aldehyde.[8] Recrystallization of this compound from absolute ethanol gave colorless crystals; yield 80%, m.p. 156.8–157.6°. 2,6-Di-*t*-butylphenol (Eastman Kodak Co.) was recrystallized from ethanol; m.p. 37.0–38.0°.

Galvinoxyl was prepared after Coppinger[9] and recrystallized five times by dissolving in Merck reagent grade carbon tetrachloride and evaporating slowly under a stream of prepurified nitrogen at room temperature. It was of 98.0% purity based on optical density at 770 mμ, and the value of ϵ_{770} = 607 observed for a previous sample of 100.2% purity by titration.[2]

***tert*-Butylperoxyoxalyl chloride** was synthesized as described in Part VI[3] and used without further purification.

Di-*tert*-butyl Monoperoxyoxalate.—A solution of 2.50 g. of *tert*-butyl alcohol and 2.8 g. of pyridine in 15 ml. of pentane was added dropwise over an hour to a solution of 5.95 g. of freshly prepared *tert*-butylperoxyoxalyl chloride in 15 ml. of pentane at −2 to −8° with stirring. The precipitation of white pyridinium chloride occurred immediately. After stirring for 30 minutes longer the mixture was carefully washed twice each with 10% sulfuric acid, water, 10% sodium bicarbonate solution and water. The pentane layer was dried with anhydrous magnesium sulfate overnight at −25°. The pentane was evaporated under vacuum at 0° to leave 5.0 g. (69%) of colorless liquid di-*tert*-butyl monoperoxyoxalate.

Anal. Calcd. for $C_{10}H_{18}O_5$: C, 55.03; H, 8.31. Found: C, 55.96; H, 8.52.

Chromatography on Florisil afforded only one fraction, identical in its infrared spectrum with the original material. The infrared spectrum could not be determined without the intrusion of absorptions due to decomposition products. The principal peaks observed in carbon tetrachloride which did not increase, or which decreased, with time were at 3.33, 5.58, 5.73, 6.87, 7.20, 7.32, 7.79, 8.05, 8.95 and 9.74 μ.

Di-*tert*-butyl monoperoxyoxalate decomposes at room temperature with evolution of carbon dioxide. When it is not diluted the decomposition may become violent. After a short time at room temperature the solutions used for determination of the infrared spectrum showed an increasing peak at 4.25 μ due to carbon dioxide.

Analysis of Decomposition Products.—The methods used were essentially those previously described.[1] In one run a solution of 0.5620 g. of di-*tert*-butyl monoperoxyoxalate in 10 ml. of cumene was degassed four times and allowed to decompose at 24.6° for 36 hours. There was 4.62 millimoles of condensable gas formed, and no non-condensable gas. After complete absorption of the carbon dioxide on Ascarite, 0.62 millimole of gas remained whose infrared spectrum showed bands corresponding to the known spectra of isobutane and isobutylene.[10,11] The residual gas was shown by its mass spectrum to be a mixture of 0.54 millimole of isobutane with 0.08 millimole of isobutylene, by comparison with published spectra.[12] The peaks at masses 43 and 56 being taken as standards, the intensities at 41, 42, 50, 51, 53, 55, 57 and 58 agreed with those calculated for this mixture within a mean deviation of 3.6 units on the scale of 660 for the most intense peak.

Comparison of the infrared spectrum of the volatile, non-gaseous products in cumene with the spectra of authentic *tert*-butyl alcohol and di-*tert*-butyl carbonate indicated that only these compounds were present and that they had been formed in the amounts of 1.48 and 1.10 millimoles, respectively. A mixture of *tert*-butyl alcohol and di-*tert*-butyl carbonate in these proportions gave an infrared spectrum in cumene identical with that of the reaction product.

The residue in the reaction flask amounted to 0.2492 g. of a white solid melting over the range from 90 to 100°, which was identified as dicumyl.

The product study in the presence of galvinoxyl was carried out in a similar manner, except that the non-volatile residue was not isolated or characterized.

Kinetic Studies.—The rate measurements were made by the infrared technique described in earlier papers of this series.[13] A calibration curve of the intensity of the characteristic perester peak at 5.58 μ as a function of concentration of the perester was prepared, and this curve was used in determining perester concentration in the aliquots taken from the thermostated solution of the perester in cumene.

The rate determinations in the presence of galvinoxyl were made as described by Bartlett and Funahashi,[2] the disappearance of the scavenger being followed by its ultraviolet absorption.

Acknowledgment.—We thank the National Institutes of Health for a grant in support of this work.

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[8] M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, **22**, 1435 (1957).

[9] G. M. Coppinger, *J. Am. Chem. Soc.*, **79**, 501 (1957).

[10] R. S. Rasmussen and R. R. Brattain, *J. Chem. Phys.*, **15**, 120 (1947).

[11] R. S. Rasmussen, *ibid.*, **16**, 712 (1948).

[12] American Petroleum Institute Research Project 44, Mass Spectral Data, Serial Nos. 5 and 28.

[13] P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.*, **80**, 1404 (1958).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE 39, MASS.]

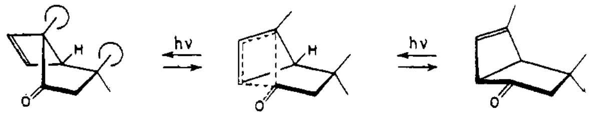
Photochemical Reactions. X.[1,2] Experiments with 1,3,5-Cycloöctatrien-7-one and Cycloöctatetraene Epoxide

BY G. BÜCHI AND EDWARD M. BURGESS[3]

RECEIVED DECEMBER 18, 1961

Irradiation of 1,3,5-cycloöctatrien-7-one in hexane solution yielded bicyclo[4.2.0]octa-4,7-dien-2-one. The anticipated bicyclo[2.2.2]octadienone was not detected. On exposure to ultraviolet light in methanol solution the monocyclic ketone was transformed to a methyl octa-1,3,5-trienoate of unknown configuration which on subsequent equilibration was partly converted to the known *trans-trans*-ester. Pyrolysis of cycloöctatrienone and its photoisomer furnished benzene, *o*-vinylphenol and *o*-vinylphenyl acetate. Cycloöctatetraene epoxide rapidly polymerizes to unrecognizable products on irradiation, but on pyrolysis at 260° it is isomerized to β-cycloheptatrienecarboxaldehyde which in turn is transformed to the γ-isomer by heating at 330°. Thermal treatment of all three isomers at 400° yielded phenylacetaldehyde. Possible mechanisms of the various transformations are discussed.

In an earlier paper we discussed the reversible photochemical equilibration of the two ketones (1 and 3) which may proceed through an activated complex (2).



1 2 3

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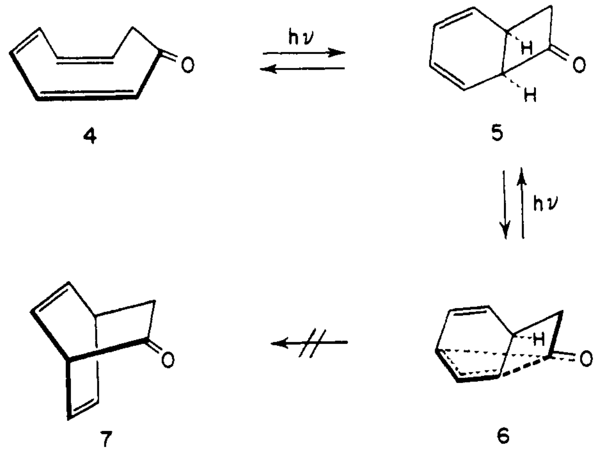
[1] Part of a program of research supported by a grant from the Godfrey L. Cabot Fund, Publication No. 74, M.I.T. Solar Energy Conversion Project.

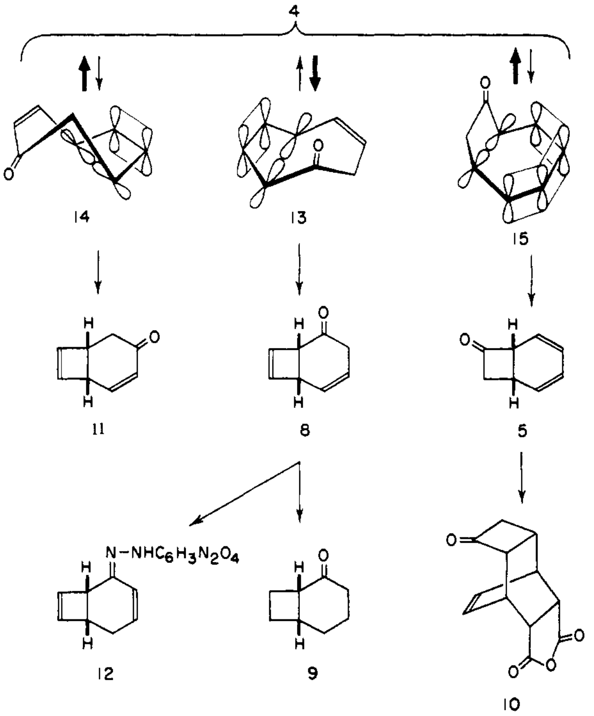
[2] Part IX, G. Büchi and Edward M. Burgess, *J. Am. Chem. Soc.*, **82**, 4333 (1960).

[3] National Science Foundation Predoctoral Fellow 1960–.

To uncover similar rearrangements with other β,γ-unsaturated ketones and hoping to find an expedient synthesis of bicyclo[2.2.2]octadienone (7) we investigated the photochemistry of 1,3,5-cycloöctatrien-7-one (4). This hypothesis required (a) the presence of a valence tautomer 5 in the photochemical equilibrium, (b) proximity of carbonyl group and one double bond in the activated complex 6 and (c) stability of the bridged ketone 7 to ultraviolet light.



When 4 was irradiated in pentane solution with a mercury arc during 21 days it was transformed to a photoisomer (30% yield) readily separable from starting material and some polymer by rapid fractional distillation. The new isomer is thermally unstable and on prolonged storage, even at 0°, it slowly reverts to 4. It exhibited infrared absorption (in CCl_4) at 1710 (cyclohexanone), 3050, 3150, 1650, 700 and 755 cm.$^{-1}$ (*cis*-disubstituted double bonds presumably in rings with different strain). Further, the ultraviolet spectrum, λ^{EtOH} 210 mμ (ε 2,300), $\lambda_{\text{max}}^{\text{EtOH}}$ 288 mμ (ε 110), is that of a non-planar β,γ-unsaturated ketone as indicated by the high intensity $n \rightarrow \pi^*$-transition.[2,4] Catalytic reduction yielded a tetrahydroketone which was identical with the known bicyclo[4.2.0]octan-2-one (9).[5] The structure of the photoisomer is now defined as 8 because the spectral data demand absence of any conjugation and evidence for *cis*-fused rings is provided by the *cis* configuration of the reduction product 9. As anticipated, bicyclo-[4.2.0]oct-4,7-dien-2-one (8) is sensitive to acidic reagents and on treatment with 2,4-dinitrophenylhydrazine hydrochloride it was transformed to a derivative with $\lambda_{\text{max}}^{\text{EtOH}}$ 382 mμ (ε 28,800) tentatively assigned structure 12. Infrared spectra of cyclooctatrienone (4) before and after irradiation exhibit absorption at 1765 cm.$^{-1}$ of equally low intensity which may be attributed to the presence of small amounts of a valence tautomer (5).[6] This suggests that the thermal equilibrium between 4 and 5 favors the monocyclic ketone by a large factor and consequently any 5 formed in a photochemical change should revert to starting material by a dark reaction. Although we have no evidence for participation of 5 in the photochemical equilibrium, it is pertinent to state that the geometry of the transition state 15 leading to its formation is not unduly strained and clearly involved in the genesis of Diels–Alder adducts[7] (*e.g.*, 10) from 4 and dienophiles. Similarly, both excited states 13 and 14 with two twisted double bonds each are sterically feasible. The absence of 11 among the photoproducts agrees with prediction (assuming thermal stability at room temperature) because this valence tautomer should exhibit high intensity ultraviolet absorption in the region of the spectrum used while the non-conjugated ketone 8 does not. An analogous argument has been used frequently to predict the steady state concentrations of isomers in photochemical reactions.[8]



After irradiation of 4 in the presence of hydrochloric acid or toluenesulfonic acid (*cf.* ref. 2) also failed to produce bicycloöctadiene (7) we studied the thermal behavior of cycloöctatrienone (4) and its photoisomer 8 at 300°. Both pyrolysates consisted of benzene,[9] *o*-vinylphenol (18) and *o*-vinylphenyl acetate (19) but 7 again was absent. The following sequence accounts for the products observed: (a) thermal equilibration of all four isomers 4, 5, 8 and 11; (b) fragmentation of the cyclobutanone 5 to benzene and ketene; and (c) isomerization of 5 to the hypothetical *cis-cis*-ketene 16. The last change is terminated by recyclization to a cyclohexadienone (20) followed by irreversible tautomerization to the more stable

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(4) S. Winstein, L. deVries and R. Orlowski, *J. Am. Chem. Soc.*, **83**, 2020 (1961); C. F. Wilcox, Jr., S. Winstein and W. G. McMillan, *ibid.*, **82**, 5450 (1960); H. Labhart and G. Wagnière, *Helv. Chim. Acta*, **42**, 2219 (1959); H. Birnbaum, R. C. Cookson and N. Lewin, *J. Chem. Soc.*, 1224 (1961), and earlier papers by Cookson.

(5) We are indebted to Professor A. C. Cope for a sample of this ketone and the corresponding 2,4-dinitrophenylhydrazone.

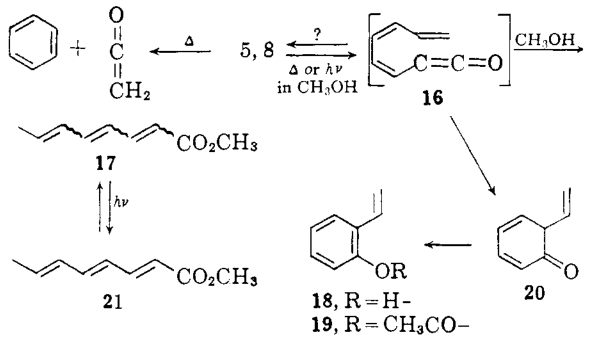
(6) See also A. C. Cope and B. D. Tiffany, *J. Am. Chem. Soc.*, **73**, 4158 (1951).

(7) A. C. Cope, S. F. Schaeren and E. R. Trumbull, *ibid.*, **76**, 1096 (1954).

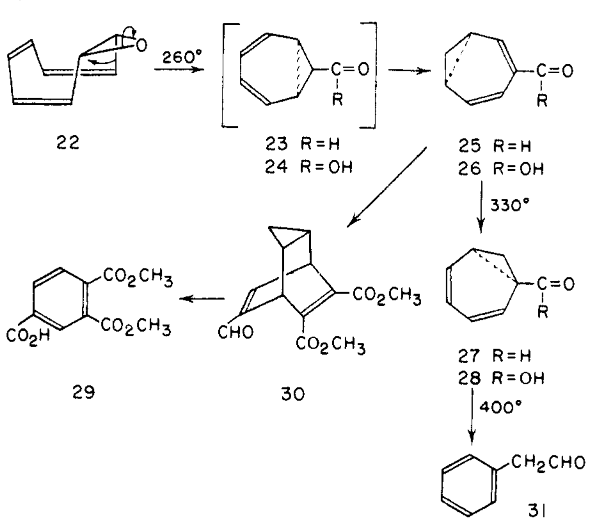
(8) *Cf.* ref. 2 and earlier reports cited.

(9) The formation of benzene by pyrolysis of 4 is mentioned in ref. 6.

phenol **18** which is partly acetylated to **19** by ketene liberated in the degradation. Fragmentation of the two other valence tautomers **8** and **11** to phenol and acetylene is energetically unfavorable because two vinylic bonds would have to be cleaved and indeed no phenol was detected. The argument for the intervention of a ketene (**16**) is strengthened by formation of a methyl-1,3,5-octatrienoate (**17**), λ_{max}^{EtOH} 304 mμ (ϵ 31,800), of unknown configuration on irradiation of cyclooctatrienone (**4**) and its photoisomer **8** in methanol solution. On subsequent photochemical equilibration in pentane solution this ester was partly converted to the known methyl all-*trans*-1,3,5-octatrienoate, m.p. 74–75°, λ_{max}^{EtOH} 301 mμ (ϵ 37,700). The ring cleavage observed was predicted earlier[10] and is analogous to the known transformations of cyclohexadienones,[11] chrysanthenone[12] and sultones[13] to aliphatic esters or sulfonic esters, respectively, which have been postulated to originate from intermediate ketenes or sulphens. The absence of monomeric *o*-vinylphenol among the irradiation products of **4** could be attributed to (a) rapid light induced polymerization or (b) the nonpolar solvent which might prohibit production of the ketene **16**. Neither possibility can be excluded at present.



Irradiation of cyclooctatetraene epoxide (**22**) in pentane or methanol solution led to rapid polymerization and no monomeric substances became available. Of greater interest was its behavior on pyrolysis and at 260° it was transformed to three isomers. The major product (45% yield) had ν_{max} 1690 (C=O), 1610 (C=C), 2720 and 2820 (CHO) cm.$^{-1}$, λ_{max}^{EtOH} 221 mμ (ϵ 11,680), 287 mμ (ϵ 6,740), and on catalytic reduction in the presence of palladium-on-charcoal it yielded cycloheptanecarboxaldehyde identified as the 2,4-dinitrophenylhydrazone. Oxidation with silver ions at room temperature caused conversion to β-cycloheptatrienecarboxylic acid (**26**) identical with an authentic sample.[14,15] Assuming that no isomerization occurred during oxidation the new aldehyde is β-cycloheptatriencarboxaldehyde (**25**). This is supported by the infrared spectrum of its adduct (**30**) with dimethyl acetylenedicarboxylate which possessed bands at 2710, 2820, 1690 (α,β-unsaturated aldehyde) and 1730 cm.$^{-1}$. Pyrolytic cleavage of **30** followed by oxidation produced an acid corresponding in melting point to dimethyl 4-carboxy-1,2-phthalate (**29**). The second product (5% yield) resulting from the thermal treatment of **22** became available for study when we established its identity with an aldehyde formed in 74% yield when **25** is heated at 330°. It exhibited ultraviolet absorption at 215 mμ (ϵ 11,400), 305 mμ (ϵ 3,500) and infrared data are in agreement with those anticipated for a conjugated aldehyde. Oxidation produced γ-cycloheptatriencarboxylic acid (**28**)[14,15] and the corresponding aldehyde is thus **27**. A third product (5% yield) formed in the initial pyrolysis of **22** at 260° was not available in sufficient quantity for complete characterization, but its infrared spectrum with bands at 1720 and 1550 cm.$^{-1}$ suggests that it may have been norcaradiencarboxaldehyde (**23**). Finally it was possible to convert **27** to phenylacetaldehyde (**31**) by heating at 400°.



The formation of the various aldehydes by thermal treatment under increasingly drastic conditions might be explained by initial rearrangement of the epoxide **22** to norcaradienecarboxaldehyde (**23**) a process stereoelectronically more favorable than that leading to the ketone **4**. If this is accepted the relative abundance of isomers **23**, **25** and **27** actually observed requires a rapid transformation of **23** to the β-isomer **25**. In consonance with this proposal methyl norcaradienecarboxylate (ester of **24**) is smoothly isomerized to the β-ester (ester of **26**) by heating at 160°.[16] Although the intramolecular nature of this change is not established, a mechanism outlined in **32** (arrows) accounts for the products observed. An analogous six-center reaction process (**33** arrows) accommodates the rearrangement of the β-aldehyde **25** to the γ-isomer **29** and the greater thermodynamic stability of the linearly conjugated γ-aldehyde is in accordance with the order of stability ascertained previously[16] for the corresponding cycloheptatrienecarboxylic acids.

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(10) D. H. R. Barton, *Helv. Chim. Acta*, **42**, 2604 (1959).

(11) D. H. R. Barton and G. Quinkert, *J. Chem. Soc.*, 1 (1960).

(12) J. J. Hurst and G. H. Whitman, *ibid.*, 2864 (1960).

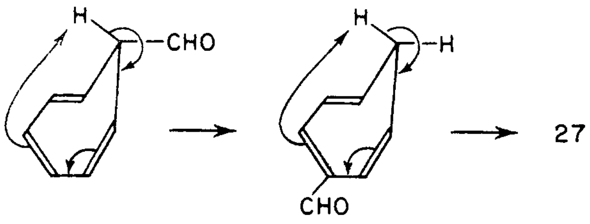
(13) E. Henmo, P. deMayo, A. B. M. Abdus Sattar and A. Stoessl, *Proc. Chem. Soc.*, 238 (1961).

(14) Kindly provided by Professor W. von E. Doering, Yale University.

(15) W. von E. Doering, G. Laber, R. Vonderwahl, N. F. Chamberlain and R. B. Williams, *J. Am. Chem. Soc.*, **78**, 5448 (1956).

(16) C. Grundmann and G. Ottmann, *Ann.*, **582**, 163 (1953).

Furthermore, the activated complex **32** must be of lower energy than **33** and this agrees also with the mechanism proposed because the electrons partially freed in the carbon–hydrogen bond breaking process are stabilized by the aldehyde group in **32** but not in **33**.



32 33

The final transformation of **27** to phenylacetaldehyde (**31**) remains mechanistically obscure and it is conceivable that an acid-catalyzed rather than a thermal process is involved.[17]

Acknowledgments.—We are indebted to the National Science Foundation (Grant 7424) for financial support of this investigation and to the Badische Anilin und Sodafabrik for a generous gift of cycloöctatetraene.

Experimental[18]

Cycloöctatetraene Oxide (22) and Cycloöctatrienone (4).—Cycloöctatetraene oxide (b.p. 75–76°, 12 mm.) was prepared from cycloöctatetraene by epoxidation with peracetic acid and cycloöctatrienone (b.p. 89–90°, 6 mm.) by base-catalyzed rearrangement of the epoxide according to the procedure of Cope and Tiffany.[6]

Bicyclo[4.2.0]oct-4,7-dien-2-one (8).—A solution of cycloöctatrienone (24.9 g., 0.207 mole) in 500 ml. of *n*-pentane was irradiated for 21 days. The *n*-pentane was removed under reduced pressure and the residual oil fractionated through a 40-cm. spinning band column at 6 mm. pressure. A colorless fraction, b.p. 67–68°, was collected and consisted of 7.615 g. (30.6%) of bicyclo[4.2.0]-oct-4,7-dien-2-one, $\nu_{\max}^{\mathrm{CCl_4}}$ 645, 700(s), 755(s, CS_2), 1235, 1265, 1310, 1710(s), 2920, 3050 and 3150(wk) cm.$^{-1}$; $\lambda_{\max}^{\mathrm{EtOH}}$ 288 mμ (ϵ110), λ^{EtOH} 210 mμ (ϵ 2,300).

Anal. Calcd. for C_8H_8O: C, 79.97; H, 6.71. Found: C, 79.29; H, 6.84.

The fraction of b.p. 89–90° consisted of 9.572 g. of starting material.

The bicyclo[4.2.0]oct-4,7-dien-2-one slowly isomerized to cycloöctatrienone upon storage at 0° under nitrogen; attempted redistillation of these samples invariably led to complete isomerization.

Treatment of the bicyclic ketone with 2,4-dinitrophenylhydrazine in methanol containing a trace of HCl gave a red precipitate which was chromatographed over neutral alumina (activity I, Woelm). Elution with chloroform followed by two recrystallizations from ethyl acetate–ethanol gave long red needles of the 2,4-dinitrophenylhydrazone of bicyclo[4.2.0]oct-3,7-dien-2-one (**12**), m.p. 194–194.5°, $\lambda_{\max}^{\mathrm{CHCl_3}}$ 382 mμ (ϵ 28,800).

Anal. Calcd. for $C_{14}H_{12}O_4N_4$: C, 56.00; H, 4.00. Found: C, 56.28; H, 3.97.

Bicyclo[4.2.0]octan-2-one (9).—Bicyclo[4.2.0]oct-4,7-dien-2-one (153 mg., 1.275 millimoles) was hydrogenated over 10 mg. of 20% palladized charcoal in 10 ml. of diethyl ether at 0° and 1 atmosphere pressure. After 80 minutes, 2.12 equivalents of hydrogen had been consumed and uptake ceased. The ether was removed by evaporation under reduced pressure and the residual oil distilled in a micro-Hickman still to afford 111 mg. (70%) of a clear oil whose infrared spectrum was identical with that of an authentic sample of bicyclo[4.2.0]octan-2-one.[5]

Treatment with 2,4-dinitrophenylhydrazine in methanol containing a trace of HCl at room temperature gave the 2,4-dinitrophenylhydrazone which was recrystallized twice from methanol to afford yellow needles, m.p. 179–180°, both pure and mixed with an authentic sample.[5] Both 2,4-dinitrophenylhydrazones had identical infrared spectra (KBr).

Thermal Aromatization of Cycloöctatrienone (4) and Bicyclo[4.2.0]oct-4,7-en-2-one (8).—Cycloöctatrienone (3.6 g., 0.03 mole) was pyrolyzed at the rate of 30 mg./min. at 300° with a nitrogen flow of 10 ml./min. The pyrolyzate was a mixture of three components in the ratio 1:1:1 as indicated by the chromatography of a small sample in the vapor phase over Dow-Corning silicone oil (No. 550) at 180°. The component eluted first was collected and, upon infrared spectra comparison, proved to be benzene. The remainder of the pyrolyzate was fractionated through a 20-cm. spinning band column at 0.9 mm. pressure to afford *o*-vinylphenol (**18**), b.p. 58–59°, n^{25}D 1.5834, 0.74 g.; and *o*-vinylphenyl acetate (**19**), b.p. 69–70°, n^{25}D 1.4560, 0.458 g.

The pyrolysis of bicyclo[4.2.0]oct-4,7-dien-2-one under the same conditions afforded an identical mixture.

A small sample of *o*-vinylphenol was treated with excess bromine in chloroform at room temperature for 12 hours. The chloroform and excess bromine were removed by distillation under reduced pressure and the brown residue recrystallized from benzene–petroleum ether six times to afford colorless prisms of (3,5-dibromo-2-hydroxyphenyl)-1,2-dibromoethane, m.p. 105° (lit.[19] m.p. 105).

o-Vinylphenol (200 mg., 1.67 millimoles) from the pyrolysis in 1.5 ml. of 10% aqueous sodium hydroxide was cooled by shaking in an ice-bath while acetic anhydride (0.5 ml.) was added over a period of 20 minutes. The resulting suspension was extracted rapidly with two 50-ml. portions of ether and the combined extracts washed once with 25 ml. of 2% aqueous sodium hydroxide and then twice with 50-ml. portions of water. The ether layer was dried over magnesium sulfate and the ether removed by evaporation under reduced pressure. Chromatography of the residual oil in the vapor phase over Dow-Corning silicone oil (No. 550) at 180° afforded 130 mg. (48%) of a clear oil whose infrared spectrum was identical with that of the *o*-vinylphenyl acetate obtained by the pyrolysis of cycloöctatrienone.

o-Vinylphenyl acetate (101 mg., 0.623 millimole) from the pyrolysis was hydrogenated over 10 mg. of 20% palladized charcoal in 2 ml. of absolute ethanol at 25.5° and 1 atm. pressure. After 6 minutes, 1.2 equivalents of hydrogen had been consumed and uptake ceased. The ethanol was removed by evaporation under reduced pressure and the residual oil distilled in a micro-Hickman still (bath temp. 110°, 7 mm.) to afford 82 mg. (80%) of *o*-ethylphenyl acetate identical by infrared spectra comparison with an authentic sample prepared by the acetylation of *o*-ethylphenol in the above manner.

Methyl *cis-trans*-1,3,5-Octatrienoate (17).—Cycloöctatrienone (15.0 g., 0.125 mole) in 150 ml. of methanol was irradiated with an immersible low intensity mercury dis-

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[17] W. Reppe, O. Schlichting, K. Klager and T. Toepel, *ann.*, **560**, 1 (1948).

[18] Microanalysis are by Dr. S. M. Nagy and associates, Massachusetts Institute of Technology Microanalytical Laboratory. Melting points were taken on a Kofler hot-stage microscope and are corrected. Boiling points are uncorrected. Ultraviolet spectra were measured on a Cary recording spectrophotometer, model II, and infrared spectra were measured on a Perkin–Elmer recording spectrophotometer, model 21, with a sodium chloride prism. The listings of infrared bands include those which are relevant to the structural argument and other medium and strong bands. Helium was used as the eluent gas for all vapor phase chromatograms and the specified liquid phases (30%) were supported by 60–80 mesh fire-brick packed in 8 mm. × 200 cm. columns.

The pyrolysis apparatus consisted of a vertical Pyrex tube (18 × 1 cm., filled two-thirds full with $^3/_{16}$-inch. diameter Pyrex helices) equipped with a nitrogen and sample inlet capillary at the top and a removable collection tube immersed in a Dry Ice–acetone-bath at the bottom. A thin wire in the inlet capillary permitted control of the rate of addition of the sample. Heating was accomplished with an external electrical heating jacket fitted with a thermocouple.

Irradiations unless otherwise indicated were performed in a flask fitted with an immersible quartz mercury arc lamp ("Labortauchlampe S81," Quartzlampengesellschaft Hanau), a reflux condenser and a nitrogen inlet. The irradiation flask was cooled in a circulating water-bath and the solution agitated with a stream of nitrogen admitted through a fritted disk.

[19] R. A. Smith and J. B. Niederl, *J. Am. Chem. Soc.*, **53**, 806 (1931).

charge tube for 8 days. The solution was agitated with a slow stream of nitrogen and the temperature was maintained at 15° by means of an external circulating water-bath. The methanol was removed under reduced pressure and the residual oil fractionated through a 40-cm. spinning band column at 1.0 mm. pressure. A straw-colored fraction, b.p. 70–70.5°, was collected and after redistillation through a 20-cm. spinning band column afforded 6.19 g. (31%) of clear methyl *cis-trans*-1,3,6-octatrienoate which was homogeneous to vapor phase chromatography; b.p. 110° (8 mm.), n^{25}D 1.5787; $\nu_{max}^{CCl_4}$ 690, 735(CS_2), 870, 1000(broad), 1140, 1175, 1260(broad), 1430 1620, 1715(s), 2850(sh), 2950 and 3020 cm.$^{-1}$; λ_{max}^{EtOH} 304 mμ (ϵ 31,800).

Anal. Calcd. for $C_9H_{12}O_2$: C, 71.05; H, 7.89. Found: C, 70.74; H, 7.72.

A fraction of b.p. 63–64° (1.0 mm.) consisted of 1.22 g. of starting ketone.

Micro-hydrogenation of the ester over pre-reduced 20% palladized charcoal in methanol led to an uptake of exactly three equivalents of hydrogen.

Methyl ***trans*-1,3,5-Octatrienoate (21).**—Methyl *cis-trans*-1,3,5-octatrienoate (2.0 g., 0.0132 mole) in 200 ml. of *n*-pentane was irradiated for 24 hours. The *n*-pentane was removed by distillation under reduced pressure and the white crystalline residue recrystallized from *n*-pentane twice to afford 600 mg. (30%) of methyl *trans*-1,2,5-octatrienoate as colorless needles, m.p. 74–75° both pure and mixed with an authentic sample. Both samples had identical infrared spectra (CCl_4).

Authentic methyl *trans*-1,3,5-octatrienoate was prepared from sorbaldehyde[20] by a Knoevenagel condensation followed by esterification according to the procedure of Kuhn and Hoffer.[21]

β-Cycloheptatriencarboxaldehyde (25).—Cycloöctatetraene oxide (15 g., 0.125 mole) was pyrolyzed at the rate of 30 mg./min. under a nitrogen flow of 10 ml./min. at *exactly* 260°. The dark-brown pyrolyzate was fractionated through a 40-cm. spinning band column at 8 mm. pressure. A small forerun of toluene (infrared spectra comparison) was collected and then a fraction, b.p. 65–67°, consisting of 4.48 g. of starting epoxide followed by a fraction, b.p. 83–84°, consisting of 6.708 g. (44.7%) of β-cycloheptatriencarboxaldehyde, n^{25}D 1.5672; $\nu_{max}^{CCl_4}$ 670, 725, 795, 875, 1160(s), 1550-(wk), 1610(wk), 1690(s), 2720, 2820, 2960 and 3030 cm.$^{-1}$; λ_{max}^{EtOH} 287 mμ (ϵ 6,740), 221 mμ (ϵ 11,680).

Anal. Calcd. for C_8H_8O: C, 80.00; H, 6.66. Found: C, 80.15; H, 6.82.

Vapor phase chromatography of the original pyrolyzate indicated 5% of an additional component which after collection exhibited infrared absorption at 1720 and 1550 cm.$^{-1}$.

Upon standing at room temperature in 3% methanolic HCl the aldehyde was recovered unchanged in a quantitative yield.

Treatment of the aldehyde with 2,4-dinitrophenylhydrazine in methanol containing a trace of HCl gave the 2,4-dinitrophenylhydrazone which after four recrystallizations from ethyl acetate afforded lustrous violet-red prisms, m.p. 210.5–211° dec., $\lambda_{max}^{CHCl_3}$ 383 mμ (ϵ 65,000).

Anal. Calcd. for $C_{14}H_{12}O_4N_4$: C, 56.00; H, 4.00. Found: C, 56.27; H, 4.15.

Cycloheptanecarboxaldehyde.—β-Cycloheptatriencarboxaldehyde (317 mg., 2.64 millimoles) was hydrogenated over 10 mg. of 20% palladized charcoal in 5 ml. of absolute ethanol at 1 atmosphere pressure. After 75 minutes, 3.24 equivalents of hydrogen had been consumed and the hydrogenation was stopped. The ethanol was removed by evaporation under reduced pressure. The residual mixture was chromatographed in the vapor phase over Dow–Corning silicone oil (No. 550) at 150° and the major component (102 mg.) collected. Treatment with 2,4-dinitrophenylhydrazine in methanol containing a trace of HCl gave a yellow precipitate which was recrystallized from ethanol–ethyl acetate to afford light yellow needles, m.p. 133–134°, both pure and mixed with an authentic sample of cycloheptanecarboxaldehyde 2,4-dinitrophenylhydrazone.

β-Cycloheptatriencarboxylic Acid (26).—From 2.47 g. of silver nitrate and 0.62 g. of sodium hydroxide a precipitate of silver oxide was prepared and dissolved in 15 ml. of cond. ammonium hydroxide. β-Cycloheptatriencarboxaldehyde (400 mg., 3.33 millimoles) in 10 ml. of ethanol was added to the silver ammonium complex with stirring. A silver mirror began to deposit immediately and stirring was continued for 12 hours. The mixture was filtered through a Celite bed which was subsequently washed with 50 ml. of ethanol. The filtrate and washings were reduced to one-fourth volume under reduced pressure and washed twice with 50-ml. portions of ether, acidified with concd. HCl and extracted with six 50-ml. portions of ether. The combined acidic ether extracts were dried over magnesium sulfate and the ether removed by evaporation under reduced pressure. The light brown residual oil (306 mg.) was taken up in benzene and chromatographed over 20 g. of silica gel (Davidson). Elution with chloroform afforded 290 mg. (64.2%) of a colorless oil which crystallized immediately when scratched with a glass rod. An analytical sample of β-cycloheptatriencarboxylic acid was obtained after six recrystallizations from pentane; m.p. 57.5–58° both pure and mixed with an authentic sample.[14,15] Both samples had identical infrared spectra (KBr).

γ-Cycloheptatriencarboxaldehyde (27).—β-Cycloheptatriencarboxaldehyde (2.084 g., 0.0174 mole) was pyrolyzed at a rate of 10 mg./min. under a nitrogen flow rate of 10 ml./min. at 330° and the collected pyrolyzate recycled twice more to yield 2 g. of dark yellow oil. After distillation from a Claisen flask at 14 mm. pressure there was obtained 1.511 g. (73.6%) of γ-cycloheptatriencarboxaldehyde, b.p. 92.5–93° (14 mm.), n^{25}D 1.5680; $\nu_{max}^{CCl_4}$ 660(wk), 700, 725-(wk), 1150, 1610, 1685(s), 2720, 2820, 3000(sh) and 3040 cm.$^{-1}$; λ_{max}^{EtOH} 215 mμ (ϵ 11,400), 305 mμ (ϵ 3,500).

Anal. Calcd. for C_8H_8O: C, 80.00; H, 6.66. Found: C, 79.63; H, 6.72.

The γ-isomer exhibited the same acid stability as the β-isomer.

Treatment with 2,4-dinitrophenylhydrazine in methanol containing a trace of HCl gave the 2,4-dinitrophenylhydrazone which after four recrystallizations from ethyl acetate afforded red needles, m.p. 214.5-215°, $\lambda_{max}^{CHCl_3}$ 390 mμ (ϵ 29,000).

Anal. Calcd. for $C_{14}H_{12}O_4N_4$: C, 56.00; H, 4.00. Found: C, 55.80; H, 4.00.

γ-Cycloheptatriencarboxylic Acid (28).—Oxidation of γ-cycloheptatriencarboxaldehyde (200 mg., 1.666 millimoles) by the same procedure described previously for the β-isomer afforded 170 mg. (75.3%) of γ-cycloheptatriencarboxylic acid as colorless needles, m.p. 62–63°, both pure and mixed with an authentic sample.[11] Both samples had identical infrared spectra (CCl_4).

Thermal Aromatization of γ-Cycloheptatriencarboxaldehyde (27).—γ-Cycloheptatriencarboxaldehyde (1.8 g., 0.015 mole) was pyrolyzed at a rate of 10 mg./min. under a nitrogen flow rate of 10 ml./min. at 400°. The pyrolyzate was recycled three times and the final pyrolyzate subjected to preparative vapor phase chromatography (6 mm. × 2.4 m. column; employing Dow–Corning 550 silicone oil, 20%, supported by 40–60 mesh firebrick and as an eluent, nitrogen). The major component (683 mg., 37.9%) had an infrared spectrum identical with that of phenylacetaldehyde (**31**) except for the region 1260–1120 cm.$^{-1}$.

Treatment with 2,4-dinitrophenylhydrazine in methanol containing a trace of HCl gave yellow needles of the 2,4-dinitrophenyldrazone of phenylacetaldehyde, m.p. 120–121°, both pure and mixed with an authentic sample. Both derivatives had identical infrared spectra (KBr).

Tricyclo[2.2.2.1^{7,8}]non-2,5-en-2,3-carboxymethyl-5-carboxaldehyde (36).—β-Cycloheptatrienecarboxaldehyde (3.00 g., 0.025 mole) and 5.28 g. of dimethyl acetylenedicarboxylate in 5 ml. of *p*-xylene were heated to 140° for 8 hours under a nitrogen atmosphere. The *p*-xylene was removed by distillation under reduced pressure and the residual oil was taken up in benzene and chromatographed over 200 g. of silica gel (Davidson). A mixture of starting materials (3.337 g.) was eluted with benzene and the crude Diels–Alder adduct (4.657 g.) was eluted with 8% ether–benzene. After rechromatography over 80 g. of Florisil, elution with 5% ether–benzene afforded 2.150 g. (32.8%) of the clear oily tricyclo[2.2.2.1^{7,8}]non-2,5-en-2,3-carboxymethyl-5-carboxaldehyde. An analytical sample was obtained by distillation in a micro-Hickman still (0.03 mm., *ca.* 165°); $\nu_{max}^{CCl_4}$ 700(wk), 1125, 1270(s), 1435, 1610(wk), 1640(wk), 1690, 1730(s), 2710. 2820. 2960 and 3000 cm.$^{-1}$; λ^{EtOH} 210 mμ (ϵ 14,000).

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[20] F. G. Fisher and O. Wiedemann, *Ann.*, **513**, 251 (1934).

[21] R. Kuhn and M. Hoffer, *Ber.*, **63**, 2164 (1930).

Anal. Calcd. for $C_{14}H_{14}O_5$: C, 64.12; H, 5.35. Found: C, 64.27; H, 5.57.

Treatment with 2,4-dinitrophenylhydrazine in methanol containing a trace of HCl gave the 2,4-dinitrophenylhydrazone which after three recrystallizations from ethyl acetate afforded orange plates, m.p. 230–231°, $\lambda_{max}^{CHCl_3}$ 375 mμ (ε 28,000).

Anal. Calcd. for $C_{20}H_{18}O_8N_4$: C, 54.29; H, 4.07. Found: C, 54.41; H, 4.32.

Pyrolysis of the adduct (1.0 g., 3.82 millimoles) diluted with 10 ml. of toluene at 400° afforded 740 mg. of a dark oil after removal of the toluene. After chromatography over Florisil and elution with 5% ether–benzene there was obtained 415 mg. of a yellow oil which had the desired infrared absorption at 3020(sh), 2980, 2850, 2750, 1720(broad) and 1605 cm.$^{-1}$. The oily aldehyde rapidly formed a 2,4-dinitrophenylhydrazone and was oxidized easily with potassium permanganate in acetone–water to yield nearly quantitatively colorless needles of dimethyl 4-carboxy-1,2-phthalate (**29**), m.p. 121–122° (lit.[22] m.p. 121°).

Anal. Calcd. for $C_{11}H_{10}O_6$: C, 55.46; H, 4.63. Found: C, 55.60; H, 4.24.

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[22] I. Heilbron, "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1953, Vol. IV, p. 589.

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Mechanism of Thiamine Action: a Model of 2-Acylthiamine[1]

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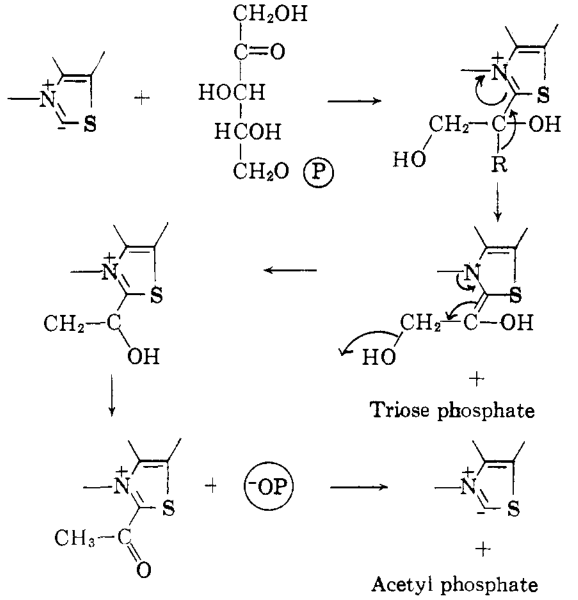
2-Benzoyl-3,4-dimethylthiazolium iodide was prepared and its reactions were studied. This compound reacts very rapidly with methanol to produce methyl benzoate and 3,4-dimethylthiazolium iodide. The biological implications of this reaction are discussed.

The mechanism of all reactions catalyzed by thiamine can be explained in terms of a 2-thiazolium anion.[2] A logical extension of the mechanism for decarboxylation can be made to the phosphoketolase catalyzed reaction[3] in which xylulose-5-phosphate reacts with phosphate ion to give acetyl phosphate and glyceraldehyde-3-phosphate.



All reactions in this mechanism appear plausible except perhaps the last reaction in which 2-acylthiazolium ion reacts with phosphate ion to produce acetylphosphate. Such a reaction would not only require that 2-acylthiazolium ions be "energy rich" but also that they cleave rapidly upon attack by a nucleophile. In order to obtain information about the reactivities of 2-acylthiazolium compounds, 2-benzoyl-3,4-dimethylthiazolium iodide was prepared and its reactivity toward various nucleophiles was studied. 2-Benzoyl-3,4-dimethylthiazolium iodide was prepared by methylating 2-benzoyl-4-methylthiazole obtained by dichromate oxidation of 2-(α-hydroxybenzyl)-4-methylthiazole. The methylation of 2-benzoyl-4-methylthiazole was difficult. Difficulties in methylation prompted us to prepare the ethylene glycol ketal of 2-benzoyl-4-methylthiazole and to methylate this compound. The methylated ketal was quite stable in neutral ethanol (crystallized from ethanol) but was cleaved to benzoic acid in acidic aqueous solution. Later it was found that methylation of 2-benzoyl-4-methylthiazole in dimethylformamide gave fair yields of an unpure product while methylation in acetonitrile gave slightly poorer yields of a product of higher purity. A solution of methyl iodide and dimethylformamide was found to produce tetramethylammonium iodide under our reaction conditions, and presumably this was the impurity present in the product prepared in dimethylformamide. The impurity could be eliminated by recrystallization from acetonitrile.

Experimental

N,N-Dimethylformamide was placed over phosphorus pentoxide 3-6 days then distilled 2–4 times *in vacuo* (20–40 mm.) from phosphorus pentoxide. The distillate was stored in glass-stoppered flasks over phosphorus pentoxide. Immediately before use the dimethylformamide was distilled once *in vacuo* over potassium carbonate and once with no drying agent.

Practical acetonitrile was distilled (81–82°) over phosphorus pentoxide five or six times. Before use, the acetonitrile was distilled twice from potassium carbonate and once with no drying agent.

2-Benzoyl-4-methylthiazole.—2-(α-Hydroxybenzyl)-4-methylthiazole prepared according to Erlenmeyer, Baumann and Sorkin[4] was oxidized with sodium dichromate in glacial acetic acid as described by Erne and Erlenmeyer.[5] The white

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[1] For previous papers in this series see F. White and L. L. Ingraham, *J. Am. Chem. Soc.*, **82**, 4114 (1960), and C. P. Nash, C. W. Olsen, F. White and L. L. Ingraham, *ibid.*, **83**, 4106 (1961).

[2] R. Breslow, *ibid.*, **79**, 1762 (1957); **80**, 3719 (1958).

[3] E. C. Heath, J. Hurwitz, B. L. Horecker and A. Ginsburg, *J. Biol. Chem.*, **231**, 1009 (1958).

[4] H. Erlenmeyer, H. Baumann and E. Sorkin, *Helv. Chim. Acta.*, **31**, 1978 (1948).

[5] M. Erne and H. Erlenmeyer, *ibid.*, **31**, 652 (1948).