attacked during acid hydrolysis to yield glycerol and a 2-carbon alcohol that remains attached to the base fraction.

The observation that the periodate-oxidized nucleosides show entirely different chromatographic properties after treatment with glycine buffer in contrast to treatment with solutions of sodium hydroxide or borax seem to suggest the formation of a complex between the dialdehyde compounds and glycine. This concept is now being explored with particular attention directed to the alkaline reactions of periodate-oxidized nucleoside 5′-phosphates.

In investigations related to the determination of base sequence in ribopolynucleotides. two groups[32,38] have reported that oxidized nucleoside 5′-phosphates readily degrade in the presence of glycine buffer at *p*H 10.5 to produce inorganic phosphate. Preliminary investigations in this Laboratory indicate that periodate-oxidized nucleoside 5′-phosphates form addition compounds (α-hydroxy amine derivatives),[39,40] not only with glycine but also with ammonia and primary amines, and that phosphate is not eliminated during the formation of these complexes. It appears that these compounds slowly release inorganic phosphate in the *p*H range of 8 to 11 and rapidly when the compounds are acidified.

[38] D. M. Brown, M. Fried and A. R. Todd, *Chemistry & Industry*, 352 (1953); *J. Chem. Soc.*, 2206 (1955).

[39] M. M. Sprung, *Chem. Revs.*, **26**, 297 (1940).

[40] D. French and J. T. Edsall, *Advances in Protein Chem.*, **2**, 277 (1945).

[Contribution from the Department of Chemistry of the University of Calfironia, Los Angeles 24, Calif.]

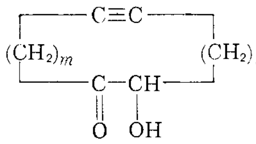
Macro Rings. XXII. 6-Hydroxy-7-keto-*trans*-cyclodecene and Derivatives[1]

By Donald J. Cram and Lyle K. Gaston[2]

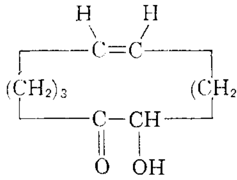
Received July 18, 1960

When submitted to the acyloin reaction, dimethyl *trans*-5-decenedioate gave about a 50% yield of 6-hydroxy-7-keto-*trans*-cyclodecene, which was converted to a number of derivatives. Transannular effects in both reactions and spectral properties were observed. Attempts to ring close dimethyl 5-undecynedioate failed.

Previous studies demonstrated that although a twelve-membered carbocyclic ring containing a carbon–carbon triple bond (Ia) could be closed with the acyloin reaction, the corresponding transformation failed when applied to the preparation of the ten-membered homolog (Ib).[3] However, an acyloin reaction gave a yield of cyclic olefin II substantially better than was obtained in the preparation of sebacoin, the saturated analog.[3] The purpose of this investigation was to explore further the steric limitations of the acyloin reaction, and to make available systems amenable to a study of transannular effects.



Ia, $m = n = 4$
b, $m = n = 3$
c, $m = 4$, $n = 3$



II

Syntheses and Reactions.—The *trans*-olefinic acyloin V was prepared from *trans*-olefin IV which in turn was obtained from the known acetylenic diacid III.[3] The yield in this acyloin reaction (about 50%) compares with the 80% yield of II and 60% yield of sebacoin obtained under similar conditions. Thus the ends of *trans*-olefin IV can be brought together without creation of great strain. The identity of V was demonstrated through its infrared spectrum, and by its conversion to sebacoin by catalytic hydrogenation. Acetylation of V gave acetate VII, whereas oxidation of V with cupric acetate gave diketone VI.[4]

An attempt to reduce acyloin acetate VII to the *thioketal* of 6-keto-*trans*-cyclodecene with trimethylenedithiol[5] resulted in a more deep-seated reduction, which led to the thioketal of cyclodecanone (VIII). The reduction of an isolated carbon–carbon double bond by a mercaptan is unprecedented, and it therefore seems probable that some transannular mechanism is operative which involves both the acyloin and olefinic linkages.

Acetylenic ester IX was prepared by the indicated sequence, but gave only polymer and starting material on repeated attempts at ring closure by the acyloin reaction. Clearly, the smallest ring containing a carbon–carbon triple bond that can be closed by the acyloin reaction is twelve-membered.

Spectra.—Table I gives the positions in the infrared spectra of the carbonyl band of a number of alicyclic ketones. Within experimental error, in these medium rings the corresponding ketones, acyloins and α-diketones all have the same carbonyl stretching frequency. As the alicyclic ketones get larger, the carbonyl band decreases in frequency until a minimum is reached in the ten-membered ring.[6] This effect seems to be associated with an increase in the C–C–C bond angle of the carbonyl group which is largest with the ten-membered

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[1] This work was sponsored by the Office of Ordnance Research, U. S. Army.

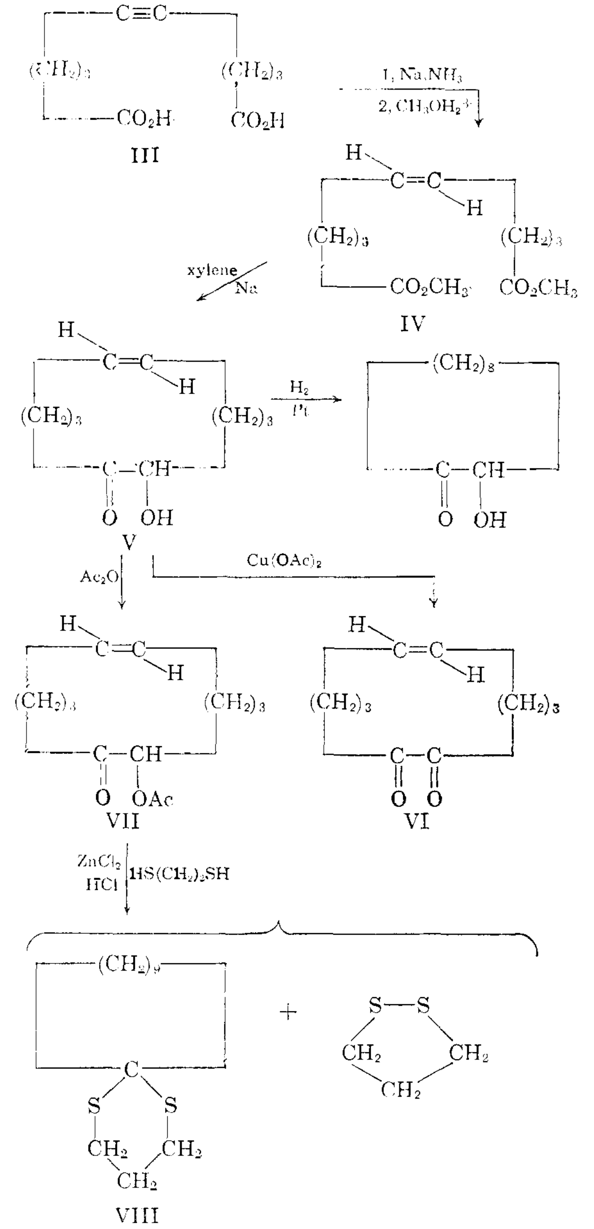
[2] Dow Predoctoral Fellow, 1956–1957.

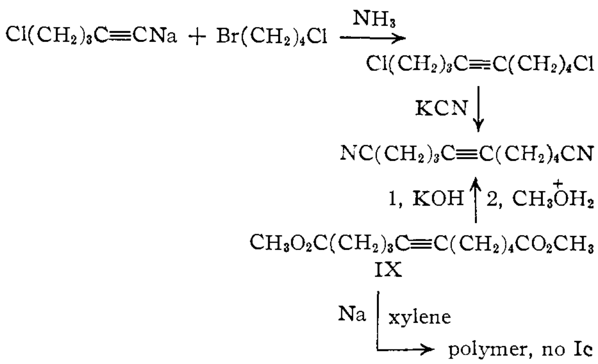
[3] D. J. Cram and N. L. Allinger, This Journal, **78**, 2518 (1956).

[4] Bismuth oxide [W. Rigby, *J. Chem. Soc.*, 793 (1951)] oxidation failed to give diketone.

[5] D. J. Cram and M. Cordon, This Journal, **77**, 1810 (1955).

[6] T. Burer and H. H. Gunthard, *Helv. Chim. Acta*, **39**, 365 (1956).





$Cl(CH_2)_3C\equiv CNa + Br(CH_2)_4Cl \xrightarrow{NH_3} Cl(CH_2)_3C\equiv C(CH_2)_4Cl \xrightarrow{KCN} NC(CH_2)_3C\equiv C(CH_2)_4CN \xrightarrow{1,\ KOH;\ 2,\ CH_3\overset{+}{O}H_2} CH_3O_2C(CH_2)_3C\equiv C(CH_2)_4CO_2CH_3$ IX

IX $\xrightarrow{Na,\ xylene}$ polymer, no Ic

ring ketone.[6,7] The introduction of a *trans*-double bond into the ten-membered acyloin or diketone seems to increase further the C–C–C bond angle of the carbonyl group, as might be expected. Further evidence of strain in the three ten-membered *trans*-olefins is found in the absorptions associated with the *trans*-double bond. Allinger[8] compared the spectra of *trans*-4-octene (C=C stretch, 1670 cm.$^{-1}$ and C—H bend, 968 cm.$^{-1}$), with that of *trans*-cycloöctene (C=C stretch, 1670 cm.$^{-1}$ and C—H bend, 968 cm.$^{-1}$), with that of *trans*-cycloöctene (C=C stretch, 1658 cm.$^{-1}$ and C—H bend, 981 cm.$^{-1}$), and concluded that the frequency of the C=C stretch decreased and of the C—H bend increased as the double bond was constrained in the ring. Our three cyclic *trans*-olefins V, VI and VII exhibit absorptions associated with C=C stretch which ranged from 1649 to 1656 cm.$^{-1}$, and with C—H bend at 958 to 988 cm.$^{-1}$. Thus the double bonds in these three ten-membered ring olefins seems to be under greater strain than that in *trans*-cycloöctene.

TABLE I

INFRARED STRETCHING FREQUENCY OF ALICYCLIC KETONES

Compound	Carbonyl band, cm.$^{-1}$	Reference
Cyclohexanone	1718	6
Cycloöctanone	1704	6
Cyclodecanone	1705	6
Sebacoin	1704	[a]
1,2-Cyclodecanedione	1700	[a]
6-Hydroxy-7-keto-*trans*-cyclodecene	1693	This work
6,7-Diketo-*trans*-cyclodecene	1693	This work
Cyclododecanone	1713	[b]
7-Hydroxy-8-keto-*cis*-cyclododecene	1707	[b]
7-Hydroxy-8-ketocyclododecyne	1705	[b]
7,8-Diketo-cyclododecyne	1705	[b]

[a] A. T. Blomquist, R. E. Burge and A. C. Sucsy, THIS JOURNAL, 74, 3636 (1952). [b] N. L. Allinger and D. J. Cram, unpublished work.

Table II records the maxima in the ultraviolet absorption spectrum of 6,7-diketo-*trans*-cyclodecene (VI), and of a number of related cyclic compounds. The long wave length bands of VI 6,7-diketo-*trans*-cyclodecene and 7,8-diketocyclododecyne indicate that the carbonyl groups are either eclipsed or *trans* to one another.[9] An examination of molecular models indicates that the *trans* arrangement is preferred.

TABLE II

ULTRAVIOLET ABSORPTION SPECTRA[a]

Compound	λmax, mμ	ε	λmax, mμ	
6,7-Diketo-*trans*-cyclodecene	242	510		
	246	510		
	253	510		
	259	520		
	280	560	396	30
6,7-Diketo-*cis*-cyclodecene[3]	255	483	402	10
7,8-Diketocyclododecyne[3]	238	907	412	21
6-Keto-*trans*-cyclodecene[10]	258	472	302	73

[a] Solvent, ethanol; spectra taken on Cary recording spectrophotometer, model 11 PMS.

The unusual absorption band at 258 mμ found in the spectrum 6-keto-*trans*-cyclodecene[10] is present in the spectra of *cis*- and *trans*-6,7-diketocyclo-

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[7] L. L. Ingraham in M. S. Newman's "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 506.

[8] N. L. Allinger, THIS JOURNAL, **80**, 1953 (1958).

[9] N. J. Leonard and P. M. Mader, *ibid.*, **72**, 5388 (1950).

[10] N. J. Leonard and F. H. Ownes, *ibid.*, **80**, 6039 (1958).

decenes and of 7,8-diketocyclododecyne. In the *trans*-diketone, the band possesses considerable fine structure, whose maxima range from 242 to 280 mμ. The fine structure is absent in the bands of the *cis* isomer and the acetylenic diketone. These bands are attributable[10] to transannular interactions between C=C and C=O in the excited states of the molecule.

Experimental

***trans*-5-Decenedioic Acid.**—A mixture of 35 g. of 5-decynedioic acid[3] (m.p. 109–110°) and 150 ml. of water was just neutralized with 6 *N* sodium hydroxide solution, and the resulting solution was lyophilized. The resulting disodium salt (42 g. or 0.173 mole) was added to a solution of 40 g. (1.74 gram atoms) of sodium dissolved in 300 ml. of liquid ammonia. The resulting mixture was heated in a stainless steel bomb fitted with a glass liner, and was stirred for 6 days at 70°. Excess sodium was decomposed with methanol, the solution was evaporated, and water was added. The solution was cooled, and concentrated hydrochloric acid was added until the mixture was strongly acidic. When cooled, solid separated which was recrystallized twice from ether–pentane to give 7.3 g. of slightly impure *trans*-5-decenedioic acid, m.p. 108–112°. The filtrates contained mixtures of this *trans*-acid and unreduced acetylenic acid. A small sample of the olefinic acid was recrystallized twice from ether–pentane to give m.p. 115–116°. The infrared spectrum of the *trans*-acid in a KBr disk gave the following bands of interest: 2990–3500 cm.$^{-1}$, strong, broad (hydrogen-bonded O–H stretch); 1690 cm.$^{-1}$, very strong (acid carbonyl); 976 cm.$^{-1}$, medium (*trans*-olefin, out of plane hydrogen bending).

Anal. Calcd. for $C_{10}H_{16}O_4$: C, 59.98; H, 8.06. Found: C, 59.99; H, 7.90.

The dimethyl ester of *trans*-5-decenedioic acid was prepared with methanol and sulfuric acid in 85% yield, b.p. 134–136 (5 mm.), n^{25}D 1.4486. The infrared spectra (neat) showed the following bands of interest: 1730 cm.$^{-1}$, very strong (ester carbonyl); 980 cm.$^{-1}$, strong (*trans*-olefin).

Anal. Calcd. for $C_{12}H_{20}O_4$: C, 63.16; H, 8.83. Found: C, 63.36; H, 8.66.

6-Hydroxy-7-keto-*trans*-cyclodecene (V).—A solution of 13.8 g. (0.0608 mole) of the dimethyl ester of *trans*-5-decenedioic acid in 950 ml. of xylene was added over 9 hours to 6.05 g. (0.263 gram atom) of sodium dispersed in 1 liter of refluxing xylene.[3] The reaction mixture was cooled to 0°, and excess acetic acid was added to decompose the excess sodium and neutralize the salt. Water was added, and the mixture filtered. The xylene layer was washed twice with water, dried, and the solvent evaporated under vacuum. Distillation at 5 mm. of the residual oil gave a small forerun (0.73 g., b.p. 95–109°), and 5.19 g. (51%) of slightly yellow acyloin, n^{25}D 1.5019, b.p. 109–115°. A small sample was redistilled for analysis, n^{25}D 1.5052.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.19; H, 9.68.

A small sample, 0.203 g., of this acyloin was shaken with 0.050 g. of prereduced platinum oxide in methanol under an atmosphere of hydrogen. After the reaction was over (22.1 ml. of hydrogen or 74% of one mole was absorbed), the reaction mixture was filtered, the solvent was evaporated, and the residue was crystallized from pentane to give 0.015 g. of sebacoin, m.p. 38.5–39.5°, undepressed by admixture with an authentic sample. An additional 0.093 g. of sebacoin was isolated from the filtrates.

6-Acetoxy-7-keto-*trans*-cyclodecene (VII).—Acyloin V (1.00 g., 0.0060 mole) was added to a solution of 5 ml. of acetic anhydride and 1 ml. of dry pyridine, and the resulting solution was allowed to stand for 4 days. The mixture was shaken with ice and dilute hydrochloric acid, the ether solution was washed with sodium bicarbonate solution, and then with water. The ether layer was dried, evaporated, and the resulting oil was chromatographed on 40 g. of neutral activity III[11] alumina. The first six 25-ml. pentane fractions from the column gave a yellow oil, distillation of which at 105° and 1 mm. produced 0.682 g. (55%) of the acyloin acetate (VII), n^{25}D 1.4829.

Anal. Calcd. for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63. Found: C, 68.32; H, 8.67.

6,7-Diketo-*trans*-cyclodecene (VI).—A solution of 0.200 g. (0.0019 mole) of acyloin V in 0.3 ml. of methanol was added to a solution of 0.475 g. (0.0024 mole) of cupric acetate monohydrate in 1.0 ml. of 50% aqueous acetic acid.[12] The mixture was refluxed for 1.5 minutes, cooled, and filtered. Water was added and the mixture was extracted with ether. The ether solution was washed with sodium carbonate solution, water, dried and evaporated to a yellow oil. Chromatography of this oil on 8 g. of neutral, activity I alumina gave with a pentane developer four 25-ml. fractions, which were combined and evaporated. Distillation of the residue at 115° (5 mm.) gave 0.047 g. (24%) of diketone VI, n^{25}D 1.4987.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.38; H, 8.34.

Attempted Preparation of Trimethylenethioketal of 6-Keto-*trans*-cyclodecene.—To 0.200 g. of 6-acetoxy-7-keto-*trans*-cyclodecene was added a mixture of 0.300 g. of freshly fused and powdered zinc chloride and 0.5 ml. of trimethylenedithiol in 10 ml. of benzene.[5] The mixture was saturated with hydrogen chloride and stirred for 12 hours. The benzene was decanted and washed with sodium hydroxide solution and water. The solution was dried and evaporated to an oil, which was chromatographed on 8 g. of neutral, activity I alumina,[11] and developed with pentane. The first five 25-ml. fractions of pentane eluate were combined and distilled at 0.5 mm. to give two fractions: bath temperature 95°, 0.034 g. of starting material; bath temperature 160°, 0.040 g. (17%) of a thioketal. The second fraction was redistilled for analysis, n^{25}D 1.5570. The infrared spectrum (liquid film) showed no absorption above 3000 cm.$^{-1}$ or between 1500–2600 cm.$^{-1}$, and little absorption between 925–1000 cm.$^{-1}$. Weak bands were observed at 695 and 675 cm.$^{-1}$. The spectrum was identical with that reported for the trimethylenethioketal of cyclodecanone,[5] which distilled at a bath temperature of 160° (0.8 mm.), n^{25}_{D} 1.5620.

Anal. Calcd. for $C_{13}H_{22}S_2$: C, 64.40; H, 9.14. Calcd. for $C_{13}H_{24}S_2$: C, 63.87; H, 9.90. Found: C, 63.50; H, 10.10.

1,9-Dichloro-4-nonyne.—Sodium (5.8 g., 0.252 gram atom) was converted to sodamide in 0.9 l. of liquid ammonia. To this solution was added dropwise 24.48 g. (0.238 mole) of 5-chloro-1-pentyne.[13] After the mixture was stirred for 30 minutes, 41.0 g. (0.238 mole) of tetramethylene chlorobromide[14] was added dropwise over 30 minutes. The solution was stirred and the ammonia allowed to evaporate over a period of 4 hours. Ammonium sulfate, pentane and then water were added. The organic phase was extracted with pentane, and the pentane extracts were combined, washed with dilute hydrochloric acid, saturated sodium bicarbonate and water. The solution was dried, evaporated, and to the residue was added a few crystals of hydroquinone. The yellow oil was distilled at 5 mm. to give a forrun of 6.21 g. (b.p. below 107°), and a main fraction, b.p.107–115°, weight 15.6 g. (34%), n^{25}D 1.4841.

Anal. Calcd. for $C_9H_{14}Cl_2$: C, 55.97; H, 7.31. Found: C, 56.26; H, 7.26.

1,9-Dicyano-4-nonyne.—To a solution of 15.6 g. (0.081 mole) of 1,9-dichloro-4-nonyne in 88 ml. of ethanol was added a solution of 15.8 g. (0.243 mole) of potassium cyanide and 2.0 g. of potassium iodide in 35 ml. of water.[15] The resulting solution was refluxed for 24 hours, and then an additional 15.8 g. of potassium cyanide and 2.0 g. of potassium iodide was added, and the mixture was refluxed for 23 hours. Ethanol, 67 ml., was evaporated through a Vigreux column. The remaining aqueous solution was shaken with ether and water, the ether layer was washed with water, with sodium thiosulfate and water. The ether was dried, and evaporated to give an oil, which was distilled

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(11) H. Brockmann and H. Schodder, *Ber.*, **74B**, 73 (1941).

(12) A. T. Blomquist and H. Goldstein in *Org. Syntheses*, **36**, 77 (1956).

(13) K. N. Campbell, F. C. Fatora and B. K. Campbell, *J. Org. Chem.*, **17**, 1141 (1952).

(14) M. S. Newman and J. H. Wotiz, THIS JOURNAL, **71**, 1291 (1949).

(15) This reaction is patterned after that of J. R. Ruhoff in "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 292.

to give the following fractions at 2 mm.; b.p. 25–158°, 1.17 g.; b.p. 158–160°, 8.17 g. (58%), $n^{25}D$ 1.4723. A small sample of the latter fraction was redistilled for analysis, $n^{25}D$ 1.4718.

Anal. Calcd. for $C_{11}H_{14}N_2$: C, 75.82; H, 8.10. Found: C, 75.71; H, 7.87.

5-Undecynedioic Acid.—A solution of 8.17 g. (0.0469 mole) of 1,9-dicyano-4-nonyne in 56 ml. of ethanol and 14 ml. of water containing 10.5 g. of potassium hydroxide was refluxed for 10 hours. Ethanol (22 ml.) was allowed to evaporate, and the solution was cooled and made strongly acidic with concentrated hydrochloric acid. The product that separated was collected, dried and recrystallized from benzene; 7.92 g. (80%), m.p. 78–79°. A sample for analysis was recrystallized four times from ether–pentane; m.p. 79.5–81°.

Anal. Calcd. for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.09; H, 7.51.

Dimethyl 5-undecynedioate was prepared in the usual way in 89% yield from 5-undecyne-1,11-dioic acid, methanol and sulfuric acid catalyst; b.p. 150-151° (5.5 mm.), $n^{25}D$ 1.4578.

Anal. Calcd. for $C_{13}H_{20}O_4$: C, 64.89; H, 8.39. Found: C, 64.76; H, 8.18.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OHIO UNIVERSITY, ATHENS, O.]

Reactions of Diolefins at High Temperatures. III. Reversible Dissociation of 1,5-Alkadienes and Sensitization of Cyclization by Allyl Bromide[1,2]

BY WILLIAM D. HUNTSMAN

RECEIVED JULY 7, 1960

The behavior of several simple 1,5-alkadienes at 460° has been investigated. 2-Methyl-1,5-hexadiene yields 1,5-hexadiene and 2,5-dimethyl-1,5-hexadiene; the reversibility of this reaction was demonstrated by pyrolyzing an equimolar mixture of 1,5-hexadiene and 2,5-dimethyl-1,5-hexadiene whereupon 2-methyl-1,5-hexadiene was formed. The product from 1,5-heptadiene contains 1,5-hexadiene, 3-methyl-1,5-hexadiene, 3-methyl-1,5-heptadiene and 1,5-heptadiene; a mixture very similar in composition is obtained from 3-methyl-1,5-hexadiene. These reactions are rationalized in terms of a reversible dissociation mechanism involving allylic free radicals. Small amounts (*ca.* 1%) of allyl bromide sensitize the formation of cyclic products from 1,5-diolefins at 460°. For example, cyclohexene and benzene are obtained from 1,5-hexadiene, while benzene, toluene, vinylcyclopentane, and 1-, 3- and 4-methylcyclohexene are formed from both 1,5-heptadiene and 3-methyl-1,5-hexadiene. A free radical chain mechanism is believed to operate in the cyclization reaction.

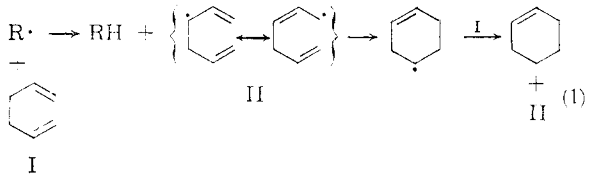
Introduction

Although the behavior of 1,5-hexadiene at high temperatures has been carefully studied, little work has been reported on the higher 1,5-alkadienes. In this paper the results of a study of some simple 1,5-alkadienes are reported.

The primary step in the thermal decomposition of 1,5-hexadiene appears to be the formation of allyl free radicals by homolytic cleavage of the central carbon–carbon bond; abstraction of hydrogen atoms from 1,5-hexadiene or other hydrogen donors by the allyl radicals leads to propylene, the major pyrolysis product.[3] Indeed the presence of allyl radicals during the pyrolysis of 1,5-hexadiene has been demonstrated by mass spectrometry.[4] Szwarc estimates the bond dissociation energy of the central bond in 1,5-hexadiene to be 38 kcal./mole, a value which is much lower than those found for simple alkanes.[5] It is generally agreed that the weakening of this bond is due to the high degree of resonance stabilization of the allyl radical.

It has also been demonstrated that allyl radicals, generated by the pyrolysis of allyl halides and other derivatives, may recombine to give 1,5-diolefins. For example, allyl radicals and 1,5-hexadiene were detected mass spectrometrically during the pyrolysis of allyl iodide,[4] and in the same way, β-methylallyl radicals and 2,5-dimethyl-1,5-hexadiene were shown to be formed by the pyrolysis of β-methylallyl iodide.[6] The formation of 1,5-hexadiene by the pyrolysis of 4-phenyl-1-butene apparently involves the dimerization of allyl radicals.[7]

Substantial amounts of cyclohexene and benzene are formed by the pyrolysis of 1,5-hexadiene at 540°, and it has been postulated that hexadienyl radicals (II), formed from 1,5-hexadiene through hydrogen abstraction, are forerunners of cyclization as illustrated by eq. 1.



Another type of thermal reaction—the Cope rearrangement—occurs at temperatures considerably below those at which dissociation occurs.[8] For example, the interconversion of 1,5-heptadiene and 3-methyl-1,5-hexadiene occurs slowly at 300° by an intramolecular mechanism.

Results and Discussion

Reversible Dissociation.—The product obtained by pyrolysis of 2-methyl-1,5-hexadiene (III) at 460° consisted largely of unchanged (III) along with smaller amounts of 1,5-hexadiene (I) and 2,5-dimethyl-1,5-hexadiene (IV). From an experiment in which the contact time was 21 seconds, the liquid product contained 4% (I) and 3% (IV);

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(1) Paper II of this series: W. D. Huntsman, V. C. Solomon and D. Eros, THIS JOURNAL, **80**, 5455 (1958).

(2) This research was supported by the United States Air Force, through the Office of Scientific Research of the Air Research and Development Command under contract No. AF18(600)546. The author acknowledges with gratitude the financial aid provided by the National Science Foundation for the purchase of the Perkin-Elmer model 21 infrared spectrophotometer used in this study (NSF-G3912).

(3) C. D. Hurd and H. T. Bollman, *ibid.*, **55**, 699 (1933).

(4) F. P. Lossing, K. U. Ingold and I. H. S. Henderson, *J. Chem. Phys.*, **22**, 621 (1954).

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(7) L. M. Porter and F. F. Rust, THIS JOURNAL, **78**, 5571 (1956).

(8) H. Levy and A. C. Cope, *ibid.*, **66**, 1684 (1944).