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]

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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 0.025N to 0.005N 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).

[4] K. Schlögl, *Monatsh Chem.* **88**, 601 (1957).

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

[6] A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya, and O. A. Nesmeyanova, *Doklady Akad. Nauk S.S.S.R.*, **97**, 459 (1954).

[7] R. A. Benkeser, D. Goggin and G. Schroll, *J. Am. Chem. Soc.*, **76**, 4025 (1954).

[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.

this anhydride from the acid and N,N'-dicyclohexylcarbodiimide gave a substance which analyzed correctly for N,N'-dicyclohexyl-N-ferrocenoylurea, m.p. 161°. Neutral, acidic, or weakly alkaline hydrogen peroxide caused oxidation of the iron in the acid chloride. Reaction of the chloride in pentane-pyridine with *t*-butyl hydroperoxide also resulted in oxidation of the iron.

EXPERIMENTAL[14]

Ferrocenoic acid, prepared by metallation and carbonation of ferrocene,[7,8] melted at 208–210° (*cf.* 208.5°,[15] 195–205°,[6] 225–230°[16]). Potentiometric titration in 95% aqueous acetone gave N.E. 232, Calcd. 230, with the equivalence point at pH reading 8.75 on a Beckman pH meter with glass and calomel electrodes. This pH reading was used when following the kinetics of solvolysis of ferrocenoyl chloride as described below.

Ferrocenoyl chloride. Ferrocenoic acid (2.3 g.) in 30 ml. of benzene was allowed to react with 2.5 g. of phosphorus pentachloride (nitrogen atmosphere) as described.[4] The residue, after removal of solvent and phosphorus oxychloride, was dissolved in pentane, washed with dilute base, water, then dried over anhydrous magnesium sulfate. Evaporation (cold) of the solvent gave a solid m.p. 46–47° which, after careful recrystallization from pentane, gave 1.2 g. of red crystals, m.p. 49°.

Anal. Calcd. for $C_{11}H_9Cl\,Fe\,O$: C, 53.69; H, 3.65; Fe, 22.70. Found: C, 53.79; H, 3.99; Fe, 22.73. The compound gave a strong Beilstein test. Its spectrum showed λ_{max} 458 mμ(ϵ = 200) and λ_{min} 398 mμ(ϵ = 120). Bands for the carbonyl (5.66μ), unsubstituted ferrocene ring[17] (6.94, 9.02, 10.00, 12.16μ) and a monosubstituted ferrocene ring[15] (10.69μ) were present. Concentrated aqueous ammonia converted the chloride to the amide, m.p. 167–168° (lit.[3] value, 167–169°).

The chloride (0.8 g.) was refluxed with an excess of sodium peroxide (0.5 g.) in 50 ml. of anhydrous ether (3 drops of water added) for 5 hr. After decomposing the excess of sodium peroxide by water under ice-cooling, enough ether was added to dissolve the insoluble part between the two layers. The ether layer was washed with water, dried, and the solvent evaporated. The yellow solid (0.5 g.) was recrystallized from pentane, m.p. 141–142°, and presumed to be *ferrocenoic anhydride.*

Anal. Calcd. for $C_{22}H_{18}O_3Fe_2$: C, 59.77; H, 4.10; Fe, 25.27. Found: C, 59.43; H, 4.41; Fe, 25.62. The infrared spectrum showed carbonyl (5.62, 5.80μ), and other bands at 6.89, 8.05, 9.02, 9.40, 9.58, 9.99, and 11.02μ.

N,N'-dicyclohexyl-N-ferrocenoylurea. Ferrocenoic acid (0.5 g.) and 0.5 g. of N,N'-dicyclohexylcarbodiimide in 20 ml. of tetrahydrofuran were allowed to stand (dry nitrogen atmosphere) at room temperature for 15 hr. The solvent was removed and the residue washed with ether and recrystallized twice from hexane, m.p. 161°.

Anal. Calcd. for $C_{24}H_{31}O_2N_2Fe$: C, 66.20; H, 7.18; N, 6.44; Fe, 12.85. Found: C, 65.87; H, 7.49; N, 6.58; Fe, 12.62.

Rate measurements. Acetone was carefully purified[18] and conductivity water was used. The solvent was prepared by diluting 50 ml. of water to 1 l. with acetone. For duplicate experiments, 0.852 g. of ferrocenoyl chloride was dissolved in 100 ml. of solvent and the solution divided between two stoppered flasks, maintained at 25.0 ± 0.1°. At convenient intervals, 5 ml. aliquots were withdrawn, quenched by running into 50 ml. of pure cold acetone, then titrated immediately with 0.0128N sodium hydroxide, using pH 8.75 on a Beckman instrument (*vide supra*) for the end point. The total titers (26.72, 26.85 ml.) were in good agreement with the calculated (26.8 ml.). Typical data are given in Table I.

TABLE I

SOLVOLYSIS OF FERROCENOYL CHLORIDE IN 95% AQUEOUS ACETONE, 25.0°

t, Min.	Ml. of 0.0128N Base/5 Ml. Aliquot	$k_1 \times 10^{-5}$, sec.$^{-1}$
0[a]	4.12	...
28	7.27	8.88
42	8.86	9.31
67	10.92	8.87
90	12.48	8.59
126	15.05	8.85
252	20.35	8.39
end	26.72	...
	Av. $k_1 = 8.81 \pm 0.22 \times 10^{-5}$ sec.$^{-1}$	

[a] Zero time is taken as time first aliquot was removed.

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(14) Microanalyses by Spang Microanalytical Laboratory, Ann Arbor, Mich., and Clark Microanalytical Laboratory, Urbana, Ill.

(15) K. L. Rinehart, Jr., K. L. Motz and S. Moon, *J. Am. Chem. Soc.*, **79**, 2749 (1957).

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Benzhydryl Ethers of N-2-Hydroxyethyl-O,N-dialkylhydroxylamines

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The discovery that diphenhydramine, N-2-diphenylmethoxyethyl-N,N-dimethylamine hydrochloride, $(C_6H_5)_2CHO\text{-}CH_2CH_2N(CH_3)_2\cdot HCl$ is a useful antihistaminic drug with a high incidence of sedation in full therapeutic doses led to an extensive study of this amine and related compounds.[1]

Utilizing methods similar to those used in the synthesis of the corresponding amines,[1b,c] namely, the interaction of benzhydryl bromide and N-2-hydroxyethyl-O,N-dialkylhydroxylamines in presence of potassium carbonate according to the equation

$$(C_6H_5)_2CHBr + HOCH_2CH_2N(R)OR \xrightarrow{K_2CO_3} (C_6H_5)_2CHO\text{—}CH_2CH_2N(R)OR$$

two N-2-diphenylmethoxyethyl-O,N-dialkylhydroxylamines have been prepared.

Some of the pharmacological properties of the following compounds have been determined by Dr. C. A. Stone of the Merck Institute for Thera-

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