to be $Ru_2C_{24}H_{32}$ (exact mass 524.059). The complex nmr spectrum of this species suggests that it is not the simple analog of **4**, $Ru_2(COD)_2(COT)$.

Cyclooctatetraene complexes of Os(0) were prepared similarly from $[Os(COD)Cl_2]_x$. In contrast to the Ru case, spectroscopically pure Os(COD)(COT) was isolated in *ca.* 25% yield. The known complex, $Os(COD)(C_8H_{10})$,[12] was isolated in 1–2% yield.

The method of reduction by $[COT]^{2-}$ can be extended to the preparation of Ru(0) complexes containing phosphine ligands, *i.e.*, $Ru(PPh_3)_2(COT)$ and $Ru(PPhMe_2)_3(COT)$. The former was isolated as yellow crystals in 50% yield by the reaction of $[K^+]_2[COT]^{2-}$ with $RuCl_2(PPh_3)_4$ and the latter as orange crystals in 20% yield from $[Ru_2Cl_3(PPhMe_2)_6]^+Cl^-$. Presumably steric considerations prevent isolation of $Ru(PPh_3)_3(COT)$.

$Ru(PPh_3)_2(COT)$, Ru(NBD)(COT), and Os(COD)(COT) are the first complexes of these metals containing tridentate cyclooctatetraene. (The temperature-dependent nmr spectra of the latter two are analogous to that for $Mo(COT)(CO)_3$.[8]) It appears, however, that tridentate bonding is tenuous since Ru(0) species[14] containing bidentate COT[15] are formed in seconds at room temperature in the presence of phosphorus ligands or carbon monoxide, *viz.*

$$\mathrm{Ru(NBD)(COT)} \xrightarrow{L} \mathrm{Ru(NBD)(COT)(L)}$$
$$L = \mathrm{CO,\ PPh_3,\ PPhMe_2,\ PEt_3,\ P(OMe)_3}$$

Interestingly, there is evidence which suggests that the tendency for COT to prefer bidentate coordination may also play an active role in determining catalytic activity (at least under mild conditions) by allowing the reagents involved to gain access to the metal center. For example, (1) Ru(NBD)(COT) and $Ru(PPh_3)_2(COT)$ are active catalysts (or catalyst precursors) for the hydrogenation of 1-butene under mild conditions (1–2 atm of H_2, 25–60°) while $Ru(NBD)(COT)(PPhMe_2)$ and $Ru(PPhMe_2)_3(COT)$ are essentially inactive under similar conditions and (2) ethylene reacts irreversibly with Ru(NBD)(COT) in C_6D_6 to yield species other than the simple adduct, $Ru(NBD)(COT)(C_2H_4)$, as judged by nmr examination of the resultant solution. The above observations should be compared with the extensive investigation of the catalytic activity of $Fe(COT)_2$[1] where similar arguments could be invoked.

Preliminary studies suggest that bidentate COT is reasonably labile and that Ru(0)–COT complexes may therefore serve as preparative materials, *viz.*

$$\mathrm{Ru(NBD)(COT)} \xrightarrow[\mathrm{C_6H_6\ reflux\ 1\ hr}\ \ 50\%\ \mathrm{yield}]{\mathrm{P(OCH_2)_3CC_2H_5}} \mathrm{Ru(NBD)[P(OCH_2)_3CC_2H_5]_3} + \mathrm{COT}$$

Analogous reactions with phosphines (L, *e.g.*, $PPhMe_2$) suggest (by nmr) that more complicated mixtures containing (*inter alia*) $Ru(NBD)L_3$ and $RuL_x(COT)$ (x = 2 or 3) are produced. The scope of this method for preparation of a variety of Ru(0) complexes containing group Va ligands is presently under active investigation.[16]

Acknowledgment. R. R. S. gratefully acknowledges support in the form of a National Science Foundation Postdoctoral Fellowship.

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[14] Corresponding studies of Os(COD)(COT) behavior have not yet been completed.

[15] In monomeric complexes of metals in the iron triad bidentate COT is bonded through a conjugated double bond system. There is no evidence to suggest deviation from this behavior.

[16] It should be noted in this context that the rearrangement of hydrocarbon ligands containing methylenic protons (such as 1,5-cyclooctadiene[13]) in complexes similar to **1**[6,12] may preclude their preparative utility in reactions of this type.

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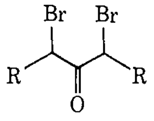
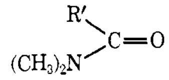
Iron Carbonyl Promoted Reaction of α,α′-Dibromo Ketones and Carboxamides. A Convenient Route to Muscarines *via* Furanones[1]

Sir:

Recently Hoffmann and coworkers reported a two-step synthesis of 3(2*H*)-furanones (**4**) which consists of reduction of α,α′-dibromo ketones (**1**) with Zn–Cu couple in the presence of carboxamides **2**, producing the dioxolane derivatives **3**, followed by acid treatment.[2] The method provides a new route to five-membered heterocycles and can be viewed formally as the construction of a carbon–oxygen bridge between the α and α′ positions of the parent dialkyl ketones. This communication describes a related method and its applicability to the synthesis of naturally occurring products.



1a, R = CH_3
b, R = C_2H_5
c, R = $CH(CH_3)_2$



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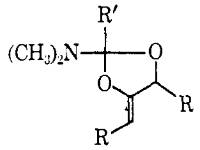

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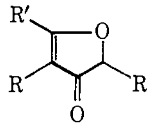

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The modification involves the adoption of $Fe_2(CO)_9$ as a reducing agent in place of Zn–Cu couple. When a mixture of the dibromo ketone **1b** (8.5 mmol) and $Fe_2(CO)_9$ (12 mmol) in dry *N*,*N*-dimethylformamide (DMF) (35 ml) was stirred at 25° for 12 hr under nitrogen, the desired cyclic adduct **4** (R = C_2H_5 and R′ = H) was obtained in 64% yield after the usual

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[1] Carbon–Carbon Bond Formations Promoted by Transition Metal Carbonyls. VIII. This work was presented in part at the 5th International Conference on Organometallic Chemistry, Moscow, Aug 16–21, 1971, Abstract No. 25. Part VII of this series: R. Noyori, K. Yokoyama, and Y. Hayakawa, *J. Amer. Chem. Soc.*, **95**, 2722 (1973).

[2] H. M. R. Hoffmann, K. E. Clemens, E. A. Schmidt, and R. H. Smithers, *ibid.*, **94**, 3201 (1972); B. K. Carpenter, K. E. Clemens, E. A. Schmidt, and H. M. R. Hoffmann, *ibid.*, **94**, 6213 (1972); M.-A. Barrow, A. C. Richards, R. H. Smithers, and H. M. R. Hoffmann, *Tetrahedron Lett.*, 3101 (1972).

work-up (78% yield by nmr analysis).[3,4] Representative results are given in Table I. *N*,*N*-Dimethylacetamide and *N*,*N*-dimethylbenzamide could be used in place of DMF. Attempted reaction of α,α'-dibromoacetone with DMF failed to give the cyclic adduct.

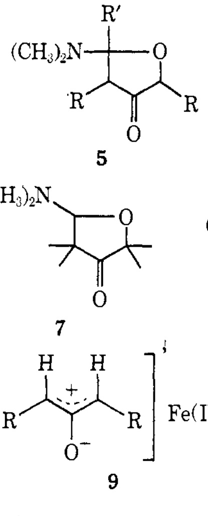
Table I. Iron Carbonyl Promoted Furanone Synthesis from α,α'-Dibromo Ketones and Carboxamides[a]

Dibromide 1	Amide 2[b]	Furanone 4[c] R	Furanone 4[c] R′	Yield, %[d]
1a	DMF	CH_3	H	53[e,f]
1b	DMF	C_2H_5	H	78, 64[e]
1b	$CH_3CON(CH_3)_2$	C_2H_5	CH_3	51
1b	$C_6H_5CON(CH_3)_2$	C_2H_5	C_6H_5	42[e]
1c	DMF	$CH(CH_3)_2$	H	90[g]
1c	$CH_3CON(CH_3)_2$	$CH(CH_3)_2$	CH_3	87[g]
1c	$C_6H_5CON(CH_3)_2$	$CH(CH_3)_2$	C_6H_5	83

[a] Reaction was carried out at 20–25° for 10–48 hr using **1** and $Fe_2(CO)_9$ in a mole ratio of 1:1.2. The progress of the reaction was conveniently monitored by glpc. Reaction conditions were not optimized. [b] DMF and $CH_3CON(CH_3)_2$ were used as solvents. $C_6H_5CON(CH_3)_2$ (20 equiv to each equiv of **1**) was used in benzene solution. [c] The structure was determined on the basis of spectral data (ir, uv, nmr, and mass). Furanones are usually air sensitive (especially under basic conditions). [d] Determined by nmr analysis of the crude product. [e] Isolated yield. [f] Anhydrous ethylenediaminetetraacetic acid disodium salt (EDTA) (3 equiv to each equiv of **1**) was added to the reaction system. When the reaction was carried out in the absence of EDTA, an efficient masking agent of Fe ions, the yield of the adduct was reduced considerably. [g] Result obtained after heating the crude product at 110° for 10 min.

Apparently the formation of the furanones **4** proceeds by way of the thermally labile adducts of type **5**. In certain cases (*e.g.*, when R is a bulky group), the complete elimination of the amine moiety required heating at an elevated temperature for a short period. The sterically crowded adduct **6**[5] (obtained from 3,5-dibromo-2,2,6,6-tetramethylheptan-4-one and DMF in 98% yield) was thermally stable, and remained unchanged even upon heating in toluene at 110° for 20 min. As expected, reduction of 2,4-dibromo-2,4-dimethylpentan-3-one, which has no hydrogen atoms at positions α to the carbonyl group, in DMF (25°, 8 hr) gave rise to the stable adduct **7**, although in low yield (3%); the major product was 2,4-dimethylpent-1-en-3-one (80%). The reaction of **1c** and a lactam, *N*-methylpyrrolidone (25°, 48 hr), proceeded through unisolable spiro-fused dihydrofuranone(s) to give ultimately the aminofuranone **8** in 26% yield.[6]

The present cyclo coupling reaction can be explained by assuming the intermediacy of the oxyallyl–Fe(II) species of type **9** (L = Br^-, CO, and amide, etc.).[7] When the reduction of **1c** with $Fe_2(CO)_9$ was carried out in a 1:1 mixture of DMF and furan at 25° for 24 hr, **5** (R = $CH(CH_3)_2$ and R′ = H) and the furan adduct **10** (cis isomer) were obtained in 65 and 27% yields, respectively. The intermediate **9** (R = $C(CH_3)_3$) generated in benzene solution is known to undergo the neopentyl-type rearrangement.[7] Under the present reaction conditions, however, it was trapped efficiently by DMF, prior to the skeletal change, to afford the adduct **6**.[8]



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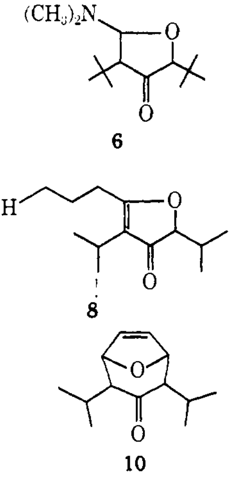

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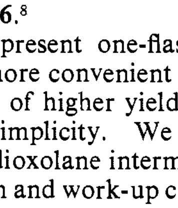

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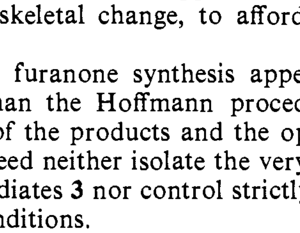

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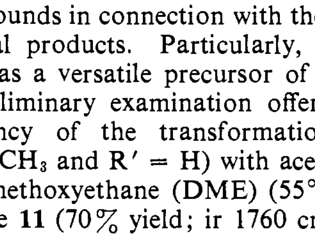

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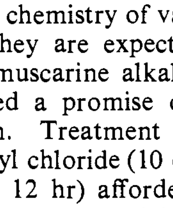

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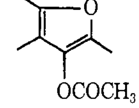
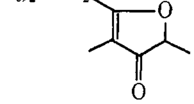
The present one-flask furanone synthesis appeared to be more convenient than the Hoffmann procedure[2] in view of higher yield of the products and the operational simplicity. We need neither isolate the very unstable dioxolane intermediates **3** nor control strictly the reaction and work-up conditions.

Furanones thus obtained are an important class of compounds in connection with the chemistry of various natural products. Particularly, they are expected to serve as a versatile precursor of muscarine alkaloids.[9] A preliminary examination offered a promise of the efficiency of the transformation. Treatment of **4** (R = CH_3 and R′ = H) with acetyl chloride (10 equiv) in dimethoxyethane (DME) (55°, 12 hr) afforded the acetate **11** (70% yield; ir 1760 cm⁻¹). Mannich reaction of **11** using 40% $(CH_3)_2NH$–37% HCHO (1.5 equiv each) in CH_3COOH (70°, 45 min) gave **12** (80%; ir 1760 cm⁻¹), exposure of which to 70% $HClO_4$–DME (1:2.5 mixture) at 50° for 30 min gave the furanone **13** in 80% yield.[10] Its conversion to **14** (two isomers) was accomplished by treating with Li–C_2H_5OH–liquid NH_3 at −35° (60%; ir 3400 cm⁻¹; nmr δ 2.45 (s, $N(CH_3)_2$)). Quaternization with CH_3I afforded 4-methylmuscarine iodides **15**, which displayed physiological activities



11, R = H
12, R = $CH_2N(CH_3)_2$



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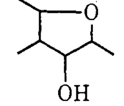

14, R = $CH_2N(CH_3)_2$
15, R = $CH_2N^+(CH_3)_3I^-$

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[3] All new compounds gave correct elemental analyses and/or molecular peaks in exact mass spectra. Unless otherwise stated, all ir and nmr spectra were taken in CCl_4 solution.

[4] Spectral characteristics were: ir (neat) 1700 (C═O) and 1617 cm⁻¹ (C═C); nmr δ 0.97 (t, J = 7.0 Hz, CH_3), 1.08 (t, J = 7.0 Hz, CH_3), 1.5–2.4 (m, CH_2CH_3), 4.21 (d of d, J = 4.5 and 7.0 Hz, $CHCH_2CH_3$), and 7.90 (m, ═CH); uv (C_2H_5OH) 272 nm (log ϵ 3.68).

[5] Spectral characteristics were: ir 1746 cm⁻¹ (C═O); nmr δ 0.97, 1.02 (2 s, $C(CH_3)_3$), 1.93 (d, J = 8.5 Hz, COC*H*CH), 2.48 (s, $N(CH_3)_2$), 3.18 (s, OCH), and 4.59 (d, J = 8.5 Hz, COCHC*H*); no uv absorptions.

[6] Spectral characteristics were: ir 1690 (C═O) and 1620 cm⁻¹ (C═C); uv (C_2H_5OH) 274 nm (log ϵ 4.04).

[7] R. Noyori, Y. Hayakawa, M. Funakura, H. Takaya, S. Murai, R. Kobayashi, and S. Tsutsumi, *J. Amer. Chem. Soc.*, **94**, 7202 (1972).

[8] At present, it is unclear whether the adducts of type **5** arise directly from **9** and amides **2** or else by way of the labile dioxolane isomers **3**, though the latter could not be detected during the reactions.

[9] Reviews: C. H. Eugster, *Advan. Org. Chem.*, 2, 427 (1960); S. Wilkinson, *Quart. Rev., Chem. Soc.*, **15**, 153 (1961).

[10] Spectral data are: ir 1698 (C═O) and 1623 cm⁻¹ (C═C); nmr δ 1.37 (d, J = 7.0 Hz, CHC*H*₃), 1.66 (s, ═CCH_3), 2.25 (s, $N(CH_3)_2$), 3.25 (s, NCH_2), and 4.24 (q, J = 7.0 Hz, CH).

characteristic of muscarine alkaloids. The products stimulated the smooth muscle of the intestinal tract, thereby increasing tone and motility. These actions were inhibited by atropine.[11]

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(11) Full details of these results will be presented in a forthcoming paper.

*Book Reviews**

Annual Reports on the Progress of Chemistry. Volume 68. 1971. Section A: General, Physical, and Inorganic Chemistry. Section B: Organic Chemistry. The Chemical Society, London. 1972. Section A: xvi + 546 pp. £6.00. Section B: xvi + 627 pp. £7.00.

This steadfast companion to the chemist hard-pressed by the burgeoning literature shows an inexorable growth in size, notwithstanding the efforts of the Senior Reporters at containment. The recent development of the Specialist Periodical Reports Series has not been sufficient to arrest the expansion completely.

The subjects of the chapters are too varied and too predictable to warrant listing them all here, but, as examples, "Molecular Acoustics" and "Application of Molecular Sieve Zeolites to Catalysis" in Section A, and "Electron Spectroscopy for Chemical Analysis" in Section B, might not ordinarily be expected. A 20-page section on "Electro-organic Chemistry" attests to the current vigor in this previously rather quiet area; as the reporters state, "It would seem that the organic chemist and the electrochemist are at last coming to terms with each other." It is good to see the continuing alertness of the publishers to the changing face of chemistry.

BIDICS—1971: Bond Index to the Determinations of Inorganic Crystal Structures. By I. D. Brown, C. P. Weiss, and K. K. Wu (McMaster University). Institute for Materials Research, Hamilton, Ontario, Canada. 1972. 126 pp. $7.50.

This is a soft-bound volume, produced by offset from typescript, which covers the subject as reported in the international literature in 1971. Similar indexes for 1969 and 1970 are also available ($3.00 each). The Index is a bibliography, arranged by bond type, in alphabetical order of the elements concerned; thus, for example, all structure determinations involving Ag–M bonds are listed first, and the last group of entries are those for compounds with Zn–M bonds. The entries cover one line only and give the literature reference, the length of the particular bond cited, the method used, and identification of the compound by name or formula. This is difficult information to track down, and this compilation appears to be potentially very useful.

Ion Implantation. Edited by F. H. Eisen (NAR Science Center) and L. T. Chadderton (University of Copenhagen). Gordon and Breach, New York, N. Y. 1971. xii + 467 pp. $22.50.

The Proceedings of the First International Conference on Ion Implantation and Semiconductors (1970) are presented in this volume. The papers were originally published in the journal *Radiation Effects* and are here collected between hard covers. Each paper is in complete, formal condition, including abstract, authors' addresses, diagrams, etc. The subject matter is heavily oriented toward silicon and the effects of bombardment by ions, atoms, etc., on its solid-state properties. There is no subject index.

Molecular Mechanisms of Antibiotic Action on Protein Biosynthesis and Membranes. Edited by E. Muñoz, F. Garcia-Ferrandiz, and D. Vázquez. American Elsevier, New York, N. Y. 1973. xvi + 804 pp. $27.50.

This volume contains the proceedings of an international symposium held in Spain in 1971, consisting of 42 papers plus the opening and closing addresses. The papers are evidently photoreproduced from the typescripts submitted by the authors, for the type faces are varied, but the quality of presentation is very good. The papers report original research, but it is not clear to what extent the material may have been or may be going to be published in journal articles as well. A useful feature is an appendix of 25 pages listing antibiotics with their structural formula. There is a general subject index as well as an antibiotic index.

Nonaqueous Electrolytes Handbook. Volume I. Edited by G. J. Janz and R. P. T. Tomkins (Rensselaer Polytechnic Institute). Academic Press, New York, N. Y. 1972. xiii + 1108 pp. $55.00.

This book consists of an immense quantity of carefully arranged and tabulated data that will be of use to a broad range of chemists. There are seven main sections: Physical Properties of Solvents (single and mixed); Solvent Purification; Electrical Conductance (of solutions); Diffusion; Density (of solutions); Viscosity (of solutions); and Transference Numbers. There is also a large appendix of additional data and a Compound Index. The entries are all keyed to references to the original literature, which is covered through 1971. The editors state that they have not attempted to repeat all the information in Walden's pioneer work "Elektrochemie Nichtwässeriger Lösungen" (1924), but have emphasized more recent contributions. Even though the editors were assisted by seven other contributors, the effort required must have been really consuming; the result seems to be worth it!

Progress in Surface and Membrane Science. Volume 5. Edited by J. F. Danielli (State University of New York), M. D. Rosenberg (University of Minnesota), and D. A. Cadenhead (State University of New York). Academic Press, New York, N. Y. 1972. xii + 353 pp. $21.45.

This book maintains the high quality of the four previous volumes. At first sight it would appear that the various chapters are too different to be of interest to any one reader. However, people interested in surface and membrane science will find it very stimulating to read the various chapters even if the specific subjects are not of immediate interest to them. For example, two of the chapters are concerned with biological membranes and are stimulating to read even if the subject is remote from one's field. The book begins with a very useful chapter on "The Mössbauer Effect in Surface Science" by M. C. Hobson, Jr. This will certainly stimulate readers to look into this technique for studying surfaces. The next two chapters have a great deal of practical as well as theoretical interest and are concerned with "Surface Functional Groups on Carbon and Silica" by V. L. Snoeyink and Walter J. Weber, Jr., and "Wetting Phenomena Pertaining to Adhesion" by Harold Schonhorn. The following chapter is biological in interest and is concerned with "The Physical State of Phospholipids and Cholesterol in Monolayers, Bilayers, and Membranes" by M. C. Phillips. A very useful and timely chapter follows on "Heterocoagulation" by S. Usui, which the reviewer found of particular value and interest. The final chapter by D. J. Triggle on "The Effects of Calcium on Excitable Membranes and Neurotransmitter Action" is again connected with biological membranes and although highly specialized is well written and should be interesting and useful to all researchers in the membrane field.

The overall impression received is that the book is a valuable

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* Unsigned book reviews are by the Book Review Editor.