until all the solid had melted. Stirring was continued and the bath temperature was raised to 340° and held there until evolution of hydrogen bromide had ceased (approximately 20–30 min). The Wood's metal bath was removed; the reaction mixture was cooled to approximately 100°, poured into an 800-ml beaker, and cooled to room temperature. Pentane (300 ml) was added; the solid was broken into fine pieces, filtered off by suction, and washed thoroughly twice with 300-ml portions of pentane. The pentane filtrates were combined, washed with 200 ml of 20% sodium hydroxide, and dried over anhydrous magnesium sulfate. The pentane extract was then passed through a 25-mm diameter column filled to 35 cm in depth with alumina. Distillation of the pentane solution gave 87 g (82–86%) of 2-bromonaphthalene; no impurities were detectable by vapor phase chromatography or nuclear magnetic resonance analysis.

Registry No.—Triphenylphosphine, 603-35-0; 2-bromonaphthalene, 580-13-2.

The Pyrolysis of 2-Acetoxycyclodecanone
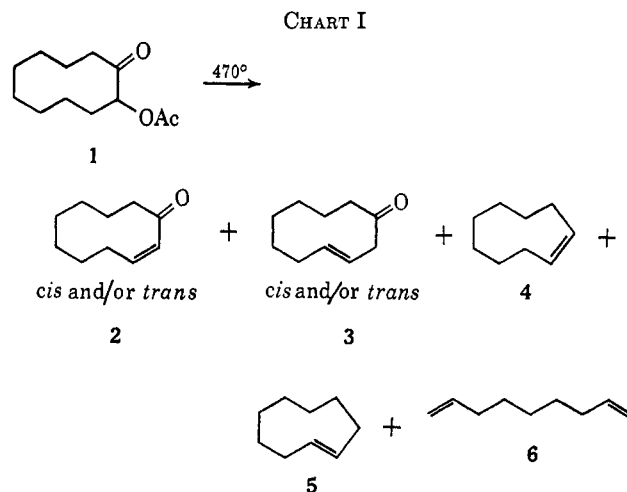
ROBERT G. CARLSON AND JOHN H. BATEMAN

Department of Chemistry, University of Kansas, Lawrence, Kansas 66044

In connection with another study we required a convenient route to 2-cyclodecenone (2). The only reported preparation of this compound involved the pyrolytic dehydration of 2-hydroxycyclodecanone over alumina at 330–350°.[1] The spectral and chemical properties reported for 2 by Leonard and Owens[1] and the recent studies of Heap and Whitham[2] on 2-cyclononenone led us to suspect that the product obtained by the dehydration of 2-hydroxycyclodecanone was a mixture of conjugated and nonconjugated cyclodecenones. We therefore attempted the preparation of 2 by pyrolysis of 2-acetoxycyclodecanone (1).

Pyrolysis of 1 by passing the ester down a tube packed with glass beads and maintained at 470° produced a mixture of products which consisted chiefly of nine-carbon olefins along with a smaller amount of a mixture of cyclodecenones (Chart I). The nine-carbon olefins were separated by a combination of fractional distillation and preparative vapor phase chromatography (vpc) and identified as *cis*-cyclononene (4), *trans*-cyclononene (5), and 1,8-nonadiene (6). The cyclodecenone fraction consisted of a mixture of conjugated and nonconjugated isomers as discussed below. A small-scale run in which the relative amounts of products were determined by vpc before fractionation gave the following percentages of products: 30% cyclononenes, which contained the *cis* and *trans* isomers in a ratio of 7:1; 6% 1,8-nonadiene; and 23% the mixture of cyclodecenones and 8% unreacted 1. In various runs the ratio of *cis*- to *trans*-cyclononene varied from 7:1 to 3.5:1. In addition to the products characterized there were several unidentified products present in minor amounts.

The cyclodecenone obtained by this procedure exhibited an ultraviolet maximum at 225 mμ (ϵ 3180) in ethanol, considerably higher than the extinction coefficient reported by Leonard.[1] Catalytic hydro-

(1) N. J. Leonard and F. H. Owens, *J. Am. Chem. Soc.*, **80**, 6039 (1958).
(2) N. Heap and G. H. Whitham, *J. Chem. Soc. (B)*, 164 (1966).

CHART I

genation afforded cyclodecanone in quantitative yield. Other evidence, however, clearly indicated that the cyclodecenone was a mixture of at least two isomers. The nmr spectrum showed a doublet at δ 3.0 ($J = 7$ cps) with some fine splitting consistent with the presence of a methylene group between a double bond and carbonyl group[3] and indicated the presence of 3. Integration of the nmr spectrum indicated that 2 and 3 were present in a ratio of ca. 2:1. The olefinic region of the nmr spectrum is of interest. The absorption at lowest field consists of a doublet at δ 6.2 ($J = 12.0$ cps) and corresponds (by integration) to one proton of the major component, the α,β-unsaturated ketone 2. Generally in α,β-unsaturated ketones the β hydrogen appears at lowest field, presumably owing to deshielding by contribution from resonance structures of the type shown below.[4] If the β hydrogen
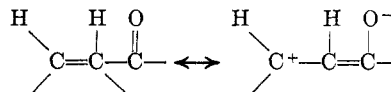
of 2 were at lowest field, however, a more complex pattern than a doublet should result from coupling with the γ hydrogens. It thus appears that for 2 the α hydrogen appears at lower field than the β hydrogen and indicates that in the ground state the more stable conformation does not involve coplanarity of the double bond and the carbonyl group. A similar nmr spectrum has been reported by Eaton[5] for *trans*-2-cyclooctenone. No conclusive evidence as to the stereochemistry of the double bonds in 2 and 3 is available. The infrared spectrum of the mixture shows absorption corresponding to both *cis* and *trans* double bonds and the coupling constants of the olefinic protons in the nmr spectrum ($J = ca.$ 11–12 cps) can be interpreted in terms of either *cis* or *trans* double bonds. Thus far all attempts to separate the mixture of cyclodecenones have been unsuccessful.

The formation of olefins containing one carbon less than the expected product appears to be a general

(3) In 3-cycloheptenone the C-2 methylene appears as a doublet at δ 3.1.[3]
(4) N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry. Illustrations from the Steroid Field," Holden-Day, Inc., San Francisco, Calif., 1964, p 90.
(5) P. E. Eaton and K. Lin, *J. Am. Chem. Soc.*, **86**, 2087 (1964).

reaction for α-acetoxy ketones.[6-9] For example, Johnson[7] has reported that the pyrolysis of 2-acetoxycyclohexanone produces cyclopentene in yields of up to 62%. The formation of ring-contracted products in the pyrolysis of cyclic α-acetoxy ketones may occur by a 1,3 elimination similar to that proposed by Spencer.[9] A 1,3 elimination of this type may account
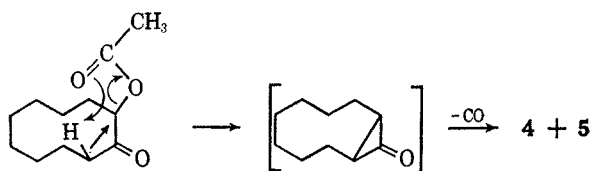
for the formation of tricyclene derivatives in the pyrolysis of xanthates[10] and amine oxides.[11] The 1,8-nonadiene formed in this reaction must arise by rearrangement of the *trans*-cyclononene under the reaction conditions.[12]

A choice can be made between the proposed 1,3 elimination and other possible mechanisms such as cleavage to a diradical[8] by use of appropriately labeled model compounds, and we are currently examining such systems.

Experimental Section[13]

Preparation of 2-Acetoxycyclodecanone (1).—A solution of 49.47 g (0.291 mole) of crude 2-hydroxycyclodecanone,[14] 27.4 ml (0.291 mole) of acetic anhydride, and 400 ml of dry pyridine was stirred overnight at 60° under nitrogen and for an additional 24 hr at room temperature. The reaction mixture was diluted with 300 ml of ether, washed repeatedly with 5% hydrochloric acid, and dried. Removal of the solvent under reduced pressure followed by distillation afforded 56.95 g (92%) of yellow liquid, bp 94–103° (0.2 mm) [lit.[15] bp 116–117° (4 mm)]. Vapor phase chromatographic analysis[16] revealed the presence of 98% 1 and 2% of 1,2-cyclodecanedione. Final purification by distillation on an Annular still afforded the pure acetate. The product exhibits infrared absorption[17] at 1745 (ester C=O) and 1725 cm^{-1} (ketone C=O) and nmr absorption at δ 5.00 (1 H, doublet of doublets, J = 6.0 and 2.0 cps, CH$_2$—C(O)H—C(=O), 3.55 (2 H, multiplet, CH$_2$—C(=O), 2.09 (3 H, singlet, CH$_3$—C(=O)-O), and unresolved absorption in the region 1.0–2.0 (14 H).

(6) J. Cologne and J. C. Dubin, *Compt. Rend.*, **250**, 553 (1960).

(7) K. L. Williamson, R. T. Keller, G. S. Fonken, J. Szmuszkovicz, and W. S. Johnson, *J. Org. Chem.*, **27**, 1612 (1962).

(8) J. Cologne and J. C. Dubin, *Bull. Soc. Chim. France*, 1180 (1960).

(9) T. A. Spencer, S. W. Baldwin, and K. W. Schiegel, *J. Org. Chem.*, **30**, 1294 (1965).

(10) H. R. Nace, *Org. Reactions*, **12**, 57 (1962). For example, it has been reported [G. Komppa and R. H. Roschier, *Ann.*, **429**, 175 (1922)] that camphenilyl S-methyl xanthate was pyrolyzed to give apobornylene and apocyclene.

(11) A. C. Cope and E. R. Trumbull, *Org. Reactions*, **11**, 317 (1960). J. McKenna and J. B. Slinger [*J. Chem. Soc.*, 2759 (1958)] have reported that pyrolysis of the amine oxide of bornylamine produces bornylene and tricyclene.

(12) A. T. Blomquist and P. R. Taussig, *J. Am. Chem. Soc.*, **79**, 3505 (1957).

(13) All boiling points are uncorrected. The infrared spectra were recorded on a Beckman IR-8 recording spectrophotometer. Ultraviolet spectra were recorded on a Beckman DB spectrophotometer. Nuclear magnetic resonance spectra were recorded on a Varian A-60 instrument using tetramethylsilane as an internal standard. Gas chromatography studies utilized an Aerograph A-90-P or F and M Model 700 gas chromatograph with thermal conductivity detectors. Unless otherwise stated magnesium sulfate was employed as the drying agent.

(14) N. L. Allinger, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 840.

(15) A. T. Blomquist, R. E. Barge, and A. C. Sucsy, *J. Am. Chem. Soc.*, **74**, 3636 (1952).

(16) A 5 ft × 0.25 in. column packed with 15% 1,2,3-tris(2-cyanoethoxy)-propane on 60/70 Analabs Anakrom ABS was employed.

(17) Determined as a solution in carbon tetrachloride.

Pyrolysis of 2-Acetoxycyclodecanone.—Pyrolyses were conducted in a 0.75 × 30 in. Pyrex tube filled with 0.25-in. glass beads mounted vertically and surrounded by an electric heating oven. The glass beads were either new or had been carefully cleaned so as to be free of carbon. A slow stream of prepurified nitrogen was passed through the column during the pyrolysis. The temperature was measured by means of a thermocouple on the outside of the Pyrex tube at the midpoint. The effluent from the column was passed through a series of three traps cooled with a Dry Ice–acetone mixture.

In a typical run 14.22 g (0.067 mole) of 2-acetoxycyclodecanone was pyrolyzed by dropping the pure ester through the column at 467° at a rate of *ca*. 1 ml/min. When the addition was complete, the column was allowed to cool and washed with ether. The material in the traps was taken up with ether and the combined ethereal solutions were washed with saturated sodium bicarbonate solution and dried. Removal of the solvent afforded 8.80 g of product. Vapor phase chromatographic analysis[18] revealed the presence of three major products and a small amount of starting material. Fractional distillation on a micro spinning-band column gave the following relatively pure fractions which were characterized as described below: fraction I, 0.207 g, bp 28–30° (14 mm); fraction II, 1.871 g, bp 74° (29 mm); and fraction III, 2.966 g, bp 50–55° (0.23 mm).

Fraction I.—This fraction was identified as 1,8-nonadiene (6) on the basis of the following evidence. The product was greater than 95% pure by vpc and determination of the molecular weight by mass spectrometry gave a value of 124. The product exhibits infrared absorption[17] at 3090 (olefinic hydrogens), 1645 (C=C), and 988 and 910 cm^{-1} (CH=CH$_2$), and nmr absorption[17] at δ 4.8–6.2 (6 H, complex absorption typical of a terminal vinyl group), 2.08 (4 H, broad multiplet CH$_2$ adjacent to double bond), and 1.40 (6 H, multiplet, aliphatic CH$_2$). Finally comparison of infrared spectra and vpc retention times with an authentic sample[19] completed the identification.

Fraction II.—This fraction was identified as a mixture of *cis*-cyclononene (4) and *trans*-cyclononene (5) on the basis of the following evidence. The product gave a single peak by vpc[20] and determination of the molecular weight by mass spectrometry gave a value of 124. The product exhibits infrared absorption[17] at 3015 (olefinic hydrogens), 1655 (C=C), 980 ($_H^H$>C=C<$_H$), and 710 cm^{-1} ($_H$>C=C<$_H$); and nmr absorption[17] at δ 5.42 (2 H, complex multiplet, olefinic hydrogens), 2.18 (4 H, complex multiplet, CH$_2$ adjacent to double bond), and 1.46 (10 H, aliphatic CH$_2$). Catalytic hydrogenation over palladium–charcoal produced cyclononane in quantitative yield. The *cis* and *trans* isomers were separated by preparative vpc[21] and their infrared spectra were identical with the published spectra.[22]

Fraction III.—This fraction was identified as a mixture of 2-cyclodecenone (2) and 3-cyclodecenone (3) on the following basis. Catalytic hydrogenation over palladium–charcoal at atmospheric pressure afforded a quantitative yield of cyclodecanone, identical in all respects with an authentic sample. The product exhibits ultraviolet absorption at λ$_{max}^{EtOH}$ 224 mμ (ε 3180) and infrared absorption[17] at 3020 (olefinic hydrogens), 1705 (shoulder, C=O), 1689 (conjugated C=O), and 1629 cm^{-1} (C=C). The nmr spectrum[17] of the mixture shows absorption at δ 6.21 (doublet, J = 12.0 cps), 5.62 (complex multiplet), 3.0 (doublet, J = 7.0 cps), and complex absorption in the region 1.0–2.6. Integration of the spectrum indicated that 2 and 3 were present in the ratio of *ca.* 2:1. The coupling constants cited above were confirmed by determination of the nmr spectrum at 100 Mc.

Registry No.—1, 10035-92-4; 6, 4900-30-5; 4, 933-21-1; 5, 3958-38-1; *trans*-3, 10035-96-8; *cis*-2, 10035-97-9; *trans*-2, 10035-98-0; *cis*-3, 10060-20-5.

(18) A 6 ft × 0.25 in. column packed with 17% diethylene glycol succinate on 60/80 Chromosorb W was employed.

(19) Chemical Samples Co., Columbus, Ohio.

(20) A 5 ft × 0.25 in. column packed with 15% diethylene glycol succinate on 60/70 Analabs Anakrom ABS was employed.

(21) A 4 ft × 0.25 in. column packed with 28% of a solution of 4-methyl-4-nitropimelonitrile (84%), tetraethylene glycol (8.4%), and silver nitrate (7.6%) on 60–80 Chromosorb W was employed. This column was reported to effect separation of *cis*- and *trans*-cyclononene [A. C. Cope, P. T. Moore, and W. R. Moore, *J. Am. Chem. Soc.*, **82**, 1744 (1960)].

(22) A. T. Blomquist, L. H. Liu, and J. C. Bohrer, *ibid.*, **74**, 3643 (1952).
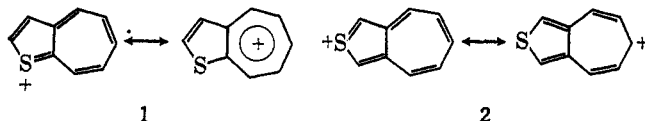

2-Thiaazulen-6-one and the 2-Thiaazulenium Cation. New 10-π-Electron Aromatic Systems

MARTIN WINN[1] AND F. G. BORDWELL

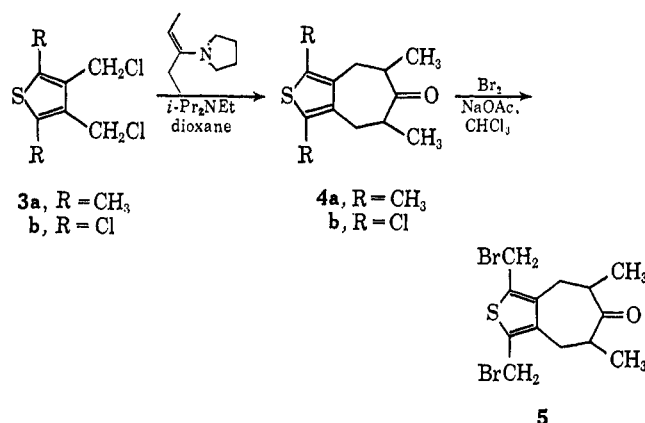*Department of Chemistry, Northwestern University, Evanston, Illinois 60201*

The observation that the 1-thiaazulenium cation (1) is relatively stable ($pK_R = +6$ in water)[2] prompted us to attempt the synthesis of 2-thiaazulenium cation (2) in order to determine its stability, relative to 1, by pK measurements. It would be interesting to compare the relative stability of these cations with the relative stability of their neutral analogs, benzo[b]thiopene (stable) and benzo[c]thiophene (very reactive).[3] Although synthesis of the parent cation (2) was not achieved, we were successful in preparing several derivative of 2 and of the analogous 2-thiaazulen-6-ones.

The readily accessible 2,5-dimethyl-3,4-bis(chloromethyl)thiophene[4] underwent cyclization[5] with the pyrrolidine enamine of 3-pentanone in good yield to give the fused thiophene–cycloheptanone system (**4a**),

but this could not be aromatized to **6a** by bromination followed by dehydrobromination. The bromination of the methyl groups on the thiophene ring competed successfully with the introduction of the second bromine on the seven-membered ring. Under certain conditions, methyl bromination was the exclusive result (giving **5**).

The enamine cyclization failed with 2,5-di-t-butyl-3,4-bis(chloromethyl)thiophene, presumably because of steric hindrance.

Cyclization of 3,4-bis(chloromethyl)-2,5-dichloro-thiophene (**3b**) (prepared by chloromethylation of 2,5-dichlorothiophene) with the pyrrolidine enamine of 3-pentanone gave **4b** in fair yield. In contrast to **4a**, this compound was easily converted to the thiaazulenone (**6b**) by bromination–dehydrobromination.
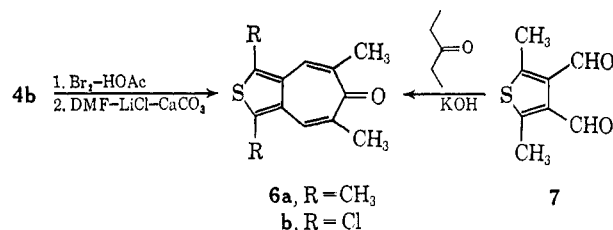
The tetramethyl compound (**6a**) was synthesized from the aldehyde (**7**) and 3-pentanone by the method of Theile.[6] Dialdehyde **7** was prepared from 2,5-dimethyl-3,4-diiodothiophene[7] by treating with butyllithium followed by dimethylformamide as described by Robba, *et al.*;[8] **7** has been recently synthesized from **3a** by another method.[9]

Thiaazulenone **6a** is deep yellow; **6b** is pale yellow. In contrast to benzo[c]thiophene, they are unreactive to maleic anhydride. The carbonyl bands in the infrared are at 6.36 and 6.21 μ, respectively. This shows that there is electron delocalization in the molecule and that the electronegative chlorine atoms in **6b** hinder delocalization of electrons from sulfur to oxygen relative to the effect of the methyl groups in **6a**. A similar effect is noted in the ultraviolet spectrum. The dichlorodimethyl compound (**6b**) has a lower λ_{max} in the ultraviolet than the tetramethyl compound **6a** (2680 *vs.* 2740 A). This is the opposite of
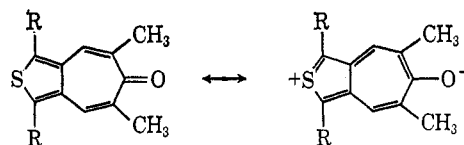
the effect of substituting a chlorine for a methyl on a benzene ring.

In trifluoroacetic acid (TFA), the tetramethyl compound (**6a**) forms a purple solution. The color change is accompanied by a change in the nmr spectrum; the singlet at 2.60, doublet at 2.22, and quartet at 7.45 observed in chloroform all become singlets in TFA (at 2.71, 3.02, 8.68).[10] This is consistent with the formation of cation **8a**. Although the dichlorodimethyl

(1) National Science Foundation Predoctoral Fellow, 1962–1963; Texaco Fellow, 1963–1964; Ethyl Corp. Fellow, 1964–1965. Abstracted in part from the Ph.D. Dissertation of M. Winn, Northwestern University, Aug 1965.

(2) $K_R = $ [ROH][H⁺]/[R⁺][H₂O]: R. Turnbo, D. L. Sullivan, and R. Pettit, *J. Am. Chem. Soc.*, **86**, 5630 (1964).

(3) R. Mayer, H. Kleinert, S. Richter, and K. Gewald, *Angew. Chem. Intern. Ed. Engl.*, **1**, 115 (1962); *J. Prakt. Chem.*, **20**, 244 (1963); M. P. Cava and N. M. Pollack, *J. Am. Chem. Soc.*, **88**, 4112 (1966); B. D. Tilak, H. S. Desai, and S. S. Gupte, *Tetrahedron Letters*, 1953 (1966).

(4) R. Gaertner and R. G. Tonkyn, *J. Am. Chem. Soc.*, **73**, 5872 (1951); Y. A. Goldbarb and M. S. KondaKova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 495 (1956); *Chem. Abstr.*, **50**, 16745 (1956).

(5) F. G. Bordwell and M. Winn, *J. Org. Chem.*, **32**, 42 (1967).

(6) J. Theile and E. Weitz, *Ann.*, **377**, 1 (1911).

(7) S. Gronowitz and R. Beselin, *Arkiv Kemi*, **21**, 349 (1963).

(8) M. Robba, R. C. Moreau, and B. Roques, *Compt. Rend.*, **259**, 3568 (1964).

(9) K. Dimroth, G. Pohl, and H. Follmann, *Ber.*, **99**, 634 (1966).

(10) The numbers are parts per million (ppm) downfield from tetramethylsilane.