analogues, ref 35 (1-substituted tropanols) and 33 (6-alkoxytropeines), respectively.
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# Iron Carbonyl Promoted Reaction of α,α′-Dibromo Ketones and Aromatic Olefins Leading to 3-Arylcyclopentanones. The [3 + 2] Cycloaddition Involving an Allylic Cation[1,2]

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**Abstract:** Reactive oxyallyl-Fe(II) intermediates, generated from secondary or tertiary α,α′-dibromo ketones and iron carbonyls, cycloadd across aryl-substituted olefins in 3 + 2 → 5 manner, producing 3-arylcyclopentanones in fair to good yields. As the by-product open-chain olefinic ketones via electrophilic olefinic substitution are formed. In certain cases, 2-alkylidenetetrahydrofurans are produced as well. As the olefinic substrate, styrene, alkylated styrenes, anethole, indene, 1,1- and 1,2-diphenylethylene, ferrocenylethylene, etc., may be used. In order to achieve smooth reaction, placement of a carbocation-stabilizing group at the arylated olefinic carbon or in the aromatic ring is favorable. Competition experiments have revealed that the relative reactivities decrease in the order of α-methylstyrene > styrene > β-methylstyrene, implying that both electronic and steric factors are controlling the ease of the cycloaddition. The $[_{\pi}2 + {}_{\pi}2]$-type cycloaddition forming cyclopentanones is fully accounted for in terms of a stepwise mechanism involving a zwitterionic intermediate. The experiment by use of *cis*-β-deuteriostyrene has indicated that the [3 + 2] cycloaddition proceeds in a stereospecific fashion regardless of the stepwise nature, whereas the electrophilic substitution goes in a nonstereospecific manner. Possible structures of the zwitterions involved in these reactions are discussed.

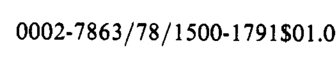
Synthesis of five-membered carbocycles is usually accomplished by intramolecular cyclization of open-chain bifunctional compounds.[3,4] In certain cases, ring contraction of cyclohexanones[5] and ring enlargement of cyclobutane derivatives[6] are employed for this purpose. In contrast, there are only little syntheses by intermolecular cyclocombination of odd- and even-numbered carbon units, viz., a 1 + 4 → 5 or 3 + 2 → 5 manner.[3,7] The latter is apparently ascribed to the scarcity of odd-numbered reactive species which are capable of participating in such cyclocoupling reactions. This paper describes a new reaction which falls into this category.

## General Consideration

Recently reactive allylic moieties have been highlighted as a promising three-carbon unit. Their cycloaddition across olefinic double bonds has received considerable attention from not only theoretical or mechanistic interest but also from synthetic importance. The possible [3 + 2] cycloadditions are formally classified into three cases, eq 1–3, according to the number of π electrons present in the allylic system. Among them the cycloaddition between allyl anions and olefins, eq 1, is regarded as a thermally allowed $[_{\pi}4_{s} + {}_{\pi}2_{s}]$ reaction,[8] and several examples of this anionic cycloaddition are known.[9] Cycloaddition of an allyl radical and olefin, given by eq 2, is viewed as a $[_{\pi}3_{s} + {}_{\pi}2_{s}]$ process and might be taken as a thermally allowed reaction according to the simple orbital-symmetry consideration[8] but some doubts arose about this analysis as well.[10] In practice, no example is known for the cycloaddition of this type. The relevant reverse reaction, decomposition of cyclopentyl radicals to allyl radicals and olefins, was examined in some detail and the stereochemical results indicated the retrocycloaddition to be stepwise in nature.[11] The third type of reaction via a four-electron transition state, eq 3, is imposed to be thermally forbidden by the orbital symmetry factors and has not been investigated to any great extent. To date, no evidence has been provided for the cationic [3 + 2] cycloaddition occurring in a concerted manner. This type of cycloaddition, though not attained in a synchronous fashion, may take place by a two-step mechanism under certain circumstances, however.[12] Such scheme, as outlined in eq 4, consists of initial electrophilic attack of an allyl cation onto olefinic substrate and subsequent cyclization of the cationic intermediate **1** to form the cyclopentyl cation **2**. Each step in this process is in principle microscopically reversible and hence the following demands must be satisfied in order that the equilibrium shifts so far to the right, thereby completing the formal [3 + 2] cycloaddition. Firstly, the intermediate **1** must have stability

(1)

(2)



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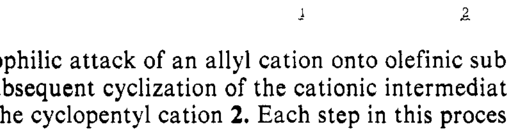

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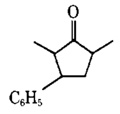
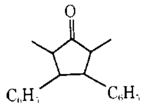
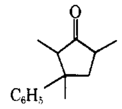
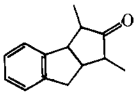
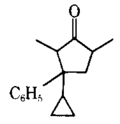
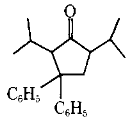
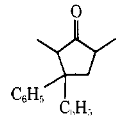
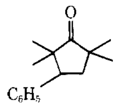
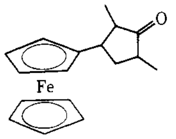
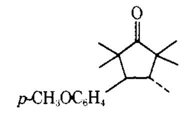
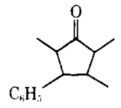
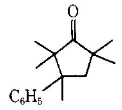
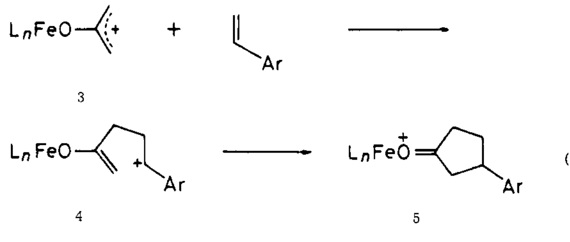
**Table I.** Iron Carbonyl Promoted Reaction of α,α′-Dibromo Ketones and Aromatic Olefins

| Dibromide | Aromatic olefin | Cycloadduct[a] | IR in $CCl_4$ $\nu_{C=O}$, $cm^{-1}$ | % yield[b] | Dibromide | Aromatic olefin | Cycloadduct[a] | IR in $CCl_4$ $\nu_{C=O}$, $cm^{-1}$ | % yield[b] |
|---|---|---|---|---|---|---|---|---|---|
| 6 | Styrene[c] |  **9** | 1740[d]<br>1737[e] | 65 | 6 | *trans*-Stilbene |  **15** | 1738[d] | 30 |
| 6 | α-Methylstyrene[c] |  **10** | 1735[d]<br>1742[e] | 70 | 6 | Indene |  **16** | 1737[d] | 45[f] |
| 6 | α-Cyclopropylstyrene |  **11** | 1736[d] | 95[f] | 7 | 1,1-Diphenylethylene |  **17** | 1728[h] | 44[i] |
| 6 | 1,1-Diphenylethylene |  **12** | 1744[d]<br>1733[e] | 70[g] | 8 | Styrene[c] |  **18** | 1734 | 23[j] |
| 6 | Ferrocenylethylene[c] |  **13** | 1736[d] | 30[f] | 8 | *trans*-Anethole |  **19** | 1733 | 55[k,l] |
| 6 | *trans*-β-Methylstyrene |  **14** | 1738[d] | 20[f] | 8 | α-Methylstyrene |  **20** | 1736 | 5[m] |

[a] A mixture of diastereomers was obtained when 6 or 8 was employed as a starting bromide. [b] Isolated yield based on the dibromo ketone. [c] Considerable polymerization of olefin took place. [d] Trans isomer with respect to $C_2$ and $C_5$ alkyl groups. [e] Cis isomer with respect to $C_2$ and $C_5$ alkyl groups. [f] Although the cyclocoupling reaction formed a mixture of two diastereomeric adducts, a single epimer was obtained after silica gel TLC or distillation. [g] 4-Methyl-6,6-diphenylhex-5-en-3-one (**21**) was also obtained in 7% yield. [h] Absorption of a mixture of two diastereomers. [i] 3-Isopropyl-7-methyl-1,1-diphenylhept-1-en-4-one (**22**) was obtained in 11% yield. [j] *trans*-2,4,4-Trimethyl-6-phenylhex-5-en-3-one (**23**) was formed in 23% yield. [k] In addition the enone **24**, and the cyclic ether **37** were obtained in 3 and 30% yields, respectively. [l] A single epimer. The *p*-methoxyphenyl and methyl at $C_4$ are trans to each other. [m] In addition there were obtained *trans*-2,4,4-trimethyl-6-phenylhept-5-en-3-one (**25**, 37%), 2-isopropylidene-3,3,5-trimethyl-5-phenyl-1-oxacyclopentane (**26**, 16%), and 2,4,4-trimethyl-6-phenylhept-6-en-3-one (**27**, 11%).

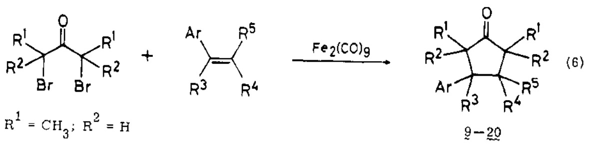
comparable with that of the allyl cation. Secondly, the resulting five-membered cation **2** is required to be even more stable than **1** or, if not so, it has to undergo further irreversible transformation, leading to neutral final products, by a proper action such as elimination of proton or other cationic species, addition of nucleophiles, and so on. Accordingly, it appears to be crucial to select suitable three- and two-carbon components bearing substituent(s) that provides such driving forces. We have selected as the bifunctional three-carbon unit the oxyallyl-iron(II) species of type **3**[13] and aryl-substituted olefins as the trapping agent (eq 5). This choice fulfills ideally the above-described requirements. An oxygen atom attached to the central sp²-hybridized carbon of **3** decreases the stability of the allylic moiety to a considerable extent, compared with that of ordinary allyl cations,[14] facilitating the first electrophilic addition process. The resulting cation **4** is highly stabilized by the aryl substituents. Here again the presence of the oxygen atom makes the subsequent cyclization step easy, because the scheme forms the stable oxonium ion **5**,[15] from which the Lewis acid eliminates giving a neutral cyclopentanone product. Cooperation of these electronic factors makes the forward process feasible. Thus the iron carbonyl promoted reaction of α,α′-dibromo ketones and aromatic olefins presents the first example of clean cationic 3 + 2 → 5 cycloaddition.



(5)

## Results and Discussion

**Cyclocoupling Reaction of α,α′-Dibromo Ketones and Aryl-Substituted Olefins.** Some examples of the reaction of eq 6 are given in Table I. Typically, the reaction of 2,4-dibromopentan-3-one (**6**) (10 mmol), 1,1-diphenylethylene (40 mmol), and $Fe_2(CO)_9$ (12 mmol) at 60 °C for 14 h in benzene gave *cis*- and *trans*-2,5-dimethyl-3,3-diphenylcyclopentanone (*cis*- and *trans*-**12**) as the major products in 70% combined yield. In addition, a small amount (7%) of 4-methyl-6,6-diphenylhex-5-en-3-one (**21**) was obtained. Structural determination of the adducts rested on the spectral data as well as elemental analysis.

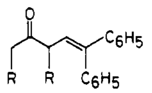


**6**, $R^1 = CH_3$; $R^2 = H$

**7**, $R^1 = CH(CH_3)_2$; $R^2 = H$

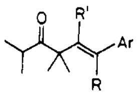
**8**, $R^1 = R^2 = CH_3$

**9**–**20**



**21**, $R = CH_3$

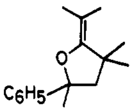
**22**, $R = CH(CH_3)_2$



**23**, $Ar = C_6H_5$; $R = R' = H$

**24**, $Ar = p\text{-}CH_3OC_6H_4$; $R = H$; $R' = CH_3$

**25**, $Ar = C_6H_5$; $R = CH_3$, $R' = H$



**26**

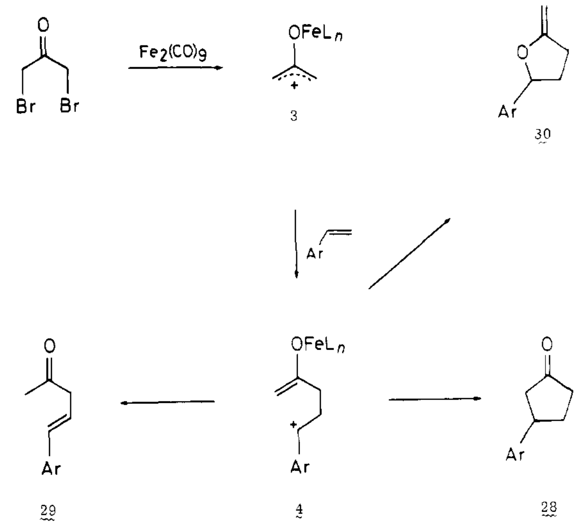
Reaction with tertiary dibromo ketones often led to another type of 1:1 adduct. Thus the reaction of the dibromo ketone **8** and α-methylstyrene afforded the alkylidenetetrahydrofuran derivative **26** in 16% yield together with the expected products. The adduct **26** remained unchanged upon exposure to the reaction conditions. A similar phenomenon was found in the reaction of **8** and *trans*-anethole as well. Such a trend forming enol ethers was peculiar to the reaction of tertiary dibromo ketones and was not observed in the coupling reaction with secondary dibromides.

Although the present cyclocoupling reaction finds considerable generality, α,α′-dibromoacetone failed to yield the olefin adducts. The reaction of α,α,α′,α′-tetrabromoacetone and styrene was attempted without success. Tetrahydrofuran (THF) as solvent accelerates the reduction of dibromo ketones but is unfavorable for the cationic coupling reaction. Regarding the reducing agent, $Fe_2(CO)_9$ is the most effective, and $Fe(CO)_5$, though less effective, may also be used. When aromatic olefin–$Fe(CO)_4$ complexes were used, the reaction proceeded rather sluggishly and did not give a better result than the standard procedure. Attempted reaction of **6** and styrene with zinc–copper couple in benzene or 1,2-dimethoxyethane gave no cyclopentanone products.

**Reaction Mechanism. A. Reactive Intermediate.** All available evidence shows the presence of oxyallyl–Fe(II) species[13] as the reactive intermediate of the [3 + 2] reaction. Control experiments indicated that 2,2-dimethylcyclopropanone does not react with 1,1-diphenylethylene. Notably both cyclopropanones[16] and oxyallyl species[17] equally cycloadd across 1,3-dienes in a [3 + 4] fashion, while only oxyallyls react with aromatic olefins in a [3 + 2] manner.

**B. Reaction Course.** As has been discussed above, the cycloaddition reaction of an allyl cation and olefin belongs to the thermally forbidden $[_\pi 2 + {}_\pi 2]$ process according to the orbital symmetry rule and, in consequence, it is submitted to proceed by a stepwise mechanism. The foregoing observations are fully in accord with the mechanism outlined in Scheme I, where, for the sake of simplicity, reaction of unsubstituted oxyallyl and a monosubstituted olefin is taken up. Electrophilic attack of the oxyallyl species **3** on the olefinic substrate forms the zwitterionic intermediate **4**. Its ring closure affords the cyclopentanone **28**, while prototropy therefrom yields the olefinic ketone **29**. The former is viewed as a formal result of [3 + 2] cycloaddition of the oxyallyl species and olefins, while formation of the latter is envisaged as electrophilic *olefinic* substitution of the oxyallyl cation.[18] In certain cases, especially when the carbon terminus of the enolate moiety of **4** is sterically crowded, ring closure at the oxygen terminus, **4** → **30**, can compete with the normal cyclization, **4** → **28**.[19]

Scheme I



**Relative Reactivities of Arylated Olefins.** Although most olefins listed in Table I are known to form the iron tetracarbonyl complexes, yield of the products or readiness with which the coupling reaction takes place seems independent of ease of the complex formation. Even indene, which forms little iron complex,[21] can produce the cycloadduct in a fair yield. Rather, the product yield appears to depend primarily on the stability of the intermediary carbocations of type **4**.

α-Cyclopropylstyrene reacted quite smoothly with **6**, giving the cycloadduct **11** in high yield. The smoothness of this reaction is easily understood by considering the great carbocation-stabilizing ability of phenyl and cyclopropyl groups.[22] Although α-cyclopropylstyrene–$Fe(CO)_4$ complex rearranges easily to *trans*-2-phenyl-1,3-pentadiene–$Fe(CO)_3$ complex,[23] there were obtained no adducts resulting from such rearranged diene ligand.

The intermolecular competition experiments by use of methylated styrenes revealed that the rate of the cyclocoupling reaction is affected by not only the electronic factors but also the steric environment around the carbon–carbon double bond. First, the result of the reaction of **6** in a 1:1 mixture of α-methylstyrene and styrene (large excess) at 55 °C indicated that the reaction with α-methylstyrene is approximately three times faster than that with unsubstituted styrene. A similar reaction with a 1:1 mixture of *trans*-β-methylstyrene and styrene afforded only the styrene adduct **9**. Such a reactivity sequence of the aromatic olefins, α-methylstyrene > styrene > β-methylstyrene, bears parallel to the well-known order in the cationic polymerization.[24] The acceleration caused by α-methylation can be ascribed to an increase in stability of the carbocation of type **4**, whereas the deceleration with the β-methyl group is presumably due to the sizable steric hindrance in the transition state of the electrophilic attack.

Attempted reaction of *trans*-β-methylstyrene and the tertiary dibromide **8** failed to produce the cyclopentanone adduct, while its *p*-methoxy derivative, *trans*-anethole, cyclocoupled with **8** to give the cyclopentanone **19** in 55% yield. The total yield of three types of 1:1 adducts went up to 88% in this case. This could be again ascribed to the electrodonative property of the methoxyl group.

Although the complexity of the present reaction system does not permit the more systematic examination of substituent effects, these findings clearly indicate the involvement of the zwitterionic intermediates in the rate-determining step of the reaction. These intermediates, we feel, form mostly by the reaction of oxyallyl–Fe(II) species and uncomplexed olefins. The initial olefin–iron(0) π complex formation seems not to

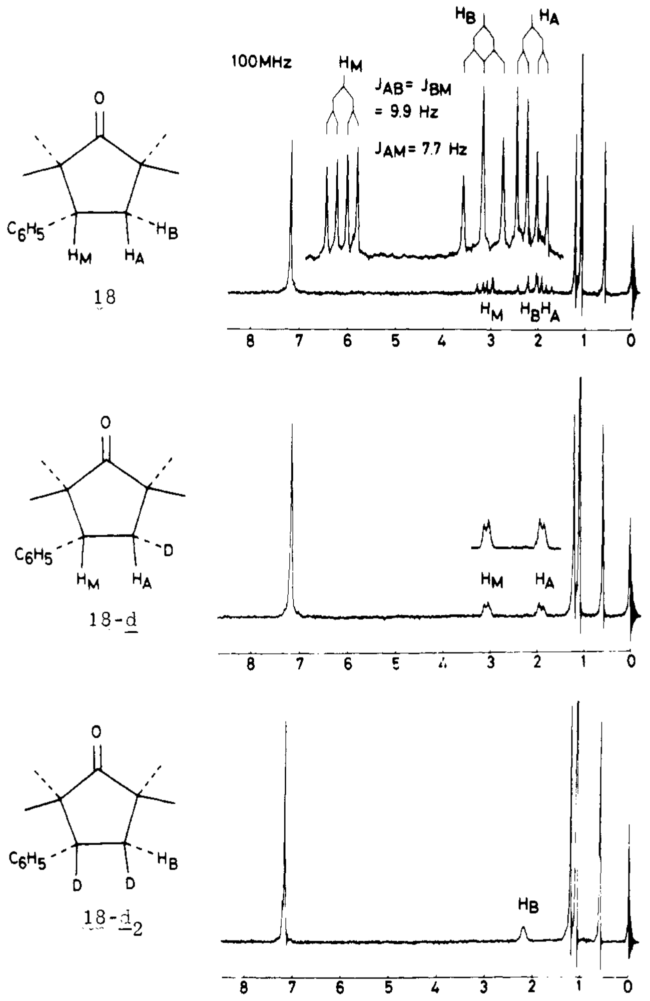
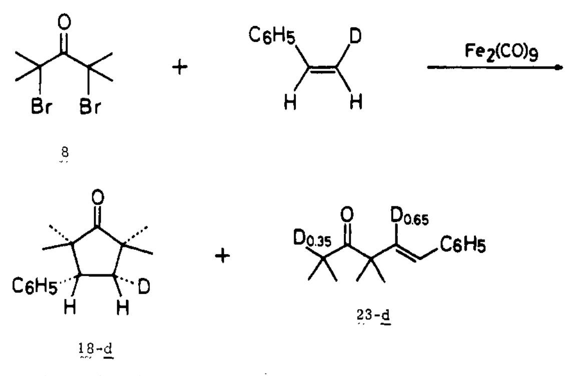


Figure 1. NMR spectra of **18**, **18**-*d*, and **18**-$d_2$ (60 MHz, $CCl_4$).

be a requisite for the cyclocoupling reaction but, at most, to provide merely the advantage of bringing the two reactants in close distance together, thereby facilitating the intermolecular reaction.

**Steric Course of the Reaction.** In order to gain further insight into this new reaction, the stereochemistry has been examined with *cis*-β-deuteriostyrene as olefinic substance. When the reaction was carried out under the standard conditions at 60 °C for 24 h, isomerization of the deuteriostyrene took place to some extent (10-20%).[25] Fortunately, this trouble could be removed by using the following modified procedure. Firstly, $Fe_2(CO)_9$ was mixed with a twofold excess of the dibromide **8** in benzene and the suspension was stirred at 50 °C for 15 min. Then the deuteriostyrene was added and the resulting mixture was stirred for an additional 1 h at the same temperature. After workup the cyclopentanone **18**-*d* and the olefinic ketone **23**-*d* were obtained in 6 and 3% yields, respectively. In this case no noticeable isomerization of the starting styrene had taken place.



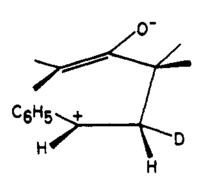
**A. The [3 + 2] Cycloaddition.** In order to establish the stereochemistry of the cyclopentanone product, the dideuterated derivative, *cis*-3,4-dideuterio-2,2,5,5-tetramethyl-3-phenylcyclopentanone (**18**-$d_2$), was synthesized independently. As can be seen from the NMR spectra of the cyclopentanones **18**, **18**-*d*, and **18**-$d_2$ (Figure 1), the stereochemical relationship of the phenyl and deuterium of **18**-*d* was determined unambiguously as cis. Thus the starting aromatic olefin has proved to enter into the overall cycloaddition *stereospecifically* with retention of configuration.

**B. Electrophilic Olefinic Substitution.** The open-chain adduct **23**-*d* was configurationally homogeneous and contaminated with <1% of the cis isomer **31**. Notably the deuterium atom that had been present at the styrene cis, β position was incorporated in **23**-*d* at both vinylic (65%) and carbonyl α positions (35%), as determined by NMR analysis. Neither the cyclopentanone **18** nor the cis olefin **31** was convertible to **23** upon exposure to the reaction conditions. Thus the olefinic substitution reaction is concluded to proceed in a *nonstereospecific* manner with respect to the starting styrene.

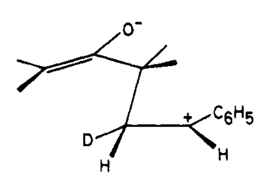
**C. Inspection of the Structures of the Zwitterionic Intermediates.** Although both [3 + 2] cycloaddition and olefinic substitution are simply considered to occur via a common zwitterion of type **4**, further scrutinies are required to explain these contrasting stereochemical results.

Although stereospecificity in cycloaddition may be conceived as a criterion of the concertedness,[26,27] certain stepwise reactions are known to go with a high degree of stereospecificity.[28,29] In principle the degree of stereospecificity in a stepwise process depends on relative rates of ring closure of the intermediate and its internal rotation inverting stereochemistry. The stereospecific nature of the present [3 + 2] reaction is presumably ascribed to involvement of the U-shaped intermediate **32U** formed by cisoid approach[30] of the oxyallyl and aromatic olefin. In this species, the structure is fixed rigidly by a charge-transfer or Coulombic attraction between the enolate and cationic center. Alternatively, bond formation between the charged termini may be quite rapid. In any event such electrostatic interactions are considered to prevent the structure from rotating around the $C_6H_5CH^+$-CDH single bond; thereby the original stereochemistry is preserved throughout the reaction.[31]

On the other hand, the lack of stereospecificity displayed by the olefinic substitution reaction is best explained in terms of the Z-shaped intermediate **32Z** arising from either transoid approach of the two π components or conformational change of **32U**.[33] Here interactions between the charged moieties are of negligible importance in keeping the stereochemical integrity. The phenyl-stabilized cation **32Z** can rotate easily to afford the conformers capable of causing prototropy, as outlined in Scheme II. Thus the rotamer **32a** formed by the 60° rotation suffers deprotonation to give the olefinic product **33**, where the original olefin stereochemistry is retained, while the initial 120° rotation, giving **32b**, followed by transfer of deuterium, leads to the keto olefin with inverted stereochemistry, **34**. Mixing of these two pathways appears to result in the overall nonstereospecific transformation. The cis olefins **35** and **36** are

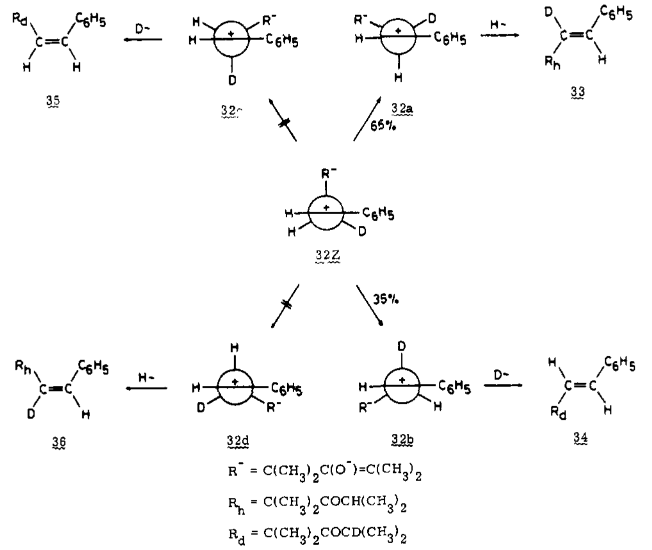


32U



32Z

Scheme II



$R^- = C(CH_3)_2C(O^-){=}C(CH_3)_2$

$R_h = C(CH_3)_2COCH(CH_3)_2$

$R_d = C(CH_3)_2COCD(CH_3)_2$

not produced, because the sterically crowded precursors **32c** and **32d**, respectively, are unfavorable to form.[34]

## Experimental Section

**General.** Melting points are uncorrected. Infrared (IR) and nuclear magnetic resonance (NMR) spectra were taken in $CCl_4$. IR spectra were recorded on a JASCO Model DS-402G spectrophotometer with matched 0.1-mm path length NaCl cells. Carbonyl absorptions of the cyclopentanones **9–20** are listed in Table I. JEOL Model C-60H, Varian NV-21, or Varian HA-100D spectrometers were used to determine NMR spectra. Untraviolet (UV) spectra were obtained in ethanol using a Perkin-Elmer Model 202 or Hitachi Model 323 spectrometer. Mass spectra were run on a Hitachi RMU-6C instrument at 70 eV. Microanalyses were done at the Microanalytical Center of Kyoto University, Faculty of Engineering of Nagoya University, and the Research Laboratory of Fujisawa Pharmaceutical Co.

**Chromatography.** Analytical gas-liquid chromatography (GLC) was done with a Hitachi 063 or Yanagimoto Model G-8 instrument, and preparative scale GLC on a Varian Model 1700 thermal conductivity gas chromatograph with helium as a carrier gas at the noted temperature. Separation of components was accomplished on the following columns: A, 15% Silicone SE-30 on Chromosorb W AW (3/8 in. × 10 ft); B, 3% Silicone OV-1 on Chromosorb W AW (3 mm × 2 m); C, 12% poly(ethylene glycol) adipate on Neopak 1A (3/8 in. × 13 ft); D, 5% poly(ethylene glycol) adipate on Neopak 1A (3 mm × 2 m); E, 14% Silicone SE-30 on Chromosorb W AW (3 mm × 1 m). Analytical thin layer chromatography (TLC) was carried out on an E. Merck Kieselgel $PF_{254}$-precoated slide (2 × 10 cm, 0.25-mm layer). Preparative scale TLC was done with a 20 × 20 cm glass plate coated with 1.0-mm thickness of E. Merck silica gel $PF_{254}$. E. Merck Kieselgel 60 (70–230 mesh) was used for column chromatography.

**Solvents and Materials.** Dibromo ketones,[35] $Fe_2(CO)_9$,[36] Zn/Cu couple,[37] ferrocenylethylene,[38] $CH_2Cl_2$ solution of 2,2-dimethylcyclopropanone,[39] and *cis*-β-deuteriostyrene[40] were prepared by the known procedures. Dibromo ketones were purified immediately before use by passing through a short column packed with basic alumina (Woelm, activity I). Benzene was distilled from $LiAlH_4$ and stored under $N_2$. All liquid aromatic olefins for the cyclocoupling reaction and solvents for chromatography were used after simple distillation of commercial materials. Other organic and inorganic reagents as well as $D_2$ gas (Matheson) were employed without further treatment of commercially supplied ones.

**General Procedure.** The cyclocoupling reaction and workup were generally performed as follows. In a two-necked flask equipped with a magnetic stirrer, a rubber septum, and a three-way stopcock fitted with a nitrogen- or argon-filled balloon was placed $Fe_2(CO)_9$, and the flask was evacuated and flushed with the inert gas. To the flask were added successively benzene, an aryl-substituted olefin, and a dibromo ketone through the rubber septum by a syringe. The resulting mixture was magnetically stirred at the stated temperature. After the reaction was complete, the mixture was diluted with ethyl acetate or ethyl acetate-benzene (30–50 mL). The organic mixture was washed with saturated $NaHCO_3$ solution and $KNO_3$ solution, dried over $Na_2SO_4$, and concentrated with a rotary evaporator under reduced pressure (60–90 mm) at 25–50 °C. Chromatography was done on a silica gel coated plate or a silica gel packed column using the described solvent system as eluent. When the separation of products was performed by preparative TLC, ethyl acetate was used for extraction of product from silica gel. Elution course of the column chromatography was monitored by TLC. Products on the plate were detected by irradiation of UV light (254 nm), spray of $Ce(SO_4)_2$ in 65% $H_2SO_4$ or phosphomolybdic acid in 10% ethanol followed by heating, or exposure to $I_2$ vapor. Analytical samples were collected by bulb-to-bulb distillation or recrystallizations of the chromatographed materials.

Some reactions afforded the cyclopentanones as a mixture of two diastereomers, which were usually homogeneous on TLC but separable on GLC. The isomeric ratio was dependent on the reaction and workup conditions (temperature, period, etc.). The diastereomeric mixture could be converted to a single (or nearly so) epimer which has trans relationship[41] with respect to the $C_2$ and $C_5$ alkyl groups but stereochemistry of the remaining carbon(s) was yet unknown (except for the ketones **12** and **15**). Throughout this section, the symbols **a** and **b** refer to the major and minor isomers, respectively, obtained by the usual reaction and workup (without basic treatment or long standing).

**2,5-Dimethyl-3-phenylcyclopentanone** (**9**). A mixture of 2,4-dibromopentan-3-one (**6**, 488 mg, 2.00 mmol), styrene (417 mg, 4.00 mmol), and $Fe_2(CO)_9$ (874 mg, 2.40 mmol) in benzene (5.0 mL) was magnetically stirred at 50 °C for 14 h. Usual workup followed by preparative TLC (1:20 ethyl acetate-hexane) gave **9** as a mixture of two diastereomers ($R_f$ 0.19, 243 mg, 65% yield). Anal. ($C_{13}H_{16}O$) C, H. **9a**: NMR δ 0.65 and 1.18 (two d, $J$ = 7.2 and 6.0 Hz, respectively, 2 $CH_3$), 1.5–2.8 (m, $CH_2$ and 2 COCH), 3.2–3.7 (m, $CHC_6H_5$), 7.15 (m, $C_6H_5$); mass spectrum *m/e* 188 ($M^+$). **9b**: NMR δ 1.01 and 1.16 (two d, $J$ = 6.5 Hz, 2 $CH_3$), 1.5–3.0 (m, $CH_2$ and 3 CH), 7.15 (m, $C_6H_5$); mass spectrum *m/e* 188 ($M^+$). This diastereomeric mixture became a single epimer, **9b**, on standing for a long period or treatment with 3% ethanolic NaOH solution at room temperature for 10 min.

The reaction of **6** (244 mg, 1.00 mmol) and styrene-$Fe(CO)_4$ complex (272 mg, 1.00 mmol) prepared by the reported method[21] at 50 °C for 19 h gave, after usual workup, **9** in 16% yield and the recovery of 20% of the dibromo ketone **6** (NMR, 1,1,2,2-tetrachloroethane as an internal standard).

A mixture of Zn-Cu couple (78 mg, 1.20 mg-atoms), the dibromide **6** (244 mg, 1.00 mmol), and styrene (208 mg, 2.00 mmol) in DME (5 mL) was stirred at −5 °C for 30 min and then at 25 °C for 16 h. Usual extractive workup gave a pale green oil (287 mg), which included no cyclopentanones and other 1:1 adducts (IR, NMR, and GLC analyses).

**2,3,5-Trimethyl-3-phenylcyclopentanone** (**10**). A mixture of **6** (488 mg, 2.00 mmol), α-methylstyrene (946 mg, 8.00 mmol), and $Fe_2(CO)_9$ (874 mg, 2.40 mmol) in benzene (10 mL) was stirred at 60 °C for 12 h. Usual workup followed by preparative TLC afforded **10** as a diastereomeric mixture of two components ($R_f$ 0.25, 284 mg, 70% yield). Anal. ($C_{14}H_{18}O$) C, H. **10a**: NMR δ 0.69 and 1.17 (two d, $J$ = 7.5 and 6.0 Hz, respectively, 2 $CHCH_3$), 1.35 (s, $CCH_3$), 1.0–2.0 (m, $CH_2$), 2.0–2.5 (m, 2 $CHCH_3$), 7.15 (m, $C_6H_5$); mass spectrum *m/e* 202 ($M^+$). **10b**: NMR δ 1.06 and 1.16 (two d, $J$ = 6.5 Hz, 2 $CHCH_3$), 1.21 (s, $CCH_3$), 1.0–2.0 (m, $CH_2$), 2.0–2.5 (m, 2 $CHCH_3$), 7.15 (m, $C_6H_5$); mass spectrum *m/e* 202 ($M^+$). Treatment of a mixture of **10a** and **10b** with 3% ethanolic NaOH solution at room temperature for 10 min afforded only **10b**.

**3-Cyclopropyl-2,5-dimethyl-3-phenylcyclopentanone** (**11**). A mixture of **6** (244 mg, 1.00 mmol), α-cyclopropylstyrene (288 mg, 2.00 mmol), and $Fe_2(CO)_9$ (437 mg, 1.20 mmol) in benzene (9.0 mL) was stirred at 65 °C for 24 h. The whole mixture was worked up in a usual manner to leave an oil which consisted mainly of **11a** and **11b** (ca. 3:1 ratio based on NMR analysis). **11a**: NMR δ 0.0–0.5 (m, 2 $CH_2$ of cyclopropyl group), 0.75 and 1.17 (two d, $J$ = 7.5 and 6.5 Hz, respectively, 2 $CH_3$), 1.5–3.0 (m, $CH_2$ of five-membered ring and 3 CH), 7.15 (m, $C_6H_5$). **11b**: NMR δ 0.0–1.0 (m, 2 $CH_2$ of cyclopropyl group), 1.14 and 1.35 (two d, $J$ = 6.5 Hz, 2 $CH_3$), 1.5–2.9 (m, $CH_2$ of five-membered ring and 3 CH), 7.11 (m, $C_6H_5$). Long standing of the mixture gave crystalline **11b** ($R_f$ 0.17, 215 mg, 95% yield) as a single epimer. Recrystallizations from hexane afforded colorless prisms: mp 92–94 °C; mass spectrum *m/e* 228 ($M^+$). Anal. ($C_{16}H_{20}O$) C, H.

**Reaction of Dibromo Ketone 6 and 1,1-Diphenylethylene in the Presence of $Fe_2(CO)_9$.** A mixture of **6** (2.44 g, 10.0 mmol), 1,1-diphenylethylene (7.20 g, 40.0 mmol), and $Fe_2(CO)_9$ (4.37 g, 12.0 mmol) in benzene (20 mL) was heated at 60 °C with stirring for 14 h. The reaction mixture was generally worked up as described above, giving a pale yellow oil. Column chromatography (silica gel, 400 g, 1:10 ethyl acetate–hexane) produced 2,5-dimethyl-3,3-diphenylcyclopentanone (**12**) ($R_f$ 0.17, 1:10 ethyl acetate–hexane, 1.85 g, 70% yield) and 4-methyl-6,6-diphenylhex-5-en-3-one (**21**) ($R_f$ 0.22, 1:10 ethyl acetate–hexane, 185 mg, 7% yield). An equilibrium mixture of *trans*- and *cis*-**12** (56:44 ratio) was obtained by treatment with 3% ethanolic NaOH solution at 25 °C for 10 min. Preparative TLC of a small portion of the mixture (1:20 acetone–hexane) gave analytical samples of *trans*-**12** ($R_f$ 0.32) as prisms, mp 118–120 °C (from hexane), and *cis*-**12** ($R_f$ 0.28) as an oil.

*trans*-**12**: NMR δ 0.73 and 1.11 (two d, *J* = 7.5 and 6.5 Hz, respectively, 2 $CH_3$), 1.80–2.32 (m, $CH_2C\mathit{H}(CH_3)CO$), 2.52 and 2.55 (two d, *J* = 8.3 and 11.3 Hz, respectively, $CH_2$), 3.20 (q, *J* = 7.5 Hz, $CC\mathit{H}(CH_3)CO$), 7.15 (m, 2 $C_6H_5$); mass spectrum *m/e* 264 ($M^+$). Anal. ($C_{19}H_{20}O$) C, H.

*cis*-**12**: NMR δ 1.12 and 1.13 (two d, *J* = 7.0 Hz, 2 $CH_3$), 1.5–3.0 (m, $CH_2$ and 2 CH), 7.15 (m, 2 $C_6H_5$); mass spectrum *m/e* 264 ($M^+$). Anal. ($C_{19}H_{20}O$) C, H.

**21**: IR 1713 (C=O), 1664 $cm^{-1}$ (C=C); NMR δ 0.93 (t, *J* = 7.5 Hz, $CH_2C\mathit{H}_3$), 1.16 (d, *J* = 7.0 Hz, $CHC\mathit{H}_3$), 2.30 (m, $C\mathit{H}_2CH_3$), 3.28 (dq, *J* = 10.5 and 7.0 Hz, $C\mathit{H}CH_3$), 5.95 (d, *J* = 10.5 Hz, =CH), 7.17 (m, 2 $C_6H_5$); UV $\lambda_{max}$ 224 nm (log ε 4.12), 255 (4.10), 285 (3.47), 296 (3.37); mass spectrum *m/e* 264 ($M^+$). Anal. ($C_{19}H_{20}O$) C, H.

**2,5-Dimethyl-3-ferrocenylcyclopentanone (13).** A mixture of **6** (244 mg, 2.00 mmol), $Fe_2(CO)_9$ (437 mg, 1.20 mmol), and freshly prepared ferrocenylethylene (424 mg, 2.00 mmol) in benzene (8.0 mL) was stirred with heating at 65 °C for 14 h. Usual workup afforded a crude oil. Bulb-to-bulb distillation (bath temperature 170–180 °C, 3 mm) yielded a single crystalline ketone **13** (85 mg, 30% yield). Collection of an analytical specimen was done by recrystallizations: mp 74–76 °C (yellow plates from hexane); NMR δ 1.08 and 1.15 (two d, *J* = 7.5 and 6.0 Hz, respectively, 2 $CH_3$), 1.5–2.8 (m, $CH_2$ and 3 CH), 4.05 (m, ferrocenyl H); mass spectrum *m/e* 296 ($M^+$), 226, 186. Anal. ($C_{17}H_{20}OFe$) C, H.

**2,3,5-Trimethyl-4-phenylcyclopentanone (14).** A mixture of **6** (244 mg, 1.00 mmol), $Fe_2(CO)_9$ (437 mg, 1.20 mmol), and *trans*-β-methylstyrene (355 mg, 3.00 mmol) in benzene (3.0 mL) was stirred at 55 °C for 14 h. The reaction mixture was usually worked up. The resulting viscous oil was subjected to preparative TLC (1:10 ether–hexane), giving a single oily adduct **14** ($R_f$ 0.20, 40 mg, 20% yield): NMR δ 0.60 (d, *J* = 8.0 Hz, $CH_3$), 0.75–1.25 (complex pattern, 2 $CH_3$), 1.3–2.9 (m, 4 CH), 7.22 (m, $C_6H_5$); mass spectrum *m/e* 202 ($M^+$). Anal. ($C_{14}H_{18}O$) C, H.

**2,5-Dimethyl-3,4-diphenylcyclopentanone (15).** A mixture of **6** (488 mg, 2.00 mmol), *trans*-stilbene (721 mg, 4.00 mmol), and $Fe_2(CO)_9$ (874 mg, 2.40 mmol) in benzene (5.0 mL) was left with heating at 50 °C for 14 h. The resulting mixture was subjected to the general workup, leaving an oil. Preparative TLC (1:20 ethyl acetate–hexane) produced oily ketone **15** as a mixture of two diastereomers ($R_f$ 0.10, 79 mg, 30% yield). **15a**: NMR δ 0.77 and 1.11 (two d, *J* = 8.0 and 7.0 Hz, respectively, 2 $CH_3$), 2.1–3.0 (m, 2 CHCO), 3.20 (t, *J* = 12 Hz, $C\mathit{H}C_6H_5$), 3.83 (dd, *J* = 12 and 8.0 Hz, $C\mathit{H}C_6H_5$), 7.10 (m, 2 $C_6H_5$); mass spectrum *m/e* 264 ($M^+$). **15b** (*trans,trans,trans*-**15**[42]): NMR δ 1.11 (d, *J* = 7.0 Hz, 2 $CH_3$), 2.40 (m, 2 CHCO), 2.80 and 2.92 (two t, *J* = 8.0 Hz, 2 $C\mathit{H}C_6H_5$), 7.10 (m, 2 $C_6H_5$); mass spectrum *m/e* 264 ($M^+$).

On long standing at room temperature, the diastereomeric mixture was converted to crystalline ketone **15b**, mp 111–112 °C (hexane) (lit.[42] 111–112 °C). Anal. ($C_{19}H_{20}O$) C, H.

**6,7-Benzo-2,4-dimethylbicyclo[3.3.0]oct-6-en-3-one (16).** A mixture of $Fe_2(CO)_9$ (874 mg, 2.40 mmol), indene (930 mg, 8.00 mmol), and the dibromo ketone **6** (488 mg, 2.00 mmol) in benzene (5.0 mL) was heated at 50 °C for 14 h with stirring. After usual workup the mixture gave an oily product, which was subjected to preparative TLC (benzene) to afford a single oily ketone **16** ($R_f$ 0.25, 180 mg, 45% yield): NMR δ 0.62 and 1.08 (two d, *J* = 7.5 and 6.5 Hz, respectively, 2 $CH_3$), 2.0–3.4 (m, 2 CHCO and $C\mathit{H}CH_2$), 2.8–3.4 (m, $CH_2$), 3.80 (dd, *J* = 11.5 and 7.5 Hz, benzylic CH), 7.03 (m, aromatic H); mass spectrum *m/e* 200 ($M^+$). Anal. ($C_{14}H_{16}O$) C, H.

**Reaction of 3,5-Dibromo-2,6-dimethylheptan-4-one (7) and 1,1-Diphenylethylene in the Presence of $Fe_2(CO)_9$.** A mixture of **7** (1.50 g, 5.00 mmol), 1,1-diphenylethylene (3.60 g, 20.0 mmol) and $Fe_2(CO)_9$ (2.18 g, 6.00 mmol) in benzene (20 mL) was stirred at 70 °C for 18 h. Usual workup left a brown oil, which was distilled using bulb-to-bulb apparatus. The fraction which boiled at 160–230 °C (bath temperature, 0.03 mm) was subjected to column chromatography (silica gel 100 g, 1:40 ether–hexane), giving a mixture of 2,5-diisopropyl-3,3-diphenylcyclopentanone (**17**) and 3-isopropyl-7-methyl-1,1-diphenylhept-1-en-4-one (**22**) ($R_f$ 0.03–0.17, 1.16 g). On addition of hexane to the oil, there formed solids, which were recrystallized from hexane, affording an analytical sample of **17a**, mp 117–118 °C (476 mg, 30% yield). Concentration of the mother liquor followed by preparative GLC of the resulting oil (column A, 230 °C) gave **17** as a mixture of two unseparable epimers, **17a** and **17b** (retention time ($t_R$) 57 min, 221 mg, 14% yield) as a highly viscous oil and **22** ($t_R$ 51 min, 189 mg, 11% yield) as a colorless oil. Total yield of **17** was 44%.

**17a**: NMR δ 0.69, 0.89, 0.90, and 1.05 (four d, *J* = 7.0, 6.0, 7.0, and 6.0 Hz, respectively, 4 $CH_3$), 1.4–2.1 (m, 2 $C\mathit{H}(CH_3)_2$ and $COC\mathit{H}CH_2$), 2.35 (ddd, *J* = 12, 7.0, and 2.0 Hz, a $CH_2$ proton), 2.72 (t, *J* = 12 Hz, a $CH_2$ proton), 2.97 (m, COCHC), 6.9–7.3 (m, 2 $C_6H_5$); mass spectrum *m/e* 320 ($M^+$), 305, 277. Anal. ($C_{23}H_{28}O$) C, H.

**17b**: NMR δ 0.20 (d, *J* = 7.5 Hz, $CH(C\mathit{H}_3)_2$)), 0.6–1.3 (complex m, $CH(C\mathit{H}_3)_2$)), 1.4–2.7 (m, $CH_2$ and 2 $C\mathit{H}(CH_3)_2$)), 2.80 (d, *J* = 2.4 Hz, $COC\mathit{H}(C_6H_5)_2$)), 2.98 (m, $COC\mathit{H}CH_2$), 7.10 (m, 2 $C_6H_5$); mass spectrum *m/e* 320 ($M^+$), 305, 277.

**22**: IR 1707 $cm^{-1}$ (C=O); NMR δ 0.81 and 0.95 (two d, *J* = 7.5 and 7.0 Hz, respectively, 2 $CH(C\mathit{H}_3)_2$)), 1.7–2.3 (m, $CH_2$ and 2 $C\mathit{H}(CH_3)_2$)), 2.95 (dd, *J* = 10.5 and 9.0 Hz, COCH), 5.90 (d, *J* = 10.5 Hz, =CH), 7.17 (m, 2 $C_6H_5$); UV $\lambda_{max}$ 257 nm (log ε 4.11), 288 (3.54), 297 (3.51); mass spectrum *m/e* 320 ($M^+$), 277. Anal. ($C_{23}H_{28}O$) C, H.

**Reaction of 2,4-Dibromo-2,4-dimethylpentan-3-one (8) and Styrene in the Presence of $Fe_2(CO)_9$.** A mixture of **8** (274 mg, 1.00 mmol), $Fe_2(CO)_9$ (437 mg, 1.20 mmol), and styrene (417 mg, 4.00 mmol) in benzene (3.0 mL) was kept at 55 °C for 12 h. The mixture was worked up as usual. The resulting oil was distilled with a bulb-to-bulb system (bath temperature 200 °C, 2 mm) to yield three volatile fractions. The middle, main fraction was subjected to preparative TLC (1:20 ether–hexane), affording *trans*-2,4,4-trimethyl-6-phenylhex-5-en-3-one (**23**) ($R_f$ 0.22, 50 mg, 23% yield) and a mixture of difficultly separable two materials ($R_f$ 0.10 and 0.16, respectively). The mixture was distilled by use of a bulb-to-bulb apparatus (bath temperature 200 °C, 2 mm), giving 2,2,5,5-tetramethyl-3-phenylcyclopentanone (**18**, 50 mg, 23% yield) as crystals, mp 43–45 °C (ethanol, −30 °C).

**18**: NMR δ 0.58, 1.08, and 1.20 (three s, 1:2:1 ratio, 4 $CH_3$), 1.89 (dd, *J* = 7.2 and 9.9 Hz, a $CH_2$ proton trans to $C_6H_5$), 2.23 (t, *J* = 9.9 Hz, a $CH_2$ proton cis to $C_6H_5$), 3.10 (dd, *J* = 7.7 and 9.9 Hz, $C\mathit{H}C_6H_5$), 7.17 (m, $C_6H_5$); mass spectrum *m/e* 216 ($M^+$), 145. Anal. ($C_{15}H_{20}O$) C, H.

**23**:[43] IR 1704 (C=O), 965 $cm^{-1}$ (C=C); NMR δ 1.03 (d, *J* = 7.0 Hz, $CH(C\mathit{H}_3)_2$), 1.32 (s, $C(CH_3)_2$), 3.07 (seven lines, *J* = 7.0 Hz, $C\mathit{H}(CH_3)_2$), 6.18 (d, *J* = 16.5 Hz, $C\mathit{H}{=}CHC_6H_5$), 6.40 (d, *J* = 16.5 Hz, $CH{=}C\mathit{H}C_6H_5$), 7.23 (m, $C_6H_5$); UV $\lambda_{max}$ 254 nm (log ε 4.10), 287 (3.42), 295 (3.40) [lit.[43] 253 nm, (log ε 4.17), 285 (2.47), 293 (2.58)]; mass spectrum *m/e* 216 ($M^+$), 145. Anal. ($C_{15}H_{20}O$) C, H.

The cyclopentanone **18** was found to be stable under the reaction conditions. 2,12-Dibromocyclododecanone (6 mg, $2 \times 10^{-3}$ mmol) was treated with $Fe_2(CO)_9$ (8 mg, $2 \times 10^{-3}$ mmol) in benzene (0.1 mL) at 50 °C for 20 min. Then to the resulting mixture was added a solution of **18** (4 mg, $2 \times 10^{-3}$ mmol) in benzene (0.1 mL). The mixture was stirred at the same temperature for 22 h longer and analyzed by GLC (column B, 130 °C), indicating no consumption of **18** ($t_R$ 11.0 min).

**Reaction of 8 with *trans*-Anethole in the Presence of $Fe_2(CO)_9$.** A mixture of **8** (274 mg, 1.00 mol), $Fe_2(CO)_9$ (437 mg, 1.20 mmol), and *trans*-anethole (593 mg, 4.00 mmol) in benzene (3.0 mL) was heated at 55 °C for 12 h. Workup as described above gave a viscous oil, which was subjected to preparative TLC (1:10 ether–hexane), producing crystalline 4-*p*-methoxyphenyl-2,2,3,5,5-pentamethylcyclopentanone (**19**) ($R_f$ 0.21, 143 mg, 55% yield), oily *trans*-6-*p*-methoxyphenyl-

2,4,4,5-tetramethylhex-5-en-3-one (**24**) ($R_f$ 0.28, 8 mg, 3% yield), and crystalline 2-hydroxy-2-isopropyl-5-*p*-methoxyphenyl-3,3,4-trimethyl-1-oxacyclopentane (**37**) ($R_f$ 0.14, 78 mg, 30% yield). The last compound is presumed to arise via hydration of 2-isopropylidene-5-*p*-methoxyphenyl-3,3,4-trimethyl-1-oxacyclopentane during workup.

**19:** mp 130-132 °C (hexane); NMR δ 0.60, 0.93, 1.05, and 1.15 (four s, 4 $CCH_3$), 0.88 (d, $J$ = 6.5 Hz, $CHCH_3$), 2.28 (dq, $J$ = 13 and 6.5 Hz, $CHCH_3$), 2.65 (d, $J$ = 13 Hz, $CHC_6H_4OCH_3$), 3.80 (s, $OCH_3$), 6.80 (d, $J$ = 9.0 Hz, 2 $CH{=}COCH_3$), 7.07 (d, $J$ = 9.0 Hz, 2 $CHCH{=}COCH_3$); mass spectrum *m/e* 260 ($M^+$), 245. Anal. ($C_{17}H_{24}O_2$) C, H.

**24:** IR 1702 $cm^{-1}$ (C=O); NMR δ 0.96 (d, $J$ = 7.5 Hz, $CH(CH_3)_2$), 1.28 (s, $C(CH_3)_2$), 1.70 (d, $J$ = 1.5 Hz, $=CCH_3$), 3.22 (seven lines, $J$ = 7.5 Hz, $CH(CH_3)_2$), 3.76 (s, $OCH_3$), 6.40 (m, $=CHC_6H_4OCH_3$), 6.77 (d, $J$ = 9.0 Hz, 2 $CH{=}COCH_3$), 7.10 (d, $J$ = 9.0 Hz, 2 $CHCH{=}COCH_3$); UV $\lambda_{max}$ 261 nm (log ε 4.14); mass spectrum *m/e* 260 ($M^+$). Anal. ($C_{17}H_{24}O_2$) C, H. The double-bond stereochemistry of **24** was based on the NMR coupling constant between the vinylic methyl protons and vinyl proton; the value, 1.5 Hz, well fitted with that of *cis*-anethole ($J$ = 1.5 Hz) rather than that of *trans*-anethole ($J$ = 0 Hz).

**37:** mp 115-117 °C (hexane); IR 3200-3600 $cm^{-1}$ (OH); NMR δ 0.80 (d, $J$ = 7.5 Hz, $CHCHCH_3$), 0.95 and 1.05 (two s, $C(CH_3)_2$), 1.00 (d, $J$ = 7.0 Hz, $CH(CH_3)_2$), 1.90 (s, OH), 1.9-2.5 (m, $CHCH_3$), 3.78 (s, $OCH_3$), 4.30 (d, $J$ = 10.5 Hz, $CHC_6H_4OCH_3$), 6.75 (d, $J$ = 9.0 Hz, 2 $CH{=}COCH_3$), 7.20 (d, $J$ = 9.0 Hz, 2 $CHCH{=}COCH_3$) mass spectrum *m/e* 260 ($M^+$). Anal. ($C_{17}H_{26}O_3$) C, H.

**Reaction of 8 and α-Methylstyrene in the Presence of $Fe_2(CO)_9$.** A mixture of **8** (548 mg, 2.00 mmol), α-methylstyrene (940 mg, 8.00 mmol), and $Fe_2(CO)_9$ (847 mg, 2.40 mmol) in benzene (6 mL) was stirred at 55 °C for 24 h. After general workup, the formation of four adducts, 2,2,3,5,5-pentamethyl-3-phenylcyclopentanone (**20**) ($t_R$ 29.6 min, 5% yield based on GLC (column C, 200 °C), eicosane (141 mg, 0.50 mmol) as an internal standard), *trans*-2,4,4-trimethyl-6-phenylhept-5-en-3-one (**25**) (27.2 min, 37%), 2-isopropylidene-3,3,5-trimethyl-5-phenyl-1-oxacyclopentane (**26**) (18.8 min, 16%), and 2,4,4-trimethyl-6-phenylhept-6-en-3-one (**27**) (24.0 min, 11%) was observed. Analytical samples were obtained by GLC (column C, 200 °C).

**20:** IR 1736 $cm^{-1}$ (C=O); NMR δ 0.66, 1.19, and 1.28 (three s, 1:3:1 ratio, 5 $CH_3$), 1.91 (d, $J$ = 12.5 Hz, a $CH_2$ proton trans to $C_6H_5$), 2.70 (d, $J$ = 12.5 Hz, a $CH_2$ proton cis to $C_6H_5$), 7.0-7.5 (m, $C_6H_5$); mass spectrum *m/e* 230 ($M^+$). Anal. ($C_{16}H_{22}O$) C, H.

**25:** IR 1705 $cm^{-1}$ (C=O); NMR δ 1.01 (d, $J$ = 7.0 Hz, $CH(CH_3)_2$), 1.30 (s, $C(CH_3)_2$), 1.89 (d, $J$ = 1.5 Hz, $=CCH_3$), 2.93 (seven lines, $J$ = 7.0 Hz, $CH(CH_3)_2$), 5.76 (q, $J$ = 1.5 Hz, =CH), 7.20 (narrow m, $C_6H_5$); UV $\lambda_{max}$ 248 nm (log ε 4.01); mass spectrum *m/e* 230 ($M^+$). Anal. ($C_{16}H_{22}O$) C, H.

The geometry of **25** was confirmed on the basis of the NMR spectrum by comparison with that of α-methylstyrene in a similar manner to that for the determination of **23** as described above.

**26:** IR 1686 $cm^{-1}$ (C=C-O); NMR δ 0.85, 1.35, and 1.52 (three s, $C(CH_3)_2$ and $OCCH_3$), 1.63 and 1.76 (two s, $=C(CH_3)_2$), 2.09 (d, $J$ = 12.5 Hz, a $CH_2$ proton cis to $C_6H_5$), 2.31 (d, $J$ = 12.5 Hz, a $CH_2$ proton trans to $C_6H_5$), 7.2-7.4 (m, $C_6H_5$); mass spectrum *m/e* 230 ($M^+$). Anal. ($C_{16}H_{22}O$) C, H.

**27:** IR 1702 $cm^{-1}$ (C=O); NMR δ 0.90 (d, $J$ = 7.0 Hz, $CH(CH_3)_2$), 1.00 (s, $C(CH_3)_2$), 2.72 (s, $CH_2$), 2.93 (seven lines, $J$ = 7.0 Hz, $CH(CH_3)_2$), 4.99 and 5.20 (two narrow m, $=CH_2$), 7.22 (narrow m, $C_6H_5$); UV $\lambda_{max}$ 247 nm (log ε 4.09); mass spectrum *m/e* 230 ($M^+$). Anal. ($C_{16}H_{22}O$) C, H.

The enol ether **26** remained virtually unchanged upon exposure to the reaction conditions. A mixture of 2,12-dibromocyclododecanone (3 mg, $10^{-3}$ mmol), $Fe_2(CO)_9$ (4 mg, $10^{-3}$ mmol), and α-methylstyrene (3 mg, $2 \times 10^{-3}$ mmol) in benzene (0.1 mL) was heated at 50 °C for 20 min with stirring. To the resulting mixture was added a solution of **26** (2 mg, $10^{-3}$ mmol) in benzene (0.1 mL) and the mixture was stirred at 50 °C for 22 h. GLC analysis (column D, 165 °C) showed little change of **26** ($t_R$ 8.0 min).

**Reaction of 1,3-Dibromopropan-2-one and *trans*-β-Methylstyrene in the Presence of $Fe_2(CO)_9$.** A mixture of 1,3-dibromopropan-2-one (200 mg, 1.00 mmol), *trans*-β-methylstyrene (355 mg, 3.00 mmol), and $Fe_2(CO)_9$ (437 mg, 1.20 mmol) was heated at 55 °C with stirring for 14 h. After usual workup the IR spectrum of the reaction mixture exhibited no carbonyl absorption arising from cyclopentanone, indicating nonoccurrence of the expected adducts.

**Attempted Reaction of 2,2-Dimethylcyclopropanone and 1,1-Diphenylethylene.** In a cooled (−30 °C) 10-mL ampule, a 1 M solution of 2,2-dimethylcyclopropanone in $CH_2Cl_2$ (0.50 mL) and 1,1-diphenylethylene (360 mg, 2.00 mmol) were mixed and the ampule was sealed under $N_2$. The mixture was heated at 40 °C for 20 h and concentrated. The IR spectrum of the residual oil showed no carbonyl absorption.

**Intermolecular Competition of the Cyclocoupling Reaction among Styrene, α-Methylstyrene, and β-Methylstyrene. A. Between Styrene and α-Methylstyrene.** A mixture of $Fe_2(CO)_9$ (1.82 g, 5.00 mmol), **6** (975 mg, 4.00 mmol), styrene (4.15 g, 40.0 mmol), α-methylstyrene (4.73 g, 40.0 mmol), decane (2.84 g, 20.0 mmol), and tetradecane (9.90 mg, 0.05 mmol) in benzene (30 mL) was stirred at 55 °C. After 10 min, the first two 0.25-mL aliquots were withdrawn followed by others at 5-min until 30 min and then 10-min intervals until 60 min. One series of aliquots was used for GLC analysis (column E, 80 °C, decane as an internal standard) to determine the consumption of olefinic substrates, indicating that the styrene/α-methylstyrene ratio remained virtually unchanged under these conditions. The other series of aliquots was employed for determination of cycloadducts formation. The aliquot was concentrated and treated with 3% ethanolic NaOH solution (0.2 mL) at 25 °C for 5 min. The mixture was diluted with water (1.0 mL) and extracted with ether (0.5 mL). The resulting organic layer was subjected to GLC analysis (column E, 150 °C, tetradecane as an internal standard). The ratios of **10** ($t_R$ 10.0 min)/**9** (7.6 min) were 3.1 (10 min), 3.0 (15 min), 2.9 (20 min), 3.0 (25 min), 2.9 (30 min), 2.8 (40 min), 2.8 (50 min), and 2.8 (60 min), respectively. The plot, **10**/**9** vs. reaction time, was linear and extrapolation of the line determined the ratio of formation rate of **10**/**9** to be 3.1.

**B. Between Styrene and β-Methylstyrene.** A mixture of **6** (195 mg, 0.80 mmol), styrene (830 mg, 8.00 mmol), *trans*-β-methylstyrene (945 mg, 8.00 mmol), $Fe_2(CO)_9$ (364 mg, 1.00 mmol), decane (568 mg, 4.00 mmol), and tetradecane (1.98 mg, 0.01 mmol) in benzene (6.0 mL) was heated at 55 °C with stirring. At appropriate time intervals two reaction aliquots (0.05 mL each) were withdrawn and subjected to the same treatment as stated above. GLC (column B, 140 °C) showed that only styrene adduct **9** ($t_R$ 8.6 min) was produced (1.2, 2.5, and 5.8% yields after 5, 10, and 30 min, respectively). The adduct **14** was not detected in the aliquots at any stage of this reaction.

**Reaction of Dibromide 8 and *cis*-β-Deuteriostyrene.** A mixture of **8** (548 mg, 2.00 mmol) and $Fe_2(CO)_9$ (364 mg, 1.00 mmol) in benzene (3.0 mL) was heated at 50 °C for 15 min. To the resulting mixture was added *cis*-β-deuteriostyrene[40] (271 mg, 2.60 mmol, isotopic purity >97%) dropwise over a period of 3 min, and stirring was continued for an additional 1 h. The cooled mixture was diluted with a 1:4:10 mixture of ethyl acetate, benzene, and petroleum ether, washed with water, and dried. The organic layer was evaporated at 25 °C at 50-70, 26, and then 3 mm. The distillates were collected in receivers cooled in a dry ice-$CH_3OH$ bath. Most unreacted deuteriostyrene was recovered in the fraction at 3-26 mm contaminated with small amounts of benzene, iron carbonyls, etc. The NMR spectrum of this fraction (measured under $N_2$) showed that the deuteriostyrene was recovered without any isomerization. The remaining viscous oil was subjected to bulb-to-bulb distillation (bath temperature 140-160 °C, 2 mm). GLC analysis of the distillate (column D, 170 °C) showed the formation of 3-deuterio-2,2,5,5-tetramethyl-4-phenylcyclopentanone (**18**-*d*) ($t_R$ 7.8 min, 6% yield) and **23**-*d* ($t_R$ 10.4 min, 3% yield). Preparative GLC (column C, 170 °C) afforded analytical species of **18**-*d* as colorless crystals, mp 43-45 °C (from petroleum ether, −30 °C), and **23**-*d* as an oil, respectively. Both deuterio products **18**-*d* and **23**-*d* indicated a molecular peak at *m/e* 217 in the mass spectrum. Location of deuterium of **18**-*d* and **23**-*d* was determined by NMR analysis. The spectrum of **18**-*d* was given in Figure 1, showing that deuterium was situated only in the position cis to phenyl. In the spectrum of **23**-*d*, there was observed a heptet due to the methine proton of the isopropyl group at δ 3.07, whose integral intensity corresponded to 0.65 proton. Besides vinyl-proton signals appeared in a complex pattern combining an AB quartet with the coupling constant of 16.5 Hz (centered at δ 6.18 and 6.40) and a multiplet centered at δ 6.30, and the combined integral intensity of the signals was equivalent to 1.35 protons.

**3,3,5-Trimethyl-1-phenylhexane-1,4-dione (38).** A mixture of **8** (1.60 g, 5.83 mmol), 1-morpholinostyrene (3.00 g, 15.9 mmol), and $Fe_2(CO)_9$ (2.62 g, 7.20 mmol) in benzene (15 mL) was heated at 40 °C for 22 h with stirring. The resulting mixture was diluted with ethyl acetate (80 mL) and washed with saturated $NaHCO_3$ solution (100 mL) and brine (15 mL). The organic layer was dried and concentrated to afford a brown liquid containing mainly 5-isopropylidene-4,4-dimethyl-2-morpholino-2-phenyl-1-oxacyclopentane [NMR ($CCl_4$) $\delta$ 0.97 and 1.39 (two s, $C(CH_3)_2$), 1.61 and 1.73 (two s, $=C(CH_3)_2$), 2.28 (m, 2 $NCH_2$ and $NCCH_2$), 3.49 (t-like m, 2 $OCH_2$), 7.12 (m, $C_6H_5$)], acetophenone, and a small amount of the recovered enamine. The crude oil was dissolved in ether (50 mL), mixed with 2 N HCl (50 mL), and stirred at 25 °C for 1 h. The reaction mixture was diluted with water (100 mL) and extracted with ether (50 mL × 2). The ethereal layers were combined, washed with brine (20 mL), dried, and evaporated (25 °C, 100 mm, then 0.01 mm), giving a black oil (2.5 g). Column chromatography (silica gel, 200 g, 1:20–1:15 ether–hexane) afforded **38** ($R_f$ 0.15, 1:20 ether–hexane, 1.16 g, 86% yield) as an oil: IR 1687 $cm^{-1}$ (C=O); NMR $\delta$ 1.12 (d, $J$ = 7.0 Hz, $CH(CH_3)_2$), 1.33 (s, $C(CH_3)_2$), 2.1–2.7 (m, $CH(CH_3)_2$), 3.30 (s, $CH_2$), 7.3–7.8 and 7.9–8.1 (two m, 3:2 ratio, $C_6H_5$); UV $\lambda_{max}$ 247 nm (log $\epsilon$ 3.87); mass spectrum *m/e* 232 ($M^+$), 189 ($M^+ - CH(CH_3)_2$), 105 ($M^+ - CH_2C(CH_3)_2COCH(CH_3)_2$). Anal. ($C_{15}H_{20}O_2$) C, H.

**2,2,5,5-Tetramethyl-3-phenylcyclopent-3-enone (39).** The diketone **38** (280 mg, 12.0 mmol) was stirred with a 10% solution of $CH_3ONa$ in $CH_3OH$ (10 mL) at 25 °C for 18 h. The mixture was diluted with water and extracted with ether. The organic layer was dried and evaporated, giving crystalline 3-hydroxy-2,2,5,5-tetramethyl-3-phenylcyclopentanone: mp 123–125 °C; IR 3600–3100 (OH), 1732 $cm^{-1}$ (C=O). The crude material was heated in 85% $H_3PO_4$ (20 mL) at 120 °C. After 20 min the resulting solution was extracted with hexane. The organic layer was washed with saturated $NaHCO_3$ solution and $KNO_3$ solution and dried. Removal of the organic solvents left an oil, which was subjected to preparative TLC (1:20 ether–hexane) to afford **39** ($R_f$ 0.33, 78 mg, 28% yield): IR 1742 (C=O), 850 $cm^{-1}$ (C=C); NMR $\delta$ 1.15 and 1.25 (two s, 1:1 ratio, 4 $CH_3$), 5.90 (s, vinyl H), 7.18 (m, $C_6H_5$); UV $\lambda_{max}$ 243 nm (log $\epsilon$ 4.16), 281 (3.39); mass spectrum *m/e* 214 ($M^+$), 199, 186, 171. Anal. ($C_{15}H_{18}O_2$) C, H.

***cis*-3,4-Dideuterio-2,2,5,5-tetramethyl-3-phenylcyclopentanone (18-$d_2$).** Balloon technique was used for the catalytic deuteration. In a micro reaction vessel, **39** (13 mg, 0.05 mmol) was mixed with 10% Pd/C (4 mg) in hexane (0.1 mL) and stirred under atmospheric pressure of $D_2$ at 25 °C. After 14 h the catalyst was removed by filtration. Evaporation of the filtrate afforded the deuterio compound **18**-$d_2$ (13 mg, 98% yield), mass spectrum *m/e* 218 ($M^+$).

**Preparation of *cis*-2,4,4-Trimethyl-6-phenylhex-5-en-3-one (31).** A solution of **23** (108 mg, 0.05 mmol) and benzophenone (sensitizer, 91 mg, 0.05 mmol) in cyclohexane (3 mL) was charged in a Pyrex tube and deoxygenated by bubbling of argon for 5 min. The solution was irradiated with a 200-W high-pressure mercury lamp (<350-nm cutoff light through a 5% aqueous $CuSO_4$ filter) by cooling with running water (15–20 °C). After 5 h the reaction mixture was evaporated. GLC analysis (column D, 190 °C) of the oil showed the formation of a ca. 2:1 photoequilibrium mixture of **31** ($t_R$ 3.5 min) and **23** ($t_R$ 4.7 min). An analytical sample of **31**[42] was collected by preparative GLC separation (column C, 190 °C).

**31:** IR 1707 $cm^{-1}$ (C=O); NMR $\delta$ 0.98 (d, $J$ = 7.0 Hz, $CH(CH_3)_2$), 1.19 (s, $C(CH_3)_2$), 2.99 (seven lines, $J$ = 7.0 Hz, $CH(CH_3)_2$), 5.69 (d, $J$ = 12.5 Hz, $CH=CHC_6H_5$), 6.46 (d, $J$ = 12.5 Hz, $CH=CHC_6H_5$), 6.9–7.4 (m, $C_6H_5$); UV $\lambda_{max}$ 250 nm (log $\epsilon$ 4.03), 285 (3.17), 294 (3.11) [lit.[42] 248 nm (log $\epsilon$ 3.97), 284 (1.67), 292 (1.95)]; mass spectrum *m/e* 216 ($M^+$).

**Examination of Stability of 35 under the Dibromo Ketone–$Fe_2(CO)_9$ Reaction Conditions.** 2,12-Dibromocyclododecanone (12 mg, 4 × $10^{-3}$ mmol) was treated with $Fe_2(CO)_9$ (7 mg, 2× $10^{-3}$ mmol) in benzene (0.1 mL) containing styrene (6 mg, 6 × $10^{-3}$ mmol) at 50 °C for 20 min and to the resulting mixture was added a solution of **31** (4 mg, 2 × $10^{-3}$ mmol) in benzene (0.1 mL). The mixture was stirred at the same temperature for 22 h. Usual workup followed by GLC analysis (column D, 190 °C) indicated little formation (<1%) of **23**.

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## References and Notes

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(31) The orbital-symmetry restrictions in pericyclic reactions might be removed by the action with certain transition metals.[32] However, such kind of perturbation has never been observed in the relevant dibromo ketone–iron *carbonyl reactions; all reactions including the 3 + 4 → 7 cyclocoupling* reaction (symmetry-allowed $[_{\pi}2_s + {}_{\pi}4_s]$ process),[17] nucleophilic trapping,[13] and various intramolecular rearrangements[13] can be understood without considering any special effects of iron atom or ions. We should like to emphasize a point that the present formally symmetry-restricted cycloaddition is also rationalized on the basis of our knowledge of ordinary organic chemistry.

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# Novel Cyclopentenone Synthesis via the Iron Carbonyl Aided Cyclocoupling between $\alpha,\alpha'$-Dibromo Ketones and Enamines[1,2]

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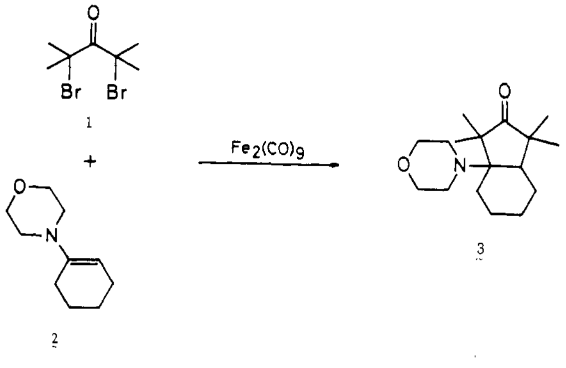
**Abstract:** Reaction of $\alpha,\alpha'$-dibromo ketones and morpholino enamines with the aid of iron carbonyls affords the corresponding 3-morpholinocyclopentanones. The adducts derived from secondary dibromo ketones and the enamines eliminate morpholine facilely, giving 2-cyclopentenones, and hence the coupling reaction provides a new, single-flask procedure for the preparation of five-membered ketones. This [3 + 2] cyclocoupling proceeds in high yield and finds a wide generality; the reaction with cyclic ketone enamines leads to bicyclo[*n*.3.0]alkenones, while the annelation using enamines of cycloalkanecarboxaldehydes gives rise to spiro[*n*.4]alkenone systems. The 7/5-fused bicyclic ketones obtained from 1-morpholinocycloheptene serve as a versatile intermediate for azulenoid synthesis.

Because cyclopentanoid derivatives are widely occurring in nature,[3] supply of a versatile and general tool for construction of five-membered ketones is very significant in synthetic chemistry. A large interest has been taken in this subject for a long time, and, as a result, a number of excellent synthetic methodologies have been elaborated.[4] This paper describes a novel, [3 + 2] type synthesis through the cyclocoupling between $\alpha,\alpha'$-dibromo ketones and enamines.

## Results and Discussion

**Cyclocoupling Reaction between $\alpha,\alpha'$-Dibromo Ketones and Enamines. A. Reaction with Tertiary Dibromide.** Reaction of the dibromo ketone **1** and enamine **2** with the aid of $Fe_2(CO)_9$ (1.0:3.0:1.2 mole ratio) was performed in dry benzene. Usual extractive workup and chromatographic purification afforded the cycloadduct **3** in 87% yield. The structure of **3** was established by IR ($\nu_{C=O}$ 1732 cm$^{-1}$) and NMR analyses.



**1**

**2**

**3**

**B. Reaction with Secondary Dibromides.** Secondary dibromo ketones can be also employed for the cyclocoupling reaction. In this case the initially formed $\beta$-morpholinocyclopentanones have an active hydrogen atom at the position $\alpha$ to the carbonyl function and hence suffered readily elimination of morpholine, giving the unsaturated ketones. Thus various cyclopentenones can be prepared in the single-flask procedure according to Scheme I. The deamination of the initial $\beta$-morpholinocyclopentanone adducts [IR 1730–1740 cm$^{-1}$ (C=O)], as usual, took place during chromatography on silica gel. When the $\alpha$ substituent R is bulky, for example, when R is isopropyl group, the elimination was not made sure by the silica gel treatment. In such a case, this purpose could be attained just by brief treatment with 3% ethanolic NaOH solution.

This cyclocoupling reaction has a wide generality. As enamines, those derived from either linear or cyclic ketones are employable. Enamines of aldehydes may be used as well. Examples of the reaction are given in Table I. As the solvent, benzene afforded the adduct in the highest yield. Use of other solvents such as tetrahydrofuran (THF) and *N,N*-dimethylformamide (DMF) gave no or little cyclocoupling products. As reducing agent iron pentacarbonyl in benzene might be also used but less effectively. Neither $\alpha,\alpha'$-dibromo-