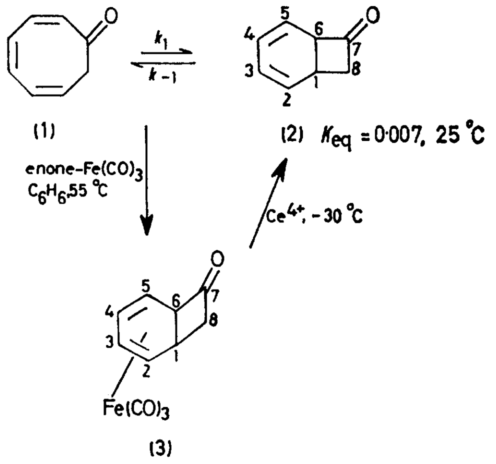
Preparation of Bicyclo[4.2.0]octa-2,4-dien-7-one *via* Trapping with Benzylideneacetoneiron Tricarbonyl

By Maurice Brookhart,* Gregory O. Nelson, Gary Scholes, and R. A. Watson
(Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514)

Summary The synthesis of bicyclo[4.2.0]octa-2,4-dien-7-one has been accomplished by trapping this unstable tautomer with benzylideneacetoneiron tricarbonyl to form the stable bicyclo[4.2.0]octa-2,4-dien-7-oneiron tricarbonyl which was then oxidatively cleaved with ceric ammonium nitrate at −30 °C to yield the title ketone.

Recently we have shown that benzylideneacetoneiron tricarbonyl [BDA-Fe$(CO)_3$] is a useful reagent for selectively trapping as iron tricarbonyl complexes the bicyclic tautomers of 1,3,5-cyclo-octatriene and its derivatives, bicyclo[6.2.0]deca-2,4,6-triene and bicyclo[6.1.0]nona-2,4,6-triene.[1] We now report the use of enoneiron tricarbonyl reagents for trapping, isolation, and study of the previously uncharacterized bicyclo[4.2.0]octa-2,4-dien-7-one (**2**). Reaction of either BDA-Fe$(CO)_3$ or 3-penten-2-oneiron tricarbonyl with 2,4,6-cyclo-octatrienone (**1**)[2] in benzene at 55 °C followed by crystallization of the crude product from pentane affords pale yellow crystals of the bicyclo[4.2.0]octa-2,4-diene-7-

oneiron tricarbonyl (**3**) in *ca.* 50% yield. Use of 3-penten-2-oneiron tricarbonyl proved more convenient in that following exchange the free 3-penten-2-one could be removed at reduced pressure. Complex (**3**) showed ^{1}H n.m.r. signals† ($CDCl_3$) at δ 2·93 (1-H), 3·47 (2-H), 5·47 (3-H), 5·65 (4-H), 3·11 (5-H), 3·47 (6-H), 2·11 (8a-H), 2·66 (8b-H) and ^{13}C n.m.r. signals at 210·9 (iron carbonyl), 204·7 (ketone carbonyl), 86·8, 85·0, 68·0, 64·8, 58·0, 48·0 and 30·1 p.p.m. downfield relative to Me_4Si.



Oxidative cleavage of (**3**) with ceric ammonium nitrate adsorbed on alumina in ether at −30 °C followed by filtration and low temperature (−20 °C) flash distillation (10^{-4} mmHg) led to isolation of a pure sample of the bicyclic dienone (**2**). The dienone (**2**) showed ^{1}H n.m.r. signals ($CDCl_3$, −30 °C) at δ 6·05 (1H), 5·91 (2H), 5·56 (1H), 4·23 (1H), 3·00—3·81 (3H).

Upon warming to 0 °C (**2**) undergoes a clean first-order isomerization to the trienone (**1**). From rate measurements using ^{1}H n.m.r. at 0 °C we find $k_{-1} = 5{\cdot}7 \times 10^{-4}\ s^{-1}$ with $\Delta G^{\ddagger} = 20{\cdot}0$ kcal mol^{-1}. Huisgen has measured k_1 from tetracyanoethylene trapping of (**2**) at 44 °C ($4{\cdot}9 \times 10^{-4}$ s^{-1}), 50 °C ($9{\cdot}8 \times 10^{-4}\ s^{-1}$) and 56·7 °C ($19{\cdot}9 \times 10^{-4}\ s^{-1}$).[3] Extrapolation of this data to 0 °C yields a value of $k_1 = 2{\cdot}0 \times 10^{-6}\ s^{-1}$ and thus an estimated K_{eq} at 0 °C of *ca.* 0·0035, $\Delta G = 3{\cdot}1$ kcal mol^{-1}. Assuming $\Delta G = 3{\cdot}1$ kcal mol^{-1} at 25 °C, $K_{eq} = 0{\cdot}0052$. This is substantially lower than Huisgen's value of 0·05 estimated from provisional ^{1}H n.m.r. data.[3] From FT-^{1}H n.m.r. measurements of the relative intensities of the δ 2·87 signal for (**1**) and the δ 4·23 signal for (**2**) we estimate K_{eq} at 25 °C to be *ca.* 0·007, $\Delta G = 2{\cdot}9$ kcal mol^{-1}, which is in close agreement with that estimated from the measured values of k_1 and k_{-1}.

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† The chemical shifts of 1-H—5-H were assigned by double resonance and deuterium decoupling experiments on 6,8,8′-trideuterio-bicyclo[4.2.0]octa-2,4,dien-7-oneiron tricarbonyl synthesized from 2,8,8′-tri-deuterio-2,4,6-cyclo-octatrienone and 3-penten-2-oneiron tricarbonyl.

[1] G. Scholes, C. R. Graham, and M. Brookhart, *J. Amer. Chem. Soc.*, 1974, **96**, 5666.

[2] A. C. Cope and B. D. Tiffany, *J. Amer. Chem. Soc.*, 1951, **73**, 4158; A. C. Cope, S. F. Schaeren, and E. R. Trumbull, *ibid.*, 1954, **76**, 1096.

[3] R. Huisgen, F. Mietzsch, G. Boche, and H. Seidl, *Chem. Soc. Spec. Publ.*, 1965, **19**, 3.