tered concentrated mixture showed 4% of the allene **3** and 96% of the acetylene **4**.

The Copper Bronze Catalyzed Reaction of Ethyl Diazoacetate with 1-Octyne.—The reaction of 2.9 g. (0.025 mole) of ethyl diazoacetate, 2.8 g. (0.025 mole) of 1-octyne, and 300 mg. of copper bronze in 40 ml. of benzene was carried out as described for the copper sulfate reaction. Distillation through a short-path still yielded 300 mg. of material which consisted of 14% of diethyl fumarate, 77% of diethyl maleate, and 9% of an unidentified component as determined by gas chromatography.[13]

Hydrogenation of the Allene 3 and Acetylene 4. A. In Ethyl Acetate.—A 260-mg. (1.31 mmoles) sample consisting of 40% of the allene **3** and 60% of the acetylene **4** in 15 ml. of ethyl acetate was hydrogenated at room temperature and atmospheric pressure over the catalyst from 30 mg. of platinum oxide. The hydrogen uptake (76.2 cc. or 2.1 equiv.) ceased after 20 min. and the reaction mixture was filtered and concentrated. The residual liquid was purified by distillation in a short-path still. The saturated ester **5** shows one peak on gas chromatography,[13,16,17] and has infrared absorption[14] at 1740 cm.$^{-1}$ (ester $C=O$) with n.m.r. peaks[14] at δ 4.0 (2H quartet with J = 7 c.p.s., $-O-CH_2-$) and 2.2 (2H triplet with J = 7 c.p.s., $-CH_2-CO-$), as well as broad absorption at δ 1.5–0.8 (20H, aliphatic C–H).

Anal. Calcd. for $C_{12}H_{24}O_2$: C, 71.96; H, 12.07. Found: C, 71.93; H, 12.15.

B. In Ethanol.—A 123-mg. (0.63 mmole) sample consisting of 40% of the allene **3** and 60% of the acetylene **4** in 12 ml. of absolute ethanol was hydrogenated at 5° and atmospheric pressure over 23 mg. of 5% palladium on carbon. The hydrogen uptake (30.6 cc. or 1.9 equiv.) ceased after 20 min. and the mixture was filtered and concentrated. The saturated ester, the only component in the residual liquid, was collected from the gas chromatograph.[17] The material has retention time and infrared spectrum[14] identical with the ester **5** obtained from hydrogenation over platinum.

Hydrolysis of the Saturated Ester 5.—A 900-mg. (4.6 mmoles) sample of the saturated ester was heated at 50° for 3 hr. with 0.6 g. of sodium hydroxide and 25 ml. of 95% ethanol. The mixture was cooled and concentrated. The residual solid was taken up in water and extracted with ether. The organic layer was concentrated to a waxy white solid which was taken up in water and acidified with dilute hydrochloric acid. The mixture was extracted with ether. The organic layer was dried, concentrated, and distilled through a short-path still to give 400 mg. of a low-melting solid. The material was shown to be pure by gas chromatography[13] and has retention time, infrared[14] and n.m.r.[14] spectra identical with those of an authentic sample of capric acid.

Ethyl Deca-3-ynoate.—The general procedure followed was that of Newman and Wotiz.[8] The Grignard reagent prepared from 0.10 mole of ethylmagnesium iodide and 9.6 g. (0.087 mole) of 1-octyne was allowed to react with gaseous formaldehyde. On working up in the usual manner 7.4 g. (60%) of 2-nonyn-1-ol, b.p. 128–132° (28 mm.), $n^{27}\text{D}$ 1.4530 [lit.[18] b.p. 62–63° (2 mm.), $n^{25}\text{D}$ 1.4541], was obtained. Gas chromatography[13] showed the material to be 95% pure. The alcohol has n.m.r. absorption[14] at δ 4.13 (2H triplet with J = 1.5 c.p.s., $-C\equiv C-CH_2-O-$), 3.76 (1H singlet, –OH), and 2.35–1.90 (2H multiplet, $-CH_2-C\equiv C-$), as well as broad absorption at δ 1.65–0.7 (13H, aliphatic C–H), and has a strong band at 3350 cm.$^{-1}$ (–OH) in the infrared spectrum.[14]

Reaction of 6.0 g. (0.043 mole) of 2-nonyn-1-ol and 0.1 ml. of pyridine in 20 ml. of anhydrous ether with 4.2 g. (0.015 mole) of phosphorus tribromide yielded on work-up 5.24 g. (60%) of 1-bromo-2-nonyne, b.p. 128–136° (28 mm.), $n^{27}\text{D}$ 1.4837 [lit.[18] b.p. 67–68° (2.5 mm.), $n^{25}\text{D}$ 1.4831]. The material has n.m.r. absorption[14] at δ 3.85 (2H triplet with J = 2.1 c.p.s., $\equiv C-CH_2-Br$) and 2.4–2.0 (2H multiplet, $-CH_2C\equiv C-$), as well as broad absorption at δ 1.7–0.7 (11H, aliphatic C–H).

A mixture of 4.0 g. (0.020 mole) of 1-bromo-2-nonyne, 3.0 g. of cuprous cyanide, 0.05 ml. of benzyl chloride, 10 mg. of anhydrous copper sulfate, and 2 ml. of xylene was heated in an oil bath kept at 150–160° for 1.5 hr. The mixture was diluted with acetone, filtered, concentrated, and distilled to give 1.8 g. (61%) of 1-cyano-2-nonyne, b.p. 81–83° (0.7 mm.), $n^{27}\text{D}$ 1.4547. The material has n.m.r. absorption[14] at δ 3.20 (2H triplet with J = 2.5 c.p.s., $-CH_2-CN$) and 2.35–1.95 (2H multiplet, $-CH_2-C\equiv C-$), in addition to absorption due to aliphatic C–H, and has weak bands at 2230 and 2290 cm.$^{-1}$ ($-C\equiv N$, $C\equiv C$) in the infrared spectrum.[14]

Into a solution of 1 ml. of water, 25 ml. of 95% ethanol, and 0.60 g. of 1-cyano-2-nonyne was bubbled hydrogen chloride until refluxing ceased and a white precipitate appeared. The mixture was concentrated, then diluted with water and extracted with ether. The organic layer was washed with sodium bicarbonate, dried, concentrated, and distilled through a short-path still to give 0.60 g. of material. Gas chromatography[13] showed the material to consist of two components, A and B, in the amounts of 42 and 58%. Pure samples of the compounds were collected. Compound A has retention time, infrared[14] and n.m.r.[14] spectra identical with that of the acetylene **4**.

Anal. Calcd. for $C_{12}H_{20}O_2$: C, 73.55; H, 10.51. Found: C, 73.41; H, 10.26.

Component B has n.m.r. absorption at δ 5.78 (0.7H) and 5.65 (0.3H) (two overlapping triplets with J = 8 c.p.s., vinyl C–H), 4.18 (2H quartet with J = 7 c.p.s., $-O-CH_2-$), 3.28 [1.5H singlet, $-C=C-CH_2-C(=O)-$], 3.24 [0.5H singlet, $-C=C-CH_2-C(=O)-$], 2.40–1.80 (2H multiplet, allylic-CH_2–), in addition to aliphatic C–H absorption, indicating that the material is a mixture of ethyl *cis*- and *trans*-3-chloro-3-decenoate. The material absorbs at 1750 (ester $C=O$) and 1660 cm.$^{-1}$ (unconjugated $C=C$) in the infrared.[14]

Anal. Calcd. for $C_{12}H_{21}ClO_2$: C, 61.91; H, 9.10; Cl, 15.24. Found: C, 62.02; H, 8.95; Cl, 15.38.

1,2-Nonadiene-3-carboxylic Acid.—The Grignard reagent from 1-bromo-2-nonyne was prepared using the method developed by Rowland, Greenlee, and Boord.[19] From 4.3 g. (0.021 mole) of the bromide was obtained after carbonation, acid hydrolysis, and recrystallization from ether–petroleum ether (b.p. 30–65°), 0.70 g. (20%) of the acid, m.p. 61–66°, which was pure by gas chromatography.[13] The acid has absorption at 1960 and 1930 cm.$^{-1}$ (terminal allene with carboxy grouping directly attached to the allenic bond),[20] broad absorption in the 3-μ region (associated –OH), and a peak at 1690 cm.$^{-1}$ (carboxyl $C=O$) in the infrared[14]; and n.m.r. peaks[14] at δ 12.25 (1H, COOH), 5.1 (2H triplet with J = 3 c.p.s., $>C=C=CH_2$), and 2.4–2.0 (2H multiplet, $-CH_2-C=C=$), as well as aliphatic C–H absorption. After recrystallization from ether–petroleum ether, the acid had m.p. 66–67°.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.27; H, 9.73.

The methyl ester, prepared by esterification with ethereal diazomethane, has bands at 1960 and 1940 cm.$^{-1}$ (allene) and a strong band at 1720 cm.$^{-1}$ (conjugated ester $C=O$) in the infrared[14] and has n.m.r. peaks[14] at δ 5.30 (2H triplet with J = 3 c.p.s., $=C=CH_2$), 3.88 (3H singlet, $-O-CH_3$), and 2.6–2.1 (2H multiplet, $-CH_2-C\equiv C$).

Acknowledgment.—The authors wish to thank Dr. J. T. Marvel for valuable discussions and helpful suggestions regarding this work.

---

(16) A gas chromatograph column packed with 10% ethylene glycol succinate suspended on Chromosorb W was employed.

(17) A gas chromatograph column packed with 15% Silicone Oil 550 suspended on base-washed ground firebrick was employed.

(18) W. J. Gensler and J. J. Bruno, *J. Org. Chem.*, **28**, 1254 (1963).

(19) Abstracts, 117th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1950. We are indebted to K. W. Greenlee for providing us with a detailed description of the apparatus and experimental procedure.

(20) J. H. Wotiz and W. D. Celmer, *J. Am. Chem. Soc.*, **74**, 1860 (1952).

Diimide. An Intermediate in the Reaction of Carbon Tetrachloride and Hydrazine

JOSEPH WOLINSKY AND TENA SCHULTZ

Department of Chemistry, Purdue University,
Lafayette, Indiana

Received June 17, 1965

The report[1,2] that nitrogen is evolved from a refluxing mixture of hydrazine and carbon tetrachloride

---

(1) S. H. Patinkin and E. Lieber, *J. Am. Chem. Soc.*, **72**, 2778 (1950).

(2) R. Stolle, *Ber.*, **37**, 3548 (1904).

attracted our attention to the possibility that diimide was involved as a transitory intermediate. Diimide is an important reducing agent and a number of methods[3] have been devised for its generation.

Patinkin and Lieber[1] identified nitrogen, hydrazine hydrochloride, chloroform, and a trace of methylene chloride as the products of the hydrazine–carbon tetrachloride reaction. They were unable to detect triaminoguanidine hydrochloride which had been reported by Stolle.[2,4] We have confirmed Patinkin and Lieber's observations and in addition have identified ammonia among the volatile products. An examination of the solid product gave no evidence for the presence of a salt other than hydrazine hydrochloride. Mass spectral examination of the gaseous products demonstrated the absence of detectable amounts of hydrogen.

The carbon tetrachloride–anhydrous hydrazine system is heterogeneous; however, this feature can be minimized by vigorous stirring and by addition of methanol. The evolution of nitrogen frequently exhibits an appreciable induction period. The induction period can be eliminated by adding a *trace* of powdered copper. The reaction proceeds violently, sometimes explosively, if more than a trace of copper is added. The reaction appears to be light catalyzed and is inhibited by thiophenol. When styrene is introduced into the system most of the styrene is polymerized, and when 1-octene is present substantial amounts of 1,1,1,3-tetrachlorononane can be isolated. These observations suggest a free-radical pathway for the oxidation of hydrazine by carbon tetrachloride (Chart I).

CHART I

$$X\cdot + CCl_4 \longrightarrow XCl + CCl_3\cdot$$

$$CCl_3\cdot + H_2NNH_2 \longrightarrow HCCl_3 + H_2NNH\cdot$$

$$H_2NNH\cdot + CCl_4 \longrightarrow CCl_3\cdot + H_2NNHCl$$

$$H_2NNHCl + H_2NNH_2 \longrightarrow H_2NNH_2\cdot HCl + HN{=}NH \text{ (or } H_2N{=}N)$$

$$2HN{=}NH \longrightarrow N_2 + H_2NNH_2$$

In keeping with the suggestion of the transitory intermediacy of diimide we find that olefins are reduced to alkanes by heating with anhydrous hydrazine and carbon tetrachloride in methanol.[5] Monosubstituted olefins such as 1-heptene and 1-octene are transformed in *ca.* 30–50% yield to *n*-heptane and *n*-octane, respectively. Carbon tetrachloride adducts account for the remainder of the starting material. Olefin reduction falls off rapidly as the degree of substitution about the carbon–carbon double bond increases. Thus, under conditions which convert 1-octene completely into *n*-octane and 1,1,1,3-trichlorononane, 2-heptene is only consumed to the extent of *ca.* 75%, cyclohexene 50%, and 1-methylcyclohexene 10%.[6]

The selectivity of this system is further demonstrated by the reduction of limonene to 4-isopropyl-1-methyl-1-cyclohexene.

While the reduction of olefins by carbon tetrachloride and hydrazine can be easily accomplished, the synthetic utility is seriously limited by the competing consumption of olefin by free-radical addition of carbon tetrachloride.

Experimental Section

Carbon Tetrachloride and Anhydrous Hydrazine.—Carbon tetrachloride (100 ml., spectral grade) and 17 g. of anhydrous hydrazine (97%) were heated and magnetically stirred in a flask equipped with a reflux condenser. The evolved gases were passed through a standardized sulfuric acid solution and were led into a water-filled inverted buret. Nitrogen evolution was determined by displacement of water. Ammonia was determined by titration of the sulfuric acid with standard alkali.[7] The amount of hydrazine hydrochloride was determined by evaporating the reaction mixture and weighing the residual solid. The results are shown in Table I.

Chloroform and anhydrous hydrazine failed to react, even in the presence of copper, after heating for 2 days. Addition of carbon tetrachloride to this mixture gave an immediate evolution of nitrogen.

TABLE I

REACTION OF HYDRAZINE WITH CARBON TETRACHLORIDE

Hydrazine, mole	CCl_4, ml.	CH_3OH, ml.	Time, days	N_2, mole	NH_3, mole	$N_2H_4\cdot HCl$, mole
0.570	100	50	6	0.161	0.066	0.290
0.578	100	50[a]	1	0.174	0.060	0.394
0.576	100	...	3.2	0.142	0.115	0.240
0.540	100[a]	...	3.2[b]	0.142	0.115	0.280

[a] Copper added. [b] 80% of the nitrogen was evolved within 12 hr.

Reduction of 1-Octene.—A mixture of 30.45 g. (0.27 mole) of 1-octene, 47.54 g. (1.44 moles) of 97% anhydrous hydrazine, 300 ml. of carbon tetrachloride, 100 ml. of methanol, and several small bits of copper wire was stirred and heated to reflux for 48 hr. The mixture was washed with water, dried, and fractionally distilled using a Todd fractionating column to yield 12.0 g. (38.7%) of *n*-octane, b.p. 120–124°, $n^{17.5}D$ 1.4004–1.4024, which was characterized by infrared, n.m.r., and mass spectroscopy ($M^+ = 114$). The distilland was further distilled under diminished pressure to give 22 g. of a colorless liquid, b.p. 102–112° (4 mm.). Gas chromatographic analysis indicated the presence of two components in a ratio of *ca.* 6:1. The major component was collected and showed $n^{14}D$ 1.4804 and displayed infrared and n.m.r. spectra identical with an authentic sample of 1,1,1,3-tetrachlorononane.[8] The minor peak exhibited $n^{15}D$ 1.4641 and appeared to be 1,1,1-trichlorononane.

Reduction of Limonene.—A mixture of 32.4 g. (0.239 mole) of limonene, 31.2 g. (0.944 mole) of 97% anhydrous hydrazine, 100 ml. of carbon tetrachloride, and 50 ml. of methanol was stirred and heated for 2 days. After the work-up described above, distillation gave 14 g. of 4-isopropyl-1-methyl-1-cyclohexene, b.p. 42–49° (7–8 mm.), $n^{15}D$ 1.4601, and *ca.* 20 g. of the carbon tetrachloride–limonene 1:1 adduct, b.p. 125–130° (1 mm.).

Acknowledgment.—We are grateful for the assistance provided by Mr. Joseph Hellmueller.

---

(3) *Cf.* A. Furst, R. C. Berlo, and S. Hooton, *Chem. Rev.*, **65**, 51 (1965); S. Hünig, H. R. Müller, and W. Thier, *Angew. Chem.*, **77**, 368 (1965); C. E. Miller, *J. Chem. Educ.*, **42**, 254 (1965).

(4) In a single instance we isolated, from a reaction of carbon tetrachloride with hydrazine hydrate, a high-melting solid which appeared to be triaminoguanidine hydrochloride. Many attempts to reproduce this result met with failure.

(5) The amount of olefin reduction in the absence of methanol is negligible.

(6) *Cf.* E. W. Garbisch and C. M. Sprecher, Abstracts, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, p. 13P, for relative rates of reduction of olefins with diimide.

(7) In one experiment the gases were led through hydrochloric acid. Evaporation of the acid solution afforded a white solid which was identified as ammonium chloride.

(8) M. S. Kharasch, E. V. Jensen, and W. H. Urry, *J. Am. Chem. Soc.*, **69**, 1100 (1947).