272 g. (2.00 moles) of *d*-limonene during 1.5 hr. The mixture was heated for 0.5 hr. The product (250.5 g., b.p. 170–173°) consisted entirely of *p*-cymene; the yield was 92.1%.

(*f*) To a solution of I prepared from 1.74 g. (0.25 mole) of lithium and 375 ml. of ethylenediamine, there was added 136 g. (1.00 mole) of *d*-limonene. The mixture was heated for 1 hr.; no gas was evolved. The product consisted entirely of *d*-limonene (124.8 g., b.p. 169–172°; 91.7% recovery).

4-Vinylcyclohexene. To a solution of I prepared from 8.33 g. (1.20 moles) of lithium and 187 ml. of ethylenediamine there was added during 0.5 hr. 21.6 g. (0.20 mole) of 4-vinylcyclohexene; gas was evolved vigorously. Heating was continued for another 2.75 hr.; during this time gas evolution continued at the rate of about 1 l. per hr. The product consisted entirely of ethylbenzene; yield 86.8%.

α-Phellandrene. (*a*) To a solution of I prepared from 8.33 g. (1.20 moles) of lithium and 187 ml. of ethylenediamine, there was added 27.2 g. (0.20 mole) of crude 2-methyl-5-isopropyl-1,3-cyclohexadiene (α-phellandrene, containing about 20% *p*-cymene). Gas was evolved vigorously. The mixture was heated for 1 hr. The product consisted entirely of *p*-cymene; the yield (corrected for *p*-cymene in the starting material) was 73.7%.

(*b*) To a solution of $H_2NCH_2CH_2NHNa$ prepared by dissolving 13.8 g. (0.60 mole) of sodium shot in 187 ml. of ethylenediamine, there was added 27.2 g. (0.20 mole) of crude α-phellandrene. The mixture was then heated for 4.5 hr. The product consisted entirely of *p*-cymene; the yield (corrected for *p*-cymene in the starting material) was 76.1%. There was also obtained a white solid, insoluble in both the aqueous and organic phases.

(*c*) A mixture of 27.2 g. (0.20 mole) of crude α-phellandrene and 190 ml. of ethylenediamine was heated at 100° for 1 hr. The product, obtained in 87.2% yield, consisted of unchanged α-phellandrene.

(*d*) To a solution of $H_2NCH_2CH_2CH_2NHLi$, prepared from 2.67 g. (0.39 mole) of lithium and 60 ml. of trimethylenediamine, there was added 6.73 g. (0.064 mole) of crude α-phellandrene. The mixture was stirred and heated for 2 hr. at 112°. The product (5.33 g.) contained about 80% of *p*-cymene and 7.5% of α-phellandrene. The yield of *p*-cymene (corrected for *p*-cymene in the starting material) was 40%.

Limonene and 4-methylcyclohexene. To a solution of I prepared from 8.33 g. (1.20 moles) of lithium and 375 ml. of ethylenediamine, there was added a mixture of 54.4 g. (0.40 mole) of *d*-limonene and 76.8 g. (0.80 mole) of 4-methylcyclohexene. Gas was evolved vigorously during the addition. The mixture was heated for 4 hr. The products and yields (mass spectrometric analyses) were: *d*-limonene, 2.5%; *p*-cymene, 87.8%; 4-methylcyclohexene, 24.1%; 1-methylcyclohexene, 63.4%. Methylcyclohexane was probably absent, but may have been formed in a yield not exceeding 0.1%.

Acknowledgment. We wish to thank John A. Queiser, Gorton Wood, and Janet L. Shultz for infrared and mass spectrometric analyses.

BRUCETON, PA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE VIRGINIA POLYTECHNIC INSTITUTE]

Synthesis of Some Trichloromethyl-2-benzylphenylcarbinols[1,2]

FRANK A. VINGIELLO, GEORGE J. BUESE, AND PETER E. NEWALLIS

Received January 24, 1958

A series of new trichloromethyl-2-benzylphenylcarbinols, which can be considered as synthetic precursors of the DDT-type molecule, have been prepared by several reaction sequences. From the toxicity data against German cockroaches it would appear that the compounds tested have little if any insecticidal activity. Many intermediates were also tested.

In connection with our studies on the mechanism of insecticidal action of DDT, 2,2,2-trichloro-1,1-bis(*p*-chlorophenyl)ethane, we have synthesized a series of trichloromethyl-2-benzylphenylcarbinols (IVa–IVd) which are synthetic precursors of the DDT-type molecule. Since many carbinols[3] of diversified structure have been synthesized and tested for insecticidal activity, we thought compounds of the type IV would be especially interesting for several reasons.

First, Fisher-Hirschfelder-Taylor models of compounds of the type IV indicate that free rotation of one phenyl group is not possible and that free rotation of the other phenyl group is severely hindered so that the trihedralized[4] configuration may be realized. Rogers, Brown, Rasmussen, and Heal[4] have pointed out the importance of a trihedralized *p,p′*-dichlorophenyl moiety in explaining the toxicity of DDT.

Second, compound IVd has other important structural features in common with DDT; namely, a trichloromethyl group and two *p*-chlorophenyl groups whose chlorine atoms are about as distant as those in DDT.

Third, compounds of the type IV are known[3] to exhibit narrow-spectrum insecticidal properties and are thus ideally suited for activity-structure studies with certain insects.

Ketones Ia and Ib are prepared in excellent yield

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(1) Presented before the Division of Organic Chemistry at the 132nd Meeting of the American Chemical Society, New York, N. Y., September 1957.

(2) This paper has been abstracted from the master's thesis of G. J. Buese and the doctorate thesis of P. E. Newallis presented to the Virginia Polytechnic Institute in 1951 and 1957, respectively.

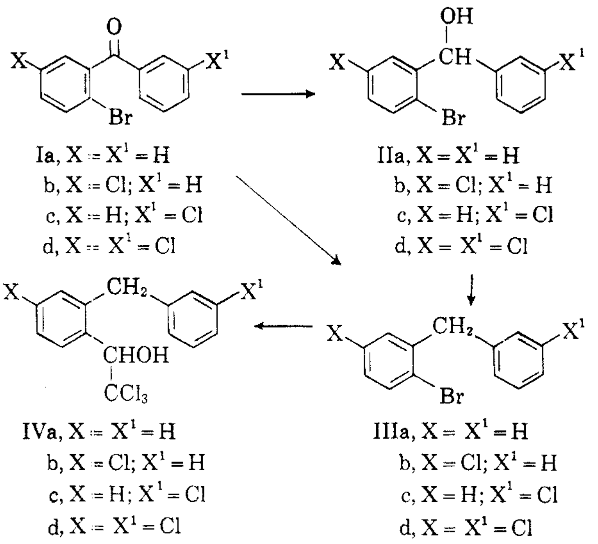
(3) R. C. Blinn, F. A. Gunther, and R. L. Metcalf, *J. Am. Chem. Soc.*, **76**, 37 (1954) and references listed there.

(4) E. F. Rogers, H. D. Brown, I. M. Rasmussen, and R. E. Heal, *J. Am. Chem. Soc.*, **75**, 2991 (1953). According to these authors the concept of trihedralization may be generalized as follows: "In compounds having one carbon atom two or three planar groups and a group sufficiently large to hinder the rotation of the planar groups, although capable of rotation itself, the planar groups will tend to positions corresponding to the sides of a trihedral angle."

by the aluminum chloride-catalyzed reaction of 2-bromobenzoyl chloride and 2-bromo-5-chlorobenzoyl chloride respectively on benzene. Ketones Ic and Id were prepared in good yield by allowing the cadmium reagent of 3-bromochlorobenzene to react with 2-bromobenzoyl chloride and 2-bromo-5-chlorobenzoyl chloride, respectively.

Reduction of these ketones, Ia–Id, with sodium borohydride[5] processed smoothly and in good yield to give the corresponding carbinols, IIa–IId. Carbinols IIa and IIc were also prepared in excellent yield by allowing 2-bromobenzaldehyde to react with the appropriate Grignard reagent.

The carbinols, IIa–IId, could be reduced to the corresponding diphenylmethanes using red phosphorus and iodine in glacial acetic acid. Although the ketones, Ia–Id, could be reduced directly to the diphenylmethanes using the same reagent, the results were erratic[6] and in our hands the two step reduction proved more satisfactory.



The addition of freshly distilled chloral to a Grignard reagent[7] prepared from IIIa, IIIb, IIIc, and IIId gave the corresponding trichloromethyl-2-benzylphenylcarbinols. These carbinols tend to decompose even when distilled at low pressures. Only IVa and IVb could be prepared analytically pure. By using a variety of methods all four carbinols could be converted to their acetates which could be purified to analytical purity.

Entomological testing[8] of the new compounds was undertaken by Dr. James M. Grayson and his staff at the Virginia Polytechnic Institute Entomology Department using standard methods of assay. From the toxicity data against German cockroaches it would appear that the new compounds have little if any insecticidal activity.

EXPERIMENTAL[9,10]

2-Bromo-5-chlorobenzoic acid. A mixture of 90 g. of cupric sulfate pentahydrate, 75 g. of sodium bromide, 50 g. of fine copper turnings, and 400 ml. of 48% hydrobromic acid was boiled vigorously for 3 hr. This hot solution was filtered through glass wool into a boiling solution of 150 g. of 2-amino-5-chlorobenzoic acid,[11] 600 ml. of 48% hydrobromic acid and 5000 ml. of water. The solution was stirred continuously during this addition and was kept boiling. A solution of 150 g. of sodium nitrite in 700 ml. of water was then added slowly, with stirring, to the hot acid solution. After addition was complete the solution was allowed to cool to room temperature and was finally cooled in an ice-salt bath. The solid which formed was filtered and recrystallized from water using a little charcoal. The fine white crystals were dried in a vacuum desiccator; yield 155 g. (75%), m.p. 148–149° (lit.,[12] m.p. 148–149°).

2-Bromo-5-chlorobenzoyl chloride. A mixture of 20 g. of the above acid and 19 g. of phosphorus pentachloride was heated in an oil bath maintained at 140° for 0.5 hr. The low boiling material was distilled under slightly reduced pressure and the residue was fractionated at 22 mm.; yield 20 g. (91%), b.p. 147–149°, m.p. 34–35° (lit.,[12] b.p. 146–147° (23 mm.), m.p. 34–35° no yield reported).

2-Bromo-5-chlorobenzophenone (Ib). A mixture of 25 g. of aluminum chloride and 180 ml. of dry benzene was cooled in an ice bath and stirred. A few drops of a solution of 39 g. of 2-bromo-5-chlorobenzoyl chloride in about 70 ml. of benzene was added immediately to prevent the benzene from freezing and then the remainder of the solution was added dropwise. The mixture was stirred overnight and allowed to warm to room temperature. The reaction mixture was then heated under reflux for three hours, cooled in an ice bath and decomposed with ice and 120 ml. of concentrated hydrochloric acid. The acid layer was separated and extracted with fresh benzene. The benzene layers were combined, washed with water, then sodium carbonate solution and again with water. The benzene solution was concentrated and fractionated under reduced pressure; yield 42 g. (93%), b.p., 172–173° (1 mm.). On standing the oil solidified; m.p. 100.5–102°. An analytical sample was prepared by recrystallization from ethanol.

Anal. Calcd. for $C_{13}H_8BrClO$: C, 52.82; H, 2.73. Found: C, 52.66; H, 2.80.

2-Bromo-3'-chlorobenzophenone (Ic). A Grignard reagent was prepared in ether from 44 g. (0.23 mole) of 3-bromochlorobenzene, 5.2 g. (0.23 mole) of magnesium. The solu-

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(5) S. W. Chaikin and W. G. Brown, *J. Am. Chem. Soc.*, 71, 122 (1949).

(6) Difficulties in using red phosphorus and iodine have been encountered before; see for example, F. A. Vingiello, A. Bořkovec, and J. Shulman, *J. Am. Chem. Soc.*, **77**, 2320 (1955).

(7) H. L. Haller, P. D. Bartlett, N. L. Drake, M. S. Newman, S. J. Cristol, C. M. Eaker, R. A. Hayes, G. W. Kilmer, B. Magerlein, G. P. Mueller, A. Schneider, and W. Wheatley, *J. Am. Chem. Soc.*, **67**, 1591 (1945); see also ref. (3).

(8) Dr. James M. Grayson of the Entomology Department at the Virginia Polytechnic Institute was responsible for conducting the assays. We are grateful to him for this work.

(9) All melting points were taken on a Fisher-Johns melting point block and are uncorrected.

(10) All analyses were carried out by the Micro-Tech Laboratories, Skokie, Ill.

(11) Purchased from Distillation Products Industries, Rochester 3, N. Y.

(12) J. B. Cohen and H. S. Raper, *J. Chem. Soc.*, **85**, 1267 (1904) prepared this compound by the nitric acid oxidation of the chlorobromotoluene and by a Sandmeyer reaction which gave a discolored product. In neither case was the yield given.

tion was cooled and 42 g. (0.23 mole) of dry, finely ground cadmium chloride was added. The mixture was stirred for an hour at the end of which the Gilman color test[13] was negative. The ether was replaced with benzene and 50 g. (0.23 mole) of 2-bromobenzoyl chloride in 50 ml. of benzene was added to the boiling solution as rapidly as possible. The mixture was stirred and heated for an additional 40 min. and then cooled and poured into a mixture of ice and dilute sulfuric acid. The acid layer was separated and extracted with benzene. The benzene layers were combined, washed with water, then with sodium carbonate solution, again with water, and finally concentrated. The residue was fractionated; yield 41 g. (61%) b.p., 182–183° (3 mm.). Crystallization from ethanol gave white crystals, m.p. 34.5–36°.

Anal. Calcd. for $C_{13}H_8BrClO$: C, 52.82; H, 2.73. Found: C, 52.93; H, 2.95.

2-Bromo-5,3'-dichlorobenzophenone (Id) was prepared using substantially the procedure given above for preparing Ic with 2-bromo-5-chlorobenzoyl chloride being used in place of 2-bromobenzoyl chloride. The product (73%) distilled at 203-206° (3 mm.). This oil crystallized on standing and was recrystallized from ethanol giving white crystals, m.p. 75–76°.

Anal. Calcd. for $C_{13}H_7BrCl_2O$: C, 47.31; H, 2.14. Found: C, 47.30; H, 2.27.

2-Bromo-5-chlorobenzhydrol (IIb). A solution of 1.3 g. (0.03 mole) of sodium borohydride in 15 ml. of distilled water was added dropwise to a stirred suspension of 20 g. (0.07 mole) of 2-bromo-5-chlorobenzophenone in 100 ml. of methanol. The mixture was warmed in a water bath at 60° for 30 min. and allowed to stand at room temperature for an additional 30 min. The mixture was then decomposed with 10% hydrochloric acid and extracted with ether. The ether solutions were combined, washed with water, dried, and concentrated. The residue was fractionated; yield 16 g. (79%) b.p. 144–147° (1 mm.). Crystallization from 30–60° petroleum ether gave white crystals, m.p. 49–49.5°.

Anal. Calcd. for $C_{13}H_{10}BrClO$: C, 52.46; H, 3.39. Found: C, 52.36; H, 3.70.

2-Bromo-3'-chlorobenzhydrol (IIc). *A. Via* $NaBH_4$ reduction of ketone. IIc was prepared using substantially the same procedure given above for IIb. There was obtained from 2-bromo-3'-chlorobenzophenone 77% of product distilling at 144–146° (0.5 mm.).

B. Via Grignard reagent. A Grignard reagent was prepared in ether from 76 g. (0.39 mole) of 3-bromochlorobenzene and 9.5 g. (0.39 mole) of magnesium. A solution of 47 g. (0.26 mole) of 2-bromobenzaldehyde[14] in 100 ml. of ether was added dropwise with stirring in the usual way, this gave 59 g. (82%) of a clear viscous oil which distilled at 178-180° (2 mm.).

Anal. Calcd. for $C_{13}H_{10}BrClO$: C, 52.46; H, 3.39. Found: C, 52.56; H, 3.64.

2-Bromo-5,3'-dichlorobenzhydrol (IId). This compound was prepared by the $NaBH_4$ reduction of 2-bromo-5,3'-dichlorobenzophenone using essentially the procedure described for IIb. The product (75%) was obtained as a clear, colorless oil distilling at 166–168° (0.5 mm.). Crystallization from 30–60° petroleum ether gave white, poorly formed crystals, m.p. 92–93°. Recrystallization from a petroleum ether-methanol mixture gave crystals melting sharply at 93.5–94°.

Anal. Calcd. for $C_{13}H_9BrCl_2O$: C, 47.02; H, 2.73. Found: C, 47.00; H, 2.87.

2-Bromodiphenylmethane (IIIa).[15] Although several different methods were used[16] to prepare this compound, the method of Bradsher and Vingiello[17] proved most satisfactory.

2-Bromo-5-chlorodiphenylmethane (IIIb). A mixture of 33 g. of 2-bromo-5-chlorobenzophenone, 33 g. of red phosphorus and 33 ml. of that portion of 48% hydriodic acid which boiled over 122° (715 mm.) was stirred and heated under reflux for 44 hr. The mixture was cooled to room temperature, 50 ml. of water was added, and the phosphorus was filtered. The acid solution was neutralized with 10% sodium hydroxide solution and extracted with ether. The ether solutions were combined, washed with water, dried over anhydrous calcium sulfate, and concentrated. The residue was distilled; yield 23 g. (72%) b.p., 168–170° (3.5 mm.).

Anal. Calcd. for $C_{13}H_{10}BrCl$: C, 55.45; H, 3.58. Found: C, 55.30; H, 3.71.

2-Bromo-3'-chlorodiphenylmethane (IIIc). This compound was prepared by the reduction of 2-bromo-3'-chlorobenzophenone using substantially the procedure described for IIb. The product (64%) was obtained as an oil distilling at 144–146° (1 mm.).

Anal. Calcd. for $C_{13}H_{10}BrCl$: C, 55.45; H, 3.58. Found: C, 55.66; H, 3.85.

2-Bromo-5,3'-dichlorodiphenylmethane (IIId). This compound was prepared by the reduction of 2-bromo-5,3'-dichlorobenzophenone using substantially the procedure described for IIb. The product (63%) was obtained as an oil distilling at 151–156° (1 mm.).

Anal. Calcd. for $C_{13}H_9BrCl_2$: C, 49.40; H, 2.87. Found: C, 49.62; H, 2.91.

Trichloromethyl-2-benzylphenylcarbinol (IVa). A Grignard reagent was prepared in ether from 40 g. (0.16 mole) of 2-bromodiphenylmethane and 3.8 g. (0.16 mole) of magnesium. The solution was heated under reflux and 26 g. (0.18 mole) of freshly distilled chloral in 50 ml. of dry ether was added rapidly.[18] The solution was then cooled and decomposed with a saturated solution of ammonium chloride. The ether was separated and the "cake" was washed with ether. The combined ether solutions were washed with water, 10% sulfuric acid, again with water, dried, and concentrated. An extremely viscous oil was obtained which distilled at 174–176° (1 mm.)[19]; yield 31 g. (61%).

Anal. Calcd. for $C_{15}H_{13}Cl_3O$: C, 57.08; H, 4.15. Found: C, 57.20; H, 4.07.

Acetate of trichloromethyl-2-benzylphenylcarbinol. A mixture of 1 g. of the above carbinol (IVa), 10 ml. of acetic anhydride, and 0.5 ml. of trifluoroacetate acid was heated under reflux for 4 hr. The solution was cooled, poured into an ice-water mixture and the fine, tan solid was filtered. Recrystallization from ethanol (Norite) gave 1 g. (84%) of white plates, m.p. 120–122°. Further recrystallizations from ethanol raised the melting point to 122–123°.[20]

Anal. Calcd. for $C_{17}H_{15}Cl_3O_2$: C, 57.10; H, 4.23; Cl, 29.74. Found: C, 57.10; H, 4.29; Cl, 29.90.

Trichloromethyl-2-benzyl-4-chlorophenylcarbinol (IVb). This compound was prepared by allowing the Grignard reagent of 2-bromo-5-chlorodiphenylmethane to react with chloral

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[13] H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

[14] Prepared according to R. Adams and E. Vollweiler, *J. Am. Chem. Soc.*, **40**, 1737 (1918).

[15] All of the diphenylmethanes (IIIa–IIId) were also made easily by the reduction of the corresponding benzhydrols (IIa–IId) using red phosphorus and iodine in acetic acid. The yields in these experiments were as follows: IIIa (77%), IIIb (71%), IIIc (66%), IIId (64%).

[16] Huang-Minlon reduction of the ketone gave only 25% yield. The aluminum chloride catalyzed condensation of 2-bromobenzyl bromide and benzene gave only 13% yield.

[17] C. K. Bradsher and F. A. Vingiello, *J. Org. Chem.*, **13**, 786 (1948).

[18] When the ether was replaced with benzene and the chloral added to the boiling benzene solution, a yield of only 22% was obtained.

[19] The distillation proceeds well if the fractionating column is warmed with an electrical heating tape.

[20] The same product was obtained in 30% yield using the Schotten-Baumann procedure and in 66% yield using the boron trifluoride method.

using substantially the procedure described for IVa. The product was obtained in 55% yield as a very viscous oil which distilled at 190–192° (1 mm.).

Anal. Calcd. for $C_{15}H_{12}Cl_4O$: C, 51.46; H, 3.46. Found: C, 51.58; H, 3.42.

Acetate of trichloromethyl-2-benzyl-4-chlorophenylcarbinol. A mixture of 2 g. of the above carbinol (IVb), 4 ml. of freshly distilled boron trifluoride etherate, and 25 ml. of glacial acetic acid was heated under reflux for 10 hr. The mixture was cooled to room temperature and poured into an ice-water mixture. A reddish yellow gum separated and was dissolved in ether. The ether solution was washed with water, a dilute sodium bicarbonate solution, and again with water. The solution was then dried and concentrated. The residue was crystallized from ethanol; yield 1.7 g. (77%), m.p. 115–116°. Several recrystallizations from ethanol raised the melting point to 116–117°.[21]

Anal. Calcd. for $C_{17}H_{14}Cl_4O_2$: C, 52.07; H, 3.60. Found: C, 52.05; H, 3.82.

Trichloromethyl-2-(3′-chlorobenzyl)phenylcarbinol (IVc). This compound was prepared by allowing the Grignard reagent of 2-bromo-3′-chlorodiphenyl-methane to react with chloral using essentially the procedure described for IVa. The product was obtained in 42% yield as a very viscous oil which distilled at 185–190° (0.1 mm.).

Acetate of trichloromethyl-2-(3′-chlorobenzyl)phenylcarbinol. This compound was prepared substantially as was the acetate of IVa using trifluoroacetic acid. Recrystallization from ethanol gave a 58% yield of white crystals; m.p. 114–115°.

Anal. Calcd. for $C_{17}H_{14}Cl_4O_2$: C, 52.12; H, 3.56.

Trichloromethyl-2-(3′-chlorobenzyl)-4-chlorophenylcarbinol (IVd). This compound was prepared by allowing the Grignard reagent of 2-bromo-5,3′-dichlorodiphenylmethane to react with chloral using substantially the procedure described for IVa. The product was obtained in 48% yield as a very viscous oil which distilled at 185–188° (0.2 mm.).

Acetate of trichloromethyl-2-(3′-chlorobenzyl)-4-chlorophenylcarbinol. This compound was prepared substantially as was the acetate of IVa using trifluoroacetic acid. Recrystallization from ethanol gave a 53% yield of white crystals; m.p. 92–93°.

Anal. Calcd. for $C_{15}H_{13}Cl_5O_2$: C, 47.87; H, 3.07. Found: C, 47.76; H, 3.12.

BLACKSBURG, VA.

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[21] The same product was obtained in 72% yield using the trifluoroacetic acid method.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

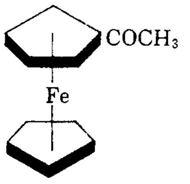
Benzoylations of Both Methyl Ketone Groups of Bisacetylferrocene with Methyl Benzoate and Alkali Amides to Form the Bis-β-diketone. Certain Derivatives[1]

CHARLES R. HAUSER AND CHARLES E. CAIN

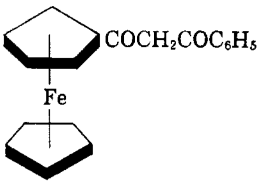
Received January 29, 1958

The benzoylations of both of the methyl ketone groups of bisacetylferrocene were effected with excess methyl benzoate and alkali amide to form the bis-β-diketone. An attempt to benzoylate only one of the methyl ketone groups was unsuccessful. The bis-β-diketone was converted to the bispyrazole, and to a copper chelate which evidently contained one molecule of the bis-β-diketone for each copper atom. Infrared data are presented for these and certain related compounds.

It has recently been shown[2] that the methyl ketone group of acetylferrocene (I) can be benzoylated with methyl benzoate by means of potassium amide to form the corresponding β-diketone (II).

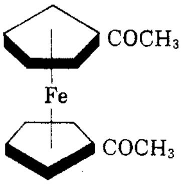


I

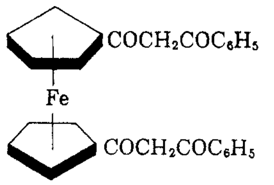


II

It has now been found that both of the methyl ketone groups of bisacetylferrocene[3] (III) can similarly be benzoylated to give the bis-β-diketone IV.[3a] For convenience these compounds are represented in the *cis*-configuration.[4]



III



IV

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(1) Supported by the National Science Foundation.

(2) Charles R. Hauser and Jacque K. Lindsay, *J. Org. Chem.*, **22**, 482 (1957).

(3) We are indebted to Linde Air Products Company, Tonawanda, N. Y., (Dr. R. L. Pruett), for a sample of this compound.

(3a) That the product was not the isomeric triacyl derivative, which might have resulted from dibenzoylation at one of the methyl ketone groups, was indicated by the absence of an infrared band at about 5.7–5.8 for the methyl ketone group which would then still be present in the molecule. Moreover, the triacyl derivative could hardly produce the bispyrazole VII and the internal copper chelate IX. Actually dibenzoylation at one of the methyl ketone groups should not be expected, since the equilibrium of similar acylations of ordinary methyl ketones with methyl benzoate is generally on the side of the anion of the β-diketone which is the monobenzoylation product (see ref. 5).

(4) Recently, D. A. Semenow and J. D. Roberts [*J. Am. Chem. Soc.*, **79**, 2741 (1957)] have presented dipole moment evidence that at least bis-*p*-chlorophenylferrocene has the *cis* configuration.