Anal. Calcd for $C_5H_7NO_4$: C, 41.4; H, 4.86; N, 9.65. Found: C, 41.4; H, 4.86; N, 9.80.

Preparation of *t*-Butylaziridine.—Ethyl N-(2-*t*-butyl-2-chloroethyl)carbamate (29.7 g, 0.145 mole) in 95% ethanol (100 ml) was added in one portion to a solution of potassium hydroxide (30.0 g, 0.550 mole) in 95% ethanol (150 ml). The solution was refluxed for 48 hr, at which time the separation of solids was complete. The reaction mixture was poured into water (1 l.) and extracted with five 200-ml portions of ether. The combined extracts were dried over anhydrous sodium sulfate and the ether was removed by distillation. The residual oil was then distilled using a 6 in. × $^3/_8$ in. column packed with glass helices to yield 2-*t*-butylaziridine, bp 116–116.5° (760 mm), and $n^{23}D$ 1.4244, as a colorless liquid (8.95 g, 60% yield). Infrared bands are λ_{max}^{neat} 3300 (NH), 1480, 1360, 1200, 895, and 860 cm^{-1}.

Anal. Calcd for $C_6H_{13}N$: C, 72.66; H, 13.21; N, 14.12. Found: C, 72.52; H, 13.32; H, 13.88.

Attempted Preparation of 2-Acetylaziridine.—Repetition of the above procedure with ethyl N-(2-acetyl-2-chloroethyl)carbamate on a 0.001-mole scale and with 2 hr of reflux time yielded a dark brown viscous oil which did not yield the aziridine on vacuum distillation.

Attempted Preparation of 2,2-Dichloroaziridine.—Repetition of the above procedure with ethyl N-(2,2,2-trichloroethyl)carbamate on a 0.01-mole scale and reaction with base for 18 hr at room temperature yielded a dark brown intractable viscous liquid.

Attempted Addition of DCU to Perfluorocyclohexene, Ethyl Vinyl Sulfone and Diethyl Maleate.—The unsaturated compound (0.05 mole) was added in one portion to a solution of DCU (8.0 g, 0.05 mole) in benzene (25 ml). With the first two unsaturated compounds, the solutions were refluxed for 72 hr; in the third case refluxing was continued for only 31 hr. There was no detectable disappearance of unsaturated compound as shown by glpc.

Registry No.—**1,** 15044-22-1; **3,** 15042-62-3; **4,** 13698-14-1; **5,** 15042-64-5; **6,** 15042-65-6; **7,** 15042-66-7; **8,** 762-07-2; **9,** 15042-67-8; **9a** (*erythro*), 15042-68-9; **9a** (*threo*), 15042-72-5; **10,** 15042-69-0; DCU, 13698-16-3; 2-*t*-butylaziridine, 13639-44-6.

The Isomerization and Cyclization of Octatrienes

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Received May 17, 1967

Interactions of the readily available mixture of 1,3,6- and 1,3,7-octatrienes with the alkali metal salts of alkyl amides have resulted in both a selective isomerization and a cyclization. In the first instance, potassium salts have selectively transformed the 1,3,6-octatrienes to 2,4,6-octatrienes and, in the second, the octatriene mixture has been converted into methylcycloheptadienes (IV). By a series of glpc and nmr determinations and by conversion to a Diels-Alder derivative, the dienes IV have been shown to be composed primarily of 1-methyl- and 2-methyl-1,3-cycloheptadiene.

The field of hydrocarbon acidity, proton exchange, and carbanions has been and remains an extremely active one in current research.[1] In this connection, we have observed that the linear trienes, 1,3,6-octatrienes (I) and 1,3,7-octatrienes (II), will undergo some unusual reactions upon treatment with strong bases. On the one hand, I in mixtures of these trienes has been found to be selectively isomerized, while, on the other, both isomers have been found to cyclize.

A mixture of 49% of I and 49% of II (2% of 4-vinylcyclohexene impurity) upon interaction with piperidinopotassium gave a product containing 46% of 2,4,6-octatrienes (III) and 48% of recovered II (eq 1). Only a trace of nondistillables was observed.

$$\underset{\text{I}}{CH_2{=}CH{-}CH{=}CH{-}CH_2{-}CH{=}CH{-}CH_3} +$$

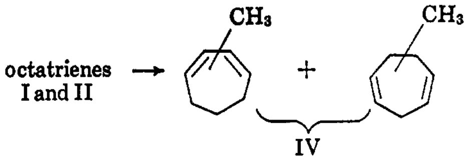
$$\underset{\text{II}}{CH_2{=}CH{-}CH{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2} \longrightarrow$$

$$\underset{\text{III}}{CH_3{-}CH{=}CH{-}CH{=}CH{-}CH{=}CH{-}CH_3} +$$

$$\underset{\text{II}}{CH_2{=}CH{-}CH{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2} \quad (1)$$

This selective isomerization appears to be general with potassium compounds of alkyl monoamines, since diethylaminopotassium and 1,1 3,3-tetramethylbutylaminopotassium were found to be equally as effective. The reaction proceeds slowly at room temperature and rapidly near 100°. Just as the compounds I and II were mixtures of at least two configurational isomers, the resultant triene III was composed of three isomers which were readily resolved by gas–liquid partition chromatography (glpc). The two major components were isolated and identified by their infrared spectra.

This selective isomerization was not observed when sodium alkyl amides were employed; instead, both I and II were consumed to give new products. These products were found to be the result of a unique cyclization which furnished a mixture of isomeric methylcycloheptadienes (IV) (eq 2). The presence of the seven-membered ring was readily demonstrated since upon hydrogenation exactly 2 moles of hydrogen were absorbed to give methylcycloheptane. This cyclization has been effected under a variety of conditions. Treatment of a mixture of octatrienes (neat) with piperidinosodium at room temperature for 19 hr gave IV in 43% yield, along with the formation of higher molecular weight materials. When the octa-



(2)

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[1] (a) A. I. Shatenshtein, "Advances in Physical Organic Chemistry," Vol. 1, V. Gold, Ed., Academic Press Inc., New York, N. Y., 1963, p 155; (b) A. Streitwieser, Jr., and J. H. Hammons, "Progress in Physical Organic Chemistry," Vol. 3, S. G. Cohen, A. Streitwieser, Jr., and R. W. Taft, Ed., Interscience, Publishers, Inc., New York, N. Y., 1965, p 41.

trienes were added to the sodium compound suspended in boiling cyclohexane, none of the starting material could be detected by glpc a few minutes after the addition was completed and IV was obtained in 66% yield. Under proper conditions, other sodium compounds, such as diethylaminosodium and sodium amide, were equally as effective. Interestingly, a reaction with piperidinosodium in boiling tetrahydrofuran (5 hr) gave both IV and III in 30 and 38% batch yields, respectively.

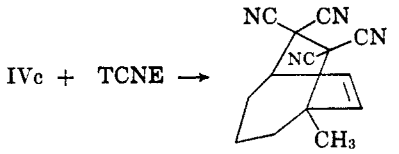
Other C_8 trienes have also been found to undergo cyclization. In accord with the above tetrahydrofuran run, samples taken prior to completion of the reactions have revealed the presence of small quantities of III upon gas chromatographic analysis. Upon treatment with piperidinosodium in boiling cyclohexane, pure III was found to cyclize to give IV in 78% yield. In contrast to the previously described potassium isomerization systems, in the presence of piperidinosodium a pure sample of II was readily converted with IV (63%) in a yield comparable to that of the mixed octatrienes. The branched chain triene, 3-methyl-1,4,6-heptatriene (V), was also found to undergo cyclization upon treatment with piperidinosodium. The products were found to be identical with those from the linear octatrienes and were obtained in high yield (84%). Surprisingly, treatment of V with piperidinopotassium also gave IV; the yield in this case was 39% with some 55% of higher molecular weight material being formed.

A careful examination of the isomerization products from the potassium bases for IV by glpc in no instance showed any evidence for the formation of IV. In fact, a mixture of octatrienes and piperidinopotassium was interacted at 150° for 4 hr, but none of the cyclization products were obtained.

The octatrienes were also treated with a number of other base systems. The alkali metal derivatives of ethylenediamine were unusual in that the lithium and potassium compounds gave low yields of both III and IV, while high molecular weight materials were the predominant product when the sodium compound was utilized. In a few runs with lithium salts of monoamines no reaction was observed.

Base-catalyzed equilibration[1] of cyclic diolefins, such as cyclohexadienes and hexahydronaphthalenes,[2] are known to produce a number of isomeric species. With the methylcycloheptadienes (IV), there exists the possibility of eight isomers with the double bonds in the ring. Employing packed glpc columns, IV could be resolved into only three fractions, and their relative distribution, under probable equilibrium for this system, was 8:23:69, in that increasing order to retention times. However, a number of other components were readily discernible upon analysis on a 150-ft capillary column containing squalane; the relative percentages of the eight most abundant peaks in the order of appearance were 3.2, 6.6, 0.4, 0.3, 24.0, 64.3, 0.1, and 1.1%. Utilizing preparatory glpc techniques, the three fractions were individually isolated, and their nmr spectra can be summarized as follows. The first fraction (IVA) had a strong doublet at τ 8.9 and an olefinic proton to nonolefinic proton ratio of 3.9:8.1. The methyl group was thus not on a double bond, and the over-all spectrum indicated that at least two components were present in agreement with the glpc data. The second (IVB) and third fractions (IVC) exhibited strong resonances at τ 8.3 and had olefinic proton to other proton ratios of 3:9. Fraction IVB exhibited some fine structural differences in that both the olefinic and methyl resonances were split 1.5 cps. Neither sample had a resonance in the τ 7.3 region (protons α to both double bonds); therefore, the spectra of IVB and IVC indicated the presence of 1-methyl- and 2-methyl-1,3-cycloheptadiene but were not sufficiently unique to distinguish between these isomers.

In an effort to resolve these structures, the third fraction (IVc) was interacted with tetracyanoethylene (TCNE) (see eq 3). The nmr spectrum of the resultant adduct (VI) had a sharp peak at τ 8.88, clearly indicating an uncoupled methyl group one carbon removed from a double bond. Overlapping the methyl peak was a broad resonance (τ 8.2–9.0) due to methylene groups; the combined methyl and methylenes measured 9.2 protons. In the olefinic region there was a complex resonance (τ 4.3–4.6) which measured 2.0 protons, while a broad resonance between τ 7.2 and 7.5 measured 0.8 protons. The latter resonance was approximately τ 0.4 downfield from the normal position for a cyclic CH group adjacent to a double bond, but the electronegative nitrile groups would be expected to effect this shift. Therefore, the olefinic to α CH proton ratio of approximately 2 to 1 was additional evidence for the adduct having the indicated structure VI, 1-methyl-8,8,9,9-tetracyanobicyclo[3.2.2]nonene-6. Therefore, fraction IVc must be primarily 1-methyl-1,3-cycloheptadiene and IVb should be 2-methyl-1,3-cycloheptadiene.



VI

(3)

The differences in base strengths and hydrocarbon acidities may account for these reaction phenomena. For any given amide, the base strength should increase as the alkali-metal cation is changed from lithium to sodium to potassium.[1,3] The difference in activity between I and II, as demonstrated toward potassium amide salts, may be due to the more acidic characteristics of the doubly allylic protons in the 5 position of I. However, the ability of the sodium salts to react with both I and II is not readily obvious, but may be associated with the heterogeneous nature of the systems. In these particular systems, the sodium derivatives could be more soluble and, therefore, more reactive than the corresponding potassium salts. This behavior is consistent with studies involving cyclohexylaminolithium, in which the soluble monomeric salt exhibited catalytic activity while the higher aggregates were comparatively unreactive.[4]

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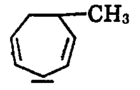
(2) R. B. Bates, R. H. Carnighan, and C. E. Staples, *J. Am. Chem. Soc.*, **85**, 3031 (1963).

(3) (a) F. Asinger, B. Fell, and P. Krings, *Chem. Ber.*, **99**, 1737 (1966); (b) D. Bethell and A. F. Cockerill, *J. Chem. Soc.*, *Sect. B*, 920 (1966).

(4) Reference 1b, p 59.

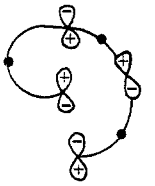
A plausible pathway for the formation of IV involves initially the transformation of the trienes to an octatrienyl anion of the type indicated by VII. In the reactions of I and II, the conjugated triene III may be formed in part as an intermediate. The heptatrienyl anion arising from V would, of course, be analogous to VII but would have the methyl substituent in the 3 position. Ring closure of either anion should give a pentadienyl anion of the type as shown by VIII with the resultant isomeric cycloheptadienes being the ultimate consequence of equilibration and proton abstraction (eq 4). Hoffmann

$$CH_3CH{=}CHCH{=}CHCH{=}CHCH_2^{-} \longrightarrow$$



VII VIII (4)

and Olofson[5] have stated that of the ten distinct planar configurations of heptatrienyl anions, the anticipated and favored anion geometrics would be the all-*cis* form IX, and the "U-sickle" and "U-W" forms. The helical configuration of the anion IX



IX

would thus seem most appropriate for closure to the seven-membered ring. This cyclization is also consistent with previous work from this laboratory,[6] in which *trans,trans,cis*-1,5,9-cyclododecatriene was converted to bicyclo[5.5.0]dodecadienes. An initial rearrangement to the conjugated triene, followed by transannular addition of a carbanion, was postulated as the mode of formation.

Experimental Section

All melting and boiling points are uncorrected. Reactions involving alkali metal compounds, or moisture- and air-sensitive derivatives thereof, were conducted in dry equipment under nitrogen. Infrared spectra were obtained on a Perkin-Elmer Infracord spectrophotometer and nmr spectra on a Varian A-60 spectrometer with tetramethylsilane as the internal standard. Analyses by gas-liquid partition chromatography (glpc) were performed on a F & M Model 720 and on a Perkin-Elmer 226 capillary chromatograph attached to a digital readout system (Model CRS-11HSB/41, Infotronic Corp.). The octadienes were prepared by the dimerization of butadiene in the presence of zero-valent nickel complexes and hydroxylic solvents.[7] Since 4-vinylcyclohexene boils at 127° and is formed along with the 1,3,6-octatrienes (I) (bp 131°) and 1,3,7-octatrienes (II) (bp 126°), the octatrienes used throughout this study were contaminated with 4-vinylcyclohexene.

Selective Isomerization of 1,3,6-Octatriene (I). A. With Piperidinopotassium.—A suspension of 0.75 g of benzylpotassium[8] in 5 ml of toluene was treated with 4.3 g of piperidine. After 30 min, the mixture was cooled in a water bath and treated with 32.5 g of octatrienes, containing 49% of I, 49% of II, and 2% of 4-vinylcyclohexene. The course of the reaction was followed by glpc with small samples being withdrawn at various intervals. Since some compound I remained after standing 2 hr, the mixture was heated. In the process of 25 min, a temperature of 93° was attained, and a glpc analysis at this time indicated all of the 1,3,6 compound had reacted. Heating was continued for 1 hr at 93 to 97°, but no further change in the product distribution could be detected. Analysis showed the product to be comprised of 48% of II, 46% of 2,4,6-octatrienes (III) (see below), and 5% of 4-vinylcyclohexene and unknown octatrienes. The reaction mixture was hydrolyzed and washed with water, and the organic layer separated and dried over calcium sulfate. The dried organic layer was distilled and three main fractions were collected boiling at 65–69° (100 mm), 69–88° (100 mm), and 88–90° (100 mm). There was only 1.9 g of residue, which upon glpc analysis was mainly III, thereby substantiating the correctness of the above glpc calculations. The first fraction was slightly impure II with the portion collected between 68 and 69° having $n^{20}{}_{\mathrm{D}}$ 1.4682. The intermediate fraction was composed of II and III. A portion of the last fraction was dissolved in methanol and cooled, and the resultant solid was filtered. This was repeated several times during which a few drops of water was added to induce crystallization. The solid was collected and sublimed at 2 mm of pressure using a Dry Ice–acetone condenser to give a colorless solid, mp 50–52°. (all-*trans*-2,4,6-Octatriene is reported to melt at 52–53°.) In addition, the infrared spectrum taken as a carbon disulfide solution was nearly identical with that of the all-*trans* compound.[9] Glpc analysis of the total product on a column containing 1,2,3-tris-(cyanoethoxy)propane was found to split the 2,4,6-octatriene peak into three components with a ratio of 66:31:3. From a sample of material prepared in an analogous manner, the first two components were isolated by glpc. The first component had retention time identical with the solid above and the infrared spectrum was superimposable with that of all-*trans*-2,4,6-octatriene.[10] Likewise, the spectrum of the second peak was identical with that of *cis,trans,trans*-2,4,6-octatriene.[11] The third or minor component in the above glpc analysis is therefore assumed to be the *cis,cis,trans* isomer of 2,4,6-octatriene.

In a repeat of the above experiment, the piperidinopotassium was treated dropwise with 75.5 g of material containing 71% of II, 27% of I, and 2% of 4-vinylcyclohexene. The mixture was then heated at approximately 100° for 1 hr, at the conclusion of which all of I had been isomerized. After the usual hydrolysis and work-up, a combination of distillation and glpc techniques revealed the presence of 52.2 g (69%) of II, with the main fraction boiling at 66–67° (100 mm), $n^{20}{}_{\mathrm{D}}$ 1.4668, and 18.9 g (25%) of isomeric trienes III, boiling mostly at 87–89° (100 mm).

B. With Diethylaminopotassium.—A suspension of 1 g of phenylpotassium[8] in 10 ml of heptane was treated with 5 ml of diethylamine followed by 15.4 g of octatrienes. The reaction mixture was stirred for 19 hr at room temperature at which time all of I had reacted. Glpc analysis of the starting material indicated the presence of 27% of II and 70% of I contaminated with 3% of 4-vinylcyclohexene, whereas the product was found to contain 24% of II and 69% of III.

C. With 1,1,3,3-Tetramethylbutylaminopotassium.—A suspension of 1 g of phenylpotassium[8] in 10 ml of heptane was treated with 4 g of 1,1,3,3-tetramethyl butyl amine and then with 19.3 g of octatrienes. After 20.5 hr at room temperature all of I had reacted. The starting material contained 13% of II, 85% of I, and 2% of 4-vinylcyclohexene, whereas the product was composed of 14% of II and 80% of III.

Cyclization of the Octatriene Mixtures. A. With Piperidinosodium.—Piperidinosodium was prepared by the interaction of 1.6 g of phenylsodium[8] suspended in 5 ml of heptane and 4.3 g of piperidine. A mixture of 20 g of octatrienes was then added; some initial warming was noted. Periodically, samples were withdrawn for glpc analyses as the mixture was stirred at room temperature. In addition to the compounds I and II, traces of III were indicated. After 19 hr, none of the

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(5) R. Hoffmann and R. A. Olofson, *J. Am. Chem. Soc.*, **88**, 943 (1966).

(6) D. L. Crain, R. F. Kleinschmidt, and H. A. Hartzfeld, Abstracts, 148th Meeting of the American Chemical Society, Chicago, Ill., Sept 1964, p 86S.

(7) For a typical method of preparation, see J. Feldman, O. Frampton, B. Saffer, and M. Thomas, presented at the 148th Meeting of the American Chemical Society, Chicago, Ill., Sept 1964, Division of Petroleum Chemistry, Preprints, p A55.

(8) Obtained from Orgmet, Hampstead, N. H.

(9) K. Alder and H. von Brachel, *Ann.*, **608**, 195 (1957).

(10) DMS-2837, Verlag Chemie, Weinheim, Bergstr., Germany; Butterworth Scientific Publications, London, England.

(11) DMS-2839, Verlag Chemie, Weinheim, Bergstr., Germany; Butterworth Scientific Publications, London, England.

octatrienes could be detected; there were instead three new glpc peaks present in a ratio of 8:23:69 with increasing retention time in that order. The reaction mixture was then hydrolyzed, and some *n*-pentane added. The organic layer was separated, dried, and stripped of solvent. Upon distillation, 8.6 g (43%) of colorless liquid was obtained in three fractions boiling between 82 and 82.5° (100 mm), of which the largest was 5 g, $n^{20}\text{D}$ 1.4960. There was 8.1 g of residue.

The infrared spectrum of the above liquid exhibited methyl group absorption at 7.3 μ and strong absorptions at 13.7, 14.05, and 14.5 μ, while the ultraviolet spectrum showed a broad band with a maxima at 252 mμ (log ϵ 3.94),[12] all of which were consistent with the material being isomeric methylcycloheptadienes (IV).

Anal. Calcd for C_8H_{12}: C, 88.8; H, 11.2. Found: C, 88.7, 88.7; H, 11.2, 11.2.

B. With Piperidinosodium in Cyclohexane.—A mixture of 100 ml of dry cyclohexane, 1.6 g of phenylsodium[8] in 5 ml of heptane, and 4.3 g of piperidine was heated to slow reflux. Octatrienes (31 g) were then added dropwise over 28 min. A sample taken 5 min after the addition was finished indicated complete reaction of the octatrienes. The mixture was then refluxed for approximately 5 hr; samples taken during this time indicated a gradual change in the methylcycloheptadiene isomers without any over-all change in concentration. On a glpc column containing Carbowax 20M the three peaks as stated above had the relative concentrations of 15:25:60 in the first sample and 8:27:65 at the end of the 5-hr period. Upon work-up, a combination of distillation and glpc techniques revealed the presence of 20.5 g (66%) of IV with the main fractions boiling between 80 and 81.5° (100 mm), $n^{20}\text{D}$ 1.4945–1.4968.

C. With Piperidinosodium in Tetrahydrofuran.—The reaction was conducted in an analogous manner to part B, except that 100 ml of dry tetrahydrofuran was used instead of cyclohexane. After heating the reaction mixture at slight reflux for 6 hr, it was hydrolyzed; following work-up and distillation, the product was recovered boiling over the range 70 to 90° (100 mm). Upon analysis by glpc on a 20-ft column containing 1,2,3-tris(cyanoethoxy)propane, this was found to contain the cyclic dienes IV in 30% batch yield and the 2,4,6-triene III in 38% yield.

When the reaction was repeated with sodium amide, instead of the piperidine compound, and the mixture refluxed for 22 hr, only IV was obtained in 58% yield.

D. With Diethylaminosodium.—In a run comparable to that of part A, a mixture of 22 g of the octatrienes and 0.016 mole of diethylaminosodium was heated at 100° for 1 hr. Work-up revealed the presence of 8.9 g (41%) of IV, bp 78–81° (100 mm), $n^{20}\text{D}$ 1.4950.

Hydrogenation of the Methylcycloheptadienes (IV).—In a Parr apparatus, 20.8 g of IV, 50 ml of glacial acetic acid, and 0.5 g of platinum oxide were treated with hydrogen at an initial pressure of 48 psi. In approximately 30 min, exactly 2 molar equiv of hydrogen were absorbed. Upon analysis by glpc, the product was found to have the same retention time as methylcycloheptane (see below). Small trace quantities of *n*-octane, ethylcyclohexane, and cyclooctane were also found to be present. In work-up, a fraction of material was collected (14 g) boiling at 73.5–74° (100 mm), $n^{20}\text{D}$ 1.4413. The infrared spectrum was superimposable with that of methylcycloheptane. An authentic sample was obtained by hydrogenation of 1-methylcycloheptene[13,14] and boiled at 73.5° (100 mm), $n^{20}\text{D}$ 1.4415 (lit. $n^{23}\text{D}$ 1.4409,[14] $n^{20}\text{D}$ 1.4410[15]).

Partial Identification of the Methylcycloheptadienes (IV). A. By Glpc and Nmr.—As stated above, the cyclics IV could be resolved into only three peaks by ordinary packed glpc columns, of which the best results were obtained on columns containing Carbowax 20M. However, by analysis on a 150-ft capillary column containing squalane, other peaks were readily discernible. For example, analysis of a mixture, obtained at what must be equilibrium conditions for the system, on a Carbowax column showed the distribution of the three peaks to be 8 to 23 to 69%, in that increasing order of retention times. On the capillary column, the relative percentages of the eight most abundant peaks in the order of appearance were 3.2, 6.6, 0.4, 0.3, 24.0, 64.3, 0.1, and 1.1%. The first peak on the Carbowax column, therefore, appears to contain two major components.

A sample of cyclic dienes IV, which analyzed 20, 20, and 60% on the Carbowax column, was fractionally separated employing that column. This sample was utilized because of the greater abundance of the first peak. Analysis on the capillary column as above showed the relative percentages of components to be 9.1, 10.8, 1.1, 0.3, 19.5, 58.5, 0.2, and 0.3%. The resultant three glpc fractions were then examined by nmr. The first fraction (IVA) exhibited an olefinic proton to nonolefinic proton ratio of 3.9:8.1 and a strong doublet at τ 8.9. The over-all spectrum thus indicated that at least two isomers were present, in agreement with the capillary column analysis, and that the methyl group was not located on a double bond. The other two samples (IVB and IVC) showed an olefinic proton to other proton ratio of 3:9 and a strong resonance near τ 8.3, and thus both have the methyl group on a double bond. Furthermore, neither has a resonance in the τ 7.3 region (methylene adjacent to two double bonds), indicating these two fractions must be 1-methyl- and 2-methyl-1,3-cycloheptadiene. The nmr spectrum of IVB, however, did exhibit fine splitting (1.5 cps) in both the olefinic and methyl group resonances.

B. Reaction of Fraction Three (IVC) with Tetracyanoethylene.—A mixture of 0.39 g (0.0036 mole) of IVC above and 5 ml of tetrahydrofuran was treated with 0.46 g (0.0036 mole) of tetracyanoethylene and allowed to stand for 4 days. The solvent was removed under reduced pressure, and the resultant solid recrystallized from a 1:1 mixture of benzene and cyclohexane to give 0.76 g of colorless solid, softening at approximately 160° and decomposing at 240°. Two additional recrystallizations did not change the melting characteristics.

Anal. Calcd for $C_{14}H_{12}N_4$: C, 71.2; H, 5.1; N, 23.7. Found: C, 71.2; H, 5.1; N, 23.5.

The nmr spectrum in deuteriobenzene solution at 70° exhibited a major resonance as a sharp peak at τ 8.88, which is characteristic of an uncoupled methyl group one carbon removed from a double bond. The integral of the protons in each resonance was 9.2 (τ 8.2–9.0, methyl peak and methylenes), 2.0 (τ 4.3–4.6, olefinic region) and 0.8 (τ 7.2–7.5, cyclic -CH adjacent to a double bond with a slight downfield shift due to the electronegative nitrile groups). In agreement with the above methyl resonance, the approximate 2:1 ratio of olefinic to α-CH protons is further evidence for the structure being 1-methyl-8,8,9,9-tetracyanobicyclo[3.2.2]nonene-6 (VI). Therefore, the fraction IVC is primarily 1-methyl-1,3-cycloheptadiene, and hence the IVB must be 2-methyl-1,3-cycloheptadiene.

Methylcycloheptadienes (IV). A. From 2,4,6-Octatrienes (III).—A suspension of 0.016 mole of piperidinosodium in 60 ml of dry cyclohexane, heated to slight reflux, was treated with a solution of 21.2 g of III in 40 ml of cyclohexane. A sample, taken 5 min after the addition was completed, indicated all of III had reacted. Work-up afforded 16.6 g (78%) of colorless liquid, bp 80.5–82° (100 mm), $n^{20}\text{D}$ 1.4964. The infrared spectrum of this material was identical with that of the cyclics of type IV prepared above.

B. From 1,3,7-Octatriene (II).—In a run conducted in an analogous manner to part A, II in cyclohexane solution with heating at reflux for 2 hr was converted to the cyclic dienes IV in 63% yield.

C. From 3-Methyl-1,4,6-heptatriene (V).—Piperidinosodium (0.016 mole) suspended in 200 ml of boiling cyclohexane was treated with 189 g of V[16] over a period of 2 hr. After an additional 1.5 hr of heating, all of the triene had been consumed. Following the usual work-up techniques, distillation afforded 158.5 g (84%) of the cyclics IV boiling mostly at 80–82° (100 mm), $n^{24.5}\text{D}$ 1.4943.

In a comparable reaction employing piperidinopotassium, instead of the sodium compound, the cyclics IV were formed in 39% yield; the predominant product was higher molecular weight materials, 55%.

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(12) 1,3-Cycloheptadiene is reported to have a broad band at 248 mμ (log ϵ 3.87): E. Pesch and S. L. Friess, *J. Am. Chem. Soc.*, **72**, 5757 (1950).

(13) Obtained from Aldrich Chem. Co., Milwaukee, Wis.

(14) H. Pines and C. T. Chen, *J. Am. Chem. Soc.*, **82**, 3562 (1962).

(15) L. R. Ruziska and C. F. Seidel, *Helv. Chim. Acta*, **19**, 424 (1936).

(16) Obtained from Copolymer Rubber and Chem. Corp., Baton Rouge, La.

Registry No.—I, 1871-53-0; II, 1002-35-3; III (all *trans*), 15192-80-0; III (*cis,trans,trans*), 14947-19-4; III (*cis,cis,cis*), 14947-20-7; IVb, 14947-21-8; IVc, 14947-22-9; VI, 15077-07-3.

Acknowledgment.—The authors wish to thank Mrs. Joy Buell for invaluable service in interpreting and compiling the nmr data and Mr. B. L. Martin for competent assistance.

Aldehyde and Ketone Condensation Reactions Catalyzed by Boric Acid

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Received May 4, 1967

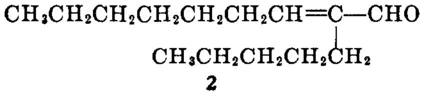
Aldol condensation and dehydration reactions using boric acid, boron oxide and 10-hydroxy-10,9-boroxarophenanthrene as catalysts were studied. Heptanal (**1**) gave 2-pentyl-2-nonenal (**2**) nearly quantitatively. Acetophenone (**3**) gave *trans*-1,3-diphenyl-2-buten-1-one (**4**). Benzaldehyde (**5**), 4-methoxybenzaldehyde (**6**), and 4-nitrobenzaldehyde (**7**) each reacted with **3** to give 1,3-diphenyl-2-propen-1-one (**8**) and substituted derivatives. Acetophenone **3** reacted at equal rates with both components of mixtures of **5** with **6** and **5** with **7**, suggesting that the rate-determining step involved only **3**. Competitive reactions of nonanal (**10**) with heptanal-2,2-d_2 (**12**) showed a deuterium isotope effect of **4**. An enol borate or a partial enol borate is suggested as an intermediate, the formation of which is rate determining.

Wayne and Adkins[2] have cited a variety of acids and bases which catalyze the aldol condensation of ketones and subsequent dehydration to form α,β-unsaturated ketones. They further observed that aluminum *t*-butoxide had advantages over many of these reagents. Both the condensation and dehydration occurred in one step, the alkoxide acting both as catalyst for the condensation and as dehydrating agent. In the latter step, inactive products are formed from the catalyst. They generally obtained high yields of the desired products. In some cases, however, small amounts of high molecular weight products were formed. Further, they found it necessary to use at least 1 mole of the alkoxide for 3 moles of the ketone.

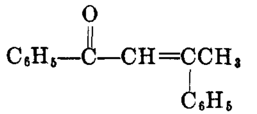
Kuivila and coworkers,[3] in a study of the reduction of carbonyl compounds with isopropyl borate, reported, in the case of heptanol (**1**), that 2-pentyl-2-nonenal (**2**) was formed through condensation and dehydration in greater yield (20.5%) than that of the reduced product, heptanal (17.5%). A large amount of higher molecular weight "condensation product" was also reported.

Now, a convenient and efficient method has been found for condensing aldehydes and ketones using boric acid or boron oxide as catalyst. The α,β-unsaturated aldehydes and ketones produced did not react further. This resulted in high yields of the primary condensation products.

Heptanal **1** under dehydrating conditions which existed (1) when boric acid was used and water was azeotropically removed or (2) when a molar quantity of "porous" boron oxide[4] was used gave nearly quantitative yields of 2-pentyl-2-nonenal **2**. Acetophenone (**3**) reacted slowly by the first method to give only *trans*-1,3-diphenyl-2-buten-1-one (**4**). Benzaldehyde (**5**), 4-methoxybenzaldehyde (**6**), and 4-nitrobenzaldehyde (**7**) each reacted with **3** to give 1,3-diphenyl-2-propen-1-one (**8**) and substituted derivatives in high yield.


$CH_3CH_2CH_2CH_2CH_2CH_2CH=\underset{\underset{CH_3CH_2CH_2CH_2CH_2}{|}}{C}-CHO$

2


$C_6H_5-\overset{\overset{O}{\|}}{C}-CH=\underset{\underset{C_6H_5}{|}}{C}CH_3$

4

Most of the work involved the use of boric acid and a solvent such as *m*-xylene which allowed water removal through the use of a Dean-Stark trap. Boric acid was only slightly soluble in this system. Varying the amount of the catalyst used had little, if any, effect on the reaction rates, suggesting that only the soluble portion was effective as a catalyst.

Increasing the concentration of **1** relative to the solvent markedly increased the rate of reaction. In several experiments with **1** using no solvent, but a stream of nitrogen to remove the water formed, the rate of formation of **2** was increased greatly. Conversion of **1** was complete in 2 hr as opposed to about 18–20 hr when *m*-xylene was used as solvent. It seems probable that the rate in these cases was limited by the efficiency of water removal. Boric acid was completely soluble in the medium in these experiments. In the absence of a solvent, however, a variety of products were formed from **1** in addition to **2**. Similarly, **3** when heated with boric acid in the absence of a solvent reacted much more rapidly to give the expected **4**, but again yielded a by-product.

The selectivity of the catalyst is demonstrated by an attempt to react the unsaturated aldehyde **2** with cyclohexanone (**9**). At the termination of the reaction, all of the **9** had disappeared to form a complicated mixture of products. At the same stage, none of the aldehyde **2** had undergone reaction.

The use of boron oxide as both catalyst and dehydrating agent potentially increases the versatility of the reaction by allowing the use of reactants such as acetone, etc., from which it is difficult to remove water. Knowledge of this variation to date is limited to **1** which gave a quantitative yield of **2** in 24 hr in refluxing dioxane.

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(1) Author to whom inquiries should be directed.

(2) W. Wayne and H. Adkins, *J. Am. Chem. Soc.*, **62**, 3401 (1940).

(3) H. G. Kuivila, S. C. Slack, and Pentti Siiteri, *ibid.*, **73**, 123 (1951).

(4) Willy Lange, *Inorg. Syn.*, **2**, 22 (1946).