EXPERIMENTAL

Cuprous chloride-Cl^{36}.[1] To a solution of cupric sulfate pentahydrate (187 mg., 0.75 mmole) and sodium chloride-Cl^{36} (44 mg., 0.75 mmole, specific activity 20.8 μc./mmole) in 0.6 ml. of water was added dropwise with shaking at room temperature, sodium sulfite (96 mg., 0.76 mmole) in 0.3 ml. of water. The mixture was centrifuged, the aqueous phase was removed with a dropper, and the precipitate of cuprous chloride-Cl^{36} was washed once with 0.5 ml. of water to which was added a very small amount of sulfurous acid to prevent oxidation. This aqueous phase was also removed by centrifugation.

The cuprous chloride-Cl^{36} was washed three times each with acetic acid, anhydrous ethanol, and anhydrous ether, centrifugation being used each time to separate the liquid phase. The product was used immediately in the next reaction.

The yield in preliminary runs was quantitative.

1,2,4,5-Tetrachlorobenzene-1-Cl^{36}. 2,4,5-Trichloroaniline (147 mg., 0.75 mmole) was diazotized in the following manner[2]: The aniline derivative was dissolved in 0.75 ml. of concentrated sulfuric acid. To this ice cold solution was added 1.88 ml. of a cold solution of sodium nitrite (1.125 mmole) in concentrated sulfuric acid. Cold 85% phosphoric acid (0.75 ml.) was then added and the dark colored solution was allowed to stand at room temperature for 1.5 hr. Initially and rather slowly, there was some precipitation, but the crystalline material gradually redissolved on intermittent shaking as the reaction progressed. The reaction solution was finally poured onto ice to give a solution with a volume of about 10 ml. The excess nitrous acid was destroyed by addition of small quantities of urea.

During the 1.5 hr. required for the diazotization reaction to take place, the cuprous chloride-Cl^{36} was prepared as described above. Following this, a solution of the cuprous chloride-Cl^{36} (0.75 mmole) and sodium chloride-Cl^{36} (65 mg., 1.13 mmole) in hydrochloric acid-Cl^{36} (0.6 ml. of 1.64 N acid, 0.98 mmole, specific activity 20.8 μc./mmole) was prepared. This solution contained a total of 2.86 mmole of chloride-Cl^{36}. Preliminary work had made it clear that a one-to-one stoichiometry, chloride to diazotized amine, gave a very poor yield of product.

The cuprous chloride-Cl^{36} solution was heated on the steam bath and the diazonium solution at room temperature was rapidly poured onto it with shaking. After 15 min. of intermittent shaking at room temperature, the product was isolated by hot benzene extraction. The benzene solution was placed in a porcelain crucible (3.3 cm. i.d. at the top) and the benzene was removed using the steam bath and a gentle stream of air. This evaporation was carried out carefully to prevent loss of product since tetrachlorobenzene sublimes very easily.

The product was purified by sublimation at atmospheric pressure in the following manner: The crucible containing the crude product was covered with a piece of Whatman No. 1 filter paper (4.25 cm.) through which were punched a large number of pin holes. This paper served to prevent sublimed product from falling back into the crucible and, more important, acted as a condensing surface for colored byproducts which do not sublime, but distill. The paper and crucible were covered with an inverted watch glass (4.2 cm.) which served as the condensing surface. The watch glass was cooled with a gentle stream of air. The crucible was heated at 275–285° for 1 hr. with the hot stage from a melting point apparatus. The tetrachlorobenzene condensed as long white needles, m.p. 137° (lit.[3] 137–141°). The yield was 92 mg. (57%); the specific activity was 20.8 μc./mmole. There was no depression in a mixed m.p. with an authentic sample of 1,2,4,5-tetrachlorobenzene.

The excess chloride-Cl^{36} used in this synthesis was recovered from the reaction mixture by treatment with barium hydroxide solution to precipitate the sulfate and phosphate, conversion to hydrochloric acid-Cl^{36} by means of Dowex-50 exchange resin in the acid form, and finally, titration of the eluate with dilute sodium hydroxide solution followed by evaporation to dryness.

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(1) R. N. Keller and H. D. Wycoff, *Inorg. Syntheses*, Vol. II, 1 (1946).

(2) J. Schoutissen, *J. Am. Chem. Soc.*, **55**, 4531 (1933).

(3) E. R. Huntress, *Organic Chlorine Compounds*, John Wiley & Sons, Inc., New York, 1948, p. 367.

Stereochemistry of 8,10-Dimethyl-2-keto-$\Delta^{1,9;3,4}$-hexahydronaphthalene

Stanley M. Bloom

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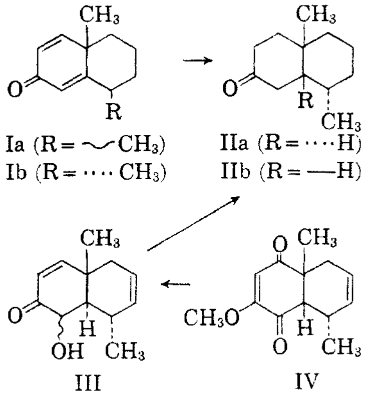
In the reported synthesis of 8,10-dimethyl-2-keto-$\Delta^{1,9;3,4}$-hexahydronaphthalene (Ia) the relationship between the methyl groups was unassigned.[1] The work described in this note establishes the missing stereochemical link and allows the assignment of (Ib) for the cyclohexadienone.



Ia (R = ∼CH$_3$)
Ib (R = ····CH$_3$)
IIa (R = ····H)
IIb (R = —H)
III
IV

Reduction of the cyclohexadienone with lithium in ammonia gave an oily saturated ketone which is shown in the sequel to be identical with *trans*-2-keto-8α-10β-dimethyldecalin (IIa) synthesized from IV. The Diels-Alder adduct IV, in which the methyl groups are fixed in the desired manner, was made from the reaction of 4-methoxy-2,5-toluquinone with *trans*-1,3-pentadiene.[2,3] The adduct on

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(1) S. M. Bloom, *J. Am. Chem. Soc.*, **80**, 6280 (1958).

(2) The *trans*-1,3-pentadiene employed in this study was not separated from any *cis* contaminant (*vide infra*). Several prior investigations have shown that the *cis*-1,3-pentadiene does not give a normal Diels-Alder adduct. For example, *cis*-1,3-pentadiene gives only polymeric material on reaction with maleic anhydride. See D. Craig, *J. Am. Chem. Soc.*, **65**, 1006 (1943); R. L. Frank, R. D. Emmick and R. S. Johnson, *J. Am. Chem. Soc.*, **69**, 2313 (1947); S. J. Averill and H. L. Trumbull, *J. Am. Chem. Soc.*, **76**, 1159 (1954) for a description of the dienophiles and the conditions employed. These facts led us to conclude that the *cis* isomer would give *only* polymeric material on reaction with 4-methoxy-2,5-toluquinone.

isomerization,[4] reduction with lithium aluminum hydride[6] and hydrolysis[5] was transformed into III. Acetylation, followed by deacetoxylation with zinc[5] and hydrogenation[5] gave IIa which was characterized by its semicarbazone and 2,4-dinitrophenylhydrazone.

The melting points of the semicarbazone and 2,4-dinitrophenylhydrazone of (IIa) synthesized *via* the adduct (IV) were in agreement with those obtained from the reduced cyclohexadienone. On admixture the derivatives from the two sources showed no melting point depressions. Lithium reduction of the cyclohexad enone (Ib) had led to (IIa).[6]

In the course of this work the semicarbazone and 2,4-dinitrophenylhydrazone of (IIb) were made and their melting points are recorded in the experimental section (*vide infra*).

EXPERIMENTAL[7]

Reduction of 8,10-dimethyl-2-keto-$\Delta^{1,9;3,4}$-hexahydronaphthalene with lithium.[8] To 200 ml. of dry ethyl ether and 500 ml. of liquid ammonia sufficient lithium was added to give a persistent blue color to the reaction medium. Lithium, 700 mg., cut into small pieces was added at once. After 5 min. the cyclohexadienone, 1.7 g. dissolved in 45 ml. of dry ethyl ether, was added at once. The ketone was followed by excess ammonium chloride which was added until the blue color was discharged. The ammonia and ether were allowed to evaporate undisturbed and the residue was taken up in water and ethyl ether. The ether layer was washed with water, dried with magnesium sulfate and taken down *in vacuo* to a heavy slightly yellow oil. The *semicarbazone* made in the usual manner was recrystallized twice from absolute ethanol for analysis, fine needles, m.p. (in an evacuated soft glass capillary) 202.5–203.0°.

Anal. Calcd. for $C_{13}H_{23}N_3O$: C, 65.78; H, 9.77. Found: C, 65.62; H, 9.99.

The *2,4-dinitrophenylhydrazone* was made in the usual way and gave orange prisms, m.p. 151.0–152.5°, after two recrystallizations from cyclohexane.

Anal. Calcd. for $C_{19}H_{24}N_4O_4$: C, 59.98; H, 6.71; N, 15.55. Found: C, 60.24; H, 6.80; N, 15.31.

Hydrogenation of 8,10-dimethyl-2-keto-$\Delta^{1,9;3,4}$-hexahydronaphthalene. The hydrogenation of the cyclohexadienone was conducted in the manner previously described,[1] with the single change that methanol was employed as the solvent. The theoretical uptake for the 206 mg. of dienone employed is 56 ml. of hydrogen while that observed was 59 ml. On work-up a pale oil was obtained which was converted to the semicarbazone in the usual manner. The derivative was crystallized three times from absolute ethanol, once from 95% ethanol, and finally from absolute ethanol, m.p. (in an evacuated soft glass capillary) 202.0–202.5°. On admixture with the *trans* isomer, m.p. (in an evacuated soft glass capillary) 196–199°.

Anal. Calcd. for $C_{13}H_{23}N_3O$: C, 65.78; H, 9.77; N, 17.71. Found: C, 65.63; H, 9.97; N, 17.94.

trans-1,4-Diketo-2-methoxy-8α,10β-dimethyl-$\Delta^{2,3;6,7}$-hexahydronaphthalene. 4-Methoxy-2,5-toluquinone,[9] 10 g., *trans*-1,3-pentadiene, 50 ml.,[10] benzene, 100 ml., and a trace of hydroquinone were heated in an autoclave at 110° for 5.5 days. The solvent was removed *in vacuo* and the thick yellow brown oil applied to Alcoa F-20 alumina, 200 g., employing ethyl ether–petroleum ether (b.p. 30–60°), 1:1. Elution with the same solvent gave after a small noncrystalline fraction, the crude semicrystalline adduct which on trituration with petroleum ether (b.p. 30–60°) melted from 90–91° and weighed 2.42 g. For analysis the adduct was taken up in a minimal of boiling dichloromethane, filtered from any insoluble material, and a large amount of petroleum ether (b.p. 30–60°) added. On concentration at the steam cone and slow cooling the compound was obtained as white leaflets. Recrystallization as above gave the adduct, m.p. 91.0–91.5°.

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 71.03; H, 7.29.

trans-1,4-Dihydroxy-2-methoxy-8α,10β-dimethyl-$\Delta^{2,3;6,7}$-hexahydronaphthalene. The method of R. B. Woodward *et al.*,[5] was employed on 2.18 g. of adduct. The reaction product on crystallization from dichloromethane–petroleum ether (b.p. 30–60°) gave soft fine needles, m.p. 136.5–137.0°.

Anal. Calcd. for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.74; H, 9.15.

trans-1-Hydroxy-2-keto-8α,10β-dimethyl-$\Delta^{3,4;6,7}$-hexahydronaphthalene. The method of R. B. Woodward *et al.*,[5] was employed on 659 mg. of diol. The crude product, which partially crystallized on scratching, weighed 530 mg. Crys-

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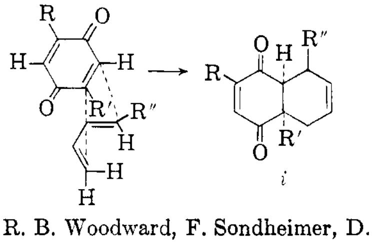
[3] The assignment IV for the adduct is supported by the work of R. B. Woodward, F. E. Bader, H. Bickel, A. J. Frey, and R. W. Kierstead, *Tetrahedron,* 2, 1 (1958) who detailed the theoretical reasons for expecting the adduct *i* (R = R′ = H, R″ = COOH) from the reaction of benzoquinone and *trans* vinylacrylic acid. In the case under discussion, the dienophile (R = OCH_3, R′ = CH_3) and the diene (R″ = CH_3) would lead to *i* (R = OCH_3, R′ = R″ = CH_3) which is the mirror image of (IV).



i

[4] While R. B. Woodward, F. Sondheimer, D. Taub, K. Heusler and W. M. McLamore, *J. Am. Chem. Soc.,* **74,** 4223 (1952) isomerized the *cis* adduct of 4-methoxy-2,5-toluquinone and butadiene by dissolving the compound in aqueous base followed by seeding with the *trans* isomer and acidification, we have found (unpublished results with Miss M. E. Kirtley that the isomerization occurs on Alcoa F-20 chromatographic alumina. In the case at hand the isomerization to the *trans* isomer was observed on purification of the crude reaction mixture (*vide infra*).

[5] R. B. Woodward, *et al.,* ref. 4, conducted a similar series of reactions, converting the adduct of 4-methoxy-2,5-toluquinone and butadiene to both *cis* and *trans*-2-keto-10-methyldecalin.

[6] The result of this study is in accord with the predictions of conformational analysis. An highly unfavorable 1:3 methyl:methyl interaction is avoided when the epimerizable C-8 methyl group assumes the equitorial (alpha) conformation.

[7] All melting points are corrected. Analyses are by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

[8] The reduction was carried out by Miss M. E. Kirtley.

[9] A gift from Dr. W. S. Knowles (Monsanto Chemical Co., St. Louis, Mo.).

[10] The *trans*-1,3-pentadiene employed in an early reaction was synthesized by the method of M. A. Dolliver, *et al., J. Am. Chem. Soc.,* **59,** 831 (1937) with modification. Potassium bisulfate was used to dehydrate the intermediate carbinol. This reagent was employed by L. F. Fieser and C. W. Wieghard, *J. Am. Chem. Soc.,* 62, 153 (1940) to obtain 2,4-dimethyl-1,3-pentadiene. No effort was made to separate the *cis* isomer for the reasons outlined in footnote 2. The diene used in the above experiment was purchased from the Phillips Petroleum Co. The same adduct was isolated with either the synthesized or purchased diene.

tallization from petroleum ether (b.p. 30–60°) and then from methanol gave the ketol, m.p. 102.5–103.5°.[11]

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.97; H, 8.39. Found: C, 74.98; H, 8.61.

trans-2-Keto-8α,10β-dimethyldecalin. The method of R. B. Woodward *et. al.*,[5] was employed to acetylate 590 mg. of the ketol (III). The crude reaction product was deacetoxylated by method A of R. B. Woodward *et al.*,[5] and the oil so obtained hydrogenated with 66 mg. of prereduced platinum oxide in 20 ml. of methanol. In 55 min., 88 ml. of hydrogen had been absorbed, the theoretical amount for two moles of hydrogen being 112 ml. The catalyst was filtered off (pyrophoric) and the solvent evaporated *in vacuo* to give a colorless oil. On examination of the infrared spectrum of the oil taken in carbon tetrachloride, bands at 5.75 microns and 5.85 microns were observed. The oil was therefore taken up in 8 ml. of glacial acetic acid and refluxed with zinc dust, 3 g., for 20 min. The zinc was filtered from the acetic acid solution and washed with several portions of ethyl acetate, the ethyl acetate washes being added to the acetic acid solution. The ethyl acetate and acetic acid were removed *in vacuo* and the residue taken up in dichloromethane and water. The dichloromethane layer was washed successively with water, saturated sodium bicarbonate solution, and water and dried with anhydrous sodium sulfate. On concentration of the dried dichloromethane solution on the steam cone an oil, weighing 300 mg., was obtained. The semicarbazone was made in the usual manner and melted from 194.5–198°. After five recrystallizations from absolute ethanol the compound was obtained as fine short needles, m.p. 202.5–203.5° (taken in an evacuated soft glass capillary). No depression was observed on admixture with the semicarbazone made from the reduced cyclohexadienone, m.p. 202.5–203.5° (taken in an evacuated soft glass capillary concurrently with the pure semicarbazone synthesized above). The pure semicarbazone was converted to the 2,4-dinitrophenylhydrazone with hot 2,4-dinitrophenylhydrazine reagent (in sulfuric acid and methanol). The 2,4-dinitrophenylhydrazone crystallized out as fine orange needles, m.p. 138.5–140.0°. On recrystallization from cyclohexane yellow orange prisms, m.p. 151.0–152.5°, were obtained. No depression was observed on admixture with the 2,4-dinitrophenylhydrazone made from the reduced cyclohexadienone, m.p. 151.0–152.5° (taken concurrently with the pure 2,4-dinitrophenylhydrazone synthesized above).

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[11] This compound was first prepared by Miss M. E. Kirtley as a part of her M.A. thesis, Smith College, 1958.

Preparation and Hydrolysis of Crystalline Ferrocenoyl Chloride[1]

Hans H. Lau and Harold Hart

Received October 8, 1958

It was our original intent to study ferrocenyl free radicals by investigating the decomposition of ferrocenoyl peroxide. This effort was thwarted[2] by lack of success in synthesizing the peroxide. But during the course of the work, ferrocenoyl chloride was prepared pure for the first time, and this note describes its preparation and properties.

Ferrocenoyl chloride has been described several times[3-5] as a red oil prepared, often in rather poor yield, as an intermediate for certain ferrocenoyl derivatives. Ferrocenoyl chloride was obtained as pure red crystals, m.p. 49°; in 48% yield from reaction of the acid[6-8] with phosphorus pentachloride. Treatment with ammonia gave ferrocenamide, m.p. 167–168° (lit.[3] value 167–169°). The spectrum in absolute ethanol showed an appreciable bathochromic shift (λ_{max} 458 mμ; λ_{min} 398 mμ) compared with ferrocene itself (440 mμ and 360 mμ, resp.) or ferrocenoic acid (445 mμ and 386 mμ, resp.). The intense carbonyl band at 5.66μ in the infrared spectrum fell in the range expected[9] for an aromatic acid chloride.

The solvolysis rate of ferrocenoyl chloride was determined in 95% acetone–5% water at 25.0 ± 0.1°. The pseudo first order rate constant, over a concentration range 0.025*N* to 0.005*N* was $8.81 \pm 0.22 \times 10^{-5}$ sec.$^{-1}$, comparable to the value of $5.40 \pm 0.03 \times 10^{-5}$ sec.$^{-1}$ for benzoyl chloride determined under similar conditions.[10] Attention should be called to the similarity of the ionization constants of the corresponding acids,[11] suggesting that both processes are rather insensitive to electronic differences between the phenyl and ferrocenyl groups.[12]

Several attempts to convert ferrocenoyl chloride to the peroxide failed. Moist ether with sodium peroxide gave only unreacted chloride and acid, by hydrolysis. Reflux with sodium peroxide in anhydrous ether gave what is presumably ferrocenoic anhydride, m.p. 141–142°, with carbonyl bands at 5.62μ and 5.80μ.[13] An attempt to prepare

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[1] We are indebted to the National Science Foundation (NSF-G 3289) for financial support of this work.

[2] Although many avenues to such radicals are undoubtedly available, they have hitherto received little attention.

[3] F. S. Arimoto and A. C. Haven, Jr., *J. Am. Chem. Soc.*, **77**, 6295 (1955).

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[5] M. Rausch, P. Shaw, D. Mayo, and A. M. Lovelace, *J. Org. Chem.*, **23**, 505 (1958).

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[8] D. W. Mayo, P. D. Shaw and M. Rausch, *Chem. and Ind. (London)*, 1388 (1957).

[9] L. J. Bellamy, *Infra-red Spectra of Complex Molecules*, John Wiley and Sons, Inc., New York, 1954, pp. 109–110.

[10] D. A. Brown and R. F. Hudson, *J. Chem. Soc.* 883 (1953).

[11] *M. Rosenblum*, Thesis, Harvard, 1953.

[12] Ferrocene is known to be more reactive toward electrophilic substitution than either benzene or anisole; see P. L. Pauson, *Quart. Rev.*, **9**, 391 (1955).

[13] See ref. 9, pp. 110–111.