well-known[1,3] to produce *n*-alkyl sodium compounds in good yield

$$R_2Hg + 2Na \longrightarrow 2NaR + Hg$$

When an excess of sodium was allowed to react with di-*s*-butylmercury at 20–25° in *n*-dodecane, a reaction occurred in which after four hours, 95% of the theoretical quantity of mercury was set free. Carbonation of the reaction mixture gave, however, only a small amount (<5%) of the expected methylethylacetic acid, together with a small amount of methylethylmalonic acid. Direct interaction of sodium with di-*s*-butylmercury in the absence of a solvent led to a slow reaction which produced butane and butene, but no detectable trace of 3,4-dimethylhexane. Again the displacement of mercury by sodium was virtually quantitative.

These results indicate that *s*-alkyl sodium compounds are relatively unstable, a result in accord with previous observations of Morton and coworkers[4] that carbonation of the mixtures obtained when 2-chloro-3-methylbutane, 2-chlorobutane and 2-chloropentane were treated with sodium led to the production of only small quantities of the expected acids. The results further demonstrate that the thermal decomposition of such substances (*s*-R–Na) does not lead to any detectable quantity of dimeric (Wurtz) product (*s*-R–)$_2$, but rather to products of disproportionation (R–H, olefin). Accordingly, it does not seem likely that any significant quantity of the dimeric product of the Wurtz reaction of an *s*-alkyl halide can arise from thermal dissociation of the intermediate *s*-alkyl sodium.

Experimental

Di-*s*-butylmercury.—This compound, b.p. 51–54° (2 mm.), was prepared in 64% yield by the procedure of Marvel and Calvery[5] with improvements by Gilman and Brown.[6] Analysis according to Whitmore and Sobatzki[7] indicated a purity of 97%.

Carbonation of *s*-Butylsodium.—To 70 ml. of purified[2] *n*-dodecane in a 125-ml. erlenmeyer flask fitted with a gas inlet tube at the base, a thermometer, a reflux condenser and a dropping funnel was added 8.2 g. (0.356 g.-atom) of sodium, cut into thin slices, and 18.5 g. (0.0589 mole) of di-*s*-butylmercury. The system was immediately swept out with purified nitrogen. Stirring was accomplished with the aid of an A. H. Thomas Co. magnetic stirrer, and the temperature of the reaction flask was maintained between 20–25° by means of a cold water-bath.

Within ten minutes the mixture became yellow and in 30 minutes had turned brown. After four hours dry carbon dioxide was bubbled through it for one hour. Then water was added cautiously over a four-hour period. The aqueous and hydrocarbon layers were separated and the amalgam removed from the aqueous solution. Upon decomposition with dilute sulfuric acid the amalgam yielded 11.3 g. (0.0563 mole, 95%) of mercury.

After extraction with pentane the aqueous layer was acidified and again extracted with pentane. On removal of the pentane there was obtained 0.5 g. of a brown liquid acid, micro b.p. 182° (uncor.). The *p*-bromophenacyl ester melted at 48–51° and gave no depression of the m.p. when admixed with an authentic specimen of the *p*-bromophenacyl ester of methylethylacetic acid (m.p. 55°).

The acidified aqueous solution was next saturated with sodium chloride and extracted with methyl ethyl ketone. Removal of the solvent gave 1.0 g. of a brown oil which partially crystallized on standing. The crystals were washed with pentane and sublimed at 118–124°. The sublimed crystals melted sharply at 124.5° (methylethylmalonic acid is reported to melt at 121°[8]).

Decomposition of *s*-Butylsodium.—An apparatus similar to that described above was used but so adapted that the evolved gases could be collected over saturated sodium chloride solution. Sodium (0.07 mole) was introduced into the flask and the system swept out with nitrogen. Di-*s*-butylmercury (0.016 mole) was then added through the dropping funnel and the mixture stirred intermittently at room temperature for a period of about eight days. The apparatus was then flushed out with a measured volume of nitrogen and the total collected gases (0.024 mole, exclusive of nitrogen) passed over bromine at −10 to 0° in a brominator similar to that described by Lucas, Dillon and Young.[9] From the loss in gas volume before and after bromination it was estimated that 0.013 mole of butene had been absorbed. The dibromobutane so obtained boiled at 72–73° (42 mm.), $n^{25}\mathrm{D}$ 1.5099 (Dillon, Young and Lucas[10] report for *meso*-2,3-dibromobutane, b.p. 72.7–72.9° (50 mm.), $n^{25}\mathrm{D}$ 1.5092; for *rac*-2,3-dibromobutene, b.p. 75.6–75.8° (50 mm.), $n^{25}\mathrm{D}$ 1.5125). The exit gases from the bromination were freed from bromine (bisulfite), dried and passed into a liquid air trap. From the change in volume it was estimated that 0.004–0.005 mole of gas was condensed by the trap. On cautious warming the condensed liquid was observed to evaporate at −6 to 3° (butane boils at −0.5°[11]).

To the residue in the reaction flask was added pentane and then water. The layers were separated and the amalgam decomposed with dilute sulfuric acid, 0.0154 mole of mercury being obtained. The dried pentane layer was found to distil practically completely as pentane (b.p. 36–37°). No trace of 3,4-dimethylhexane (b.p. 118°[2]) could be detected.

On repetition of the foregoing experiment with 0.17 g.-atom of sodium and 0.017 mole of di-*s*-butylmercury substantially the same results were obtained. Thus, 0.0166 mole of mercury was found to be present in the amalgam and 0.026 mole of gas was evolved which was estimated to contain 0.016 mole of butene.

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[4] A. A. Morton, *et al.*, This Journal, **58**, 1697 (1936); **64**, 2240 (1942).

[5] C. S. Marvel and H. O. Calvery, *ibid.*, **45**, 820 (1923).

[6] H. Gilman and R. E. Brown, *ibid.*, **52**, 3314 (1930).

[7] F. C. Whitmore and R. J. Sobatzki, *ibid.*, **55**, 1128 (1933).

[8] A. I. Vogel, *J. Chem. Soc.*, 1478 (1929).

[9] H. J. Lucas, R. T. Dillon and W. G. Young, This Journal, **52**, 1949 (1930).

[10] R. T. Dillon, W. G. Young and H. J. Lucas, *ibid.*, **52**, 1953 (1930).

[11] G. Egloff, "Physical Constants of Hydrocarbons," Vol. I, Reinhold Publishing Corp., New York, N. Y., 1939, p. 30.

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Eight-Membered Carbocycles. III. Hydrogenation of Vinylcycloöctatetraene

By Clifford E. Larrabee and L. E. Craig

The hydrogenation of a mixture of 1-phenyl-1,3-butadiene and vinylcycloöctatetraene to give a mixture of *n*-butylbenzene, 1-ethylcycloöctene and ethylcycloöctane has been reported previously.[1] It was, at first, thought that the presence of 1-ethylcycloöctene among the products might be due to interruption of the hydrogenation before it was completed. An experiment with a pure sample of vinylcycloöctatetraene showed that this was not true and a series of room-temperature hydrogenations was carried out under a variety of conditions.

Hydrogenation of vinylcycloöctatetraene in glacial acetic acid in the presence of Adams catalyst was found to proceed readily to the point of complete saturation and the formation of ethylcyclooctane. When methanol was used in place of acetic acid, it was found that the hydrogenation

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[1] L. E. Craig and C. E. Larrabee, This Journal, **73**, 1191 (1951).

stopped somewhat short of complete saturation and that the product was a mixture of 1-ethylcyclooctene and ethylcyclooctane. The products were separated by fractional distillation and identification was made by comparison with authentic samples. The pure 1-ethylcyclooöctene was resistant to hydrogenation in methanol in the presence of Adams catalyst, but readily absorbed one molar equivalent of hydrogen in acetic acid to give ethylcyclooöctane.

In the presence of either Raney nickel or palladium-on-calcium carbonate in methanol, vinylcyclooöctatetraene absorbed only four molar equivalents of hydrogen to give a product which absorbed one molar equivalent of hydrogen in acetic acid in the presence of Adams catalyst to give ethylcyclooöctane and 0.65 molar equivalent in methanol to give 1-ethylcyclooöctene and ethylcyclooöctane.

In an attempt to separate the mixture produced by Raney nickel hydrogenation, a large sample was subjected to a refined distillation; the results are given in Fig. 1. The properties of the fractions which were examined are contained in Table I. It is obvious that complete separation was not accomplished.

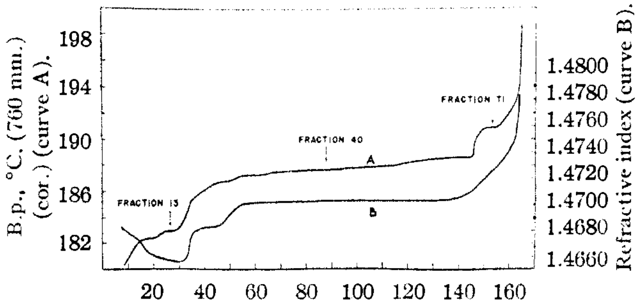


Fig. 1.—Distillation of Raney nickel hydrogenation product.

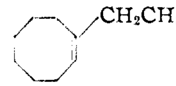
TABLE I

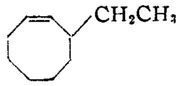
PROPERTIES OF THE RANEY NICKEL HYDROGENATION PRODUCT OF VINYLCYCLOOÖCTATETRAENE

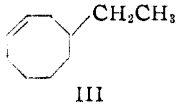
Fraction no.	B.p., °C. (cor.)	$n^{25}D$	d^{25}_4	Analyses[a] found, % Carbon	Hydrogen	Molar equivalent of hydrogen absorbed[b]
13	182.8–183.0	1.4666	0.8411	86.78	13.12	0.96
40	187.6[c]	1.4712[c]	.8518[c]	86.86	13.33	.18
71	190.8–191.9	1.4740	.8831	87.01	13.14	.35

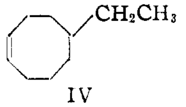
[a] Calculated for $C_{10}H_{18}$: C, 86.90; H, 13.10. [b] Hydrogenations were carried out at 30 ± 1° on samples of 1.0000 ± 0.0001 g. dissolved in 40 ml. of methanol in the presence of 0.2000 ± 0.0001 g. of Adams catalyst. Hydrogen was added from a reservoir at a constant pressure of 5 atmospheres, until no more hydrogen was absorbed. [c] Reported for 1-ethylcyclooöctene, b.p. 186.9° (cor.), $n^{25}D$ 1.4720, d^{25}_4 0.8511 (ref. 1).

The analytical data given in Table I make it seem probable that the majority of the material collected near the middle of the distillation was principally 1-ethylcyclooöctene[1] while the more completely hydrogenatable materials collected near the ends contained other ethylcyclooöctenes (II–IV). The behavior of the Raney nickel hydrogenation product upon shaking with hydrogen in the presence of Adams catalyst in methanol together with its behavior in the presence of the same catalyst in glacial acetic acid indicate that it is a mixture composed of 35% of I and 65% of II, III and IV.


I


II


III


IV

Attempts were made to identify the products of the hydrogenation by ozonolyses of various fractions. The isolations of pure crystalline carboxylic acids or dinitrophenylhydrazones were not achieved and it seemed evident that mixtures were present in all cases.

The observation that the fifth double bond of vinylcyclooöctatetraene is hydrogenated less readily than the first four is not unexpected, as the fourth double bond of cyclooöctatetraene has been found to be hydrogenated at a rate one-tenth that of the first three.[2] That conditions could be found under which the fifth double bond of vinylcyclooöctatetraene resists hydrogenation entirely is somewhat unexpected. Examination of Fisher–Hirschfelder models indicates that the hydrogen–hydrogen and carbon–hydrogen interferences are considerable in cyclooöctane but not so large in cyclooöctene. This could account for the retarded rate of hydrogenation of cyclooöctene.

The hydrogenation of vinylcyclooöctatetraene probably occurs in a random fashion except for, possibly, some orientation by the side chain, so that the last-remaining double bond may be found in any of four different positions about the eight-membered ring. (It is assumed that the vinyl group is hydrogenated in all cases as there is no obvious reason for its hydrogenation being retarded.) The results of hydrogenations show that the effect of the ethyl group on the hydrogenation of the double bonds in the ring is greatest in I and less in II, III and IV. Even in II, III and IV the effect, presumably steric, of the ethyl group is sufficient to account for the different hydrogenative behaviors of these compounds as compared to that of cyclooöctene.

Acknowledgments.—The authors are indebted to Mr. L. J. Lohr for the distillations carried out in the Podbielniak and spinning band columns, to Dr. S. T. Gross for measurement and interpretation of infrared spectra and to Mr. L. J. Frauenfelder for all analyses.

Experimental[3]

Hydrogenations of Vinylcyclooöctatetraene.—Hydrogenations of 0.1 molar amounts of vinylcyclooöctatetraene in 50 ml. of solvent were carried out in a Parr hydrogenator with a starting hydrogen pressure of three atmospheres. When the hydrogen absorption ceased, the catalyst was removed by filtration, the filtrate diluted with 200 ml. of ether, and the ether solution washed thoroughly with water. After the ether solution was dried over anhydrous sodium sulfate,

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[2] W. Reppe, O. Schlicting, K. Klager and T. Toepel, *Ann.*, **560**, 1 (1948).

[3] All boiling points are uncorrected unless otherwise indicated.

TABLE II

HYDROGENATIONS OF VINYLCYCLOÖCTATETRAENE

Experiment	Catalyst (g.)	Solvent	Molar equivalents of H_2 absorbed	Product B.p., °C.	Mm.	$n^{25}\text{D}$	Yield, %
A	10% Pd on $CaCO_3$ (5)	Methanol	4.0	89	35	1.4701	90
B	Raney nickel (5)	Methanol	3.8	181–184	..	1.4703	70.5
C	PtO_2 (0.1)	Methanol	4.5	90–92	35[a]	1.4640	79
D	PtO_2 (0.1)	Acetic acid	5.0	188.5–190	cor.[b,c]	1.4588	86

[a] Shown by infrared analysis to be 36% 1-ethylcycloöctene and 64% ethylcycloöctane.[1] [b] Physical constants and infrared absorption spectrum identical with those of ethylcycloöctane.[1] [c] This product was distilled through a 6 ft. × 13 mm. Podbielniak fractionating column.

TABLE III

HYDROGENATIONS OF ETHYLCYCLOÖCTENES

Starting material	Solvent	Molar equivalent of H_2 absorbed	Product
1-Ethylcycloöctene[a]	Methanol	0	No reaction
1-Ethylcycloöctene[a]	Acetic acid	1.0	Ethylcycloöctane[b]
Ethylcycloöctene from B of Table II	Acetic acid	1.0	Ethylcycloöctane[b]
Ethylcycloöctene from B of Table II	Methanol	0.65	1-Ethylcycloöctene[b,c] (35%) Ethylcycloöctane[b,c] (65%)

[a] Ref. 1. [b] Products identified by physical constants and infrared absorption spectra. [c] Products separated by distillation in a Piros–Glover spinning band column.

the product was isolated by fractional distillation through a 12" × 1" glass helices-packed fractionating column. The results of the hydrogenations are summarized in Table II.

Several samples of vinylcycloöctatetraene (215 g. in all) were hydrogenated in the presence of Raney nickel as above. The product was distilled through a 6 ft. by 12 mm. Podbielniak column at a reflux ratio of about 150 to 1. The results of the distillation and properties of certain cuts are given in Fig. 1 and Table I.

Hydrogenations of Ethylcycloöctenes.—Hydrogenations of 0.05–0.1 molar amounts of various ethylcycloöctenes were carried out in the Parr hydrogenator with 50 ml. of solvent and Adams catalyst. The products were isolated as above and the results of the hydrogenations are summarized in Table III.

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RECEIVED MAY 18, 1951

The Synthesis of Ethyl 2,2-Dichlorocyanoacetate[1]

BY E. T. MCBEE, J. F. HIGGINS AND O. R. PIERCE

Although Henry[2] prepared ethyl 2-chlorocyanoacetate by chlorination of ethyl cyanoacetate, the 2,2-dichloro compound has never been reported. This compound was desired as an intermediate for the preparation of a *s*-triazine. Chlorination of the ester at 140° produced the dichloro compound conveniently and in good yield. The preparation of the corresponding triazine by the method of McBee, *et al.*,[3] was not successful.

Experimental

Preparation of Ethyl 2,2-Dichlorocyanoacetate.—Ethyl cyanoacetate (226 g., 2.0 moles) was placed in a glass chlorination tube 90 cm. long and 20 cm. in diameter. Chlorine was introduced through a gas diffusion disc beneath the surface of the ester. A condenser was attached to the top of the chlorination tube. An attached water scrubber was used to remove hydrogen chloride and excess chlorine. The tube was maintained at 140° while the chlorine was introduced. Chlorine was admitted until no more was absorbed. The reaction product was then warmed on a steam-bath for two hours to remove dissolved gases and rectified under reduced pressure. A 90% yield of ethyl 2,2-dichlorocyanoacetate was obtained, b.p. 60° at 19 mm., $n^{20}\text{D}$ 1.4380, d^{20}_4 1.238. *Anal.* Calcd. for $C_5H_5Cl_2NO_2$: C, 33.2; H, 2.74. Found: C, 32.9; H, 2.74.

DEPARTMENT OF CHEMISTRY
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RECEIVED JULY 19, 1951

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(1) This paper represents part of a thesis submitted by J. F. Higgins to the Graduate School, Purdue University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy. This work was supported by the Westinghouse Electric Corporation.

(2) Henry, *Compt. rend.*, **104**, 1620 (1887).

(3) McBee, Pierce and Bolt, *Ind. Eng. Chem.*, **39**, 391 (1947).

The Reaction of Nitrous Acid with O-Alkylhydroxylamines[1]

BY JOHN E. LEFFLER AND AKSEL A. BOTHNER-BY

Many of the reactions between nitrous acid and the amino group can be described by the equation

$$R{-}NH_2 + HONO \longrightarrow R^+ + H_2O + N_2$$

The real or incipient fragment R^+ then either reacts with solvent, loses H^+, or rearranges. To the well-known formation of alcohols from primary aliphatic amines and of acids from amides there has recently been added the formation of benzanilide from benzophenone hydrazone.[2] It was therefore of interest to examine the behavior of the amino group attached to oxygen: the formation of carbonyl compounds by way of an intermediate with cationoid oxygen might well be expected.[3] However, it had already been established that O-methylhydroxylamine gives nitrous oxide and methyl alcohol,[4] and that hydroxylamine itself gives nitrous oxide and water.[5]

In the present investigation it was found that the reaction leading to nitrous oxide and ROH is fairly general. Only in the case of O-benzylhydroxylamine does there seem to be any reaction of the type anticipated; the fact that the carbonyl

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(1) Research carried out in part under the auspices of the U. S. Atomic Energy Commission.

(2) D. E. Pearson and C. M. Greer, THIS JOURNAL, **71**, 1895 (1949).

(3) J. E. Leffler, *Chem. Revs.*, **45**, 385 (1950).

(4) A. B. Boese, Jr., L. W. Jones and R. T. Major, THIS JOURNAL, **53**, 3530 (1931).

(5) W. Wislicenus, *Ber.*, **26**, 772 (1893); V. Meyer, *Ann.*, **175**, 141 (1875).