tion. The dominant factor leading to the production of II rather than I may be the greater stability of dimedon as the enol rather than the keto form.[10] Thus II with the preferred cyclohexenone ring is the observed product.

Experimental[11]

The Disodium Salt of the Dimedon Formaldehyde Derivative.—This and subsequent procedures were essentially those of Radulescu and Georgescu.[1,2] A mixture of sodium ethoxide (1.00 g of sodium, 0.0435 g.-atom) and the dimedon formaldehyde[12] derivative (5.80 g., 0.0199 mole) in 100 ml. of absolute ethanol was stirred at room temperature for 1.5 hr. affording a finely divided white crystalline precipitate. After filtration and washing with ether and ethanol, the solid was dried under vacuum for 12 hr. and weighed 6.35 g. (95%). The n.m.r. spectrum in D_2O showed three peaks at δ 0.90, 2.05, and 2.97 in the ratio 12:8:2.

Spiro[4-keto-6,6-dimethyltetrahydrobenzofuran-2(5,7,H)-1′-4′,4′-dimethylcyclohexane-2,6-dione](II).—To a suspension of the disodium salt of the dimedon–formaldehyde adduct (4.81 g., 0.0143 mole) in 80 ml. of anhydrous ether was added dropwise with stirring at room temperature during 2 hr. a solution of iodine (3.64 g., 0.0143 mole) in 80 ml. of ether. The deep brown mixture was stirred for 0.5 hr. and filtered; the precipitate was washed with sodium thiosulfate solution and water and dried. The brown solid was then dissolved in 40 ml. of chloroform and successively washed with aqueous sodium thiosulfate and water. After drying ($MgSO_4$) the solvent was evaporated *in vacuo* leaving a yellow-white solid: 3.72 g. (90%); m.p. 207–209°; $\nu_{max}^{CHCl_3}$ 1644, 1722, and 1752 cm.$^{-1}$; ν_{max}^{KBr} 1633, 1713, and 1748 cm.$^{-1}$. Recrystallization from ethanol afforded 2.91 g. (70%), m.p. 211–212°, λ_{max}^{EtOH} 267 mμ (ϵ 11800). The infrared spectra of the crude and recrystallized solids were identical.

Anal. Calcd. for $C_{17}H_{22}O_4$: C, 70.32; H, 7.64. Found: C, 70.47; H, 7.62.

The preparation of II-d_2, m.p. 210–211°, was carried out as above employing formaldehyde-d_2 which was obtained by pyrolysis of Eμ-polyoxymethylene-d_2 (Tracerlab, Waltham, Mass.).

Basic Cleavage of II.—To a solution of II (0.324 g., 1.12 mmoles) in 15 ml. of dioxane was added dropwise with stirring at room temperature 35.0 ml. of 0.0314 *N* sodium hydroxide (1.10 mmoles). After stirring 4 hr., the mixture was then acidified with 0.55 ml. of 2 *N* hydrochloric acid and extracted with methylene chloride; the extracts were washed with water and dried (Na_2SO_4); and the solvent was removed at reduced pressure leaving a yellowish white oil (0.316 g.). Crystallization was effected by dissolution in ethyl ether followed by addition of petroleum ether. Several recrystallizations from ethyl ether gave a solid with melting point 98–100°; λ_{max}^{EtOH} 269 mμ (ϵ 13,900); ν_{max}^{KBr} 1726 and 1611 cm.$^{-1}$; $\nu_{max}^{CHCl_3}$ 1637, 1708 and 1725 cm.$^{-1}$.

Dimedon Derivative of Chloroacetaldehyde.—A mixture of dimedon (3.02 g., 0.0215 mole), chloroacetaldehyde diethylacetal (1.62 g., 0.0106 mole), 15 ml. of ethanol, and 25 of ml. water was heated at reflux for 5 hr. After standing overnight the solution deposited a white-yellow solid which was filtered and washed with water. The dried material weighed 0.915 g., m.p. 211–221°. The filtrate deposited an additional 0.277 g. Crystallization of the combined solids (ethanol–acetone) yielded 0.490 g. (8%): m.p. 221–224° (lit.[4] m.p. 237.5°); λ_{max}^{EtOH} 268 mμ (ϵ 24,000)[13]; $\lambda_{max}^{CHCl_3}$ 1613, 1703 (weak), and 1735 (weak) cm.$^{-1}$; ν_{max}^{KBr} 1592, 1629, and 1637 cm.$^{-1}$. The n.m.r. spectrum (dimethyl-d_6 sulfoxide) revealed two methyl peaks at δ 0.98 and 1.07, a dimedon methylene peak at 2.22, and cyclohexenone methylene peaks at 2.29 and 2.05 with the latter a doublet (J = 2 c.p.s.) presumably due to coupling with the lone proton of the dihydrofuran ring; the dihydrofuran methylene is a complex multiplet centered at 4.50 and the single dihydrofuran proton is a multiplet centered at 4.20. A peak due to the hydroxyl proton of the dimedon moiety was not seen.[14]

Anal. Calcd. for $C_{18}H_{24}O_4$: C, 71.02; H, 7.95. Found: C, 71.34; H, 8.06.

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[10] Dimedon in aqueous solution has been found to be 95% enolic by G. Schwarzenbach and E. Felder, *Helv. Chim. Acta*, **27**, 1044 (1944).

[11] Melting points were obtained on a Kofler hot stage and are corrected. Carbon–hydrogen analyses were performed by Micro-Tech Laboratories, Skokie, Ill. Infrared spectra were determined with a Beckman IR-7 spectrophotometer, ultraviolet spectra with a Cary Model 11 spectrophotometer, and n.m.r. spectra with a Varian A-60 spectrophotometer.

[12] Prepared by the method of R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th Ed., John Wiley and Sons, Inc., New York, N. Y., 1959, p. 220.

[13] For 2,5,5-trimethylcyclohexane-1,3-dione, λ_{max}^{EtOH} 264 mμ (ϵ 13,600); ref. 5.

[14] The n.m.r. spectrum of formaldehyde bismethone does not display an enolic hydrogen peak: R. F. Brown, *et al.*, *J. Org. Chem.*, **29**, 146 (1964).

A Convenient Synthesis of Some Haloferrocenes

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Haloferrocenes constitute intermediates of considerable value for the preparation of hydroxy-,[1a–e] amino-,[1a,c] azido-,[2] thio-,[3] and cyanoferrocenes,[1c] as well as biferrocenyls[4,5] and ferrocenyl Grignard reagents.[5] Of the halo derivatives, bromo- and iodoferrocenes were first prepared by Nesmeyanov, Perevalova, and Nesmeyanova in 1955 by the action of the free halogens on mono- and 1,1′-bischloromercuriferrocene.[6] Although relatively simple and direct, the procedure has not found wide application, since, with the possible exception of iodoferrocene, the yields of haloferrocenes obtained in these reactions were poor. In the intervening years, the chloro- and bromoferrocenes have become considerably more accessible through the reaction of cupric halides with ferrocenylboronic and ferrocenyl-1,1′-diboronic acids, a procedure first introduced and largely exploited by the Russian group.[1a,7]

Our interest in the haloferrocenes, in connection with studies related to the possible existence of ferrocynes, prompted us to re-examine the use of the readily accessible chloromercuriferrocenes as potential precursors of these substances. The purpose of the present report is to set forth a general procedure which accomplishes this aim, and which constitutes an attractive alternative method for the preparation of the mono- and disubstituted bromo- and iodoferrocenes.

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[1] (a) A. N. Nesmeyanov, V. A. Sazonova, and V. N. Drozd, *Ber.*, **93**, 2717 (1960); (b) A. N. Nesmeyanov and V. A. Sazonova, *Dokl. Akad. Nauk SSSR*, **129**, 1060 (1959); (c) *ibid.*, **130**, 1030 (1960); (d) *ibid.*, **133**, 126 (1960); (e) A. Nesmeyanov, V. A. Sazonova, and V. N. Drozd, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 45 (1962).

[2] A. N. Nesmeyanov, V. N. Drozd, and V. A. Sazonova, *Dokl. Akad. Nauk SSSR*, **150**, 321 (1963).

[3] M. D. Rausch, *J. Org. Chem.*, **26**, 3579 (1961).

[4] E. G. Perevalova and O. A. Nesmeyanova, *Dokl. Akad. Nauk SSSR*, **132**, 1093 (1960); M. D. Rausch, *J. Am. Chem. Soc.*, **82**, 2080 (1960); M. D. Rausch, *J. Org. Chem.*, **26**, 1802 (1962); S. J. Goldberg and R. L. Matteson, *ibid.*, **29**, 323 (1964).

[5] H. Shechter and J. F. Helling, *ibid.*, **26**, 1034 (1961).

[6] A. N. Nesmeyanov, E. G. Perevalova, and O. A. Nesmeyanova, *Dokl. Akad. Nauk SSSR*, **100**, 1099 (1955).

[7] A. N. Nesmeyanov, V. A. Sazonova, and V. N. Drozd, *ibid.*, **126**, 1004 (1959); **131**, 1088 (1960).

We have found the chloromercuriferrocenes[8] are readily transformed to haloferrocenes by treatment with positive halogen reagents in polar media. Thus, bromoferrocene is formed in 57% yield when chloromercuriferrocene is treated with N-bromosuccinimide in dimethylformamide solution, and 1,1′-bischloromercuriferrocene is converted to 1,1′-dibromoferrocene in 47% yield under similar reaction conditions. The absence of other ferrocene derivatives in the crude reaction mixture makes isolation of the haloferrocenes especially convenient. Although comparable yields of bromoferrocene may be obtained from the reaction of chloromercuriferrocene with N-bromosuccinimide in methylene chloride, with pyridinium bromide perbromide, or with N-bromoacetamide in dimethylformamide, the concomitant formation of ferrocene as well as bromomercuriferrocene and diferrocenylmercury makes these procedures somewhat less advantageous.

Iodoferrocene may similarly be prepared from chloromercuriferrocene, in 85% yield, by treatment with N-iodosuccinimide in methylene chloride solution, while the more insoluble 1,1′-bischloromercuriferrocene is converted in dimethylformamide solution to 1,1′-diiodoferrocene in 42% yield.

These procedures appear to be confined in application to the preparation of bromo- and iodoferrocenes, since several attempts to employ them for the synthesis of chloroferrocenes were unsuccessful.

In one experiment, the direct conversion of ferrocene to 1,1′-dibromoferrocene, without isolation of the intermediate chloromercuri derivative, was shown to be feasible, but the practicability of this procedures was not further investigated.

Experimental

Halomercuriferrocenes.—A solution of 78.7 g. (0.25 mole) of mercuric acetate in 750 ml. of absolute methanol was added dropwise to a stirred solution of 93 g. (0.50 mole) of ferrocene in 500 ml. of dry benzene. The reaction was continued in a nitrogen atmosphere at room temperature for 10 hr., and then 22 g. (0.52 mole) of lithium chloride in 200 ml. of a 1:1 ethanol–water mixture was added dropwise. The resulting orange suspension was stirred at room temperature for 2 hr., then heated at reflux for 1 hr., and was finally collected, placed in a Soxhlet, and extracted with methylene chloride. The residue remaining was recrystallized from dimethylformamide to give 22.7 g. of 1,1′-bischloromercuriferrocene (18%) as a fine yellow powder, m.p. >300°.

The methylene chloride extract was washed thoroughly with water and dried over magnesium sulfate. After removal of solvent, the solid residue was sublimed *in vacuo* to remove unchanged ferrocene. In this manner, 56.9 g. of ferrocene were recovered. The unsublimed portion gave, on recrystallization from methylene chloride–petroleum ether, 59.8 g. (73%) of chloromercuriferrocene as golden platelets, m.p. 196–198° dec. (lit.[8] m.p. 194–196°).

Bromoferrocene.—A solution of N-bromosuccinimide (1.15 g., 6.4 mmoles) in 100 ml. of dry, nitrogen-flushed dimethylformamide was added dropwise to a cold, stirred solution of chloromercuriferrocene (2.10 g., 5 mmoles) in 50 ml. of the same solvent. Reaction was continued at 0° in a nitrogen atmosphere for 3 hr., after which time 200 ml. of a 10% sodium thiosulfate solution was added, and the resulting dark solution was poured into 2 l. of cold water. The aqueous solution was extracted four times with 100-ml. portions of petroleum ether, and the combined organic extract was washed with water and dried over magnesium sulfate. Evaporation of solvent left an orange oil which was taken up in Skellysolve B and chromatographed on an alumina column (Fisher, activity 1). Evaporation of solvent from the single yellow band, which developed on elution with Skellysolve B, gave 0.81 g. of an orange oil, which solidified on cooling. The material was recrystallized from cold ethanol to give 0.75 g. (57%) of bromoferrocene as yellow plates, m.p. 31–32° (lit.[4] m.p. 30–31°).

Treatment of chloromercuriferrocene with an equivalent of N-bromosuccinimide in methylene chloride solution gave bromoferrocene in 50% yield together with ferrocene (5%), diferrocenylmercury (18%), and bromomercuriferrocene (4%), m.p. 201.5–203°. This latter substance was identical by mixture melting point determination with the product obtained on treatment of acetoxymercuriferrocene with potassium bromide.

Anal. Calcd. for $C_{10}H_9BrFeHg$: C, 25.79; H, 1.95. Found: C, 25.97; H, 1.87.

With chloromercuriferrocene and pyridinium bromide perbromide, in dimethylformamide solution under similar reaction conditions, ferrocene and bromoferrocene were formed in 42 and 58% yield, respectively. N-bromoacetamide in dimethylformamide solution gave 48% of bromoferrocene and 5% of ferrocene.

1,1′-Dibromoferrocene.—Following the experimental procedure given for the preparation of bromoferrocene, bischloromercuriferrocene, on treatment with N-bromosuccinimide in dimethylformamide, gave 1,1′-dibromoferrocene, m.p. 51.5–52° (lit.[3] m.p. 50–51°), in 47% yield.

Iodoferrocene.—A solution of N-iodosuccinimide (1.2 g., 5.1 mmoles) in 100 ml. of dry methylene chloride, previously flushed with nitrogen, was added dropwise to a stirred suspension of chloromercuriferrocene (2.10 g., 5 mmoles) in 75 ml. of methylene chloride cooled in an ice bath, and maintained in a nitrogen atmosphere. After allowing the reaction to continue for 12 hr., 50 ml. of an aqueous 10% sodium bisulfite solution was added, followed by an equal volume of a 10% sodium carbonate solution. The organic layer was separated and the aqueous solution was extracted thrice with 50-ml. portions of methylene chloride. The combined organic extract was washed successively with 10% sodium carbonate solution and water, and dried over magnesium sulfate. Removal of solvent left an oil which was taken up in a small volume of Skellysolve B and chromatographed on alumina. On elution with this solvent two bands developed. The first gave 1.32 g. (85%) of iodoferrocene, m.p. 45.5–46° (lit.[4] m.p. 44–45°). The second band, eluted with methylene chloride–Skellysolve B, gave 0.34 g. of golden brown needles, m.p. 174–175.5°, after one recrystallization from this solvent pair. This compound was identical by mixture melting point with iodomercuriferrocene, prepared by treatment of acetoxymercuriferrocene with potassium iodide.

Anal. Calcd. for $C_{10}H_9FeHgI$: C, 23.43; H, 1.77. Found: C, 23.61; H, 1.97.

1,1′-Diiodoferrocene.—This substance was isolated as a red-brown oil, in 42% yield, on treatment of 1,1′-bischloromercuriferrocene with N-iodosuccinimide in dimethylformamide solution following the general procedure employed for the preparation of iodoferrocene.

Direct Conversion of Ferrocene to 1,1′-Dibromoferrocene.—A solution of 14 g. of mercuric acetate (0.044 mole) in 150 ml. of methanol was added to 3.72 g. of ferrocene (0.02 mole) dissolved in 100 ml. of dry benzene. The reaction was allowed to continue at room temperature under nitrogen for a period of 12 hr. At the end of this period 6.75 g. of sodium iodide (0.045 mole) in 100 ml. of methanol was added and the solution was stirred at room temperature for an additional 3 hr., and then finally heated at reflux for 1 hr. The mixture was cooled to 0°, 8.95 g. of N-bromosuccinimide (0.05 mole) in 150 ml. of dry methylene chloride was added slowly, and the resulting green solution was stirred at 0° for 6 hr. Aqueous sodium bisulfite solution (10%, 200 ml.) was added, the organic layer was separated, and the aqueous phase was extracted several times with methylene chloride. The combined organic extract was washed twice with 100-ml. portions of 10% sodium carbonate solution, then with water to neutrality, and finally dried over magnesium sulfate. Evaporation of the solvent left a brown oil, which on vapor phase fractometric analysis, employing a 20% QF column on Chromosorb W, indicated that it was a mixture of ferrocene and 1,1′-dibromoferrocene in a ratio of 1:9.6. No monobromoferrocene was evident in the mixture.

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[8] A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya, and O. A. Nesmeyanova, *Dokl. Akad. Nauk SSSR*, **97**, 459 (1954); M. D. Rausch, M. Vogel, and H. Rosenberg, *J. Org. Chem.*, **22**, 960 (1957).