Organic
Syntheses

A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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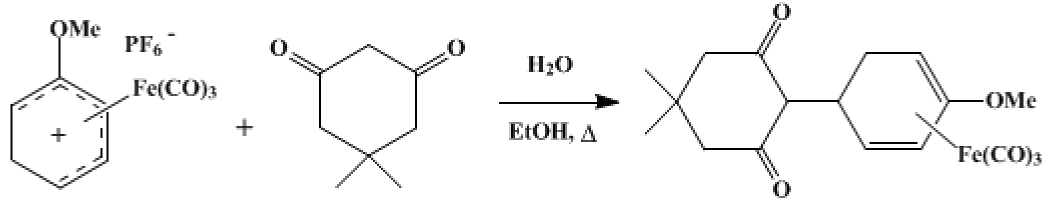
Organic Syntheses, Coll. Vol. 6, p.1001 (1988); Vol. 57, p.16 (1977).

ALKYLATION OF DIMEDONE WITH A TRICARBONYL(DIENE) IRON COMPLEX: TRICARBONYL[2-[(2,3,4,5-η)-4-METHOXY-2,4-CYCLOHEXADIEN-1-YL]-5,5-DIMETHYL-1,3-CYCLOHEXANEDIONE]IRON

[Iron, tricarbonyl[2-[(2,3,4,5-η)-4-methoxy-2,4-cyclohexadien-1-yl]-5,5-dimethyl-1,3-cyclohexanedione]-]



Submitted by A. J. Birch and K. B. Chamberlain[1].
Checked by T. Aoki, S. Kamata, and W. Nagata.

1. Procedure

A 500-ml., round-bottomed flask equipped with a condenser is charged with 5 g. (0.013 mole) of tricarbonyl[(1,2,3,4,5-η)-2,4-cyclohexadien-1-yl]iron(1+) hexafluorophosphate(1−) (Note 1), 150 ml. of water, and 50 ml. of ethanol and heated on the steam bath with occasional swirling until the salt is dissolved. Dimedone (1,3-Cyclohexanedione, 5,5-dimethyl-) (2.5 g., 0.018 mole) is dissolved in 50 ml. of ethanol by warming. The two solutions are mixed and refluxed for 15 minutes. After cooling to about 25°, the mixture is poured into 500 ml. of water with stirring, and the precipitate is collected, washed with water, and air-dried, yielding 4.4 g. of crude product. The product is recrystallized by first dissolving in a minimum volume of boiling ethanol and adding water until the first sign of turbidity. On standing under refrigeration overnight, crystallization occurs. After collection by filtration, the product is washed with water and air-dried, yielding 3.7 g. of small, white to buff-colored crystals (Note 2), which darken above 140° but do not melt. On addition of water to the filtrate a crop of 0.6 g. is obtained, giving a total yield of 4.3 g. (87%).

2. Notes

1. The preparation of this salt is described in *Org. Synth.*, **Coll. Vol. 6**, 996 (1988).
2. ^{1}H NMR (100 MHz, acetone-d_6), δ (multiplicity, number of protons): δ 1.02 (s, 6H), 1.88 (q, 1H), 2.23 (s), 2.52 (quintet), 2.48–3.52 (m)—the preceding four signals account for 10 protons—3.66 (s, 3H), 5.24 (q, 1H); IR (Nujol) cm.$^{-1}$: 2040, 1980, 1950, 1560; mass spectrum *m/e*: 388 (M+).

3. Discussion

Hexafluorophosphate and tetrafluoroborate dienyl salts react with many nucleophiles.[2] The tetrafluoroborate salts are preferred, being more soluble in organic solvents than the hexafluorophosphates.

In all cases so far investigated, including a useful direct reaction with ketones,[3] the methoxydienyl salt is substituted at the 5-position and not at the alternative 1-position. The iron tricarbonyl group can conveniently be removed from many of these adducts by the action of iron(III) chloride in ethanol.[3]

References and Notes

1. Research School of Chemistry, Australian National University, P.O. Box 4, Canberra, A.C.T. 2600, Australia.
2. A. J. Birch, P. E. Cross, J. Lewis, D. A. White, and S. B. Wild, *J. Chem. Soc. A*, 332 (1968).
3. A. J. Birch, K. B. Chamberlain, M. A. Hass, and D. J. Thompson, *J. Chem. Soc. Perkin Trans. 1*, 1882 (1973); A. J. Birch, K. B. Chamberlain, and D. J. Thompson, *J. Chem. Soc. Perkin Trans. 1*, 1900 (1973).

Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

TRICARBONYL[2-[(2,3,4,5-η)-4-METHOXY-2,4-CYCLOHEXADIEN-1-YL]-5,5-DIMETHYL-1,3-CYCLOHEXANEDIONE]IRON

Iron, tricarbonyl[2-[(2,3,4,5-η)-4-methoxy-2,4-cyclohexadien-1-yl]-5,5-dimethyl-1,3-cyclohexanedione]-

tricarbonyl[(1,2,3,4,5-η)-2,4-cyclohexadien-1-yl]iron(1+) hexafluorophosphate(1−)

ethanol (64-17-5)

iron(III) chloride (7705-08-0)

tetrafluoroborate (14874-70-5)

1,3-Cyclohexanedione, 5,5-dimethyl-,
dimedone (126-81-8)

hexafluorophosphate

TRICARBONYL(DIENE)IRON