicyclo[3.2.1]-octane fluoborate in 2 ml. of acetone was added 2 ml. of 2,2-dimethoxypropane. *The sample immediately became orange-yellow.* Anhydrous ether (10 ml.) was added and the sample

---

[15] G. V. D. Tiers, "Table of τ Values for a Variety of Organic Compounds," Minnesota Mining and Manufacturing Co., St. Paul, Minn., 1958; G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

[16] Data from heats of combustion have shown that replacement of a methylene group in a cycloalkane by a sulfur atom relieves strain due to H:H nonbonded interactions (Sj. Kaarsemaker and J. Coops, *Rec. trav. chim.*, **71**, 261 (1952)).

[17] The authors are indebted to Josef Nemeth for the microanalyses and to Oliver Norton and Dick Johnson for the n.m.r. and the infrared spectra. All transfers of analytical samples to preweighed analytical platinum boats enclosed in aluminum pigs for n.m.r. and infrared spectra were performed in a drybox through which dry nitrogen was recirculated after passing through a drying tower.

[18] C. A. Kingsbury and D. J. Cram, *J. Am. Chem. Soc.*, **82**, 1810 (1960).

was transferred to a refrigerator at 5° for 4 hr. to complete the crystallization. The supernatant liquid was decanted and the crystals were triturated with ether. These hygroscopic, electrostatic crystals were transferred to an analytical boat and dried to a constant weight prior to analysis. The infrared spectrum (Nujol) was not free of O–H absorption.

Anal. Calcd. for $C_7H_{13}BF_4O_2S$: C, 33.89; H, 5.28. Found: C, 34.07; H, 5.50.

Co-Reductions with Alkali Metals. I. Styrene and Acetone with Sodium

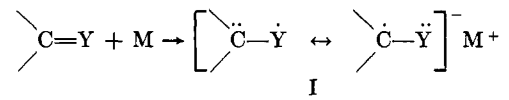
JAY K. KOCHI[1]

Department of Chemistry, Case Institute of Technology, Cleveland, Ohio, and Shell Development Company, Emeryville, California

Received February 8, 1963

The reductive condensation of styrene and acetone by sodium metal to form phenylmethylbutanols, dimethylphenylhexanediol, dimethyldiphenyloctanediols, and related co-reduction products has been examined. The formation and distribution of these condensation products are highly solvent dependent. It is postulated that the styrene radical-anion, $PhCH\overset{\cdot}{=}CH_2$, is the intermediate directly responsible for the products of co-reduction. The mechanism of the reactions is discussed with respect to the nucleophilic properties of the styrene radical-anion and the effect of solvent on the dimerization equilibrium to form styrene dimer dianion, $[Ph\ddot{C}H—CH_2—CH_2—\ddot{C}HPh]Na_2$. Initiation by electron transfer from sodium to styrene *via* the ketyl of acetone is discussed.

The addition of alkali metals to multiple bonds of organic compounds to form ion-radical intermediates I is a relatively common process.



(1)

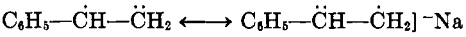
I

Y = C, O, N, etc.
M = alkali metal.

With compounds which contain carbon–carbon unsaturation, such species as I (Y = carbon) have been postulated in the sodium or lithium ammonia[2a] and amine[2b] reduction of aromatic compounds, in displacement reactions[3a] and the polymerization of conjugated olefins such as butadiene[3b,c] and styrene.[4a,b] Such intermediates as I from aromatic compounds also have been detected and studied spectroscopically.[5] In a similar manner heteropolar multiple bonds, especially between carbon and oxygen (Y = oxygen), have been subjected to reaction by alkali metals as in the pinacolic reduction of ketones,[6] acyloin condensation of esters,[7] and reduction of esters to alcohols.[8] Metal ketyls (I, Y = oxygen) have been postulated as intermediates in the reduction of these carbonyl-containing compounds, and also as "carriers" for electron transfer reactions from sodium to peroxides[9] and unsaturated compounds.[10]

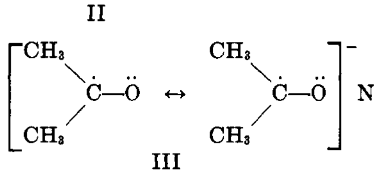
In many of these cases where ion-radicals from unsaturated compounds or metal ketyls from carbonyl compounds are formed as intermediates, condensations to yield dimers or polymers as well as simple reduction products result. Although crossed products from unlike unsaturated compounds (for example in the anionic copolymerization of monomers)[3c] or from unlike metal ketyls in mixed acyloin condensations[11] have been effected, crossed condensation between ion radicals from unsaturated compounds and ketyls appears not to have been studied.

In this series of studies we examined the chemistry of radical ions and ketyls derived *simultaneously* as intermediates from alkali metals and such organic compounds possessing unsaturated centers as aromatic, olefinic, carbonyl, and nitrile-containing compounds. In this report we wish to describe the co-reduction[12] of styrene and acetone with sodium. The possible ion-radical intermediates in this case are the styrene radical-anion (II) and the ketyl (III) from acetone.



$[C_6H_5—\dot{C}H—\ddot{C}H_2 \longleftrightarrow C_6H_5—\ddot{C}H—\dot{C}H_2]^-Na^+$

II



III

These co-reductions, under conditions in which the unsaturated and carbonyl compounds react together with sodium, differ from those condensations of alkali metal adducts of hydrocarbons with electrophilic reagents such as carbon dioxide[13] and ethylene oxide[14] described recently. In the latter cases the alkali metal is first treated with the unsaturated compound to *preform* the organoalkali metal adduct which is then treated with the electrophilic reagent in a subsequent step. These reactions are, thus, essentially those of "conventional" carbanions such as Grignard,[15] organolithium,[16]

---

(1) Department of Chemistry, Case Institute of Technology.

(2)(a) A. P. Krapcho and A. A. Bothner-By, *J. Am. Chem. Soc.*, **81**, 3658 (1959); J. J. Eisch and W. C. Kasha, *J. Org. Chem.*, **27**, 3745, 4171 (1962); (b) R. A. Benkeser, *J. Am. Chem. Soc.*, **77**, 3230, 3378, 6042 (1955).

(3)(a) D. R. Weyenberg and L. H. Toporcer, *ibid.*, **84**, 2844 (1962); (b) M. Sittig, "Sodium," Reinhold Publishing Co., New York, N. Y., 1956, pp. 313 ff.; (c) A. V. Tobolsky, *et al.*, *J. Polymer Sci.*, **31**, 115, 123 (1958).

(4)(a) M. Szwarc, M. Levy, and R. Milkovich, *J. Am. Chem. Soc.*, **78**, 2657 (1956); (b) C. Geacintov, J. Smid, and M. Szwarc, *ibid.*, **84**, 2508 (1962).

(5)(a) D. E. Paul, D. Lipkin, and S. I. Weissman, *ibid.*, **80**, 5342 (1958); 116 (1956); *J. Chem. Phys.*, **21**, 2227 (1953); **25**, 188 (1956); (b) T. L. Chu and S. C. Yu, *ibid.*, **76**, 3367 (1954); ref. 27, p. 159 f.

(6)(a) G. W. Wheland, "Advanced Organic Chemistry," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1960, p. 793 ff.; (b) J. Wieman, *Bull. soc. chim. France*, 63 (1954); *Compt. rend.*, **232**, 1941, 2029 (1951).

(7) M. Kharasch, E. Sternfeld, and F. Mayo, *J. Org. Chem.*, **5**, 362 (1940).

(8)(a) Ref. 4a, p. 286 ff.; (b) G. Darzens, *Compt. rend.*, **224**, 570 (1947); (c) S. M. McElvain, *Org. Reactions*, **4**, Chap. 4 (1948).

(9) J. F. Garst, D. Walmsley, and W. R. Richards, *J. Org. Chem.*, **27**, 2924 (1962).

(10) A. Zilkha, P. Neta, and M. Frankel, *Proc. Chem. Soc.*, 364 (1960).

(11) J. Kapron, *Compt. rend.*, **223**, 421 (1946); *Ann. chim.*, 12, **3**, 117 (1948).

(12) We wish to apply the term "co-reduction" to those condensations effected by alkali metals or related reducing agents in the presence of both components simultaneously.

(13) T. M. Lyssy, *J. Org. Chem.*, **27**, 5 (1962); C. E. Frank and W. E. Foster, *ibid.*, **26**, 303 (1961); C. E. Frank, *et al.*, *ibid.*, **26**, 307 (1961).

(14) J. F. Nobis and E. A. Allgeier, U. S. Patent 2,850,538 (1958).

(15) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954.