*Journal of Organometallic Chemistry*, 127 (1977) 193–196
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

# INVESTIGATIONS IN THE CYCLOBUTANE SERIES

## XLIII *. DIACETYLCYCLOBUTADIENEIRON TRICARBONYL AND 3,6-DIMETHYLPYRIDAZINO[4,5-*a*]CYCLOBUTADIENEIRON TRICARBONYL

ILIE G. DINULESCU, EMIL G. GEORGESCU and MARGARETA AVRAM **
*Center of Organic Chemistry, Spl. Independenţei 202B, 7000 Bucharest 15 (Romania)*
(Received July 15th, 1976)

### Summary

Acetylation of cyclobutadieneiron tricarbonyl gives the mono- and the diacetyl derivative. Some reactions of the latter, including that with hydrazine to give a pyridazinocyclobutadiene complex, are described.

### Introduction

In view of the interest in cyclobutadiene chemistry, an investigation of systems containing the cyclobutadiene ring fused to heterocyclic rings seemed appropriate. We describe below the synthesis of the 3,6-dimethylpyridazino-[4,5-*a*]cyclobutadieneiron tricarbonyl complex (I) from the 1,2-diacetylcyclobutadieneiron tricarbonyl complex (II).

### Results and discussions

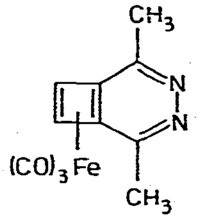
The treatment of cyclobutadieneiron tricarbonyl [2] or its monoacetyl derivative [3] with an excess of acetyl chloride in the presence of anhydrous aluminium chloride gave the 1,2-diacetylcyclobutadieneiron tricarbonyl complex (II), identical with the previously described compound [4].

Complex II undergoes normal carbonyl reactions. Reduction with sodium borohydride affords the dihydroxy derivative III, and treatment with Grignard reagents gives the tertiary alcohols IV and V, respectively.

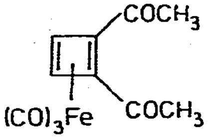
---

* For part XLII, see Ref. 1.

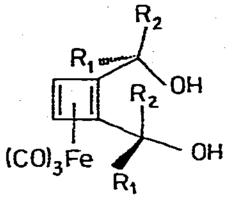
** To whom correspondence should be addressed.



I



II



III, $R_1$=$CH_3$, $R_2$=H

IV, $R_1$=$R_2$=$CH_3$

V, $R_1$=$CH_3$, $R_2$=$C_6H_5$

The spectra show good agreement with the proposed structures, and some features deserve comment. The Dreiding models of the alcohols III, IV and V show the possibility of intramolecular hydrogen bonds between the two alcohol groups. The less bulky $CH_3CHOH$ group in III may rotate freely and the hydrogen bond can be broken. Consequently, the OH band appears at 3635 cm$^{-1}$, a normal position for non-associated hydroxy groups. Since the bulkier substituents in IV hinder C—C rotation, a strong intramolecular hydrogen bond is formed ($\nu$(OH) 3475 cm$^{-1}$), leading to a frozen structure. In the latter, two methyl groups are coplanar with the cyclobutadiene ring and two are perpendicular to the cyclobutadiene ring plane, opposite to the $Fe(CO)_3$ group. The NMR data are in agreement with these suggestions. The spectrum shows only two types of methyls in the expected ratio of 2 : 2 with peaks at $\delta$ 1.23 and 1.61 ppm, respectively. A similar structure is indicated for complex V, this has an intramolecular hydrogen bond ($\nu$(OH) 3455 cm$^{-1}$), and the phenyl groups ($\delta$ 7.03 ppm) are perpendicular to the cyclobutadiene ring plane, being parallel and showing mutual shielding.

Treatment of II with hydrazine in acetic acid gives the pyridazinocyclobutadiene complex I. The NMR spectrum ($CDCl_3$, $\delta$, ppm) of I shows signals at 1.98 (s, 4 H) corresponding to the two methyl groups, and at 4.80 (s, 2 H) assigned to the complexed cyclobutadiene ring protons. The spectrum also shows the deshielding of the protons due to the proximity of the heterocyclic ring. In the IR spectrum ($CCl_4$) the carbonyl bands appear at 1992, 1998 and 2060 cm$^{-1}$. Attempts to liberate the ligand from I using oxidizing reagents ($Ce^{4+}$) [2] or reduction with lithium aluminium hydride gave no dimerization product. To our knowledge, the preparation of the internal azine I, which is a pyridazinocyclobutadiene, represents the first synthesis of a heteroarenocyclobutadiene.

## Experimental

Microanalyses were performed by Miss E. Sliam and Mrs. V. Daniel. IR spectra were recorded with a double beam UR 20 spectrophotometer. NMR spectra were recorded on a Varian A-60A spectrometer by Mr. F. Chiraleu.

### *Cyclobutadieneiron tricarbonyl*

A mixture of 2.5 g (20 mmol) *cis*-3,4-dichlorocyclobutene [5], 9.0 g (6.0

ml, 50 mmol) iron pentacarbonyl, 30 ml ether and 60.0 g lithium amalgam (0.5%) was stirred at room temperature for 24 hours. The filtered solution was distilled to give 0.4 g (10.5%) of cyclobutadieneiron tricarbonyl. IR and NMR spectra were identical with those of an authentic sample [2].

### *1,2-Diacetylcyclobutadieneiron tricarbonyl (II)*

(A). A solution of 1.91 g (10 mmol) cyclobutadieneiron tricarbonyl and 2.4 g (30.6 mmol) acetyl chloride in 40 ml carbon disulfide was treated with 8.0 g (60.0 mmol) anhydrous aluminium chloride with vigorous stirring. When the exothermic reaction had ceased, the mixture was boiled for 1 hour. After cooling, ice water was added, the product was extracted with dichloromethane and the organic layer washed with 5% aqueous sodium carbonate. The brown oily crystals remaining after evaporation of the solvent were triturated with 1.5—2.0 ml methanol. After filtration, 1.00—1.20 g (36.2—43.5%) of II was obtained as yellow crystals, m.p. 124°C (methanol) [4]. IR ($CCl_4$, $cm^{-1}$): $\nu$(CO) 1688 (from acetyl), 2008, 2022, 2078 (from iron tricarbonyl). NMR ($CS_2$, $\delta$, ppm): 2.15 (s, 6 H, 2 $CH_3$), 4.75 (s, 2 H from complexed cyclobutadiene ring). Analysis found: C, 47.46; H, 3.19; Fe, 19.72. $C_{11}H_8FeO_5$ calcd.: C, 47.87; H, 2.92; Fe, 20.23%.

(B). The procedure as above, from 2.7 g (11.6 mmol) monoacetylcyclobutadieneiron tricarbonyl [3], 2.8 g (36 mmol) acetyl chloride, 50 ml carbon disulfide and 7.5 g (56 mmol) anhydrous aluminium chloride, gave 0.90 g (28%) of II (NMR and IR spectra were identical with those of the previous sample).

### *$\alpha,\alpha'$-Dihydroxy-1,2-diethylcyclobutadieneiron tricarbonyl (III)*

A solution of 1.0 g (3.6 mmol) II in 30 ml methanol and 10 ml water was treated with 1.0 g sodium borohydride. After 3 hours the solution was diluted with water and extracted with ether. The ethereal extract was washed with water, dried and the ether was removed by distillation. The crystalline residue was washed with ether/petroleum ether 1 : 3, to give 0.3 g (30%) III, white crystals, m.p. 95°C. IR ($CCl_4$, $cm^{-1}$): $\nu$(CO) 1990, 2060 (from iron tricarbonyl); $\nu$(OH) 3635. NMR ($CDCl_3$, $\delta$, ppm): 1.15 (d, 6 H, 2 $CH_3$, $J$ 6.0 Hz), 3.05 (s, 2 H, 2 OH), 4.15 (s, 2 H from complexed cyclobutadiene ring), 4.66 (qu, 2 H, 2$\alpha$-H, $J$ 6.0 Hz). Analysis found: C, 47.09; H, 4.44; Fe, 19.89. $C_{11}H_{12}FeO_5$ calcd.: C, 47.17; H, 4.32; Fe, 19.94%.

### *$\alpha,\alpha'$-Diacetoxy-1,2-diethylcyclobutadieneiron tricarbonyl*

A solution of 0.25 g (0.89 mmol) III in 3 ml acetic anhydride was treated with a few drops of pyridine and the mixture was left at room temperature. Working up gave 0.22 g (67%) of a colourless oil. IR ($CCl_4$, $cm^{-1}$): $\nu$(OCO) 1240, $\nu$(CO) 1755 (from acetyl), 1980, 1992, 2059 (from iron tricarbonyl). NMR ($CCl_4$ + $CDCl_3$, $\delta$, ppm): 1.33 (d, 6 H, 2 $CH_3$, $J$ 6.0 Hz), 2.05 (s, 6 H, 2 $CH_3$ from acetyl), 4.23 (s, 2 H from complexed cyclobutadiene ring), 5.45 (qu, 2 H, 2$\alpha$-H, $J$ 6.0 Hz). Analysis found: C, 49.55; H, 5.15; Fe, 15.38. $C_{15}H_{16}FeO_7$ calcd.: C, 49.47; H, 4.43; Fe, 15.34%.

### *$\alpha,\alpha'$-Dihydroxy-1,2-diisopropylcyclobutadieneiron tricarbonyl (IV)*

A solution of 0.6 g (2.16 mmol) II in 30 ml ether and 5 ml THF was added to a solution of methylmagnesium iodide prepared from 0.5 g (20 mmol) magnesium, 4.4 g (30 mmol) methyl iodide and 30 ml ether. The mixture was boiled for 30 min. Water was added, followed by 5 ml of 50% acetic acid. The ethereal layer was separated, washed with 5% sodium carbonate solution until neutral, and then with water. After drying, the ether was removed and the crude oily residue was purified by chromatography on aluminium oxide (elution with ether) to give 0.15—0.20 g (21—30%) IV, m.p. 151°C (from carbon tetrachloride). IR ($CCl_4$, $cm^{-1}$): $\nu(OH)$ 3475 (assoc.), 3600 (free). NMR ($CDCl_3$, $\delta$, ppm): 1.23 and 1.61 (2s, 12 H, 4 $CH_3$), 3.23 (s, 2 H, 2 OH), 4.11 (s, 2 H from complexed cyclobutadiene ring). Analysis found: C, 50.82; H, 5.54; Fe, 17.86. $C_{13}H_{16}FeO_5$ calcd.: C, 50.68; H, 5.23; Fe, 18.13%.

*α,α'-Dihydroxy-α,α'-diphenyl-1,2-diethylcyclobutadieneiron tricarbonyl (V)*

A solution of 0.6 g (2.16 mmol) II in 30 ml ether and 5 ml THF was added to a solution of phenylmagnesium bromide prepared from 0.5 g (20 mmol) magnesium, 5.0 g (30 mmol) bromobenzene and 30 ml ether. The procedure as above gave 0.10 g (11%) of V as white crystals, m.p. 147°C (from carbon tetrachloride). IR ($CH_2Cl_2$, $cm^{-1}$): $\nu(CO)$ 1980—1990, 2055 (from iron tricarbonyl); $\nu(OH)$ 3455 (assoc.), 3595 (free). NMR ($CDCl_3$, $\delta$, ppm): 1.40 (s, 6 H, 2 $CH_3$), 3.75 (s, 2 H, 2 OH), 4.41 (s, 2 H from complexed cyclobutadiene ring), 7.03 (broad s, 10 H aromatic). Analysis found: C, 64.74; H, 5.07; Fe, 12.92. $C_{23}H_{20}FeO_5$ calcd.: C, 63.91; H, 4.66; Fe, 12.92%.

*3,6-Dimethylpyridazino[4,5-a] cyclobutadieneiron tricarbonyl (I)*

A solution of 0.5 g (1.8 mmol) II in 50 ml acetic acid was treated with 2.5 ml (2.6 g, 51 mmol) hydrazine hydrate and the red mixture was left at room temperature for 48 hours. Water (100 ml) was added and the resulting solution was treated with sodium hydrogen carbonate until neutral. The mixture was extracted with ether, and the ethereal layer washed with water and dried. Evaporation of the solvent gave a crystalline residue, which was purified by washing with methanol, yielding 0.30 g (60%) I, yellow crystals, m.p. 180°C (dec.). IR ($CCl_4$, $cm^{-1}$): $\nu(CO)$ 1992, 1998, 2060 (from iron tricarbonyl). NMR ($CDCl_3$, $\delta$, ppm): 1.98 (s, 6 H, 2 $CH_3$), 4.80 (s, 2 H from complexed cyclobutadiene ring). Analysis found: C, 48.84; H, 3.35; N, 10.46; Fe, 19.89. $C_{11}H_8FeN_2O_3$ calcd.: C, 48.56; H, 2.99; N, 10.29; Fe, 20.52%.

## References

1 O. Constantinescu-Simon, F. Chiraleu and M. Avram, Chem. Ber., in press.
2 G.F. Emerson, L. Watts and R. Pettit, J. Amer. Chem. Soc., 87 (1965) 131.
3 J.D. Fitzpatrick, L. Watts, G.F. Emerson and R. Pettit, J. Amer. Chem. Soc., 87 (1965) 3254.
4 W. Roberts, A. Wissner and R.A. Rimerman, J. Amer. Chem. Soc., 91 (1969) 6208.
5 M. Avram, I.G. Dinulescu, M. Elian, M. Fărcaşiu, E. Marica, G. Mateescu and C.D. Nenitzescu, Chem. Ber., 97 (1964) 372.