Even-Numbered *n*-Acyl and *n*-Alkyl Ferrocenes

Edwin L. DeYoung[1]

Received August 1, 1960

The Friedel-Crafts acylation with acid chlorides and aluminum chloride was one of the first reactions to be carried out with ferrocene.[2] About a dozen each of *n*-acyl- and *n*-alkyl ferrocenes with various chain lengths have since been prepared.[3-5]

TABLE I

Properties of Ferrocenes

Substituent	Color	Yield	B.P. or Solvent	M.P.[a] or n_D^{20}	Calcd. C	Calcd. H	Found C	Found H
				Acyl Substituted				
1-Ethanoyl-[b]	Red	—	Methanol	81–83°	—	—	—	—
1-Butanoyl-	Red	72%	144–146°/1.5 mm.	1.6073	65.6	6.3	65.8	6.2
1-Hexanoyl-	Orange	88%	161–163°/1.5 mm.	1.5843	67.6	7.0	67.4	7.0
1-Octanoyl-	Orange	91%	Methanol	26–27°	69.2	7.7	69.1	7.4
1-Decanoyl-	Red	84%	203–204°/1.6 mm.	1.5513	70.6	8.2	70.8	8.2
1-Dodecanoyl-	Orange	79%	Methanol	36–37°	71.7	8.6	71.7	8.5
1,1′-Dihexanoyl-	Orange	67%	Methanol	38–39°	69.1	7.8	68.8	7.7
				Alkyl Substituted				
1-Ethyl-[c]	Red	67%	107–108°/5 mm.	1.6011	—	—	—	—
1-Butyl-[c]	Red	7%	180°/3/5 mm.	1.5701	—	—	—	—
1-Hexyl-	Orange	93%	139–40°/1.5 mm.	1.5602	71.1	8.1	71.2	8.1
1-Octyl-	Orange	71%	154–155°/1.0 mm.	1.5490	72.5	8.7	72.6	8.7
1-Decyl-	Orange	90%	183–184°/1.4 mm.	1.5399	73.6	9.2	73.9	9.3
1-Dodecyl-	Yellow	96%	Methanol	35–36°	74.6	9.6	74.6	9.6
1,1′-Dihexyl-	Orange	86%	189°/1.6 mm.	1.5320	74.6	9.6	74.8	9.9

[a] Uncorrected. [b] From A. N. Nesmeyanov, E. G. Perevalova, R. V. Goloonya, and O. A. Nesmeyanova, *Doklady Akad. Nauk S.S.S.R.*, 97, 459 (1954). [c] From Ref. 3.

To complete an even-numbered series of *n*-acyl and *n*-alkyl ferrocenes, eleven new ferrocenes through dodecyl were synthesized in good yields by the methods of Rausch.[5] After purification by either distillation through a 60 × 8-mm. spinning-band column or recrystallization from methanol, the products were red to yellow liquids and low-melting solids. Table I lists the measured properties.

All of the acyl derivatives showed carbonyl infrared absorption at about 6 μ. The monosubstituted ferrocenes showed infrared absorption bands at 9 to 10 μ.[6]

Research & Development Laboratory
Standard Oil Co.
Whiting, Ind.

---

[1] Present address: RB&P Chemical & Supply Co., 1640 N. 31st St., Milwaukee 8, Wis.

[2] R. B. Woodward, M. Rosenblum, and M. C. Whiting, *J. Am. Chem. Soc.*, 74, 3458 (1952).

[3] K. L. Rinehart, R. J. Corby, and P. E. Sokol, *J. Am. Chem. Soc.*, 79, 3420 (1957).

[4] A. N. Nesmeyanov and N. S. Kochetkova, *Doklady Akad. Nauk S.S.S.R.*, 109, 543 (1956).

[5] M. D. Rausch, M. Vogel, and H. Rosenberg, *J. Org. Chem.*, 22, 1016 (1957).

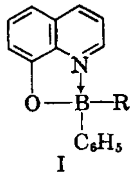
[6] M. Rosenblum, *Chem. & Ind.*, 953 (1958).

8-Quinolinol Derivatives of Borinic Acids

James E. Douglass

Received August 23, 1960

In 1955, Letsinger and Skoog reported that diarylborinic acids react with ethanolamine to form crystalline products.[1] Attempts in this laboratory to prepare such derivatives of several aralkylborinic acids were not uniformly successful, and thus attention was turned to the problem of finding a suitable reagent for making derivatives of these acids. As ethanolamine and 8-quinolinol have in common the critical reactive grouping, HO—C—C—N=, the latter was considered as a possible reagent, and indeed it was found to react with both diaryl- and aralkylborinic acids to form yellow crystalline products (I) which are readily isolated and characterized.[2] Each of the reported compounds (Table I) shows an intense green fluorescence under ultraviolet light.



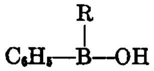
I

---

[1] R. L. Letsinger and I. Skoog, *J. Am. Chem. Soc.*, 77, 2491 (1955).

[2] R. Neu [*Z. anal. Chem.*, 142, 335 (1954)], in an article describing the use of diphenylborinic acid as a reagent for identifying certain 5-hydroxyflavones, mentioned that this acid also reacts with 8-quinolinol.

TABLE I

8-QUINOLINOL DERIVATIVES OF 

$C_6H_5—\overset{\overset{R}{|}}{B}—OH$

R	M.P.[a]	Formula	Carbon[b]		Hydrogen[b]		Boron[c]		Neut. Equiv.[d]	
			Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
C_2H_5	152–153	$C_{17}H_{16}BNO$	78.21	78.09	6.17	6.14	4.14	4.10	261	262
i-C_3H_7	87	$C_{18}H_{18}BNO$	78.56	79.23	6.60	6.58	3.93	3.88	275	275
t-C_4H_9	108–109	$C_{19}H_{20}BNO$	78.91	78.65	6.97	7.29	3.74	3.70	289	291
$C_6H_5CH_2$[e]	133–133.5	$C_{22}H_{18}BNO$	81.75	81.27	5.62	5.66	3.35	3.34	323	325
C_6H_5	204–205[f]	$C_{21}H_{16}BNO$	81.47	81.84	5.22	5.30	3.50	3.48	309	308

[a] Melting points are corrected. [b] Analyses by Drs. Weiler and Straus, Oxford, England. [c] Boron analyses by the method described by J. M. Thoburn, Dissertation, Northwestern University, 1954. [d] By titration with perchloric acid in glacial acetic acid; sample dissolved in acetic acid–acetic anhydride (4 to 1). [e] This compound does form a crystalline aminoethyl ester, m.p. 211–213°; reported[5] m.p. 208–212.5°. [f] Reported[2] m.p. 203°.

The 8-quinolinol derivatives are stable in air (no indication of decomposition over a period of several months) and resist hydrolysis in neutral aqueous ethanol (as judged by the persistence of strong fluorescence for several weeks).

Each of these compounds has an absorption maximum in chloroform in the region 397–405 mμ (ε 2700–3100). These data, joined with those of Moeller and Cohen, who found that the 8-quinolinol chelates aluminum, gallium, indium, and thallium have λ_{max} in the same region (390–401 mμ),[3] indicate that absorption near 400 mμ is characteristic of the 8-quinolinol chelates of all the Group III-A elements.

EXPERIMENTAL

Boronic acids. The previously reported ethylphenylborinic acid[4] and benzylphenylborinic acid[5] were prepared as described by Torssell[4]; the previously unreported isopropylphenylborinic acid was prepared similarly. Diphenylborinic acid was prepared by the method of Povlock and Lippincott.[6]

t-Butylphenylborinic acid. As conventional methods for the preparation of unsymmetrically substituted borinic acids[7] failed to give detectable amounts of this acid, its synthesis will be described in some detail.

A solution of t-butylmagnesium chloride (0.1 mole) in 45 ml. of dry tetrahydrofuran was added dropwise to a well stirred solution of 10.4 g. (0.10 mole) of benzeneboronic anhydride (triphenylboroxin)[8] in 150 ml. of dry tetrahydrofuran cooled to 0° and under an atmosphere of dry nitrogen. After the addition was complete (about 30 min.), stirring at 0° was continued for 1 hr. The mixture was then hydrolyzed with 100 ml. of 3M hydrochloric acid, the two layers were separated, and the solvent was evaporated under reduced pressure from the organic layer to give 2.6 g. (16%) of crude product.[9]

8-Quinolinol derivatives. An equivalent amount of 8-quinolinol (in a 20% solution of 95% alcohol) was added to a solution of the crude borinic acid (about 0.5 g. of acid per 10 ml. of 95% alcohol); in most cases the product crystallized immediately and in high yield. The crude derivatives were recrystallized from 95% alcohol, with the exception of the diphenyl derivative which was more conveniently recrystallized from methanol-tetrahydrofuran (3 to 1).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF KENTUCKY
LEXINGTON, KY.

---

(3) T. Moeller and A. J. Cohen, *J. Am. Chem. Soc.*, **72**, 3546 (1950).

(4) K. Torssell, *Acta Chem. Scand.*, **9**, 242 (1955).

(5) D. R. Nielsen, W. E. McEwen, and C. A. Vanderwerf, *Chem. and Ind.*, 1069 (1957).

(6) T. P. Povlock and W. T. Lippincott, *J. Am. Chem. Soc.*, **80**, 5409 (1958).

(7) M. F. Lappert, *Chem. Revs.*, **56**, 1015 (1956).

(8) R. M. Washburn, E. Levens, C. F. Albright, and F. A. Billig, *Org. Syntheses*, **39**, 3 (1959).

(9) For a very similar approach to the preparation of borinic acids, see J. M. Davidson and C. M. French, *J. Chem. Soc.*, 191 (1960).

5-Substituted Derivatives of 3-Methylpyrrolidinone-2

GEORGE H. COCOLAS,[1] SOUREN AVAKIAN,[2] and GUSTAV J. MARTIN[3]

Received August 18, 1960

In the light of a recent investigation[4] in which is described a concomitant addition and cyclization between acrylic esters and diethyl acetamidomalonate to form 2-pyrrolidinone derivatives, it became of interest to prepare various carboxylic acid derivatives utilizing one or both of the carboxyl groups of the pyrrolidinone prepared from diethyl acetamidomalonate and ethyl methacrylate as indicated in Fig. 1.

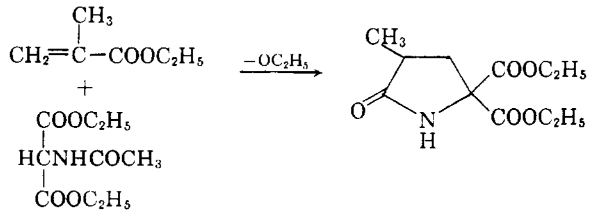


Figure 1

---

(1) Present address: School of Pharmacy, University of North Carolina, Chapel Hill, N. C.

(2) Present address: Wampole Laboratories, Stamford, Conn.

(3) Present address: W. H. Rorer, Inc., Philadelphia, Pa.

(4) G. H. Cocolas and W. H. Hartung, *J. Am. Chem. Soc.*, **79**, 5023 (1958).