

structure of tren complexes in solution seems to be rather uncertain, our observations suggest that the usual assumption of a cis-octahedral arrangement ($\text{Ni}(\text{tren})(\text{H}_2\text{O})_2^{2+}$) is correct. The two water molecules in such a structure are in different environments. The results derived from ^{17}O nmr line broadening and paramagnetic shifts are shown in Table I. The slower

Table I. Water Exchange Kinetics in tren Complexes

System	k_1 , $25^\circ \text{ sec}^{-1}$	ΔH^* , kcal/mol
$\text{Ni}(\text{tren})(\text{H}_2\text{O})_2^{2+}$	8.2×10^6 $\sim 9 \times 10^6$ ^a	8 ± 1 8 ± 1.5
$\text{Cu}(\text{tren})(\text{H}_2\text{O})_2^{2+}$	1.5×10^6 (-10°) 2.5×10^5	10.4 ± 0.3

^a The value at 25° is extrapolated from the more accurate one at -10° .

exchange is about what one would predict from our study of aliphatic amine ligands.^{2,3}

Substitution of water in the Ni-tren complex by ammonia⁴ is fairly consistent with replacement of the faster exchanging water *via* an Eigen mechanism. The reported substitutions on the Ni-tren complex by phen and bipy⁵ are slower than for NH_3 by a factor of at least 20. It has been suggested⁵ that the rate-determining step with the chelate ligands involves ring closure. Since phen and bipy when attached at one end would not be expected to affect the lability of the remaining water molecule,⁵⁻⁷ which exchanges relatively slowly, the loss of this water may be rate determining for ring closure. The ratio of water exchange rates at 25° is *ca.* 10-20, which is at least suggestive that the loss of the second water is important here. If this idea is correct, one predicts that ethylenediamine substitution on Ni-tren should be considerably more rapid than for phen or bipy; apparently this reaction has not been studied.

The case of Cu(II) is interesting because of the single relatively slow rate of exchange observed (see Table I), more like Ni(II) than Cu(II). The structure of the complex in aqueous solution is uncertain. Suggestions of trigonal-bipyramidal,⁸ tetrahedral,⁹ and cis-octahedral¹⁰ structures have been made. Polymeric forms of the Ni(II) complex are reported¹¹ but the Cu(II) species is said to be monomeric.⁸ We have measured the effect of NH_3 addition on the $^{17}\text{OH}_2$ line broadening due to the Cu-tren complex. At a 1:1 NH_3/Cu ratio the line broadening becomes very small, suggesting that a monoamine-tren complex (five-coordinate) has formed. This result suggests five coordination also for the aquo-tren complex but, of course, is not con-

clusive evidence. No shift in the $^{17}\text{OH}_2$ resonance was observed for the aquo-tren species which tends to rule out the presence of a second very rapidly exchanging water molecule.

As far as we are aware, no substitution work has been done on the copper complex which can be compared with water exchange.

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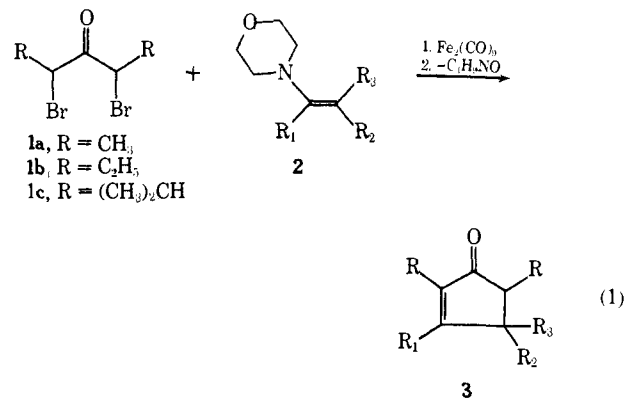
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Reaction of α, α' -Dibromo Ketones and Enamines with the Aid of Iron Carbonyls. A Novel Cyclopentenone Synthesis¹

Sir:

The construction of five-membered carbocyclic systems has been generally accomplished by intramolecular condensation of open-chain dicarbonyl compounds or dicarboxylic acid derivatives,² or ring contraction of six-membered cyclic ketones.^{3,4} This paper describes a new, facile cyclopentenone synthesis by *intermolecular* coupling of three- and two-carbon units. The general sequence (eq 1) which consists of reaction of the dibromo ketones **1** and the morpholine enamines **2** in the presence of iron carbonyls, followed by spontaneous elimination of morpholine, was achieved under mild reaction conditions, and usually in satisfactory yield.



For example, when a mixture of **1a** (10 mmol), α -morpholinostyrene (25 mmol), and $\text{Fe}_2(\text{CO})_9$ (12 mmol) in dry benzene (25 ml) was stirred at $25-30^\circ$ for 12 hr under nitrogen atmosphere, the desired cyclopentenone **3** ($\text{R} = \text{CH}_3$, $\text{R}_1 = \text{C}_6\text{H}_5$, and $\text{R}_2 = \text{R}_3 = \text{H}$) was obtained in 94% yield after silica gel chromatography: ir (CCl_4) 1696 ($\text{C}=\text{O}$) and 1626 cm^{-1} ($\text{C}=\text{C}$); uv ($\text{C}_2\text{H}_5\text{OH}$) 220 ($\log \epsilon$ 3.72) and 279 nm (4.05); nmr (CCl_4)

(2) A. G. Desai, H. W. Dodgen, and J. P. Hunt, *J. Amer. Chem. Soc.*, **92**, 798 (1970).

(3) J. P. Hunt, *Coord. Chem. Rev.*, **7**, 1 (1971).

(4) J. P. Jones, E. J. Billo, and D. W. Margerum, *J. Amer. Chem. Soc.*, **92**, 1875 (1970).

(5) R. G. Wilkins, *Accounts Chem. Res.*, **3**, 408 (1970).

(6) M. Grant, H. W. Dodgen, and J. P. Hunt, *J. Amer. Chem. Soc.*, **92**, 2321 (1970).

(7) M. Grant, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, **10**, 71 (1971).

(8) H. B. Jonassen and H. Thilemann, *Z. Anorg. Chem.*, **320**, 274 (1963).

(9) C. R. Bertsch, W. C. Fernelius, and B. P. Block, *J. Phys. Chem.*, **62**, 444 (1958).

(10) C. K. Jørgensen, *Acta Chem. Scand.*, **10**, 887 (1956).

(11) H. B. Jonassen and V. V. Ramanujam, *J. Phys. Chem.*, **63**, 411 (1959).

(1) Carbon-Carbon Bond Formations Promoted by Transition Metal Carbonyls. II. Part I: R. Noyori, S. Makino, and H. Takaya, *J. Amer. Chem. Soc.*, **93**, 1272 (1971).








(2) (a) A. T. Nielsen and W. J. Houlihan, *Org. React.*, **16**, 1 (1968); (b) R. A. Raphael, "Chemistry of Carbon Compounds," Vol. IIA, E. H. Rodd, Ed., Elsevier, New York, N. Y., 1953, p 71; (c) M. Green, G. R. Knox, and P. L. Pauson, "Rodd's Chemistry of Carbon Compounds," Vol. IIA, S. Coffey, Ed., Elsevier, New York, N. Y., 1967, p 104.

(3) For example, B. G. McFarland, "Steroid Reactions," C. Djerassi, Ed., Holden-Day, San Francisco, Calif., 1963, p 427.

(4) Recently recorded excellent methods for the synthesis of five-membered ketones: (a) (intramolecular alkylation of ketones) P. T. Lansbury, E. J. Nienhouse, D. J. Scharf, and F. R. Hilfiker, *J. Amer. Chem. Soc.*, **92**, 5649 (1970); (b) (retro-Diels-Alder process) G. Stork, G. L. Nelson, F. Rouessac, and O. Gringore, *ibid.*, **93**, 3091 (1971).

exhibited methyl signals at δ 1.22 (d, $J = 7.0$ Hz, $>CHCH_3$) and 1.91 (t, $J = 2.0$ Hz, $=CCH_3$). Some examples of the new cyclocoupling reaction are shown in Table I. $Fe(CO)_5$ as reducing agent may be used, but less effectively.

Table I. Iron Carbonyl Promoted Cyclopentenone Synthesis^a

Dibromide	Enamine 2			Product ^b	Yield, % ^c
	R ₁	R ₂	R ₃		
1a	H	CH ₃	CH ₃		83
1a	(CH ₂) ₃	H	H		75
1a	(CH ₂) ₄	H	H		100
1a	(CH ₂) ₁₀	H	H		50
1b	C ₂ H ₅	CH ₃	H		55
1c	C ₆ H ₅	H	H		72
1c	(CH ₂) ₄	H	H		77

^a Reaction was performed in dry benzene at 25° for 12 hr using 1, 2, and $Fe_2(CO)_9$ in a mole ratio of 1.0:2.5-3.0:1.2. No attempt was made to optimize the reaction conditions. In certain cases (e.g., diisopropyl derivatives), the elimination of morpholine from the β -morpholino ketone was confirmed by treating the crude products with 3% ethanolic NaOH at 25° for 5 min. ^b All new compounds gave correct elemental analyses. The structure was determined on the basis of the spectral data (ir, uv, nmr, and mass spectra). A mixture of epimers, when possible, was obtained. ^c Isolated yield based on starting dibromide.

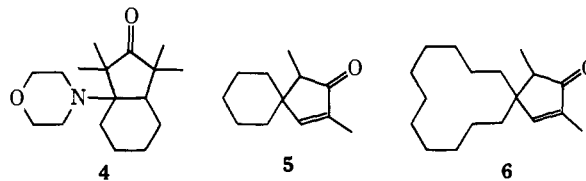
As expected, reaction of 1-morpholinocyclohexene with 2,4-dibromo-2,4-dimethylpentan-3-one bearing no hydrogen atoms at the position α to the carbonyl function gave rise to the stable β -morpholino ketone 4 in 91% yield: mp 96-97°; ir (CCl₄) 1732 cm⁻¹ (C=O) characteristic of tetraalkylated cyclopentanone.⁶ Attempted reaction of dibromides derived from acetone and other methyl ketones yielded little, if any, cyclic adducts. While not suited to the formation of unsubstituted cyclopentenones, the present synthetic reaction does produce α, α' -dialkylcyclopentenones directly, thus avoiding the tedious, multistep techniques which are required to α -alkylate cyclic ketones, particularly with bulky alkyl groups.⁷

(5) For related long-range coupling, see W. von E. Doering, M. R. Willcott, III, and M. Jones, Jr., *J. Amer. Chem. Soc.*, **84**, 1224 (1962).

(6) J. Lascombe, P. Grange, and M.-L. Josien, *Bull. Soc. Chim. Fr.*, 773 (1957).

(7) For a method of synthesis of α, α' -dialkylcyclopentanones, see R. M. Coates and R. L. Soweby, *J. Amer. Chem. Soc.*, **93**, 1027 (1971), and references cited therein.

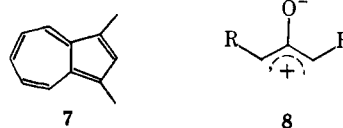
The novel annulation reaction allows for the synthesis of a variety of cyclic compounds which have not so far been readily accessible. Utilization of enamine derived from cycloalkanecarboxaldehydes provided a convenient route to spiro[*n*.3]alkenone systems.⁸ For instance, the reaction of 1a and cyclohexanecarboxaldehyde morpholine enamine under the above described conditions gave the spirofused cyclopentenone 5 in 70% yield: ir (CCl₄) 1706 (C=O) and 1640 cm⁻¹



(C=C); uv (C₂H₅OH) 237 nm (log ϵ 3.95); nmr (CCl₄) showed a finely split one-proton multiplet at δ 7.37 due to the vinylic proton. In a similar fashion, the spiro-adduct 6, mp 87-88°, was obtained in 65% yield starting with 1a and the morpholino enamine of cyclo-dodecanecarboxaldehyde.

Bicyclic adducts 3 prepared from the dibromo ketones 1 and cycloheptanone enamines could readily be converted to the azulene derivatives employing standard procedures. Thus, reduction of 3 (R = CH₃, R₁R₂ = (CH₂)₃, R₃ = H; obtained in 100% yield) with 10 equiv of NaBH₄ (in C₂H₅OH, 25°, 15 hr) followed by heating the crude products with 3 equiv of sulfur at 290-300° for 15 min gave 1,3-dimethylazulene (7) as blue crystals in 20% yield, mp 52-53° (lit.⁹ mp 54°), with spectral data identical with those recorded.⁹

Thus, by combining the present method with the previously developed cycloheptenone synthesis,¹ the dehalogenation of α, α' -dibromo ketones with iron carbonyls has become a versatile tool for synthesizing odd-numbered carbocyclic systems. The mechanism of the cyclocoupling reaction, which probably involves the zwitterions of type 8 (or the related species) interacted



by σ or π coordination with iron atoms as the key intermediates, will be presented in the near future.¹⁰

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(8) Recently recorded methods for the synthesis of spiro compounds: (a) E. J. Corey and J. I. Shulman, *J. Amer. Chem. Soc.*, **92**, 5522 (1970); (b) D. J. Dunman and R. G. Lawton, *ibid.*, **93**, 2074 (1971).

(9) Pl. A. Plattner, A. Fürst, and K. Kirasek, *Helv. Chim. Acta*, **30**, 1329 (1947).

(10) In the absence of $Fe_2(CO)_9$, no reaction was observed between 1-morpholinocyclohexene and 1a (in benzene, 25°). Reduction of 1a with $Fe_2(CO)_9$ in a 1:5 mixture of the enamine and furan (25°, 12 hr) gave 3 (R = CH₃, R₁R₂ = (CH₂)₄, and R₃ = H) and 2,4-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one in a 1:9 ratio.

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