tions under which a given separation can be made. It is anticipated that as the method is more fully explored, broader applications will suggest themselves. Its usefulness in radiochemical investigations and as a means for the isolation of pure sugars in high yield has already been demonstrated.[12]

Acknowledgments.—The authors wish to express appreciation to Dr. G. R. Noggle for his advice and assistance given to us throughout these experiments, and to Dr. W. E. Cohn for his criticisms and many constructive suggestions pertaining to the preparation of this manuscript.

Oak Ridge, Tennessee Received October 26, 1951

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[12] L. P. Zill and G. R. Noggle, 1951, work to be published.

[Contribution from the Rohm and Haas Company]

The OXO Reaction of Camphene. Structure of the Aldehyde and Derivatives

By J. C. LoCicero and R. T. Johnson

Camphene undergoes the OXO reaction without rearrangement giving an aldehyde which has been shown to be structurally related to isocamphenilanaldehyde by several methods of degradation. Oxidation of the aldehyde gives an acid which is shown to be disastereoisomeric with homocamphenilanic acid previously prepared from camphene *via* the Prins reaction.

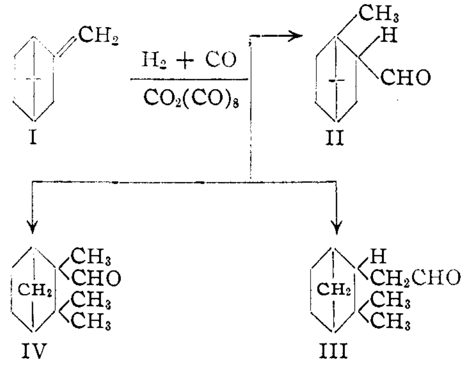
The preparation of aldehydes from olefins by the reaction of carbon monoxide, hydrogen and a cobalt catalyst under pressure has been the subject of some recent publications.[1–4a]

It has been shown[3] that under the conditions of the reaction, migration of the double bond occurs in an olefinic compound. The rearranged olefinic structure then gives rise to additional isomeric aldehydes, *e.g.*, pentene-1 gives not only hexanal and 2-methylvaleraldehyde but 2-ethylbutyraldehyde as well. With increased chain length the number of possible isomers increases accordingly depending on the number of isomeric olefins possible by the shifting of the double bond in the starting olefin.

Camphene (I) appeared to be an interesting substrate for the hydroformylation reaction because of its well known tendency to undergo the Wagner rearrangement under acidic conditions. Cobalt carbonyl hydride, which is believed to be the catalyst of the reaction,[4] is acidic and can be titrated.[5] The aldehydic product that might result on hydroformylation could be camphene 2-aldehyde (II) or an isomer.

Assuming no rearrangement to occur, the product might have the structure (III) or (IV). In view of the factors[3] which appear to regulate the position of the entering aldehyde group, structure (IV) did not appear likely.

It was found that camphene (I) underwent the OXO reaction smoothly when diluted with an equal volume of benzene using dicobalt octacarbonyl[4a] giving a liquid aldehyde (V) of constant boiling point in 65% yields. Oxidation of the aldehyde (V) with air or oxygen gives a single acid (VI) m.p. 56–57° of the same chain length. Oxidative decarboxylation of the α-hydroxy acid (VII) from the acid (VI) as well as thermal decomposition of the α-methoxy acid (IX) by the method of Darzens and Lévy[6] give isocamphenilanaldehyde (X) which is differentiated from camphenilanaldehyde solely by its oxidation in air to isocamphenilanic acid[7,8] (XI) m.p. 116–117° compared to 65° for camphenilanic acid; both aldehydes give the same semicarbazone which on hydrolysis yields isocamphenilanaldehyde.[8] Chemical oxidation of either aldehyde with potassium permanganate yields isocamphenilanic acid.[7] Recrystallization of camphenilanic acid from nitric acid gives isocamphenilanic acid.



A novel and more direct method for degrading the aldehyde (V), attended by higher yields, was found to be the oxidation of the enamine (XII) with potassium permanganate in acetone to give isocamphenilanic acid (XI).

The preceding reactions show conclusively that the hydroformylation of (I) gives a single aldehyde homologous with isocamphenilanaldehyde showing the absence of any rearrangement during the reaction. The structure of the aldehyde (V) must be that corresponding to (III).

Since the aldehyde from camphene (V = III) has been related structurally to isocamphenilanic acid, we shall refer to it henceforth as homoisocamphenilanaldehyde.

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[1] O. Roelen, U. S. Patent 2,327,000 (1943).

[2] Fiat Final Report 1000. The OXO Process. Issued by the Office of Military Government for Germany through the Office of Technical Services of the U. S. Department of Commerce, PB 81383.

[3] A. I. M. Keulemans, A. Kwantes and T. Van Bavel, *Rec. trav. chim.*, **67**, 299 (1948).

[4] H. Adkins and G. Krsek, This Journal, **70**, 383 (1948); **71**, 3051 (1949).

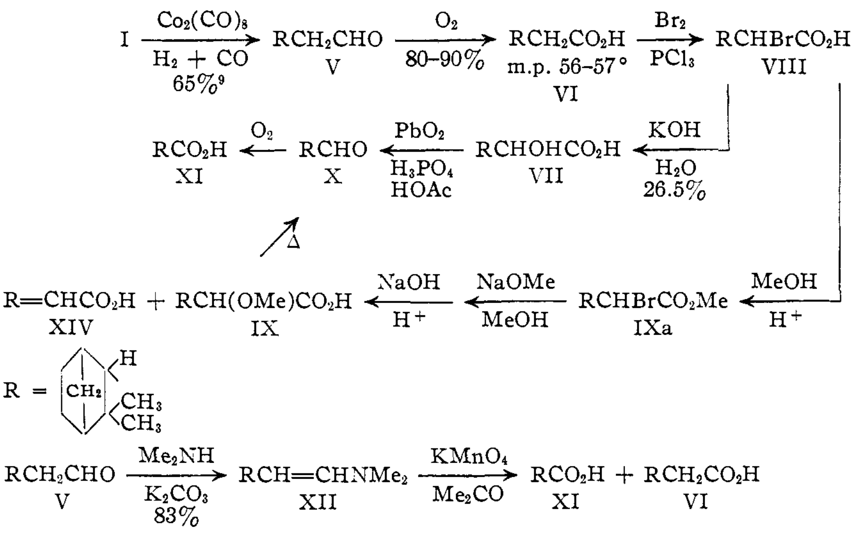
[4a] C. H. McKeever, U. S. Patents 2,476,263; 2,477,553-4 (1949).

[5] W. Reppe, "New Developments in the Chemistry of Acetylene and Carbon Monoxide," Springer-Verlag, Berlin, Göttingen, Heidelberg 1949.

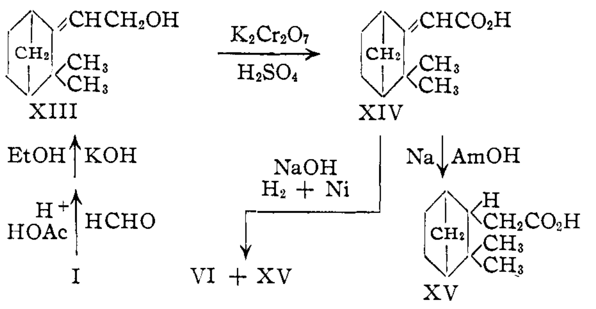
[6] G. Darzens and A. Lévy, *Compt. rend.*, **196**, 184 (1933).

[7] J. Bredt and W. Jagelki, *Ann.*, **310**, 112, 121, 129 (1900).

[8] G. G. Henderson and M. M. J. Sutherland, *J. Chem. Soc.*, **99**, 1539 (1911); G. G. Henderson and I. M. Heilbron, *ibid.*, **99**, 1887 (1911).

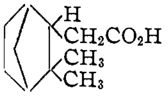


Langlois[10] reported an acid (XV), homocamphenilianic, melting at 75–76°. This was prepared by a series of reactions involving the Prins reaction on camphene (I) to give 8-camphene carbinol (XIII), chromic acid oxidation of the alcohol (XIII) to camphenilidene acetic acid (XIV) and reduction of the acid with sodium and amyl alcohol to homocamphenilanic acid (XV). Compound (XIV) was prepared as described by Langlois[10] and reduced catalytically as the sodium salt with Raney nickel. In addition to homocamphenilanic, m.p. 76–77° (XV), there was isolated homoisocamphenilanic, m.p. 56–57° (VI). Since Langlois[10] failed to mention his exact yields it is probable that he had both isomers but isolated only one. The formation of both isomers by the catalytic hydrogenation of the sodium salt is not surprising since it is known that tetrasubstituted olefins such as dimethylfumaric and maleic acids give rise to diastereoisomers on hydrogenation.[11] The close relationship of the two acids (VI) and (XV) is likewise indicated during the conversion of the bromoester (IXa) to the methoxy acid (IX) which is accompanied by the formation of varying amounts of camphenilidene acetic acid (XIV) as a result of dehydrohalogenation. This is added proof for the diastereoisomeric relation between acids (VI) and (XV).

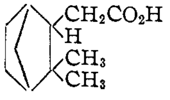


The pure diastereoisomeric alcohols were readily prepared from the acids (VI) and (XV) by reduction with lithium aluminum hydride. Catalytic reduction of 8-camphenecarbinol (XIII) gives a mixture of the isomeric alcohols whose derivatives possess melting points intermediate between those shown by the derivatives of the pure alcohols prepared from the individual acids.

Infrared and X-ray spectra data along with additional chemical data as yet incomplete have been obtained in the attempt to establish which of the acids has the *cis* or *endo* structure and which the *exo* or *trans* structure. Our present belief is that the low melting isomer (VI) has the *cis* or *endo* configuration while the higher melting isomer (XV) has the *exo* or *trans* structure. This will be the subject of a future contribution.



VI



XV

Experimental[12]

OXO on Camphene I.—In a 300-ml. autoclave are charged 60 g. of camphene, 60 ml. of benzene and 20 ml. of dicobalt octacarbonyl solution.[4a] The vessel is pressurized with 1:1 synthesis gas to 3000 p.s.i. The hydroformylation is carried out at 125–150° for 1–1.5 hours feeding additional gas as required to maintain the pressure above 3000 p.s.i. The discharged crude (137–138 g. assaying 7.1% aldehyde groups by hydroxylamine titration using the glass electrode) is stripped quickly with a water aspirator then flash-distilled through a Claisen flask followed by fractionation through a ten-inch Vigreux column. The product homoisocamphenilanaldehyde (V) (46–50 g.) is collected at 60–63° (0.7 mm.), $n^{20}\text{D}$ 1.480, d^{20}_{20} 0.975, assays 96.5–99% pure by hydroxylamine titration, the impurity probably is the corresponding alcohol. Some 10–15% of the camphene charged is recovered as a forerun either unreacted or reduced to the hydrocarbon (b.p. 36–59° (0.7 mm.)); small amounts of the aldehyde are reduced to the alcohol especially at higher reaction temperatures; the still residue usually amounts to 8–12% of the weight of aldehyde. **The 2,4-dinitrophenylhydrazone and semicarbazone** prepared in the usual way melt sharply at 148.6–148.8° and 190.8–191.3°, respectively. *Anal.* 2,4-Dinitrophenylhydrazone. Calcd. for $C_{17}H_{22}O_4N_4$: C, 59.0; H, 6.37; N, 16.18. Found: C, 59.41; H, 6.62; N, 16.36. Semicarbazone. Calcd. for $C_{12}H_{21}N_3O$: C, 64.6; H, 9.48; N, 18.82. Found: C, 64.87; H, 9.62; N, 18.94.

Homoisocamphenilanic Acid (VI).—Oxygen is passed by means of a diffusion tube into 300 g. of vigorously stirred aldehyde (V) at 50–60°, until a neutral equivalent of 193–200 is attained. The acid is distilled at 112–114° (0.65 mm.) through a ten-inch Vigreux column, then recrystallized 2–3 times from petroleum ether (40–60°); m.p. 56–57°, neutral equivalent 181.5 (theory 182).

Homoisocamphenilanyl Chloride.—100 g. of acid (VI) and 121 g. of thionyl chloride are refluxed 2–3 hours. Excess thionyl chloride is distilled off to a pot temperature of 130°. After cooling, vacuum is applied, the acid chloride is col-

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(9) The 65% represents the yield of actual aldehyde based on an *expected* yield of aldehyde from a given weight of camphene charged to the autoclave. No account is taken of the unreacted or hydrogenated camphene (10–15% of the original charge) which is recovered as a forerun; of the aldehyde which is reduced to the alcohol, nor of the 8–12% residue which probably consists of aldol condensation products and/or acetals. If these are taken into account the yield is upwards of 90%.

(10) G. Langlois, *Ann. chim.*, [9] **12**, 265 (1919).

(11) E. Ott, A. Behr and R. Schröter, *Ber.*, **61**, 2124 (1928).

(12) All melting points are corrected. All boiling points are uncorrected.

lected at 106–110° (8-9 mm.); yield 106 g., d^{20}_{20} 1.082. *Anal.* Calcd. for $C_{11}H_{17}OCl$: Cl, 17.67. Found: Cl, 17.85.

Homoisocamphenilanylamide.—This is prepared from the acid chloride (5 g.) and cold concentrated ammonia (25 ml.), m.p. 116–117° from dilute alcohol and heptane, yield 2.5–3 g. *Anal.* Calcd. for $C_{11}H_{19}ON$: N, 7.73. Found: N, 7.70.

Homoisocamphenilanylanilide.—This is prepared from the acid chloride (10 g.), freshly distilled aniline (5 g.) and 20 ml. of anhydrous pyridine. The reaction mixture, after five minutes on a steam-bath, is poured into 300 ml. of hot benzene. The solution is extracted successively with 150 ml. of hot 5% hydrochloric acid (twice), 100 ml. of hot 5% sodium carbonate (twice) and 100 ml. of hot distilled water (four times). The solution is concentrated to 150 ml. and allowed to cool. The crystals are filtered and recrystallized twice from benzene; yield 13 g., m.p. 175.8–176.4°. *Anal.* Calcd. for $C_{17}H_{33}ON$: N, 5.44. Found: N, 5.39.

α-Bromohomoisocamphenilanic Acid (VIII).—A mixture of 100 g. of acid (VI), 100 g. of bromine and 1.5 ml. of PCl_3 was heated at 65–70° overnight, then at 95–100° for five hours. The cooled mixture is stripped under vacuum (water aspirator) to a pot temperature of 80°. The residue is distilled with high vacuum giving 109 g. of product, b.p. 128° (0.28 mm.), which after two recrystallizations from heptane melts at 117.1–117.3°.

Anal. Calcd. for $C_{11}H_{17}O_2Br$: Br, 30.6. Found: Br, 30.8.

α-Hydroxyhomoisocamphenilanic Acid (VII).—This was prepared in 26% yield from the bromoacid (VIII) by the method of LeSeur.[13] Recrystallized from heptane twice, it melts at 113–113.8°; neutral equivalent found 198.4; calcd. 198.3. Some camphene is obtained as a by-product.

Methyl α-Bromohomoisocamphenilanate (IXa).—In a solution of 100 g. of the acid in 700 ml. of dry methanol is absorbed 20 g. of anhydrous hydrochloric acid. After refluxing overnight the solution is cooled, diluted with 100 ml. of benzene then washed successively with two portions of 3% sodium carbonate, thrice with water, then dried over sodium sulfate. The filtered solution is stripped under vacuum with a water aspirator to a pot temperature of 80° then subjected to distillation using an oil-pump. The product (102 g.) is collected at 96–99° (0.7 mm.), n^{20}_{D} 1.5059.

Anal. Calcd. for $C_{12}H_{19}O_2Br$: Br, 29.10. Found: Br, 29.57.

Decarboxylation of the Hydroxy Acid (VII).—Following the procedure of Baeyer and Liebig[14] 19.8 g. of the hydroxy acid (VII), 20 g. of lead dioxide, 30 g. of glacial acetic acid and 30 g. of 25% phosphoric acid were refluxed four hours with stirring. The mixture is steam distilled and the distillate is extracted with petroleum ether. The petroleum ether is stripped and the residue distilled giving 2 g. of aldehyde, b.p. 88–90° (10 mm.), m.p. 60–65°; **semicarbazone,** m.p. 188–190°; **2,4-dinitrophenylhydrazone,** m.p. 156.5–157.5°. Oxidation of a thin film of the aldehyde on a watch glass gives isocamphenilanic acid, m.p. 116–117°, neutral equivalent 167.5 (theory 168), amide m.p. 169–169.2°; Lipp,[15] *et al.*, reported 170–171°. Mixed melting points of the acid and amide with authentic samples of the compounds prepared according to the method of Henderson and Sutherland[8] and Lipp and co-workers[15] showed no depression. *Anal.* Semicarbazone. Calcd. for $C_{11}H_{19}N_3O$: N, 20.07. Found: N, 20.23. 2,4-Dinitrophenylhydrazone. Calcd. for $C_{16}H_{20}N_4O_4$: C, 57.8; H, 6.07; N, 16.85. Found: C, 57.65; H, 6.02; N, 17.1. Amide. Calcd. for $C_{10}H_{17}ON$: N, 8.38. Found: N, 8.44.

α-Methoxyhomoisocamphenilanic Acid (IX).—One hundred and two grams of α-bromoester (IXa), 40 g. of sodium methoxide and 200 ml. of anhydrous methanol are refluxed 2.5 hours. After the addition of 50 ml. of water and 30 g. of sodium hydroxide the solution is refluxed three hours. The cooled solution is acidified with hydrochloric acid (congo red) and the organic acid is extracted with benzene (250 ml.). The benzene extract is washed with water until neutral then dried by distillation of the benzene with vacuum. The pot is heated to 120° at 0.6–0.7 mm. The residue (52 g.) is crude α-methoxyhomoisocamphenilanic acid (neutral equivalent 200, theory 211.5). Attempts to purify by fractional crystallization were unsuccessful. Without further purification the crude acid is heated at 260° at 150 mm. pressure. From the low boiling cut of the degradation products (12 g. up to 120° at 20 mm.) were prepared the semicarbazone, m.p. 189–191°, and the 2,4-dinitrophenylhydrazone, m.p. 156.5–157.5°. Oxidation of the same cut gave isocamphenilanic acid, m.p. 115–117°, neutral equivalent 168.

When the etherification is carried out with larger amounts of sodium methoxide and longer reaction times the crude acid contains considerable solid material. This is filtered and recrystallized three times from heptane giving camphenilidene acetic acid (XIV), m.p. 125–126°, **amide,** m.p. 192.6–193.6°; **anilide,** m.p. 154,1–154.4°. Mixed melting points with authentic samples (Langlois[10] and Hasselstrom[16] and Hampton) show no depression.

Anal. Amide of (XIV) (from dehydrobromination of IXa). Calcd. for $C_{11}H_{17}ON$: C, 73.75; H, 9.50; N, 7.82. Found: C, 73.62; H, 9.61; N, 7.77. Anilide of (XIV) (from dehydrobromination of IXa). Calcd. for $C_{17}H_{21}ON$: C, 80.0; H, 8.24; N, 5.49. Found: C, 80.32; H, 8.25; N, 5.47.

Oxidative Degradation of Dimethylenamine of Homoisocamphenilanaldehyde (XII).—The enamine is prepared by passing 99 g. of anhydrous dimethylamine into a stirred mixture of 50 g. of anhydrous potassium carbonate and 166 g. of aldehyde (V) followed by heating one hour at 50°. The solid, after filtration, is extracted with benzene. The filtrate and extracts are stripped and the product distilled, b.p. 85–89° (2.5–2.8 mm.), n^{20}_{D} 1.4975, yield 93 g. To 110 g. of potassium permanganate in 500 ml. of anhydrous acetone are added with stirring in 0.5 hour, 33 g. of the enamine, while the temperature is maintained below 45°. After the addition is complete, agitation is continued for five hours. The acetone is evaporated and the solid residue is extracted repeatedly with hot water. The combined extracts are concentrated to about 150 ml. and acidified with hydrochloric acid. The organic solid after three recrystallizations from petroleum ether gives 7 g. of isocamphenilanic acid (XI), m.p. 116–117°, neutral equivalent 168.4 (theory 168.2), showing no depression in melting point when mixed with an authentic sample.[8] About 5.5 g. of homoisocamphenilanic acid, b.p. 106–110° (0.5–0.6 mm.) (neutral equivalent 181.5) is obtained by evaporating the mother liquors and distilling.

Camphenilidene Acetic Acid (XIV) and Its Catalytic Reduction to Diastereoisomeric Acids (VI) and (XV).—The Prins reaction on camphene to obtain 8-camphenecarbinol (XIII) is carried out essentially as described by Langlois[10] except that purification of the alcohol is carried out by fractionation through a 20-inch column packed with glass helices (b.p. 114–116° (6–7 mm.) n^{20}_{D} 1.5035) rather than by conversion to the solid acid phthalate. To 132 g. of potassium dichromate and 352 g. of sulfuric acid made up to 1600 ml. with water is added dropwise in 1.5 hours a solution of 110 g. of the carbinol (XIII) in 110 ml. of benzene maintaining the temperature at 0–5° (vigorous agitation). The solution is allowed to attain room temperature slowly and is agitated overnight. The benzene layer is separated and the water layer is extracted twice with 75 ml. of benzene. The combined extracts are washed twice with water then dried by refluxing the benzene using a Dean–Stark water separator. Through the benzene solution is passed a diffused stream of oxygen at 35–50° with vigorous agitation for 4–5 hours. The oxidized solution is poured into 300 ml. of 10% sodium hydroxide and after stirring, the water layer is separated and extracted twice with benzene, then acidified with hydrochloric acid. The organic acid which separates is taken up in hot heptane and recrystallized several times from the same solvent. About 12 g. of pure acid (XIV) (m.p. 125–126°, neutral equivalent 180.2, amide m.p. 192.5–193.5°, anilide m.p. 154–155°) are obtained along with 10–15 g. of impure acid recoverable from the mother liquors. The acid (XIV) 45 g. in 103 ml. of 10% sodium hydroxide with 7 g. Raney nickel is hydrogenated at 130–160° for 2.5–3.0 hours at 170–200 atm. The catalyst is filtered and, after adding 100 ml. of benzene, the solution is acidified with hydrochloric acid. The organic layer is washed with water, stripped of solvent under vacuum, then distilled. About

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(13) H. R. LeSeur, *J. Chem. Soc.*, **87**, 1895 (1905).

(14) A. Baeyer and H. Liebig, *Ber.*, **31**, 2106 (1898).

(15) P. Lipp, H. Dessauer and E. Wolf, *Ann.*, **525**, 271, 8 (1936).

(16) T. Hasselstrom and B. L. Hampton, This Journal, **61**, 3445 (1939).

36 g. of acid is collected at 102–104° (0.1 mm.), m.p. 57–62°. The products from four hydrogenations are combined and recrystallized together from petroleum ether. After several recrystallizations the higher melting isomer is isolated: m.p. 76–77°; neutral equivalent 182.2; **amide**, m.p. 123.8–124.2; **anilide**, m.p. 163.8–164.1° (15–20 g. from 149 g. mixture). From the first mother liquor by repeated fractional crystallization is obtained the low melting isomer (about 18 g.), **homoisocamphenilanic acid (VI)**, m.p. 56–57°, neutral equivalent 182; **amide**, m.p. 115.5–115.7°; **anilide**, m.p. 175.8–176.4°, mixed melting points of the acid and its derivatives with those obtained from the acid (VI) derived from the OXO aldehyde show no depression.

Anal. Amide of higher melting isomer (XV). Calcd. for $C_{11}H_{19}ON$: N, 7.71. Found: N, 7.72. Anilide of higher melting isomer (XV). Calcd. for $C_{17}H_{23}ON$: N, 5.44. Found: N, 5.44.

Reduction of the Isomeric Acids (VI), (XV) to the Alcohols.—The reduction is carried out on both acids with lithium aluminum hydride according to the procedure of Nystrom and Brown.[17] From 9.1 g. of acid (VI) and 3.7 g. of lithium aluminum hydride is obtained 7.3 g. of alcohol, homoisocamphenilanol, b.p. 122–123° (9 mm.), $n^{20}{}_D$ 1.4885, $d^{20}{}_{20}$ 0.9742; ***p*-nitrobenzoate**, m.p. 111.2–111.3°; **3,5-dinitrobenzoate**, m.p. 80.0–80.5°; ***α*-naphthylamine addition compound**[18] of latter, m.p. 129.5–130.5°.

Anal. *p*-Nitrobenzoate. Calcd. for $C_{18}H_{23}NO_4$: C, 68.18; H, 7.25; N, 4.42. Found: C, 68.46; H, 7.22; N, 4.49. 3,5-Dinitrobenzoate. Calcd. for $C_{18}H_{22}N_2O_6$: C, 59.7; H, 6.12; N, 7.74. Found: C, 60.06; H, 6.06; N, 7.76. 3,5-Dinitrobenzoate·*α*-naphthylamine addition compound. Calcd. for $C_{28}H_{31}N_3O_6$: C, 66.5; H, 6.16; N, 8.31. Found: C, 66.6; H, 6.26; N, 8.25.

From 9.1 g. of the higher melting isomeric acid (XV) in the same way are obtained 6.7 g. of alcohol, b.p. 139–140° (22 mm.), $n^{20}{}_D$ 1.4883, $d^{20}{}_{20}$ 0.9767; ***p*-nitrobenzoate**, m.p. 103.1–103.4°; **3,5-dinitrobenzoate**, m.p. 88.0–88.2°; ***α*-naphthylamine addition compound** of latter, m.p. 140.3–140.8°.

Anal. *p*-Nitrobenzoate. Calcd. for $C_{18}H_{23}NO_4$: C, 68.18; H, 7.25; N, 4.42. Found: C, 68.32; H, 7.37; N, 4.51. 3,5-Dinitrobenzoate. Calcd. for $C_{18}H_{22}N_2O_6$: C, 59.7; H, 6.12; N, 7.74. Found: C, 59.5; H, 6.13; N, 7.95. *α*-Naphthylamine addition compound. Calcd. for $C_{28}H_{31}N_3O_6$: C, 66.5; H, 6.16; N, 8.31. Found: C, 66.6; H, 6.10; N, 8.36.

Reduction of 8-Camphenecarbinol (XIII).—Hydrogenation of 27.6 g. of the carbinol (XIII), 120 g. of ethanol and 8 g. of Raney nickel at 160–170°, 1–1.25 hours with 120–150 atm. gives on distillation a 24-g. mixture of the isomeric alcohols, b.p. 134–135° (18 mm.). The ***p*-nitrobenzoate**, **3,5-dinitrobenzoate** and ***α*-naphthylamine addition compound** melt as follows: 107–108° (after three recrystallizations); 82–83° (after five recrystallizations) and 134–135° (after three recrystallizations), respectively. All these melting points are intermediate between those of the derivatives made above from the pure isomers.

Acknowledgment.—We are indebted to Mr. C. W. Nash and his co-workers for the microanalyses and to Mr. Harold Klenk for the preparation and purification of a few of the derivatives.

PHILADELPHIA, PENNA. RECEIVED OCTOBER 3, 1951

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[17] R. F. Nystrom and W. G. Brown, THIS JOURNAL, **69**, 2548 (1947).

[18] P. Sutter, *Helv. Chim. Acta*, **21**, 1266 (1938).

NOTES

The Dehalogenation Reaction. III. Dechlorination of 1,2-Dichloroethane and 1,1,2-Trichloroethane[1]

BY TURNER ALFREY, JR.,[2] HOWARD C. HAAS AND CHARLES W. LEWIS

RECEIVED JANUARY 22, 1952

In the course of an investigation of the dechlorination by zinc of the copolymers vinyl acetate/*trans*-dichloroethylene and vinyl acetate/trichloroethylene, it became apparent that a better understanding of the reaction could be obtained if a study were made of the prototype molecules 1,2-dichloroethane and 1,1,2-trichloroethane. In this way, the interference of side reactions such as polymer degradation could be avoided. It was found however, that after 44 days at 101.5° a 0.048 *M* solution of dichloroethane in dioxane did not react with zinc dust as evidenced by the absence of measurable amounts of chloride ion.

Experiments were then performed with 0.033, 0.064 and 0.107 *M* solutions of 1,1,2-trichloroethane in dioxane in the presence of 1.000 and 2.000 g. of zinc dust/25 ml. of solution. In every case an induction period was observed. This was followed by a linear rise in the concentration of zinc chloride up to about 40% conversion, and finally an asymptotic approach to 100% conversion, (*i.e.*, one mole of zinc chloride formed per initial mole of trichloroethane). In all cases the reactions were virtually complete (> 98%) after 3.5 days. The induction periods ranged from 4 to 7.5 hours when 2 g. of zinc was used, and from 9 to 10.5 hours when 1 g. of zinc was used. The linear conversion rates varied from 2.4%/hr. to 6.4%/hr. in a rather random fashion, and no reliable correlation could be established between these rates and the amounts of reactants used.

The induction period can be most readily understood if it is assumed that the zinc chloride produced is capable of promoting the reaction in some manner. This assumption is in accord with the observation that a 0.064 *M* solution of trichloroethane containing 1.000 g. Zn/25 ml. underwent complete dechlorination in less than 24 hours without an observable induction period in the presence of 0.025 *M* zinc chloride. However the scatter of the experimental points for an individual run was very great, so that it could not even be established if the initial rate was linear, as was observed in the previous runs. Nevertheless, it was quite evident that the time required to achieve a given conversion had been materially reduced. It is felt that the qualitative aspects of this observation should be of interest in the field of organic synthesis.

When the dechlorination of dichloroethane was

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[1] Taken in part from the Ph.D. thesis of Charles W. Lewis, Polytechnic Institute of Brooklyn, May, 1950.

[2] Dow Chemical Company, Midland, Michigan.