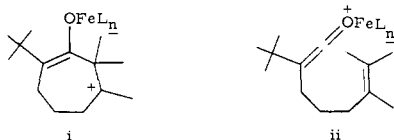


- (19) Recently Hoffmann and his co-workers attained the reductive dimerization of α,α' -dibromo ketones in *N*-methylformamide using zinc-copper couple as the reducing agent: C. Chassin, E. A. Schmidt, and H. M. R. Hoffmann, *J. Am. Chem. Soc.*, **96**, 606 (1974).
- (20) H. M. R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **12**, 819 (1973), and references cited therein.
- (21) Y. Ito, M. Asada, K. Yonezawa, and T. Saegusa, *Synth. Commun.*, **4**, 87 (1974).
- (22) G. H. Posner, C. E. Whitten, and J. J. Sterling, *J. Am. Chem. Soc.*, **95**, 7788 (1973); R. G. Carlson and W. S. Mardis, *J. Org. Chem.*, **40**, 817 (1975).
- (23) R. H. Prager and J. M. Tippett, *Tetrahedron Lett.*, 5199 (1973).
- (24) R. R. Sauers and C. K. Hu, *J. Org. Chem.*, **36**, 1153 (1971).
- (25) L. T. Scott and W. D. Cotton, *J. Am. Chem. Soc.*, **95**, 2708 (1973).
- (26) Reaction of α -bromo ketones with metal ions or metals, such as Cr(II) and Zn, usually produces metal enolates. See ref 11 and J. E. Baldwin and J. A. Walker, *J. Chem. Soc., Chem. Commun.*, 117 (1973); H. O. House, "Modern Synthetic Reactions", 2nd ed, W. A. Benjamin, Menlo Park, Calif., 1972, Chapter 3.
- (27) A. C. B. Smith and W. Wilson, *J. Chem. Soc.*, 1342 (1955).
- (28) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Verlag Chemie, Weinheim/Bergstr., Germany, 1970, pp 38-64.
- (29) W. Kirmse and H. Schütte, *Chem. Ber.*, **105**, 824 (1972); F. G. Bordwell and R. G. Scamehorn, *J. Am. Chem. Soc.*, **93**, 3410 (1971).
- (30) H. Takaya, S. Makino, Y. Hayakawa, and R. Noyori, *J. Am. Chem. Soc.*, **100**, 1765 (1978).
- (31) For cycloaddition of allyl cations to furan, see H. M. R. Hoffmann and D. R. Joy, *J. Chem. Soc. B*, 1182 (1968).
- (32) H. E. Zimmerman, D. S. Crumrine, D. Döpp, and P. S. Huyffer, *J. Am. Chem. Soc.*, **91**, 434 (1969).
- (33) H. E. Zimmerman and D. S. Crumrine, *J. Am. Chem. Soc.*, **90**, 5612 (1968); T. M. Brennan and R. K. Hill, *ibid.*, **90**, 5614 (1968).
- (34) M. T. Reetz, *Angew. Chem., Int. Ed. Engl.*, **11**, 130 (1972).
- (35) T. S. Sorensen and K. Ranganayakulu, *Tetrahedron Lett.*, 659 (1970); J. K. Crandall and S. A. Sojka, *ibid.*, 1641 (1972); W. Kirmse and H. Urbach, *Chem. Ber.*, **105**, 840 (1972).
- (36) J. K. Crandall and W. H. Machleder, *J. Am. Chem. Soc.*, **90**, 7347 (1968); J. K. Crandall, W. W. Conover, J. B. Komlin, and W. H. Machleder, *J. Org. Chem.*, **39**, 1723 (1974).
- (37) W. F. Erman, R. S. Treptow, P. Bakuzis, and E. Wenkert, *J. Am. Chem. Soc.*, **93**, 657 (1971).
- (38) C. D. Poulter and S. Winstein, *J. Am. Chem. Soc.*, **94**, 2297 (1972). The bicyclo[3.2.0]heptanone **28** could arise via the seven-membered zwitterion **i** formed through ring opening of **33** [K. B. Wiberg and G. W. Kline, *Tetrahedron Lett.*, 1043 (1963); see also S. Wolff and W. C. Agosta, *J. Chem. Soc., Chem. Commun.*, 771 (1973); R. H. Blissegia and C. J. Cheer, *ibid.*, 165 (1973)]. The path involving the ketene intermediate **ii** derived from **32** could not be excluded rigorously [S. W. Baldwin and E. H. Page, Jr., *J. Chem. Soc., Chem. Commun.*, 1337 (1972)].
- (39) H. O. House and H. W. Thompson, *J. Org. Chem.*, **28**, 164 (1963); L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy In Organic Chemistry", 2nd ed, Pergamon Press, Oxford, 1969, p 240.
- (40) As to regioselectivity of the iron carbonyl promoted cyclocoupling reactions, see ref 1.
- (41) H. M. R. Hoffmann, T. A. Nour, and R. H. Smlthers, *J. Chem. Soc., Chem. Commun.*, 963 (1972).
- (42) N. J. Turro and W. B. Hammond, *Tetrahedron*, **24**, 6017 (1968); **24**, 6029 (1968); N. J. Turro, S. S. Edelson, J. R. Williams, T. R. Darling, and W. B. Hammond, *J. Am. Chem. Soc.*, **91**, 2283 (1969); S. S. Edelson and N. J. Turro, *ibid.*, **92**, 2770 (1970); N. J. Turro, *Acc. Chem. Res.*, **2**, 25 (1969); J. F. Pazos, J. G. Pacifflci, G. O. Pierson, D. B. Sclove, and F. D. Greene, *J. Org. Chem.*, **39**, 1990 (1974); N. J. Turro and R. B. Gagosian, *J. Am. Chem. Soc.*, **92**, 2036 (1970).
- (43) R. L. Camp and F. D. Greene, *J. Am. Chem. Soc.*, **90**, 7349 (1968); T. H. Chan, B. S. Ong, and W. Mychajlowski, *Tetrahedron Lett.*, 3253 (1976).
- (44) The related diradical species **8**, even if formed, was unlikely to undergo the observed rearrangements and reactions with nucleophiles. The diradical of the type **8** was suggested as an intermediate in the photolysis of tetramethylcyclobutane-1,3-dione [R. C. Cookson, N. J. Nye, and G. Subrahmanyam, *Proc. Chem. Soc., London*, 144 (1964); N. J. Turro, W. B. Hammond, and P. A. Leermakers, *J. Am. Chem. Soc.*, **87**, 2774 (1965)].
- (45) Y. Hayakawa, K. Yokoyama, and R. Noyori, *J. Am. Chem. Soc.*, **100**, 1791 (1978); **100**, 1799 (1978).
- (46) H. O. House, "Modern Synthetic Reactions", 2nd ed, W. A. Benjamin, Menlo Park, Calif., 1972, pp 498-500, and references cited therein.
- (47) N. C. Deno, "Carbonium Ions", Vol. 2, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N.Y., 1970, pp 787-796.
- (48) Since bicyclo[3.1.1]heptan-6-one derivatives are known to be converted to bicyclo[3.2.0]heptan-6-one system by the action of acids,³⁷ it may be conceivable that the products **28** and **29** were derived from **49** under the influence of FeBr₂ formed in the progress of reaction. This possibility, however, was excluded by a control experiment: upon treatment of **49** with FeBr₂ in benzene at room temperature neither **28** nor **29** was obtained, but the starting **49** was recovered unchanged. The production of **50** and **51** would probably be due to the presence of moisture in the reaction system.
- (49) R. B. King, *Organomet. Synth.*, **1**, 93 (1965).
- (50) E. LeGoff, *J. Org. Chem.*, **29**, 2048 (1964).
- (51) C. Rappe, *Acta Chem. Scand.*, **16**, 2467 (1962).
- (52) J. Ciabattini and E. C. Nathan, III, *J. Am. Chem. Soc.*, **91**, 4766 (1969).
- (53) W. P. Wallace and H. R. Henze, *J. Am. Chem. Soc.*, **64**, 2882 (1942).
- (54) I. Elphimoff-Felkin, *Bull. Soc. Chim. Fr.*, 784 (1955).
- (55) E. A. Braude and E. A. Evans, *J. Chem. Soc.*, 3238 (1956).



Reactions of Polybromo Ketones with 1,3-Dienes in the Presence of Iron Carbonyls. New 3 + 4 → 7 Cyclocoupling Reaction Forming 4-Cycloheptenones^{1,2}

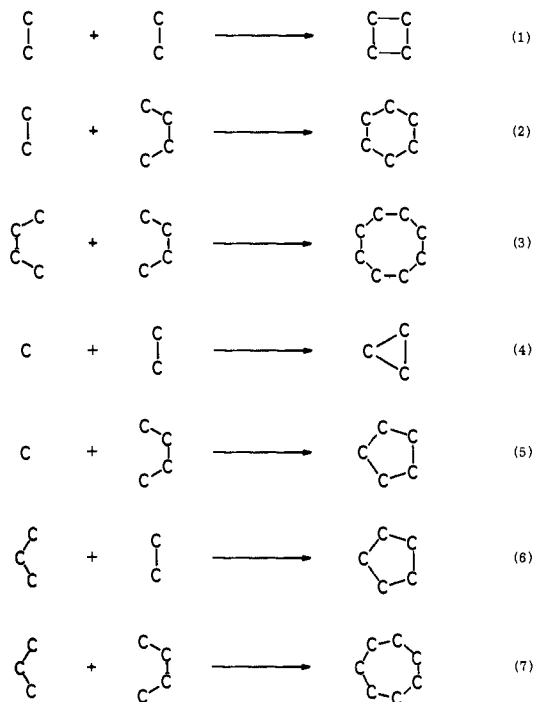
H. Takaya, S. Makino, Y. Hayakawa, and R. Noyori*

Contribution from the Department of Chemistry, Nagoya University, Chikusa, Nagoya 464, Japan. Received February 28, 1977

Abstract: Oxyallyl species generated from α,α' -dibromo ketones and iron carbonyls cycloadd to both open-chain and cyclic 1,3-dienes in a 3 + 4 → 7 manner, giving 4-cycloheptenones in fair to good yields. Cyclopentadiene and furan serve as highly efficient receptors of the oxyallyl intermediates to give bicyclic cycloadducts. Pyrrole derivatives having an electron-withdrawing group at the nitrogen atom give the 3 + 4 cyclocoupling products, while *N*-methylpyrrole or thiophene produces the electrophilic substitution products. Although reaction of 1,3-dienes and α,α' -dibromoacetone, unlike other ordinary dibromo ketones, has failed to afford any cycloheptenone adduct, the cyclocoupling with $\alpha,\alpha,\alpha',\alpha'$ -tetrabromoacetone proceeds smoothly. Thus iron carbonyl promoted reaction of tetrabromoacetone and 1,3-dienes followed by zinc-copper couple reduction formally corresponds to a 3 + 4 → 7 cyclocoupling of dibromoacetone and dienes.

The *cyclocoupling reactions*, defined broadly as ring formations by combining termini of two (or more) linear components irrespective of the detailed reaction mechanism, have occupied a most important position in the synthesis of organic structures.³⁻¹⁰ The carbocyclic ring formations are formally

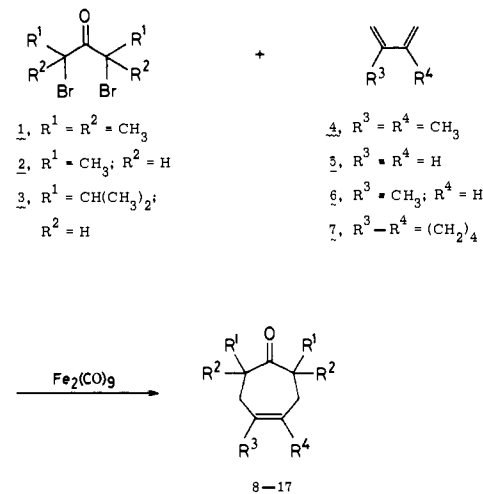
classified according to the number of carbon units which participate in the coupling reaction as shown in eq 1-7. Reaction patterns of eq 1-3, forming even-numbered homocyclic systems, have various examples. Construction of cyclobutane rings, for instance, can be easily attained by [2 + 2] photocy-



cloaddition of olefinic substrates.³ The [2 + 4] cycloaddition known as the Diels–Alder reaction is the most fundamental and general tool for obtaining six-membered carbocycles.⁴ The transition metal catalyzed cyclodimerization of butadiene to 1,5-cyclooctadiene is a representative of the [4 + 4] reactions.¹¹ It should be noted, however, that only these types of combinations, viz., coupling of two *even-numbered* carbon units, have been achieved with ease and that preparation of odd-membered carbocycles employing *odd-numbered* carbon moieties as one component is rather sparse. One widely used process categorized into the latter is cyclopropanation of olefins shown by eq 4; carbenes, their metal complexes, and ylides are generally used for obtaining three-membered carbocycles.^{12,13} There exist no general cyclocoupling reactions giving other higher odd-membered homologues such as five- and seven-membered rings,¹⁴ although their usefulness in organic synthesis has been steadily increasing. This is mainly ascribed to the lack of suitable compounds which can serve as or generate a bifunctional odd-numbered carbon unit. The preceding paper¹ demonstrated the generation of oxallyl–iron complexes from the reaction of α,α' -dibromo ketones and iron carbonyls. We now report the trapping of such reactive intermediates with various 1,3-dienes. The reaction can be viewed as a new 3 + 4 \rightarrow 7 cyclocoupling reaction ([$\pi 2 + \pi 4$] cycloaddition¹⁵) (eq 7) and provides a convenient, direct route to seven-membered ketones.

Results and Discussion

Reaction between α,α' -Dibromo Ketones and 1,3-Dienes in the Presence of Iron Carbonyls. A. Reaction with Open-Chain 1,3-Dienes. Reaction of α,α' -dibromo ketones and $\text{Fe}_2(\text{CO})_9$ in the presence of 1,3-dienes afforded the corresponding 4-cycloheptenones in moderate to good yields. For example, when a mixture of 2,4-dibromo-2,4-dimethylpentan-3-one (**1**), $\text{Fe}_2(\text{CO})_9$, and 2,3-dimethylbutadiene (**4**) in dry benzene was heated at 60 °C under nitrogen atmosphere, 2,2,4,5,7,7-hexamethyl-4-cycloheptenone (**8**) was obtained in 71% yield. This simple one-step procedure has a wide applicability in the synthesis of seven-membered ketones on preparative scales. The examples are given in Table I. Various open-chain 1,3-dienes including 1,3-butadiene (**5**) and isoprene (**6**) could be used. As well as the tertiary dibromo ketones, secondary dibromides such as 2,4-dibromopentan-3-one (**2**) and 3,5-di-

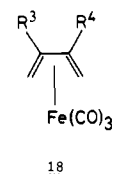


bromo-2,6-dimethylheptan-4-one (**3**) could be employed. 2,7-Dialkyl-4-cycloheptenones were usually obtained as a mixture of *cis* and *trans* isomers. Neither 2- nor 3-cycloheptenone was detected in the products.

Structures of thus obtained 4-cycloheptenones were readily determined by combination of appropriate analytical and spectroscopic methods. 2,7-Dialkyl adducts gave in the IR spectra a carbonyl absorption in a 1710–1704- cm^{-1} region and 2,2,7,7-tetraalkyl derivatives at 1685 cm^{-1} .¹⁶ In the NMR spectra, vinylic proton signals appeared at δ 5.1–5.7 and absorptions due to methyls attached to an sp^2 carbon at δ 1.7–1.8.

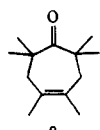
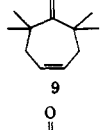
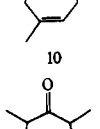
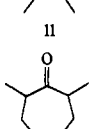
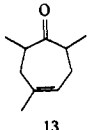
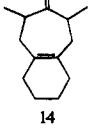
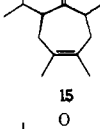
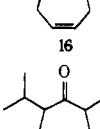
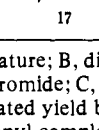
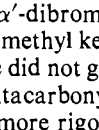
Since the present 3 + 4 \rightarrow 7 type reaction can be regarded as a concerted [$\pi 2 + \pi 4$] cycloaddition,¹⁵ it was expected that dienes with the high equilibrium concentration of the *s-cis* conformer serve as an efficient receptor of the reactive three-carbon unit.¹⁷ In fact, the reactions with **4** usually gave higher yields of the cycloheptenones than those using the diene **5** or **6**. 1,2-Bismethylenecyclohexane (**7**), in which the *s-cis* conformation is frozen by inclusion of the 2 and 3 position of the diene into a six-membered ring, is among the most effective receptors as shown in the reactions of the dibromide **2** and 1,3-dienes.

Noteworthy is the fact that the dieneiron tricarbonyl complexes of type **18**, when compared to $\text{Fe}_2(\text{CO})_9$, have weaker reducing ability and hence require forcing reaction conditions, but the use of these complexes leads to considerable improvement in yields of cycloheptenones (compare methods A and B in Table I). For example, reaction of the dibromo ketone **1**, $\text{Fe}_2(\text{CO})_9$, and free butadiene gave the 4-cycloheptenone **9** in only 33% yield, while 90% yield was obtained by the reaction of **1** and an equimolar amount of butadieneiron tricarbonyl (**18**,



$\text{R}^3 = \text{R}^4 = \text{H}$) at 80 °C. One can use directly without purification the diene–iron complexes **18** which are prepared by photoirradiation of a mixture of 1,3-diene and iron pentacarbonyl in benzene.¹⁸ The great increase in product yield is somewhat surprising, since no stable diene–Fe(II) complexes have been isolated. When a diene–Fe(0) complex reacts with a dibromo ketone, the central metal becomes Fe(II) and, consequently, the diene can no longer remain as a persistent ligand on the Fe atom. We feel that here exists certain delicate balance in timing between liberation of the diene ligand from the Fe(II) atom and the carbon–carbon bond formation pro-

Table I. Reaction of α,α' -Dibromo Ketones with Open-Chain 1,3-Dienes in the Presence of $\text{Fe}_2(\text{CO})_9$

Dibromide (mmol)	Diene (mmol)	Method ^a	Reaction condition		Product	Yield, ^b g (%)
			Temp, °C	Time, h		
1 (2.0)	4 (89)	A	60	38		(71) ^c
1 (15.0)	4 (60)	B	80	12		2.90 (100)
1 (2.0)	5 (120)	A	60	38		(33) ^c
1 (15.0)	5 (100)	B	80	4		2.26 (90)
1 (1.0)	6 (100)	A	65	38		(47) ^c
1 (13.7)	6 (60)	B	87	12		1.74 (70)
2 (1.06)	4 (9.0)	A	60	34		(46) ^c
2 (15.0)	4 (60)	B	120	4		0.82 (33)
2 (0.96)	5 (12)	A	80	16		(30) ^c
2 (15.0)	5 (120)	B	80	9		0.72 (35, 40 ^e)
2 (1.0)	6 (10)	C	25	36		(36) ^c
2 (15.0)	6 (60)	B	120	12		0.98 (43, 51 ^e)
2 (2.5)	7 (1.0)	A	63	46		0.15 (80)
3 (4.0)	4 (35)	A	60	38		(36) ^c
3 (15.0)	4 (60)	B	120	20		1.82 (55)
3 (4.0)	5 (48)	A	90	12		(44) ^c
3 (10.0)	5 (22) ^d	B	70	40		(77) ^c
3 (1.0)	6 (10)	C	25	36		(31) ^c












^aA, a mixture of dibromide, diene, and $\text{Fe}_2(\text{CO})_9$ in benzene was stirred at the specified temperature; B, dieneiron tricarbonyl complex was prepared in situ by photoirradiation of a mixture of diene and $\text{Fe}(\text{CO})_5$ and to this was added dibromide; C, a mixture of dibromide, diene, and $\text{Fe}_2(\text{CO})_9$ was irradiated by visible light at 25 °C. For details, see Experimental Section. ^bIsolated yield based on dibromide unless otherwise noted. ^cDetermined by GLC using an appropriate internal standard. ^dButadieneiron tricarbonyl complex was used.

ducing the cycloaddition product. Thus the efficiency of the 3 + 4 reaction involving open-chain dienes may be influenced by such initial π complexation. However, since the reaction goes smoothly even with substrates that do not form the stable iron complex (vide infra), the coupling reaction does not necessarily require the initial 1,3-diene complexation or the intermediacy of a discrete mixed ligand complex that bears both oxyallyl and diene ligands. Attempted coupling reaction of cyclobutadieneiron tricarbonyl and **1** failed to give any 1:1 adducts.

Unfortunately, α,α' -dibromoacetone and other dibromo ketones derived from methyl ketones such as butan-2-one and 3-methylbutan-2-one did not give the corresponding 4-cycloheptenones. Iron pentacarbonyl was also employable as the reducing agent, but more rigorous reaction conditions were required and the yield of the cycloadducts was lower than that obtained with $\text{Fe}_2(\text{CO})_9$.

B. Reaction with Cyclopentadiene. The iron carbonyl promoted reaction of the dibromide **1** and cyclopentadiene gave the known bicyclic ketone **19**¹⁹ in 82% yield (Table II). The

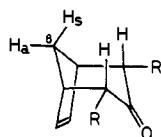
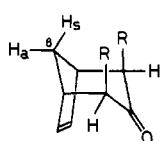
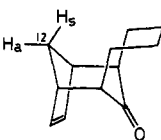
Table II. Reaction of Dibromo Ketones with Cyclic 1,3-Dienes in the Presence of $\text{Fe}_2(\text{CO})_9$

Dibromide (mmol)	Diene (mmol)	Solvent (mL)	Reaction condition		Product	Yield, g (%) ^a
			Temp, °C	Time, h		
1 (2.0)	Cyclopentadiene (125)	Benzene (10)	60	38		(82) ^b
1 (8.0)	Cyclopentadiene (144)	Benzene (20)	60	38	19	1.01 (71)
2 (4.0)	Cyclopentadiene (50)	Benzene (10)	60	25		0.492 (81, 86) ^b
20 and 21						
3 (4.0)	Cyclopentadiene (50)	Benzene (10)	90	12		0.706 (86, 93) ^b
22 and 23						
1 (1.0)	Furan (138)	None	40	38		(96) ^c
1 (8.0)	Furan (80)	Benzene (20)	40	38		1.28 (89)
28						
2 (5.0)	Furan (691)	None	40	53		0.883 (90)
29 and 30						
3 (1.0)	Furan (138)	None	40	80		(96) ^{c,d}
3 (8.0)	Furan (108)	Benzene (20)	40	80		1.26 (89) ^e
31 and 32						
26 (8.2)	Furan (368)	None	25	6		2.40 (90)
33 and 34						
2 (2.0)	2,5-Dimethylfuran (6.0)	Benzene (10)	80	16		0.28 (78)
35						
27 (2.0)	Furan (551)	None	40	45		0.140 (84)
36						
1 (6.0)	<i>N</i> -Acetylpyrrole (2.0)	Benzene (10)	40-50	18.5		0.302 (68) ^f
53						
2 (20.0)	<i>N</i> -Carbomethoxy-pyrrole (20.0)	Benzene (80)	25 ^g	10		(60) ^c
54, 55, and 56						

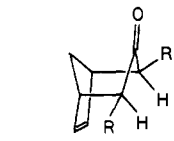
^a Isolated yield based on starting dibromide unless otherwise specified. ^b Determined by GLC. ^c Determined by NMR. ^d 76% conversion. ^e 85% conversion. ^f Isolated yield based on *N*-acetylpyrrole. ^g Irradiated by visible light.

reactive species derived from the secondary dibromide **2** reacted with cyclopentadiene to afford two types of cis adducts, **20** (46%) and **21** (40%), no trans isomer being produced. In a like manner the reaction with **3** gave **22** (47%) and **23** (46%). The cis relationship of the two alkyl substituents α to carbonyl group is apparent from the magnetic equivalence of each C_1 and C_5 , and C_2 and C_4 , protons (with or without $\text{Eu}(\text{fod})_3$). Structures of these isomers were elucidated by comparing the $\text{Eu}(\text{fod})_3$ -aided NMR spectra with those of the tricyclic ketones **24** and **25**.²⁰ The plots of the induced shift vs. the mole ratio, $\text{Eu}(\text{fod})_3/\text{substrate}$, yielded straight lines, from which the gradients of these lines, $-\Delta_{\text{Eu}}$, for each group of protons were determined. Here, intramolecular comparison of Δ_{Eu} values for the syn and anti methylene protons, H_s and H_a ,

served as a key in discerning the stereochemistries. In the ketone **24** containing a rigid chair cyclohexanone skeleton, neither H_s nor H_a is in the neighborhood of the carbonyl oxygen that acts as a Lewis base, and consequently the ratio of the induced shifts for these protons is very close to unity (Δ_{Eu} for H_s/Δ_{Eu} for $H_a = 1.05$). By contrast, in the ketone **25** where the cyclohexanone structure is rigidly constrained to a boat form, H_s lies much closer to the carbonyl oxygen than H_a , and hence the shift of H_s is greater than twice that of H_a (2.17 ratio). The structures of the ketones **20-23** are apparent when their Δ_{Eu} values are compared with those of the models **24** and **25**. The ketones that exhibit the ratios of 1.21 and 1.30 were assigned as **20** and **22** which exist mostly in chair forms, whereas the compounds displaying ratios of 1.72 and 1.71 were

20, R = CH₃22, R = CH(CH₃)₂21, R = CH₃23, R = CH(CH₃)₂

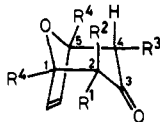
24



25

assigned as the ketones **21** and **23**, respectively. The rather large values for **21** and **23** are satisfactorily interpreted in terms of the significant contribution of the boat conformation; the repulsive 1,3 interactions between two alkyl groups at C₂ and C₄, coupled with the presence of the CH=CH bridge between C₁ and C₅, shift the equilibrium to the symmetrical boat form to a considerable extent.

C. Reaction with Furan Derivatives. The reaction with the dibromides **1–3** and furans also gave 1:1 cycloadducts in high yields. 1,3-Dibromo-1,3-diphenylpropan-2-one (**26**) and 2,4-dibromo-2-methylpentan-3-one (**27**) were employable as well. The results are shown in Table II. The furan adducts of secondary dibromides such as **2**, **3**, and **26** were mixtures of stereoisomers with respect to the alkyl substituents, while the reactions of **2** with 2,5-dimethylfuran and of **27** with furan gave only **35** and **36**, respectively.

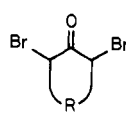
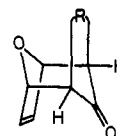
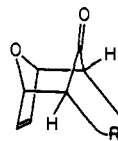
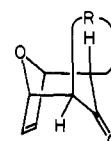
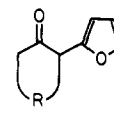
29, R¹ = R³ = CH₃; R² = R⁴ = H30, R¹ = R⁴ = H; R² = R³ = CH₃31, R¹ = R³ = CH(CH₃)₂; R² = R⁴ = H32, R¹ = R⁴ = H; R² = R³ = CH(CH₃)₂33, R¹ = R³ = C₆H₅; R² = R⁴ = H34, R¹ = R⁴ = H; R² = R³ = C₆H₅35, R¹ = R³ = R⁴ = CH₃; R² = H36, R¹ = R² = R³ = CH₃; R⁴ = H37, R¹ = CH₃; R² = R³ = R⁴ = H, andR¹ = R³ = R⁴ = H; R² = CH₃38, R¹ = R² = CH₃; R³ = R⁴ = H

The structural assignment of these oxabicyclic adducts was based on the following NMR characteristics.^{19,21,22} Firstly, the cis dialkyl derivatives have a plane of symmetry and give a much more simple spectrum compared with the trans isomers. Secondly, owing to the anisotropy effect of the oxygen atom, the signal of C₂ and C₄ axial protons appears at 0.5–0.7 ppm lower field than that of the equatorial protons. Thirdly, the bridgehead protons couple to C₂ or C₄ axial protons with

$J = 4.5\text{--}5.0$ Hz but to the equatorial protons with a very small value, $J = 0\text{--}1$ Hz.¹⁹

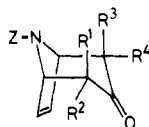
The attempted cyclocoupling reaction of α,α' -dibromoacetone and furan was totally unsuccessful. Reaction of dibromides of other methyl ketones did produce the corresponding furan adducts but the yields were not as high as those with dibromides of ordinary ketones with long alkyl chains. For example, the reaction of 1,3-dibromobutan-2-one or 1,3-dibromo-3-methylbutan-2-one gave the corresponding cycloadducts **37** and **38** in only 20–30% yields. In place of iron carbonyls, zinc–copper couple is also employable as a reducing agent,^{19–21} though it is much less effective in the reaction of open-chain 1,3-dienes.

The cyclic dibromo ketones **39–42** did not react with open-chain 1,3-dienes in satisfactory yield, but have proved to couple with cyclic 1,3-dienes in fair yields. The reaction with furan gave the tricyclic compounds, **43–48**, along with the α -sub-

39, R = (CH₂)₃40, R = (CH₂)₄41, R = (CH₂)₅42, R = (CH₂)₉43, R = (CH₂)₃ (35%)44, R = (CH₂)₄ (54%)45, R = (CH₂)₅ (27%)46, R = (CH₂)₉ (7%)47, R = (CH₂)₅ (10%)48, R = (CH₂)₉ (45%)49, R = (CH₂)₃ (35%)50, R = (CH₂)₄ (21%)51, R = (CH₂)₅ (10%)52, R = (CH₂)₉ (34%)

stituted furans **49–52** (yields given in parentheses). The stereochemistry of the tricyclic products was readily deduced by NMR analysis. The product distribution was markedly influenced by the ring size of the starting dibromo ketones and, in certain cases, reaction and workup conditions. Reaction of the six- and seven-membered dibromides **39** and **40** afforded the cis diaxial compounds **43** and **44**, respectively, while the eight-membered dibromo ketone **41** produced two cis isomers **45** and **47**. The 12-membered dibromide **42** yielded the cis and trans cycloadducts **46** and **48** with the latter predominating.²³ Since certain cycloadducts, particularly of type **47**, are rather labile in the presence of Lewis acids,²³ initially formed such adducts perhaps had isomerized to **49–52** to some extent.

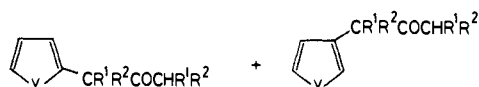
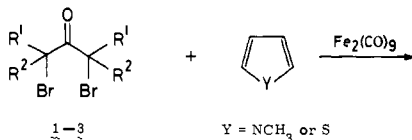
D. Reaction with Pyrrole Derivatives. Pyrroles bearing an electron-withdrawing substituent at nitrogen are also good receptors of oxyallyls (Table II). The reaction of **1** and *N*-acetylpyrrole in the presence of Fe₂(CO)₉ led to the bicyclic adduct **53** in 69% yield. Its IR spectrum exhibited intense absorptions at 1720 and 1660 cm⁻¹ attributable to the CO and NCOCH₃ moieties. The chemical shift and coupling data in the NMR spectrum were in accord with the assigned structure. The reduction of **2** with Fe₂(CO)₉ in the presence of *N*-carbomethoxypyrrole was accelerated by irradiation of visible light (>350 nm) to give three stereoisomeric cycloadducts, two cis isomers **54** and **55** and one trans isomer **56** (3:2:2 ratio), in 60% combined yield.^{2c} In the IR spectra of all these adducts strong bands due to the NCOOCH₃ and CO functions occurred in a 1710–1700-cm⁻¹ region. The cis isomers **54** and **55** exhibited a six-proton doublet attributable to two equivalent



- 53, $R^1 = R^2 = R^3 = R^4 = \text{CH}_3$; $Z = \text{COCH}_3$
54, $R^1 = R^3 = \text{H}$; $R^2 = R^4 = \text{CH}_3$; $Z = \text{COOCH}_3$
55, $R^1 = R^3 = \text{CH}_3$; $R^2 = R^4 = \text{H}$; $Z = \text{COOCH}_3$
56, $R^1 = R^4 = \text{H}$; $R^2 = R^3 = \text{CH}_3$; $Z = \text{COOCH}_3$

methyl groups, whereas the trans isomer **56** showed two three-proton doublets.

The reaction of the dibromides **1–3** with *N*-methylpyrrole did not give bicyclic adducts but resulted in the formation of the α - and β -substitution products **57–62** in good yields.



- 57, $Y = \text{NCH}_3$;
 $R^1 = R^2 = \text{CH}_3$ (31%)
58, $Y = \text{NCH}_3$;
 $R^1 = R^2 = \text{CH}_3$ (51%)
59, $Y = \text{NCH}_3$;
 $R^1 = \text{CH}_3$; $R^2 = \text{H}$ (48%)
60, $Y = \text{NCH}_3$;
 $R^1 = \text{CH}_3$; $R^2 = \text{H}$ (33%)
61, $Y = \text{NCH}_3$; $R^1 = \text{CH}(\text{CH}_3)_2$;
 $R^2 = \text{H}$ (62%)
62, $Y = \text{NCH}_3$; $R^1 = \text{CH}(\text{CH}_3)_2$;
 $R^2 = \text{H}$ (13%)
63, $Y = \text{S}$; $R^1 = \text{CH}_3$;
 $R^2 = \text{H}$ (37%)

Structure determination of these isomers was made by NMR; a signal due to the pyrrole α proton appeared at lower field (δ 6.3–6.5) than that of the β one (δ 5.7–6.1).²⁴

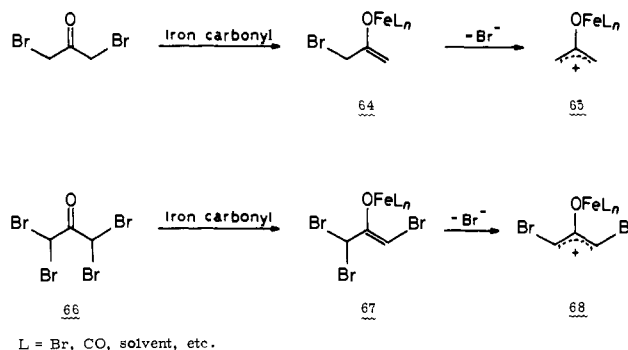
E. Reaction with Thiophene. The reaction of **2** with thiophene afforded only the α -substitution product **63** in 37% yield. No β product was formed.

Thus the reaction course of the oxyallyl species and five-membered heterocycles is highly dependent on the heteroatoms and the substituents. The formation of β -substitution products is a result of an electrophilic aromatic substitution by cationic oxyallyl-iron species, while the α -substitution compounds could arise via either a direct electrophilic substitution of the heterocycles by oxyallyl-iron intermediates or (and in part) initial cycloaddition followed by thermal or an acid-catalyzed isomerization.^{24,25} An aromatic substitution to pyrrole and thiophene occurs at both α and β positions, and the α to β ratio is strongly influenced by the nature of electrophilic reagent, heteroatom, solvent, reaction temperature, etc.²⁶ The failure of the cycloaddition with *N*-methylpyrrole and thiophene, undergoing substitution reaction, is contrasted with the behavior of cyclopentadiene, furan, and *N*-acetyl- or *N*-carbo-methoxypyrrole, and should be to the eminent aromatic character in the former five-membered dienes.²⁷ The same trend has been observed in the Diels-Alder reaction.²⁸ The isomer distribution in the cyclocoupling reaction with cyclopentadiene, furan, and pyrroles is variable depending on the structures of both cyclic dienes and dibromo ketones. However, the stereochemical result does not depend on whether the dibromide is either meso or *dl* isomer. The controlling factors may include the population of configurational isomers of the oxyallyl intermediate (W, sickle, and U forms are possible for 1,3-dialkyl-2-oxyallyls) and electronic structures of

the diene affecting the relative stabilities of the transition states, but the exact origin of such selectivities has not yet been elucidated.

The 3 + 4 Cyclocoupling Reaction by the Use of Tri- and Tetrabromo Ketones. The limitation of the above described 3 + 4 \rightarrow 7 cyclocoupling reaction apparently arises from the type of starting dibromides employable for the reaction. Attempted reactions with α, α' -dibromoacetone and 1,3-dienes did not produce any detectable amount of 1:1 cycloadducts, though the starting dibromide was consumed rapidly. Dibromides derived from other methyl ketones did not give satisfactory results either. Accordingly, in order to remove these limitations and to make the present procedure usable as a general tool for the synthesis of seven-membered ketones, it was required to discover suitable precursors which are synthetically equivalent to these methyl ketone dibromides.

This problem was successfully solved by employing, in place of the α, α' -dibromo ketones, further brominated substrates. The failure of the reaction with dibromoacetone is prevalently ascribed to high reactivity of the initially formed enolate **64** and instability of the unsubstituted oxyallyl species **65**.¹ Further introduction of bromine atoms at the α and α' positions, however, perturbs strongly the reactivity and stability of these intermediates. The bromine atom decreases the reactivity of the enolate **67** markedly by steric crowding and at the same time increases the stability of the oxyallyl **68** by the electronic



$L = \text{Br}, \text{CO}, \text{solvent}, \text{etc.}$

(mesomeric) effect,²⁹ thereby making the desired intermolecular coupling reaction feasible.

Thus the modified procedure consists of the generation of 1,3-dibromoxyallyl **68** from $\alpha, \alpha, \alpha', \alpha'$ -tetrabromoacetone (**66**) and removal of bromine atoms from the resulting cyclocoupling products. For example, the reaction of **66** and $\text{Fe}_2(\text{CO})_9$ in refluxing furan under nitrogen gave after ordinary workup a mixture of two crystalline adducts **69** and **70** (90:10 ratio), in

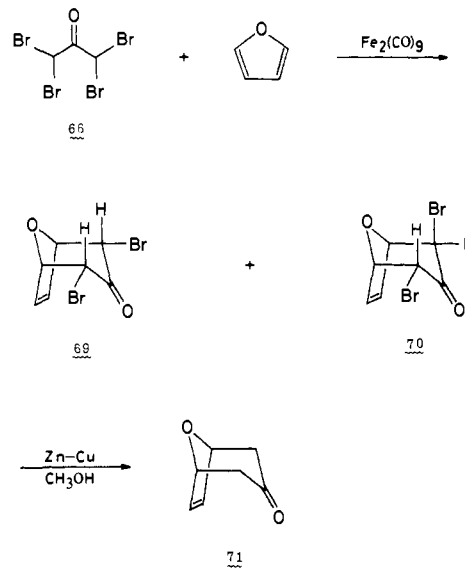







Table III. Synthesis of Bicyclo[3.2.1]oct-6-en-3-ones and the 8-Oxa Derivatives Using Tri- or Tetrabromo Ketones

Starting bromide (mmol)	Diene (mL)	Product	Yield, g (%)
$\alpha,\alpha,\alpha',\alpha'$ -Tetrabromoacetone (10.0)	Furan (40)		1.76 (63) ^a
$\alpha,\alpha,\alpha',\alpha'$ -Tetrabromoacetone (5.0)	Cyclopentadiene (1.0)		0.29 (47, 60) ^b
1,1,3,3-Tetrabromobutan-2-one (2.0)	Furan (10)		(63) ^c
1,1,3-Tribromo-3-methylbutan-2-one (2.0)	Furan (10)		0.37 (93) ^d
1,1,3-Tribromo-3-methylbutan-2-one (5.0)	Cyclopentadiene (1.0)		0.52 (69, 83) ^{b,e}

^a Yield of the dibromides **69** and **70**. The bromine atoms were removed quantitatively to give **71** (see Experimental Section). ^b Determined by GLC. ^c Yield of this volatile product was determined by NMR. ^d Yield of 2-bromo-4,4-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one. Conversion of this bromide to **38** was done quantitatively. ^e Reference 35.

63% combined yield. The stereochemistry was deduced by the NMR spectra.²² The bromine atoms in these adducts were easily removed by brief treatment with zinc-copper couple in methanol containing 5% ammonium chloride to give the desired reduction product **71** in 100% yield. Similarly, the reaction of tetrabromoacetone and cyclopentadiene with the aid of Fe(CO)₅ followed by the reduction with zinc-copper couple led to the bicyclic ketone **72** in 60% yield (Table III).

Since these products, **71** and **72**, have no alkyl substituents at positions α to the carbonyl group, this process can be envisaged formally as the 3 + 4 \rightarrow 7 cycloaddition between unsubstituted oxallyl and 1,3-dienes. 2-Methoxyallyl cation generated from the corresponding allyl halide and a silver salt is known to react with cyclic 1,3-dienes, but only in low yield.^{30,31} Parent cyclopropanone fails to undergo the [3 + 4] cycloaddition reaction giving seven-membered ketones,^{10,24}

This modified process has found a wide applicability as shown in Table III. For instance, polybromo derivatives of methyl ketones can be used and unsymmetrically substituted bicyclic ketones **37**, **38**, and **73** were prepared by this procedure. Although direct synthesis of **37** and **38** from the corresponding α,α' -dibromo ketones and furan was attained in only moderate yield (20 and 31%, respectively), the present two-step procedure using tribromo ketones gave these compounds in much improved yields (63 and 93%, respectively).

Thus, in a formal sense, we can now generate 2-oxallyls with all kinds of substitution patterns, i.e., unsubstituted one as well as mono-, 1,1-di-, 1,3-di-, tri-, and tetraalkylated species.

Conclusion

The existing methodologies for obtaining seven-membered carbocycles have been limited to expansion of six-membered rings and certain cyclocondensation reactions.³² The [3 + 4] type cycloaddition has been attained using cyclopropanones and certain 1,3-dienes,¹⁰ but the three-membered ketones are

rather difficult to prepare and unstable. We have described here an iron carbonyl promoted cyclocoupling reaction between polybromo ketones and 1,3-dienes forming 4-cycloheptenones in good yields. The [3 + 4] annulation is quite general and attained by a simple procedure using readily accessible, self-stable starting materials. The applications have been found in the synthesis of various troponoids,³³ tropane derivatives,³⁴ and other terpenic compounds.³⁵

Experimental Section

General. All melting and boiling points are uncorrected. Infrared (IR) spectra were recorded on a JASCO Model DS-402G spectrometer in carbon tetrachloride. Nuclear magnetic resonance (NMR) spectra were taken in carbon tetrachloride unless otherwise indicated at 60 MHz on a JEOL Model C-60H spectrometer or at 100 MHz on a Varian Model HA-100D instrument. The chemical shifts are recorded in parts per million relative to tetramethylsilane as an internal standard. Singlet, doublet, triplet, quartet, and multiplet were abbreviated to s, d, t, q, and m, respectively. Yields by NMR were obtained using tetralin as an internal standard. Low-resolution mass spectra were obtained at 70 eV on a Hitachi Model RMU-6C spectrometer. Exact mass spectra were taken in a laboratory of Professor A. Tatematsu, Department of Pharmaceutical Science, Meijo University. Analytical gas chromatography (GLC) was performed on a Yanagimoto Model G-8 or a Hitachi Model 063 gas chromatograph equipped with flame ionization detector using an appropriate internal standard. Preparative GLC work was conducted on a Varian Model 1700 thermal conductivity instrument. Columns used follow: A, 3 mm \times 2 m 5% Silicone OV-22 on 100–120 mesh Chromosorb W HP; B, 3 mm \times 1.5 m 2% Silicone OV-17 on 80–100 mesh Diasolid L; C, $\frac{3}{8}$ in. \times 10 ft 15% Silicone OV-17 on 60–80 mesh Chromosorb W AW; D, $\frac{3}{8}$ in. \times 7 ft 33% Apiezon grease L on 60–80 mesh Neopak 1A; E, 3 mm \times 2 m 5% Apiezon grease L on 60–80 mesh Diasolid M; F, 3 mm \times 3 m 5% Apiezon grease L on 60–80 mesh Neopak 1A; G, $\frac{3}{8}$ in. \times 7 ft 10% Apiezon grease L on 60–80 mesh Neopak 1A; H, 3 mm \times 0.75 m 10% Apiezon grease L on 60–80 mesh Neopak 1A; I, 3 mm \times 1 m 10% Silicone SE-30 on 80–100 mesh Chromosorb W AW; J, 3 mm \times 2 m 10% Silicone SE-30 on 80–100 mesh Chromosorb W AW; K, 4 mm \times 2 m 15% Silicone SE-30 on 60–80 mesh Chromosorb W AW. Analytical thin layer chromatography (TLC) was done on E. Merck Kieselgel GF₂₅₄ or PF₂₅₄ precoated plates (0.25-mm layers). Preparative TLC separation was conducted using 20 \times 20 cm glass plates coated with a 1.0-mm thick layer of E. Merck Kieselgel PF₂₅₄. The position of spots is shown by *R_f* values. For column chromatography E. Merck Kieselgel 60 (70–230 mesh) or Woelm basic alumina (activity I, 70–290 mesh) was used. Microanalytical works were carried out at the Microanalytical Center of Kyoto University.

Materials. α,α' -Dibromo ketones **1–3**, **26**, **27**, and **39–42**, and polybromo ketones **66**, 1,1,3,3-tetrabromobutan-2-one, and 1,1,3-tribromo-3-methylbutan-2-one were prepared by the method of Rappe.³⁶ The dibromides were used as obtained and no efforts to separate diastereoisomers were made. Liquid dibromo ketones were purified by passing through a short alumina column before use. Polybromo ketones, especially ones derived from cyclic ketones, are allergenic and use of rubber gloves is recommended for handling these materials. Diiron nonacarbonyl [Fe₂(CO)₉] was obtained according to the procedure of King³⁷ and dried in vacuo over KOH. 1,3-Diene-iron tricarbonyl complex **18** was synthesized from the corresponding 1,3-diene and iron pentacarbonyl following the photochemical process.¹⁸ 2,3-Dimethylbutadiene,³⁸ 1,2-bismethylenecyclohexane,³⁹ cyclopentadiene,⁴⁰ *N*-acetylpyrrole,⁴¹ *N*-carbomethoxypyrrole,⁴² and zinc-copper couple⁴³ were prepared by the literature methods. Furan was purified by refluxing on KOH followed by distillation. Commercial *N*-methylpyrrole and thiophene were distilled from CaH₂ before use. Benzene was distilled on phosphorus pentoxide prior to use.

Reaction of α,α' -Dibromo Ketones and 1,3-Dienes. Reaction and Workup Conditions. Reactions of α,α' -dibromo ketones and 1,3-dienes with the aid of iron carbonyls were carried out by the following three procedures.

Procedure A. Diiron nonacarbonyl (2.40 mmol) was placed in a 100-mL thick-wall reaction ampule connected to a three-way stopcock equipped with a rubber septum and a nitrogen inlet tube. The system was filled with dry nitrogen by five evacuation-flush with nitrogen

cycles. To this was added a mixture of dry benzene (10 mL), a 1,3-diene (20.0 mmol), and an α,α' -dibromo ketone (2.00 mmol) with a syringe and the tube was sealed under nitrogen. The mixture was stirred at 60–90 °C for several hours and then cooled to ambient temperature. The resulting precipitates were removed by filtration through a pad of Celite 545 (ca. 2 g) and the filtrate was concentrated by a rotary evaporator to give a yellow oil. Yields were obtained by GLC analysis using an appropriate internal standard. For the isolation of the adducts the residue was directly subjected to preparative TLC followed by distillation using a Kugelrohr apparatus. Otherwise, the mixture was distilled in vacuo and then the distillate was purified by preparative GLC.

Procedure B. In a 300-mL pressure bottle was placed $\text{Fe}(\text{CO})_5$ (20.0 mmol). The system was evacuated and flushed with nitrogen. Then a mixture of a 1,3-diene (60.0 mmol) and dry benzene (20.0 mL) was introduced with a syringe. The mixture was irradiated at 60 °C for 6–30 h with a 200-W high-pressure mercury lamp. The bottle was opened and an aliquot of the mixture was analyzed by NMR (dioxane as an internal standard) to confirm the quantitative formation of the diene-iron tricarbonyl complex. To this was added a solution of an α,α' -dibromo ketone (15.0 mmol) in a small amount of benzene. The mixture was again covered with nitrogen and heated at 70–120 °C for several hours. To an aliquot of the reaction mixture was added an appropriate internal standard and the mixture was analyzed by GLC using the specified column. The remaining reaction mixture was filtered through a pad of Celite 545 (ca. 2 g) and the filtrate was concentrated by a rotary evaporator to give a pale yellow oil. This oil was dissolved in acetone (20 mL), mixed with solid $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (10 mmol), and stirred at room temperature for 15 min to decompose the remaining diene-iron tricarbonyl complex. The slurry was then passed through a short column packed with Celite 545 (2 g) and the filtrate was concentrated under reduced pressure. The residue was dissolved in methylene chloride (40–50 mL) and washed with four 20-mL portions of 5% aqueous solution of ethylenediaminetetraacetic acid disodium salt (EDTA disodium salt). The organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated by a rotary evaporator to give a yellow oil, distillation of which under reduced pressure using a Kugelrohr apparatus yielded the 1:1 adduct as a colorless oil. Analytical samples were obtained by preparative TLC, GLC, or a combination of both.

Procedure C. Diiron nonacarbonyl (1.30 mmol) was placed in a 50-mL pressure bottle and the air in the vessel was replaced by nitrogen by five evacuation-flush with nitrogen cycles. To this was introduced a mixture of a dibromo ketone (1.00 mmol), a 1,3-diene (10.0 mmol), and dry benzene (2.5 mL). The mixture was irradiated at room temperature for 36 h by a 200-W high-pressure mercury lamp using a 10% aqueous solution of cupric sulfate as a filter. The reaction mixture was worked up as described in procedure B.

2,2,4,5,7,7-Hexamethyl-4-cycloheptenone (8). **Procedure A.** A mixture of $\text{Fe}_2(\text{CO})_9$ (1.60 g, 4.40 mmol), the dibromo ketone **1** (540 mg, 2.00 mmol), 2,3-dimethylbutadiene (**4**, 7.28 g, 88.5 mmol), dry benzene (5.0 mL), and a small amount of hydroquinone was heated at 60 °C for 38 h with occasional shaking. Workup gave a yellow oil (290 mg). GLC analysis (column E, 100 °C, tetradecane as an internal standard) indicated the production of **8** in 71% yield. The analytical sample of **8** was obtained by preparative GLC (column D, 165 °C, retention time (t_R) 20 min): IR 1685 cm^{-1} (C=O); NMR δ 1.07 (s, 4 CH_3), 1.79 (s, 2 =CCH₃), 2.25 (s, 2 =CCH₂); mass spectrum m/e 194 (M^+), 123 ($M^+ - 71$) (base peak), 110 ($M^+ - 84$), 109 ($M^+ - 85$). Anal. ($\text{C}_{13}\text{H}_{22}\text{O}$) C, H.

Procedure B. A mixture of $\text{Fe}(\text{CO})_5$ (3.92 g, 20.0 mmol), **4** (4.93 g, 60.0 mmol), and dry benzene (20.0 mL) was irradiated at 55 °C for 6.5 h. To this was added the dibromo ketone **1** (4.08 g, 15.0 mmol) and the mixture was kept at 80 °C for 12 h. The reaction mixture was worked up to give a brown oil (6.20 g), which was distilled under reduced pressure affording **8** (2.90 g, 100%) as a colorless oil, bp 120–130 °C (0.02 mm). The product was homogeneous on GLC and TLC analyses.

2,2,7,7-Tetramethyl-4-cycloheptenone (9). **Procedure B.** A mixture of $\text{Fe}(\text{CO})_5$ (3.92 g, 20.0 mmol), **5** (5.40 g, 100 mmol), and benzene (20.0 mL) was irradiated by visible light at 60 °C for 30 h. NMR analysis of the aliquot indicated that **18** ($R^3 = R^4 = \text{H}$) was formed quantitatively. To this was added the dibromo ketone **1** (4.08 g, 15.0 mmol) and the mixture was kept at 80 °C for 4 h. GLC analysis (column A, 80 °C) indicated that only one product was formed. Workup gave a red oil (3.38 g), which was distilled in vacuo yielding

9 (2.26 g, 90%), bp 90–100 °C (0.02 mm). The analytical sample was obtained by preparative GLC (column D, 165 °C, t_R 20.0 min): IR 1685 cm^{-1} (C=O); NMR δ 1.11 (s, 4 CH_3), 2.2–2.3 (m, 2 CH_2), 5.70 (t, $J = 3.0$ Hz, 2 =CH); mass spectrum m/e 166 (M^+), 123 ($M^+ - 43$), 95 ($M^+ - 71$) (base peak), 82 ($M^+ - 84$), 81 ($M^+ - 85$). Anal. ($\text{C}_{11}\text{H}_{18}\text{O}$) C, H.

Procedure A. A mixture of $\text{Fe}_2(\text{CO})_9$ (1.60 g, 4.40 mmol), **1** (540 mg, 2.00 mmol), **5** (6.50 g, 120 mmol), dry benzene (5.0 mL), and a small amount of hydroquinone in an ampule was kept at 60 °C for 38 h with occasional shaking. Workup followed by GLC analysis (column E, 100 °C, dodecane as an internal standard) showed that **9** was formed in 33% yield.

2,2,4,7,7-Pentamethyl-4-cycloheptenone (10). **Procedure B.** In a pressure bottle $\text{Fe}(\text{CO})_5$ (3.92 g, 20.0 mmol) was mixed with isoprene (**6**, 4.09 g, 60.0 mmol) and dry benzene (20 mL), and the resulting suspension was irradiated by visible light at 60 °C for 6 h. To this was added the dibromo ketone **1** (3.74 g, 13.7 mmol) and the mixture was kept at 87 °C for 12 h. Workup gave a yellow oil (3.10 g), which was distilled under reduced pressure affording **10** (1.74 g, 70%) as a colorless oil, bp 120–130 °C (3 mm). An analytically pure sample was obtained by preparative GLC (column D, 150 °C, t_R 24.0 min): IR 1685 cm^{-1} (C=O); NMR δ 1.10 (s, 2 CH_3), 1.12 (s, 2 CH_3), 1.80 (s, =CCH₃), 2.1–2.3 (m, 2 CH_2), 5.4–5.8 (m, =CH); mass spectrum m/e 180 (M^+), 109 ($M^+ - 71$) (base peak), 96 ($M^+ - 84$), 95 ($M^+ - 85$). Anal. ($\text{C}_{12}\text{H}_{20}\text{O}$) C, H.

Procedure A. To $\text{Fe}_2(\text{CO})_9$ (800 mg, 2.20 mmol) placed in a 50-mL reaction ampule was added a mixture of **1** (272 mg, 1.00 mmol), **6** (6.81 g, 100 mmol), and dry benzene (5.0 mL). The mixture was kept at 65 °C for 38 h with occasional shaking and cooled to room temperature. The mixture was worked up to give a yellow oil, which was analyzed by GLC (column E, 100 °C) indicating that the adduct **10** (t_R 8.0 min) was obtained in 47% yield.

2,4,5,7-Tetramethyl-4-cycloheptenone (11). **Procedure B.** Iron pentacarbonyl (3.92 g, 20.0 mmol) was placed in a pressure bottle under nitrogen. To this was added a mixture of **4** (4.93 g, 60.0 mmol) and dry benzene (20.0 mL) and the solution was irradiated at 55 °C for 6 h, where the quantitative formation of 2,3-dimethylbutadiene-iron tricarbonyl (**18**, $R^3 = R^4 = \text{CH}_3$) was proved by NMR analysis. To this was added the dibromo ketone **2** (2.66 g, 15.0 mmol) and the mixture was kept at 120 °C for 4 h. The reaction mixture was worked up to give a yellow-green oil (3.60 g). Distillation in vacuo yielded a pale yellow oil (2.56 g), bp 90–100 °C (3 mm). Its TLC purification (1:10 ether-hexane) gave oily **11** (R_f 0.15, 819 mg, 33%). An analytically pure sample was obtained by preparative GLC (column D, 165 °C): IR 1708 cm^{-1} (C=O); NMR δ 0.97 (d, $J = 6.0$ Hz, 2 CH_3), 1.72 (s, 2 =CCH₃), 1.7–2.8 (m, 2 CH_2 and 2 CH); mass spectrum m/e 166 (M^+), 151 ($M^+ - 15$), 137 ($M^+ - 29$), 124 ($M^+ - 42$), 123 ($M^+ - 43$), 109 ($M^+ - 57$) (base peak), 96 ($M^+ - 70$), 95 ($M^+ - 71$). Anal. ($\text{C}_{11}\text{H}_{18}\text{O}$) C, H.

Procedure A. A mixture of $\text{Fe}_2(\text{CO})_9$ (437 mg, 1.20 mmol), **4** (728 mg, 8.85 mmol), and dry benzene (5.0 mL) was stirred at 60 °C and to this was added dropwise a solution of the dibromo ketone **2** (259 mg, 1.06 mmol) and dodecane (15.7 mg, 0.09 mmol, and internal standard for GLC analysis) in benzene (4.0 mL) over a period of 34 h. Workup gave a crude oil, which was analyzed by GLC (column E, 120 °C) indicating that the adduct **11** was produced in 46% yield.

The coupling products of secondary dibromo ketones and 1,3-dienes, though homogeneous on TLC and GLC, in most cases consisted of two stereoisomers as was revealed by careful examination of the 100-MHz NMR spectra. For example, ten-time expansion of the δ 0.5–1.5 region of the spectrum of **11** showed that absorptions due to methyl protons were composed of two doublets separated by only 1 Hz (δ 1.02 and 1.03). Such difficult-to-separate isomers were analyzed as the mixtures throughout this paper.

2,7-Dimethyl-4-cycloheptenone (12). **Procedure B.** A mixture of $\text{Fe}(\text{CO})_5$ (3.92 g, 20.0 mmol), **5** (6.50 g, 120 mmol), and dry benzene (20.0 mL) was irradiated by visible light at 55 °C for 14 h. Then the dibromo ketone **2** (3.66 g, 15.0 mmol) was added and the mixture was kept without light at 80 °C for 9 h. Workup gave a dark brown oil (8.91 g), which was distilled in vacuo yielding crude **12** (1.07 g, 80% pure by NMR analysis, 40% yield). Preparative TLC separation (1:10 ether-hexane, two developments) afforded **12** (0.72 g, 35%). An analytical sample of **12** was obtained by preparative GLC (column G, 140 °C): IR 1710 cm^{-1} (C=O); NMR δ 1.05 (d, $J = 6.0$ Hz, 2 CH_3), 1.6–3.0 (m, 2 CH_2 and 2 CH), 5.6–5.8 (m, 2 =CH); mass spectrum m/e 138 (M^+), 110 ($M^+ - 28$), 96 ($M^+ - 42$), 95 ($M^+ - 43$), 82 (M^+

– 56), 81 ($M^+ - 57$), 68 ($M^+ - 70$), 67 ($M^+ - 71$) (base peak). Anal. ($C_9H_{14}O$) C, H.

Procedure A. A mixture of $Fe_2(CO)_9$ (441 mg, 1.20 mmol), **5** (650 mg, 12.0 mmol), the dibromo ketone **2** (234 mg, 0.96 mmol), dodecane (14.3 mg, 0.08 mmol, an internal standard for GLC analysis), and dry benzene (2.5 mL) was heated at 80 °C for 16 h with occasional shaking. Workup followed by analysis of the reaction mixture by GLC (column E, 120 °C) indicated that **12** was formed in 30% yield.

2,4,7-Trimethyl-4-cycloheptenone (13). **Procedure B.** A mixture of $Fe(CO)_5$ (3.92 g, 20.0 mmol), **6** (4.09 g, 60.0 mmol), and dry benzene (20.0 mL) placed in a 300-mL pressure bottle was exposed to visible light at 55 °C for 20 h. The quantitative formation of the diene-iron tricarbonyl complex **18** ($R^3 = CH_3$, $R^4 = H$) was confirmed by NMR. To this was added the dibromo ketone **2** (3.66 g, 15.0 mmol) and the mixture was stirred at 120 °C for 12 h. Workup gave a brown oil (4.20 g), which was distilled in vacuo to give a pale yellow oil (3.10 g), bp 70–150 °C (0.02 mm). Redistillation of the product afforded crude **13** (1.45 g) as a colorless oil, bp 87–91 °C (0.02 mm). GLC analysis (column K, 150 °C) indicated that **13** (t_R 18.0 min) was produced in 51% yield accompanied by another 1:1 adduct (t_R 11.0 min, 12%). TLC separation (1:10 ether–hexane) gave a pure sample of **13** (0.98 g, 43%). An analytically pure sample was obtained by GLC purification (column K, 150 °C): IR 1708 cm^{-1} (C=O); NMR δ 1.04 (d, $J = 6.0$ Hz, 2 CH_3), 1.69 (br s, CH_3), 1.5–3.0 (m, 2 CH_2 and 2 CH), 5.1–5.5 (m, =CH); mass spectrum m/e 152 (M^+), 110 ($M^+ - 42$), 109 ($M^+ - 43$), 95 ($M^+ - 57$), 91 ($M^+ - 61$), 82 ($M^+ - 70$), 81 ($M^+ - 71$). Anal. ($C_{10}H_{16}O$) C, H. The by-product was tentatively assigned as 2,3,5-trimethyl-3-vinylcyclopentanone based on its spectral properties: IR 1745 (C=O), 1640 (C=C), 990, 915 cm^{-1} (CH=CH₂); NMR ($CDCl_3$) δ 0.94 (s, CH_3), 1.14 (d, $J = 7.0$ Hz, 2 CH_3), 1.6–3.0 (m, CH_2 and 2 CH), 4.8–5.2 (m, CH=CH₂), 5.5–6.0 (m, CH=CH₂); mass spectrum m/e 152 (M^+).

Procedure C. A mixture of $Fe_2(CO)_9$ (461 mg, 1.27 mmol), the dibromo ketone **2** (244 mg, 1.00 mmol), isoprene (**6**, 680 mg, 10.0 mmol), dodecane (17.0 mg, 0.10 mmol, a GLC internal standard), and benzene (2.5 mL) was irradiated by visible light in a 50-mL Pyrex ampule at room temperature for 36 h. Workup followed by GLC analysis (column B, 80 °C) showed that the compound **13** was produced in 36% yield.

3,5-Dimethylbicyclo[5.4.0]undec-1(7)-en-4-one (14). This compound was prepared by a modified method of procedure A. Diiron nonacarbonyl (697 mg, 2.49 mmol) was placed in a 30-mL two-necked flask equipped with a serum cap and a three-way stopcock carrying a nitrogen-filled rubber balloon. The system was flushed with nitrogen and to this was added a solution of 1,2-bismethylenecyclohexane (108 mg, 1.00 mmol) in dry benzene (2.5 mL) followed by the dibromo ketone **2** (608 mg, 2.49 mmol). The mixture was magnetically stirred at 62–64 °C for 46 h, then cooled to room temperature, and poured into 15 mL of a saturated $NaHCO_3$ solution. To this was added ethyl acetate (60 mL) and the solid material was removed by filtration through a pad of Celite 545. The organic layer was separated and the aqueous layer was extracted with two 10-mL portions of ethyl acetate. The combined extracts were dried over Na_2SO_4 and the solvent was evaporated to give a dark brown oil (0.261 g). Purification by silica gel chromatography (1:1 benzene–hexane) yielded the adduct **14** (0.153 g, 80%) as a colorless oil which was homogeneous on GLC analysis (column I, 110 °C): IR 1705 (C=O), 1660 cm^{-1} (C=C); NMR δ 1.03 (d, $J = 6.5$ Hz, 2 CH_3), 1.4–1.6 (m, 2 CH_2), 1.7–2.3 (m, 4 =CCH₂), 2.6–3.0 (m, 2 $CHCH_3$); mass spectrum m/e 192 (M^+). Anal. ($C_{13}H_{20}O$) C, H.

2,7-Diisopropyl-4,5-dimethyl-4-cycloheptenone (15). **Procedure B.** The diene-iron tricarbonyl complex **18** ($R^3 = R^4 = CH_3$) was synthesized by irradiation of a mixture of $Fe(CO)_5$ (3.92 g, 20.0 mmol), 2,3-dimethylbutadiene (**4**, 4.93 g, 60.0 mmol), and dry benzene (20.0 mL) at room temperature for 39 h. To this was added the dibromo ketone **3** (4.50 g, 15.0 mmol) and the mixture was stirred at 120 °C for 20 h. Usual workup gave a yellow oil (4.83 g). Distillation in vacuo gave a yellow oil (3.47 g), bp 120–140 °C (3 mm), which was purified by preparative TLC (1:10 ether–hexane) to give **15** (R_f 0.50, 1.82 g, 55%) as a pale yellow oil. An analytical sample was obtained by further GLC purification (column G, 190 °C): IR 1704 cm^{-1} (C=O); NMR δ 0.7–1.1 (complex, 2 $CH(CH_3)_2$), 1.70 (s, 2 CH_3), 1.5–2.5 (m, 2 CH_2 , 2 CH, and 2 $CH(CH_3)_2$); mass spectrum m/e 222 (M^+), 208 ($M^+ - 14$), 180 ($M^+ - 42$), 140 ($M^+ - 82$), 137 ($M^+ - 85$), 123 ($M^+ - 99$), 110 ($M^+ - 112$). Anal. ($C_{15}H_{26}O$) C, H.

Procedure A. A mixture of $Fe_2(CO)_9$ (1.61 g, 4.40 mmol), the di-

bromo ketone **3** (1.20 g, 4.00 mmol), and the diene **4** (2.91 g, 35.4 mmol) in dry benzene (10.0 mL) was stirred at 60 °C for 38 h. After usual workup the reaction mixture was analyzed by GLC (column E, 150 °C) indicating that the cycloadduct **15** was formed in 36% yield.

2,7-Diisopropyl-4-cycloheptenone (16). **Procedure B (with Some Modification).** Butadiene-iron tricarbonyl complex (**18**, $R^3 = R^4 = H$) was prepared by the standard photochemical procedure and purified by distillation. The complex (4.27 g, 22.0 mmol) was mixed with the dibromo ketone **3** (3.00 g, 10.0 mmol) in benzene (4.0 mL) and the mixture was stirred at 70 °C for 40 h. Analysis of the reaction mixture by GLC (column E, 120 °C) indicated that the adduct **16** was produced in 77% yield. The reaction mixture was diluted with carbon tetrachloride (20 mL), washed with water, and dried. Evaporation of the solvent followed by distillation in vacuo gave crude **16** (1.80 g), bp 50–78 °C (3 mm). In the early fraction, some starting diene-iron tricarbonyl complex (2.2 g) was recovered, bp 30–40 °C (3 mm). A high-boiling fraction (400 mg, bp 80–150 °C (2 mm)) was also obtained, but no effort to elucidate the structure was done. An analytically pure sample of **16** was obtained by preparative TLC (R_f 0.30, 1:1 benzene–hexane) followed by GLC purification (column G, 190 °C): IR 1710 cm^{-1} (C=O); NMR δ 0.87 (d, $J = 6.0$ Hz, 2 $CH(CH_3)_2$), 1.5–2.7 (m, 2 CH_2 , 2 CH, and 2 $CH(CH_3)_2$), 5.5–5.7 (m, 2 =CH); mass spectrum m/e 194 (M^+), 179 ($M^+ - 15$), 152 ($M^+ - 42$), 151 ($M^+ - 43$), 149 ($M^+ - 45$), 140 ($M^+ - 54$), 138 ($M^+ - 56$), 125 ($M^+ - 69$), 123 ($M^+ - 71$), 110 ($M^+ - 84$), 109 ($M^+ - 85$), 94 ($M^+ - 100$), 82 ($M^+ - 112$). Anal. ($C_{13}H_{22}O$) C, H.

Procedure A. A mixture of the dibromo ketone **3** (1.20 g, 4.00 mmol), $Fe_2(CO)_9$ (1.60 g, 4.40 mmol), and butadiene (**5**, 2.60 g, 48.0 mmol) in dry benzene (10.0 mL) was heated at 90 °C for 12 h. Workup as usual gave a crude oil (0.80 g). GLC analysis (column E, 150 °C) indicated that the adduct **16** was formed in 44% yield.

2,7-Diisopropyl-4-methyl-4-cycloheptenone (17). **Procedure C.** A mixture of **3** (300 mg, 1.00 mmol), $Fe_2(CO)_9$ (445 mg, 1.23 mmol), isoprene (**6**, 680 mg, 10.0 mmol), and benzene (2.5 mL) was irradiated by visible light at room temperature for 36 h. The crude mixture (220 mg) obtained after usual workup, when analyzed by GLC (column I, 160 °C) using tetradecane as an internal standard, indicated that the product **17** (t_R 7.0 min) was produced in 31% yield in addition to a cyclopentanone adduct (t_R 5.0 min, 8%). An analytical sample of **17** was obtained by TLC (R_f 0.35, 1:1 benzene–hexane) followed by GLC separation (column G, 190 °C): IR 1705 cm^{-1} (C=O); NMR δ 0.7–1.0 (complex, 2 $CH(CH_3)_2$), 1.69 (s, CH_3), 1.6–2.8 (m, 2 CH_2 , 2 CH, and 2 $CH(CH_3)_2$), 5.3–5.6 (m, =CH); mass spectrum m/e 208 (M^+), 193 ($M^+ - 15$), 165 ($M^+ - 43$), 152 ($M^+ - 56$), 140 ($M^+ - 68$), 109 ($M^+ - 99$). Anal. ($C_{14}H_{24}O$) C, H. The cyclopentanone by-product was tentatively assigned as 2,5-diisopropyl-3-methyl-3-vinylcyclopentanone: IR 1735 (C=O), 1640 (C=C), 1000, 916 cm^{-1} (CH=CH₂); NMR ($CDCl_3$) δ 0.8–1.2 (m, 2 $CH(CH_3)_2$), 1.6–2.8 (m, CH_2 , 2 CH, and 2 $CH(CH_3)_2$), 4.9–5.2 (m, CH=CH₂), 5.5–6.0 (m, CH=CH₂); mass spectrum m/e 208 (M^+), 193 ($M^+ - 15$), 165 ($M^+ - 43$), 151 ($M^+ - 57$), 123 ($M^+ - 85$), 110 ($M^+ - 98$), 109 ($M^+ - 99$), 95 ($M^+ - 113$).

2,2,4,4-Tetramethylbicyclo[3.2.1]oct-6-en-3-one (19). **Procedure A.** A mixture of the dibromo ketone **1** (544 mg, 2.00 mmol), $Fe_2(CO)_9$ (1.60 g, 4.40 mmol), cyclopentadiene (8.24 g, 125 mmol), and dry benzene (10 mL) was stirred at 60 °C for 38 h. Usual workup gave crude **19** (280 mg). GLC analysis (column E, 100 °C) using dodecane as an internal standard showed that **19** (t_R 8.0 min) was produced in 82% yield. An analytical sample was obtained by preparative GLC (column D, 165 °C). The IR, NMR, and mass spectra of **19** were identical with those of an authentic sample.¹⁹

A similar reaction using **1** (2.18 g, 8.00 mmol), $Fe_2(CO)_9$ (4.37 g, 12.0 mmol), cyclopentadiene (6.33 g, 95.9 mmol), and dry benzene (20 mL) was carried out. Additional introduction of cyclopentadiene (3.15 g, 47.7 mmol) and workup as usual gave a brown oil (9.36 g). Silica gel chromatography (1:10 ether–hexane) afforded oily **19** (1.01 g, 71%) which was homogeneous on GLC analysis.

2,4-Dimethylbicyclo[3.2.1]oct-6-en-3-ones (20 and 21). **Procedure A.** A mixture of $Fe_2(CO)_9$ (1.76 g, 4.84 mmol), the dibromo ketone **2** (978 mg, 4.00 mmol), cyclopentadiene (3.29 g, 49.8 mmol), benzene (10.0 mL), and a trace amount of hydroquinone was stirred at 60 °C for 25 h and worked up in a usual manner. Analysis of the reaction mixture (600 mg) by GLC (column H, 100 °C) using dodecane as an internal standard indicated that **20** (t_R 8.0 min) and **21** (t_R 6.5 min) were formed in 86% combined yield in a ratio of 47:53. Preparative

TLC separation (1:1 benzene-hexane) gave pure samples of **20** (R_f 0.35, 232 mg, 38%) and **21** (R_f 0.31, 260 mg, 43%). The spectral properties of the products were identical with those reported.¹⁹ When the Eu(fod)₃-induced shifts vs. the mole ratio Eu(fod)₃/substrate were plotted, a linear correlation was found for each group of protons. The gradients ($-\Delta E_u$, ppm/mol of Eu(fod)₃ per mol of substrate, of these lines follow: **20** (0.18 M in CCl₄), 4.7 (H_{8a}), 5.0 (H₁, H₅, H₆, and H₇), 5.7 (H_{8s}), 9.8 (CH₃), 12.5 (H₂ and H₄); **21** (0.16 M in CCl₄), 3.9 (H₆ and H₇), 4.7 (H_{8a}), 5.3 (H₁ and H₅), 8.1 (H_{8s}), 10.2 (CH₃), 18.2 (H₂ and H₄). The following coupling constants were determined: **20**, $J_{1,2} = J_{4,5} = 3.0$, $J_{8a,8s} = 11.0$ Hz; **21**, $J_{1,2} = J_{4,5} < 2$, $J_{1,8a} = J_{5,8a} = 5.0$, $J_{8a,8s} = 12.0$ Hz.

2,4-Diisopropylbicyclo[3.2.1]oct-6-en-3-ones (22 and 23). Procedure A. To Fe₂(CO)₉ (1.61 g, 4.40 mmol) placed in a 100-mL reaction ampule was added a mixture of the dibromo ketone **3** (1.20 g, 4.00 mmol), cyclopentadiene (3.29 g, 49.8 mmol), and benzene (10.0 mL), and the mixture was stirred at 90 °C for 12 h. The reaction mixture was worked up as usual to give a crude product (800 mg). GLC analysis (column E, 150 °C, tetradecane as an internal standard) indicated that the adducts **22** and **23** were formed in 93% combined yield in equal amounts. The reaction mixture was then subjected to TLC separation (1:4 chloroform-benzene) to give **22** (R_f 0.30, 360 mg, 44%) and **23** (R_f 0.35, 346 mg, 42%). Analytical samples were obtained by preparative GLC (column G, 190 °C). **22**: IR 1695 cm⁻¹ (C=O); NMR δ 0.92 and 1.00 (two d, $J = 6.0$ Hz, 2 CH(CH₃)₂), 1.5-2.2 (m, CH₂ and 2 CHCH(CH₃)₂), 2.7-2.9 (m, 2 =CCH), 5.96 (br s, 2 =CH); mass spectrum m/e 206 (M⁺), 191 (M⁺ - 15), 163 (M⁺ - 43), 149 (M⁺ - 57), 140 (M⁺ - 66), 125 (M⁺ - 81), 121 (M⁺ - 85), 107 (M⁺ - 99), 91 (M⁺ - 115), 79 (M⁺ - 127), 77 (M⁺ - 129). Anal. (C₁₄H₂₂O) C, H. **23**: IR 1703 cm⁻¹ (C=O); NMR δ 0.85 and 0.95 (two d, $J = 6.0$ Hz, 2 CH(CH₃)₂), 1.6-2.5 (m, CH₂ and 2 CHCH(CH₃)₂), 2.8-3.1 (m, 2 =CCH), 5.86 (br s, 2 =CH); mass spectrum m/e 206 (M⁺), 191 (M⁺ - 15), 163 (M⁺ - 43), 149 (M⁺ - 57), 140 (M⁺ - 66), 125 (M⁺ - 81), 121 (M⁺ - 85), 107 (M⁺ - 99), 91 (M⁺ - 115), 79 (M⁺ - 127). Anal. (C₁₄H₂₂O) C, H. The $-\Delta E_u$ values derived from the Eu(fod)₃-aided NMR spectra of **22** (0.18 M in CCl₄) and **23** (0.18 M in CCl₄) follow: **22**, 2.7 and 3.7 (CH(CH₃)₂), 3.3 (H_{8a}), 3.8 (H₁, H₅, H₆, and H₇), 4.3 (H_{8s}), 10.4 (CH(CH₃)₂, H₂ and H₄); **23**, 2.8 (H₆ and H₇), 3.2 and 6.5 (CH(CH₃)₂), 3.5 (H_{8a}), 4.1 (H₁ and H₅), 6.0 (H_{8s}), 7.9 (CH(CH₃)₂), 14.9 (H₂ and H₄). The coupling constants observed follow: **22**, $J_{1,2} = J_{4,5} < 2$, $J_{1,8a} = J_{5,8a} = 5.0$, $J_{8a,8s} = 11.0$ Hz; **23**, $J_{1,2} = J_{4,5} < 2$, $J_{1,8a} = J_{5,8a} = 5.0$, $J_{8a,8s} = 11.0$ Hz.

The NMR spectra of **24** and **25** obtained by the literature procedure²¹ were measured in the presence of Eu(fod)₃. The $-\Delta E_u$ values obtained follow: **24** (0.14 M in CCl₄), 2.9 (H₃ and H₄), 3.3 (H₂ and H₅), 3.8 (H_{12a}), 4.0 (H_{12s}), 10.4 (H₁ and H₆); **25** (0.21 M in CCl₄), 4.3 (H₃ and H₄), 4.6 (H_{12a}), 5.2 (H₂ and H₅), 10.0 (H_{12s}), 18.4 (H₁ and H₆). The coupling constants determined follow: **24**, $J_{1,2} = J_{5,6} < 2$, $J_{12a,12s} = 12.0$ Hz; **25**, $J_{1,2} = J_{5,6} = 7.0$, $J_{12a,12s} = 12.0$ Hz.

Attempted Reaction of Cyclobutadiene-Iron Tricarbonyl with 2,4-Dibromo-2,4-dimethylpentan-3-one (1). A solution of cyclobutadiene-iron tricarbonyl (10.0 mg, 0.05 mmol) and **1** (14.3 mg, 0.05 mmol) in dry benzene (0.2 mL) was placed in an ampule under argon and kept at 45 °C for 14.5 h, and then at 70-80 °C for 5 h. After cooling the mixture was poured into aqueous NaHCO₃ and extracted five times with 1:10 ether-hexane, and the combined extracts were dried. Evaporation of the solvent gave a brown oil (10.0 mg). An IR spectrum of the oil showed a carbonyl band at only 1704 cm⁻¹, indicating that no cyclopentanone derivatives were formed.

2,2,4,4-Tetramethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (28). A mixture of **1** (272 mg, 1.00 mmol) and Fe₂(CO)₉ (437 mg, 1.20 mmol) in furan (10 mL) was heated at reflux for 38 h. Usual workup gave a pale yellow oil (227 mg). The yield of **28** determined by NMR analysis was 96%. An analytical sample was obtained by preparative TLC (1:10 ether-benzene). The IR and NMR spectra were identical with those of an authentic sample.²⁴

In another experiment a mixture of **1** (2.18 g, 8.00 mmol), Fe₂(CO)₉ (3.64 g, 10.0 mmol), furan (5.44 g, 80.0 mmol), and benzene (20 mL) was stirred at 40 °C for 38 h. After workup a yellow-green oil was obtained (1.80 g), which was purified on silica gel chromatography (1:10 ether-hexane) to afford **28** (1.28 g, 89%).

2,4-Dimethyl-8-Oxabicyclo[3.2.1]oct-6-en-3-ones (29 and 30). A mixture of Fe₂(CO)₉ (2.18 g, 6.00 mmol), the dibromo ketone **2** (1.22 g, 5.00 mmol), and furan (50 mL) was stirred at 40 °C. After 24 h, Fe₂(CO)₉ (1.09 g, 3.00 mmol) was added renewedly, and the mixture

was maintained at this temperature for an additional 29 h. Workup afforded a crude mixture of **29** and **30** (883 mg, 90%, 44:56 ratio by NMR analysis). TLC separation (1:2 ether-hexane, two developments) followed by purification by GLC (column G, 110 °C) gave pure samples of **29** (R_f 0.54) and **30** (R_f 0.48). The IR and NMR spectra were identical with those of the reported ones.¹⁹

2,4-Diisopropyl-8-oxabicyclo[3.2.1]oct-6-en-3-ones (31 and 32). A mixture of Fe₂(CO)₉ (437 mg, 1.20 mmol), the dibromo ketone **3** (300 mg, 1.00 mmol), and furan (10 mL) was stirred at reflux. After 40 h, Fe₂(CO)₉ (220 mg, 0.60 mmol) and furan (10 mL) were added renewedly, and the mixture was further stirred for an additional 40 h. Workup gave a yellow oil (220 mg). Yields of **31** and **32** were determined by NMR analysis (96% combined yield based on the consumed starting dibromo ketone (76% conversion)). A 77:23 ratio was obtained by GLC analysis (column E, 150 °C). TLC separation (1:10 ether-hexane, two developments) afforded pure samples of **31** (R_f 0.39) and **32** (R_f 0.29). **31**: mp 34.5-35.5 °C (from cyclohexane); IR 1713 cm⁻¹ (C=O); NMR δ 0.88 and 1.00 (two d, $J = 6.5$ Hz, 2 CH(CH₃)₂), 1.6-2.3 (m, 2 CH(CH₃)₂), 2.40 (dd, $J = 4.5$ and 6.5 Hz, 2 CHCO), 4.88 (d, $J = 4.5$ Hz, 2 OCH), 6.13 (br s, 2 =CH); mass spectrum m/e 208 (M⁺), 165 (M⁺ - 43) (base peak), 123 (M⁺ - 85), 109 (M⁺ - 99), 81 (M⁺ - 127). Anal. (C₁₃H₂₀O₂) C, H. **32**: mp 34-35 °C (from cyclohexane); IR 1710 cm⁻¹ (C=O); NMR δ 0.8-1.2 (m, 2 CH(CH₃)₂), 1.7-2.4 (m, 2 CH(CH₃)₂), 1.71 (d, $J = 9.0$ Hz, CHCO), 2.48 (dd, $J = 4.5$ and 9.0 Hz, CHCO), 4.83 (br s, OCH), 4.86 (d, $J = 4.5$ Hz, OCH), 6.16 (br s, 2 =CH); mass spectrum m/e 208 (M⁺), 165 (M⁺ - 43) (base peak), 123 (M⁺ - 85), 109 (M⁺ - 99), 81 (M⁺ - 127). Anal. (C₁₃H₂₀O₂) C, H.

For synthesis of **31** and **32** on a preparative scale, a mixture of **3** (2.40 g, 8.00 mmol), Fe₂(CO)₉ (3.27 g, 9.00 mmol), furan (5.44 g, 80.0 mmol), and benzene (20 mL) was stirred at 40 °C for 40 h. After addition of Fe₂(CO)₉ (1.60 g, 4.39 mmol) and furan (1.87 g, 27.5 mmol) and stirring at the same temperature for further 40 h, the reaction mixture was worked up to give a pale yellow-green oil (2.13 g). Silica gel chromatography (1:10 ether-hexane) gave the starting dibromo ketone **3** (0.36 g, 15%) and a mixture of **31** and **32** (1.26 g, 75:25 ratio, 89% based on the consumed **3**).

2,4-Diphenyl-8-oxabicyclo[3.2.1]oct-6-en-3-ones (33 and 34). A mixture of the dibromo ketone **26** (3.00 g, 8.20 mmol), Fe₂(CO)₉ (4.00 g, 11.0 mmol), and furan (25 g) in tetrahydrofuran (30 mL) was stirred at room temperature for 6 h. To this was added benzene (80 mL) and the mixture was washed with water. The organic layer was dried and concentrated to give a crystalline material (2.3 g). Recrystallization of the residue from ethanol gave pure **34** (1.20 g, 45%), mp 151-152 °C (lit.²¹ 152-153 °C). Concentration of the mother liquor followed by recrystallization of the residue from hexane gave **33** (1.20 g, 45%), mp 135-135.5 °C (lit.²¹ 134-135 °C). The IR and NMR spectra of these samples were superimposable on those of authentic samples.²¹

1,2,4,5-Tetramethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (35). A mixture of Fe₂(CO)₉ (873 mg, 2.40 mmol), 2,5-dimethylfuran (576 mg, 6.00 mmol), and the dibromo ketone **2** (4.88 mg, 2.00 mmol) in dry benzene (10 mL) was heated at reflux. After 16 h, the reaction mixture was worked up to give **35** as highly subliming, pale yellow crystals. Yield of **35** determined by NMR analysis was 73%. TLC purification (1:2 ether-hexane, two developments) gave pure **35** (R_f 0.40, 280 mg, 78%); mp 66-67 °C; IR 1710 cm⁻¹ (C=O); NMR δ 0.93 (d, $J = 7.5$ Hz, 2 CHCH₃), 1.43 (s, 2 CCH₃), 2.39 (q, $J = 7.5$ Hz, 2 CHCH₃), 5.93 (br s, =CH); mass spectrum m/e 180 (M⁺), 137 (M⁺ - 43), 124 (M⁺ - 56), 123 (M⁺ - 57), 109 (M⁺ - 71) (base peak). Anal. (C₁₁H₁₆O₂) C, H.

2,2,4-Trimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (36). A mixture of 2,4-dibromo-2-methylpentan-3-one (516 mg, 2.00 mmol), Fe₂(CO)₉ (873 mg, 2.40 mmol), and furan (10 mL) was stirred at reflux for 45 h. Workup followed by preparative TLC (1:10 ether-hexane) gave **36** (R_f 0.20) as a pale yellow oil (140 mg, 84%), whose NMR spectrum was identical with the reported one.¹⁹

2-Methyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (37). A mixture of Fe₂(CO)₉ (436 mg, 1.20 mmol), 1,3-dibromobutan-2-one (230 mg, 1.00 mmol), and furan (5.0 mL) was heated at reflux for 12 h. Usual workup gave a brown oil (37 mg), which was dissolved in carbon tetrachloride (5 mL). After 24 h at room temperature the resulting precipitates were filtered off and the filtrate was concentrated to give **37** (28 mg, 20%) as a mixture of 2 α - and 2 β -methyl isomers (52:48 ratio). Pure sample of each isomer was obtained by preparative GLC (column D, 110 °C). The IR and NMR spectra of the products were

identical with those of the reported ones.^{19,24}

2,2-Dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (38), 1,3-Dibromo-3-methylbutan-2-one (488 mg, 2.00 mmol), $\text{Fe}_2(\text{CO})_9$ (873 mg, 2.40 mmol), and furan (10 mL) were mixed and stirred at reflux for 12 h. Workup as usual gave a pale yellow oil (187 mg). Purification by TLC (1:5 ethyl acetate–hexane, two developments) gave pure **38** (R_f 0.26, 105 mg, 31%). The IR and NMR spectra were identical with those reported.¹⁹

Reaction of 2,6-Dibromocyclohexanone (39) and Furan in the Presence of $\text{Fe}_2(\text{CO})_9$. A mixture of $\text{Fe}_2(\text{CO})_9$ (873 mg, 2.40 mmol), the dibromo ketone **39** (525 mg, 2.05 mmol), and furan (10 mL) was stirred at reflux and the progress of the reaction was monitored by GLC (column I, 150 °C). After 30 h, the mixture was worked up to give a mixture of (1 α ,6 α ,2 β ,5 β)-11-oxatricyclo[4.3.1.1^{2,5}]undec-3-en-10-one (**43**) and 2-(2-furyl)cyclohexanone (**49**, 345 mg). NMR analysis showed that **43** and **49** were produced in 70% combined yield (50:50 ratio). Preparative TLC (1:2 ether–hexane) gave pure **43** (R_f 0.14) and **49** (R_f 0.33). **43**: mp 45.5–46 °C; IR 1727 cm^{-1} (C=O); NMR δ 1.7–2.9 (m, 3 CH_2 and 2 CH), 4.84 (br s, 2 OCH), 6.30 (br s, 2 =CH); mass spectrum m/e 164 (M^+), 136 ($\text{M}^+ - 28$), 107 ($\text{M}^+ - 57$) (base peak). Anal. ($\text{C}_{10}\text{H}_{12}\text{O}_2$) C, H. **49**: IR 1721 cm^{-1} (C=O); NMR δ 1.6–2.7 (m, 4 CH_2), 3.4–3.9 (m, CHCO), 6.0–6.4 (ABM, OCH=CHCH), 7.25 (ABM, OCH=); mass spectrum m/e 164 (M^+), 120 ($\text{M}^+ - 44$), 108 ($\text{M}^+ - 56$) (base peak). Anal. ($\text{C}_{10}\text{H}_{12}\text{O}_2$) C, H.

Reaction of 2,7-Dibromocycloheptanone (40) with Furan in the Presence of $\text{Fe}_2(\text{CO})_9$. A mixture of $\text{Fe}_2(\text{CO})_9$ (874 mg, 2.40 mmol), the dibromo ketone **40** (540 mg, 2.00 mmol), and furan (12 mL) was heated at reflux for 62 h. Workup gave a yellow oil (569 mg). The NMR analysis indicated that (1 α ,6 α ,2 β ,5 β)-12-oxatricyclo[4.4.1.1^{2,5}]dodec-3-en-11-one (**44**) and 2-(2-furyl)cycloheptanone (**50**) were formed in 54 and 21% yields, respectively. Pure samples of **44** (R_f 0.35), mp 50–51 °C (from cyclohexane), and **50** (R_f 0.78) were obtained by TLC separation (1:2 ether–hexane, two developments). The IR and NMR spectra of **44** were identical with those reported.²³ **50**: IR 1716 cm^{-1} (C=O); NMR δ 1.2–3.0 (m, 5 CH_2), 3.5–3.9 (m, CHCO), 6.0–6.4 (ABM, OCH=CHCH), 7.27 (ABM, OCH=); mass spectrum m/e 178 (M^+), 149 ($\text{M}^+ - 29$), 107 ($\text{M}^+ - 71$) (base peak), 94 ($\text{M}^+ - 84$). Anal. ($\text{C}_{11}\text{H}_{14}\text{O}_2$) C, H.

Reaction of 2,8-Dibromocyclooctanone (41) with Furan in the Presence of $\text{Fe}_2(\text{CO})_9$. The authors reported that the compounds **45** and **51** were produced in 60 and 23% yields, respectively, based on NMR analysis.^{2b} Later studies, however, revealed that the starting dibromo ketone **41** had been contaminated with 2,2,8-tribromocyclooctanone. The reaction using the pure dibromo ketone **41** afforded **45** and **51** in lower yields. A mixture of $\text{Fe}_2(\text{CO})_9$ (437 mg, 1.20 mmol), **41** (282 mg, 0.99 mmol), and furan (10 mL) was stirred at reflux for 46 h. Usual workup afforded a brown oil (170 mg). Preparative TLC (1:1 ether–hexane, two developments) afforded pure (1 α ,7 α ,8 β ,11 β)-13-oxatricyclo[5.4.1.1^{8,11}]tridec-9-en-12-one (**45**), mp 49.5–52 °C (from cyclohexane) (R_f 0.49, 53 mg, 27%), 2-(2-furyl)cyclooctanone (**51**) (R_f 0.68, 20 mg, 10%) accompanied by cyclooctanone (R_f 0.59, 53 mg, 40%), and (1 β ,7 β ,8 β ,11 β)-13-oxatricyclo[5.4.1.1^{8,11}]tridec-9-en-12-one (**47**) (R_f 0.38, 19 mg, 10%). The products **45** and **47** showed identical IR and NMR spectra with those of the reported ones.²³ **51**: IR 1712 cm^{-1} (C=O); NMR δ 0.9–2.8 (m, 6 CH_2), 3.5–3.9 (m, CHCO), 5.9–6.3 (ABM, OCH=CHCH), 7.22 (ABM, OCH=); mass spectrum m/e 192 (M^+), 108 ($\text{M}^+ - 84$), 107 ($\text{M}^+ - 85$), 95 ($\text{M}^+ - 97$), 94 ($\text{M}^+ - 98$), 91 ($\text{M}^+ - 101$), 81 ($\text{M}^+ - 111$). Anal. ($\text{C}_{12}\text{H}_{16}\text{O}_2$) C, H.

Reaction of 2,12-Dibromocyclododecanone (42) with Furan in the Presence of $\text{Fe}_2(\text{CO})_9$. A mixture of $\text{Fe}_2(\text{CO})_9$ (437 mg, 1.20 mmol), **42** (340 mg, 1.00 mmol), and furan (12 mL) was heated at reflux with stirring for 40 h. Workup gave a yellow oil (270 mg). TLC separation (1:2 ether–hexane, two developments) gave (1 α ,11 α ,12 β ,15 β)-17-oxatricyclo[9.4.1.1^{12,15}]heptadec-13-en-16-one (**46**) (R_f 0.34, 17 mg, 7%), its isomer **48** (R_f 0.43, 112 mg, 45%), and 2-(2-furyl)cyclododecanone (**52**) (R_f 0.80, 84 mg, 34%). The compounds **46**, mp 148–155 °C (from cyclohexane, in a sealed tube), and **48**, mp 58–60 °C (from cyclohexane), exhibited IR and NMR spectra identical with those reported.²³ **52**: IR 1715 cm^{-1} (C=O); NMR δ 1.0–1.7 (m, 9 CH_2), 2.33 (t, $J = 3.0$ Hz, CH_2CO), 3.6–4.0 (m, CHCO), 6.06 and 6.23 (ABM, OCH=CHCH), 7.27 (ABM, OCH=); mass spectrum m/e 248 (M^+), 220 ($\text{M}^+ - 28$), 107 ($\text{M}^+ - 141$), 94 ($\text{M}^+ - 154$) (base peak). Anal. ($\text{C}_{16}\text{H}_{24}\text{O}_2$) C, H.

Attempted Reaction of α,α' -Dibromoacetone with Furan in the

Presence of $\text{Fe}_2(\text{CO})_9$. A mixture of $\text{Fe}_2(\text{CO})_9$ (2.40 g, 6.60 mmol), α,α' -dibromoacetone (650 mg, 3.00 mmol), and furan (10 mL) was placed in a reaction ampule and heated at 60–70 °C for 43 h. The dibromo ketone was consumed completely, but no adducts were detected by GLC (column E, 100 °C).

8-Acetyl-2,2,4,4-tetramethyl-8-azabicyclo[3.2.1]oct-6-en-3-one (53), Diiron nonacarbonyl (1.10 g, 3.02 mmol) was placed in a 50-mL two-necked flask equipped with a serum cap and a nitrogen balloon. After the system was flushed with nitrogen, dry benzene (10 mL), the dibromo ketone **1** (1.62 g, 5.96 mmol), and *N*-acetylpyrrole (218 mg, 2.00 mmol, freshly distilled from NaH) were successively added through the rubber septum by a syringe. The mixture was stirred at 40–50 °C for 18.5 h. The reaction mixture was diluted with ethyl acetate (15 mL), washed with three 10-mL portions of saturated NaHCO_3 solution followed by brine (5 mL), and dried. Concentration of the organic layer gave an orange oil (1.2 g), which was subjected to column chromatography on silica gel (25 g). Elution with 1:3 ethyl acetate–hexane followed by evaporation of the solvents gave some unreacted **1**. The fractions eluted with ethyl acetate afforded **53** (302 mg, 68%) as pale yellow crystals. Recrystallization from hexane gave an analytical sample: IR 1720 (C=O), 1660 cm^{-1} (NCOCH₃); NMR δ 1.02 (s, 2 CH_3), 1.23 (s, CH_3), 1.30 (s, CH_3), 2.08 (s, COCH₃), 4.32 (br s, NCH), 4.92 (br s, NCH), 6.42 (br s, 2 =CH); mass spectrum m/e 221 (M^+), 206 ($\text{M}^+ - 15$), 178 ($\text{M}^+ - 43$), 164 ($\text{M}^+ - 57$), 151 ($\text{M}^+ - 70$), 150 ($\text{M}^+ - 71$), 109 ($\text{M}^+ - 112$), 108 ($\text{M}^+ - 113$). Anal. ($\text{C}_{13}\text{H}_{19}\text{NO}_2$) C, H, N.

8-Carbomethoxy-2,4-dimethyl-8-azabicyclo[3.2.1]oct-6-en-3-ones (54–56). In a 100-mL two-necked flask equipped with a serum cap and a rubber balloon filled with nitrogen was placed $\text{Fe}_2(\text{CO})_9$ (10.0 g, 27.5 mmol) and the flask was flushed with nitrogen. To this were added benzene (80 mL), *N*-carbomethoxypyrrole (2.50 g, 20.0 mmol), and **2** (4.88 g, 20.0 mmol), and the mixture was stirred and irradiated by visible light at room temperature for 10 h. GLC analysis (column B, 80 °C) of the aliquot indicated that the starting dibromo ketone **2** was consumed completely. To the reaction mixture were added ethyl acetate (100 mL) and a saturated aqueous solution of NaHCO_3 – KNO_3 (200 mL) and the mixture was extracted four 50-mL portions of ethyl acetate. The combined extracts were dried and concentrated in vacuo to give a brown oil (5 g). Column chromatography on basic alumina (200 g, 1:10–1:5 ether–benzene) gave a mixture of **54**, **55**, and **56** (2.50 g, 60% by NMR) in 42:29:29 ratio. An analytical sample of each product was obtained by repeated preparative TLC (1:10 ethyl acetate–hexane, R_f 0.53 (**54**), 0.32 (**55**), and 0.28 (**56**)). **54**: mp 60–61 °C (from hexane); IR 1705 cm^{-1} (C=O and NCOOCH₃); NMR δ 0.99 (d, $J = 6.5$ Hz, 2 CHCH_3), 2.62 (m, 2 CHCH_3), 3.70 (s, OCH₃), 4.56 (narrow m, 2 NCH), 6.26 (br s, 2 =CH); mass spectrum m/e 209 (M^+). Anal. ($\text{C}_{11}\text{H}_{15}\text{NO}_3$) C, H, N. **55**: IR 1705 cm^{-1} (C=O and NCOOCH₃); NMR δ 0.99 (d, $J = 7.0$ Hz, CHCH_3 (eq)), 1.21 (d, $J = 6.5$ Hz, CHCH_3 (ax)), 2.33 (br q, $J = 6.5$ Hz, $\text{CH}(\text{eq})\text{CH}_3$), 2.71 (m, $\text{CH}(\text{ax})\text{CH}_3$), 3.68 (s, OCH₃), 4.66 (m, NCH), 6.25 (m, 2 =CH); mass spectrum m/e 209 (M^+). Anal. ($\text{C}_{11}\text{H}_{15}\text{NO}_3$) C, H, N. **56**: mp 60–61 °C (from hexane); IR 1705 cm^{-1} (C=O and NCOOCH₃); NMR δ 1.25 (d, $J = 7.0$ Hz, 2 CHCH_3), 2.27 (br q, $J = 7.0$ Hz, 2 CHCH_3), 3.70 (s, OCH₃), 4.64 (narrow m, 2 NCH), 6.22 (narrow m, 2 =CH); mass spectrum m/e 209 (M^+). Anal. ($\text{C}_{11}\text{H}_{15}\text{NO}_3$) C, H, N.

Reaction of the Dibromo Ketone 1 with *N*-Methylpyrrole in the Presence of $\text{Fe}_2(\text{CO})_9$. A mixture of $\text{Fe}_2(\text{CO})_9$ (874 mg, 2.40 mmol), *N*-methylpyrrole (486 mg, 6.00 mmol), the dibromo ketone **1** (544 mg, 2.00 mmol), and dry benzene (10 mL) was stirred at 40 °C for 18 h under nitrogen. The reaction was monitored by GLC (column J, 130 °C). To the reaction mixture was added saturated KNO_3 solution (30 mL) and the mixture was extracted with five 20-mL portions of ethyl acetate. The combined extracts were washed with water and dried. Evaporation of the solvent afforded a crude mixture of 2,4-dimethyl-2-(2-*N*-methylpyrrolyl)pentan-3-one (**57**) and 2,4-dimethyl-2-(3-*N*-methylpyrrolyl)pentan-3-one (**58**) as a yellow oil. Yields of **57** and **58** determined by NMR were 31 and 51%, respectively. Analytical samples of these products were obtained by preparative GLC (column D, 150 °C). **57**: IR 1703 cm^{-1} (C=O); NMR δ 0.84 (d, $J = 6.0$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.46 (s, 2 CH_3), 2.6–3.1 (m, $\text{CH}(\text{CH}_3)_2$), 3.42 (s, NCH₃), 5.8–6.1 (ABM, NCH=CHCH), 6.40 (ABM, NCH=); mass spectrum m/e 193 (M^+), 123 ($\text{M}^+ - 70$), 122 ($\text{M}^+ - 71$) (base peak), 108 ($\text{M}^+ - 85$), 107 ($\text{M}^+ - 86$), 106 ($\text{M}^+ - 87$), 94 ($\text{M}^+ - 99$). Anal. ($\text{C}_{12}\text{H}_{19}\text{NO}$) C, H. **58**: IR 1700 cm^{-1} (C=O); NMR δ 0.84 (d, $J = 7.0$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.33 (s, 2 CH_3),

2.6–3.1 (m, $\text{CH}(\text{CH}_3)_2$), 3.62 (s, NCH_3), 5.85 (ABM, $\text{NCH}=\text{CH}$), 6.3–6.5 (ABM, 2 $\text{NCH}=\text{CH}$); mass spectrum m/e 193 (M^+), 123 ($\text{M}^+ - 70$), 122 ($\text{M}^+ - 71$) (base peak), 107 ($\text{M}^+ - 86$), 106 ($\text{M}^+ - 87$), 94 ($\text{M}^+ - 99$). Anal. ($\text{C}_{12}\text{H}_{19}\text{NO}$) C, H.

Reaction of the Dibromo Ketone 2 with *N*-Methylpyrrole in the Presence of $\text{Fe}_2(\text{CO})_9$. A suspension of $\text{Fe}_2(\text{CO})_9$ (874 mg, 2.40 mmol) in a mixture of 2 (488 mg, 2.00 mmol), *N*-methylpyrrole (486 mg, 6.00 mmol), and benzene (10 mL) was stirred at 40 °C for 70 h under nitrogen. The reaction mixture was worked up as described above to give a brown oil. NMR analysis of the mixture indicated that 2-(2-*N*-methylpyrrolyl)pentan-3-one (59) and 2-(3-*N*-methylpyrrolyl)pentan-3-one (60) were formed in 48 and 33% yields, respectively (80% conversion). Preparative GLC (column C, 170 °C) gave analytical samples of 59 and 60. 59: IR 1713 cm^{-1} ($\text{C}=\text{O}$); NMR δ 0.91 (t, $J = 7.0$ Hz, CH_2CH_3), 1.41 (d, $J = 7.0$ Hz, CHCH_3), 2.0–2.5 (m, CH_2CO), 3.50 (s, NCH_3), 3.65 (q, $J = 7.0$ Hz, CHCH_3), 5.8–6.0 (ABM, $\text{NCH}=\text{CHCH}$), 6.45 (ABM, $\text{NCH}=\text{CH}$); mass spectrum m/e 165 (M^+), 108 ($\text{M}^+ - 57$) (base peak), 107 ($\text{M}^+ - 58$), 93 ($\text{M}^+ - 72$). Anal. ($\text{C}_{10}\text{H}_{15}\text{NO}$) C, H. 60: IR 1715 cm^{-1} ($\text{C}=\text{O}$); NMR δ 0.94 (t, $J = 7.5$ Hz, CH_2CH_3), 1.26 (d, $J = 7.5$ Hz, CHCH_3), 2.1–2.6 (m, CH_2CO), 3.61 (s, NCH_3), 3.52 (q, $J = 7.5$ Hz, CHCH_3), 5.87 (ABM, $\text{NCH}=\text{CH}$), 6.3–6.5 (ABM, 2 $\text{NCH}=\text{CH}$); mass spectrum m/e 165 (M^+), 107 ($\text{M}^+ - 58$) (base peak), 106 ($\text{M}^+ - 59$), 92 ($\text{M}^+ - 73$), 57 ($\text{M}^+ - 108$). Anal. ($\text{C}_{10}\text{H}_{15}\text{NO}$) C, H.

Reaction of the Dibromo Ketone 3 with *N*-Methylpyrrole in the Presence of $\text{Fe}_2(\text{CO})_9$. A mixture of $\text{Fe}_2(\text{CO})_9$ (874 mg, 2.40 mmol), *N*-methylpyrrole (486 mg, 6.00 mmol), and 3 (600 mg, 2.00 mmol) in benzene (10 mL) was stirred at 40 °C for 60 h. Consumption of the dibromo ketone 3 (50% conversion) was confirmed by GLC (column J, 150 °C). Workup as described above gave a yellow oil. NMR analysis of the crude product revealed that 2,6-dimethyl-3-(2-*N*-methylpyrrolyl)heptan-4-one (61) and 2,6-dimethyl-3-(3-*N*-methylpyrrolyl)heptan-4-one (62) were produced in 62 and 15% yields, respectively, based on the consumed 3 (50% conversion). TLC separation (1:10 ether–hexane, two developments) gave pure samples of 61 (R_f 0.33) and 62 (R_f 0.26). 61: IR 1705 cm^{-1} ($\text{C}=\text{O}$); NMR δ 0.6–1.1 (four d, $J = 7.0$ Hz, 2 $\text{CH}(\text{CH}_3)_2$), 1.7–2.7 (m, $\text{CH}(\text{CH}_3)_2$ and CH_2CO), 3.19 (d, $J = 10.5$ Hz, CHCO), 3.50 (s, NCH_3), 5.8–6.0 (ABM, $\text{NCH}=\text{CHCH}$), 6.41 (ABM, $\text{NCH}=\text{CH}$); mass spectrum m/e 221 (M^+), 136 ($\text{M}^+ - 85$) (base peak), 121 ($\text{M}^+ - 100$). Anal. ($\text{C}_{14}\text{H}_{23}\text{NO}$) C, H. 62: IR 1710 cm^{-1} ($\text{C}=\text{O}$); NMR δ 0.6–1.0 (four d, 2 $\text{CH}(\text{CH}_3)_2$), 1.8–2.5 (m, 2 $\text{CH}(\text{CH}_3)_2$ and CH_2CO), 3.30 (d, $J = 10.5$ Hz, CHCO), 3.60 (s, NCH_3), 5.7–5.9 (ABM, $\text{NCH}=\text{CH}$), 6.3–6.5 (ABM, 2 $\text{NCH}=\text{CH}$); mass spectrum m/e 221 (M^+), 136 ($\text{M}^+ - 85$) (base peak), 121 ($\text{M}^+ - 100$); exact mass spectrum m/e 221.1805 (calcd for $\text{C}_{14}\text{H}_{23}\text{NO}$, 221.1778).

Reaction of the Dibromo Ketone 2 with Thiophene in the Presence of $\text{Fe}_2(\text{CO})_9$. A mixture of $\text{Fe}_2(\text{CO})_9$ (876 mg, 2.40 mmol), 2 (488 mg, 2.00 mmol), and thiophene (504 mg, 6.00 mmol) in benzene (10 mL) was irradiated by visible light at room temperature for 35 h. The reaction mixture was diluted with benzene (30 mL) and washed three times with water. The organic layer was dried and concentrated in vacuo to give a reddish oil (376 mg). TLC purification (alumina, 1:10 ether–hexane) gave 2-(2-thienyl)pentan-3-one (63) (62 mg, 37% yield based on the consumed starting bromide, 50% conversion) as a colorless oil: IR 1724 ($\text{C}=\text{O}$), 1460, 697 cm^{-1} ; NMR δ 0.97 (t, $J = 7.0$ Hz, CH_2CH_3), 1.44 (d, $J = 7.0$ Hz, CHCH_3), 2.42 (q, $J = 7.0$ Hz, CH_2CH_3), 3.94 (q, $J = 7.0$ Hz, CHCH_3), 6.7–7.0 (ABM, $\text{SCH}=\text{CHCH}$), 7.12 (ABM, $\text{SCH}=\text{CH}$); mass spectrum m/e 168 (M^+), 111 ($\text{M}^+ - 57$) (base peak). Anal. ($\text{C}_9\text{H}_{12}\text{OS}$) C, H.

Reaction of Tri- and Tetrabromo Ketones with Furan in the Presence of $\text{Fe}_2(\text{CO})_9$. 8-Oxabicyclo[3.2.1]oct-6-en-3-one (71). In a dry 100-mL two-necked flask equipped with a rubber septum and an efficient condenser connected with a bubbler was placed a mixture of tetrabromoacetone (66, 3.73 g, 10.0 mmol) and $\text{Fe}_2(\text{CO})_9$ (3.46 g, 10.0 mmol), and the flask was evacuated and flushed with nitrogen. To the mixture was added furan (40 mL) over a 5-min period through the rubber septum by a syringe. The resulting mixture was stirred at reflux for 48 h under nitrogen and then to this was added water (30 mL) and ethyl acetate (30 mL). The resulting insoluble materials were removed by filtration through a pad of Celite 545. The pad was washed with ethyl acetate. The filtrate and washings were combined and the organic layer was separated. The aqueous layer was extracted with five 20-mL portions of ethyl acetate and the combined organic layers were dried. Concentration of the solution afforded a brown oil which was subjected to column chromatography (silica gel, 150 g, 1:10 ethyl

acetate–hexane), giving a 9:1 mixture of 2 α ,4 α -dibromo-8-oxabicyclo[3.2.1]oct-6-en-3-one (69) and the trans isomer 70 (R_f 0.19, 1.76 g, 63% combined yield) as colorless crystals. These products were sensitive to air and heat and tinged with dark brown on long storage at room temperature and under atmosphere. 69: mp 119–120 °C; IR (CHCl_3) 1746 cm^{-1} ($\text{C}=\text{O}$); NMR (CDCl_3) δ 4.85 (d, $J = 4.5$ Hz, 2 CHBr), 5.17 (br d, $J = 4.5$ Hz, 2 OCH), 6.58 (br s, 2 $=\text{CH}$); mass spectrum m/e 284, 282, 280 (1:2:1 ratio) (M^+). Anal. ($\text{C}_7\text{H}_6\text{O}_2\text{Br}_2$) C, H. 70: mp 111–113 °C; IR (CHCl_3) 1747, 1734 cm^{-1} ($\text{C}=\text{O}$); NMR (CDCl_3) δ 4.20 (d, $J = 1.5$ Hz, $\text{CH}(\text{eq})\text{Br}$), 5.08 (dd, $J = 1.5$ and 1.9 Hz, $\text{CH}(\text{eq})\text{BrCH}$), 5.16 (m, $\text{CH}(\text{ax})\text{BrCH}$), 6.38 and 6.65 (finely split AB q, $J_{\text{AB}} = 6.0$ Hz, 2 $=\text{CH}$); mass spectrum m/e 284, 282, 280 (1:2:1 ratio) (M^+). Anal. ($\text{C}_7\text{H}_6\text{O}_2\text{Br}_2$) C, H.

A mixture of the dibromides 69 and 70 (300 mg, 1.06 mmol) was stirred with zinc–copper couple (1.00 g, 15.3 mg-atoms) in methanol (10 mL) saturated with NH_4Cl at room temperature for 10 min. The reaction course was monitored by TLC (R_f 0.58 (69 and 70), 0.26 (71), 1:3 ethyl acetate–hexane). The reaction mixture was filtered and the filtrate was diluted with saturated EDTA disodium salt solution (25 mL) and extracted with three 20-mL portions and then four 10-mL portions of methylene chloride. The organic layers were combined and dried. Removal of the solvent under atmospheric pressure through a 21-cm Vigreux column produced 71 in a crystalline form (130 mg, 100%). This very volatile product was purified by sublimation at ca. 70 °C (0.01 mm), mp 37–39 °C (lit.⁴⁴ 38 °C). The IR, NMR, and mass spectra were identical with those reported.⁴⁴

Bicyclo[3.2.1]oct-6-en-3-one (72). A mixture of dry THF (2.0 mL), benzene (10 mL), freshly distilled cyclopentadiene (1.0 mL), and $\text{Fe}(\text{CO})_5$ (1.17 g, 5.98 mmol) was stirred at 80 °C under argon, and to this was added dropwise a solution of tetrabromoacetone (1.87 g, 5.00 mmol) in 1:1 cyclopentadiene–benzene (7.5 mL) over 25 min. The resulting mixture was stirred for an additional 20-min period at the same temperature. After cooling, the reaction mixture was diluted with benzene (15 mL) and methanol (12 mL) saturated with NH_4Cl and then vigorously shaken with zinc–copper couple (3.80 g, 57.8 mg-atoms) for 15 min. To this were added methylene chloride (200 mL) and saturated EDTA disodium salt solution (100 mL) and the solid materials were removed by filtration. The methylene chloride layer was separated and the aqueous layer was extracted twice with methylene chloride (50 and 30 mL). The combined organic layers were dried and the solvent was evaporated to afford a black oil (3 g), which was dissolved in methylene chloride (30 mL). The solution was added dropwise to vigorously stirred pentane (300 mL). The resulting precipitates were removed by filtration and the filter cake was washed with pentane (50 mL). The combined filtrate and washing were concentrated in vacuo to leave a brown oil (1.7 g) containing the desired adduct 72 (60% yield by GLC analysis (column L, 90 °C)). This oil was subjected to column chromatography on silica gel (15 g). Elution with 1:1 benzene–hexane (120 mL) followed by methylene chloride (100 mL) afforded 72 as a crystalline solid (289 mg, 47%), which was identified by comparison of the NMR spectrum with the reported one.⁴⁵ Distillation gave an analytical sample (170 mg), bp 80–100 °C (bath temperature), mp 99–100 °C (lit.⁴⁴ 100 °C).

2-Methyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (37). A mixture of 1,1,3,3-tetrabromobutan-2-one (776 mg, 2.00 mmol), $\text{Fe}_2(\text{CO})_9$ (728 mg, 2.00 mmol), and furan (10 mL) was stirred at room temperature for 24 h and worked up. Treatment of the crude product (1.0 g) with zinc–copper couple (400 mg, 6.15 mg-atoms) in 2:1 methanol–acetone (15 mL) saturated with NH_4Cl at room temperature for 3 h was followed by extractive workup with methylene chloride. The resulting brown oil was passed through a short column of basic alumina to afford an orange oil (ca. 800 mg). Its NMR analysis (benzene as an internal standard) indicated the formation of 37 in 63% yield as a mixture of 2 α - and 2 β -methyl isomers (55:45 ratio). A pure sample of 37 was obtained by preparative GLC (column D, 110 °C) and the structure was determined on the basis of the spectral data.^{19,25}

2,2-Dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (38). A mixture of 1,1,3-tribromo-3-methylbutan-3-one (646 mg, 2.00 mmol), $\text{Fe}_2(\text{CO})_9$ (728 mg, 2.00 mmol), and furan (10 mL) was stirred at reflux for 40 h. Workup as described above afforded 2-bromo-4,4-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one as colorless crystals (371 mg, 93%); mp 93–94 °C; IR 1729 cm^{-1} ($\text{C}=\text{O}$); NMR δ 1.00 and 1.35 (two s, 2 CH_3), 4.36 (br s, $\text{OCHCH}(\text{CH}_3)_2$), 4.73 (d, $J = 4.5$ Hz, CHBr), 5.00 (d, $J = 4.5$ Hz, OCHCHBr), 6.37 (br s, 2 $=\text{CH}$); mass spectrum m/e 232 and 230 (1:1 ratio) (M^+), 151 ($\text{M}^+ - \text{Br}$) (base peak). Reduction of the cycloadduct (49.0 mg, 0.21 mmol) with

zinc-copper couple (400 mg, 6.12 mg-atoms) in methanol (2.0 mL) saturated with NH_4Cl (25 °C, 30 min) followed by extractive workup with methylene chloride and evaporation of the solvents gave rise to crystalline **38** (33 mg, 100%), mp 47–50 °C, whose IR and NMR spectra were identical with reported ones.¹⁹

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References and Notes

- Carbon-Carbon Bond Formations Promoted by Transition Metal Carbonyls. 17. For the previous paper (part 16) in this series, see R. Noyori, Y. Hayakawa, H. Takaya, S. Murai, R. Kobayashi, and N. Sonoda, *J. Am. Chem. Soc.*, preceding paper in this issue.
- For preliminary communications of this work, see (a) R. Noyori, S. Makino, and H. Takaya, *J. Am. Chem. Soc.*, **93**, 1272 (1971); (b) R. Noyori, Y. Baba, S. Makino, and H. Takaya, *Tetrahedron Lett.*, 1741 (1973); (c) R. Noyori, S. Makino, Y. Baba, and Y. Hayakawa, *ibid.*, 1049 (1974); (d) R. Noyori, S. Makino, T. Okita, and Y. Hayakawa, *J. Org. Chem.*, **40**, 806 (1975).
- Photochemical cycloadditions: O. L. Chapman and G. Lenz, *Org. Photochem.*, **1**, 200 (1967); A. Schönberg, "Preparative Organic Photochemistry", Springer-Verlag, West Berlin, 1968, p 109; K. J. Crowley and P. H. Mazzocchi, "The Chemistry of Alkenes", Vol. 2, J. Zabicky, Ed., Interscience, New York, N.Y., 1970, p 267; A. A. Lamola and N. J. Turro, "Energy Transfer and Organic Photochemistry", Interscience, New York, N.Y., 1970.
- Diels-Alder reactions: M. C. Kloetzel, *Org. React.*, **4**, 1 (1948); H. L. Holmes, *ibid.*, **4**, 60 (1948); L. W. Butz and A. W. Rytina, *ibid.*, **5**, 136 (1949); A. Onischenko, "Diene Synthesis", Oldbourne Press, London, 1964; A. Wassermann, "Diels-Alder Reactions", Elsevier, Amsterdam, 1965; J. Sauer, *Angew. Chem., Int. Ed. Engl.*, **5**, 211 (1966); J. Sauer, *ibid.*, **6**, 16 (1967).
- 1,2:1,2-Cycloadditions: J. D. Roberts and C. M. Sharts, *Org. React.*, **12**, 1 (1962); P. D. Bartlett, *Science*, **159**, 833 (1968); L. L. Müller and J. Hamer, "1,2-Cycloaddition Reactions", Interscience, New York, N.Y., 1967.
- 1,3-Dipolar cycloadditions: R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **2**, 565, 633 (1963); **7**, 321 (1968); R. Huisgen, R. Grashey, and J. Sauer, "Chemistry of Alkenes", S. Patai, Ed., Interscience, New York, N.Y., 1964, p 739.
- 1,3-Anionic cycloadditions: T. Kauffmann, *Angew. Chem., Int. Ed. Engl.*, **13**, 627 (1974). Other polar cycloadditions: R. Gompper, *ibid.*, **8**, 312 (1969); R. R. Schmidt, *ibid.*, **12**, 212 (1973).
- J. Hamer, "1,4-Cycloaddition Reactions", Academic Press, New York, N.Y., 1967.
- H. Ulrich, "Cycloaddition Reaction of Heterocumulenes", Academic Press, New York, N.Y., 1967.
- Cycloaddition of cyclopropanones: N. J. Turro, *Acc. Chem. Res.*, **2**, 25 (1969).
- G. Wilke, *Angew. Chem., Int. Ed. Engl.*, **2**, 105 (1963); P. Heimbach, *ibid.*, **12**, 975 (1973); H. Müller, D. Wittenberg, H. Seibt, and E. Scharf, *ibid.*, **4**, 327 (1965); C. Hoozand and Hubel, "Organic Syntheses via Metal Carbonyls", I. Wender and P. Pino, Ed., Interscience, New York, N.Y., 1968; C. W. Bird, "Transition Metal Intermediates in Organic Synthesis", Academic Press, New York, N.Y., 1967; J. P. Candlin, K. A. Taylor, and D. T. Thompson, "Reaction of Transition Metal Complexes", American Elsevier, New York, N.Y., 1968.
- W. Kirmse, "Carbene Chemistry", 2nd ed., Academic Press, New York, N.Y., 1971.
- A. W. Johnson, "Ylide Chemistry", Academic Press, New York, N.Y., 1966.
- Some direct syntheses of five- and seven-membered rings have been developed. $1 + 4 \rightarrow 5$ type reactions: P. Pino and A. Miglierina, *J. Am. Chem. Soc.*, **74**, 5551 (1952); D. Seebach, N. R. Jones, and E. J. Corey, *J. Org. Chem.*, **33**, 300 (1968); E. J. Corey and S. W. Walinsky, *J. Am. Chem. Soc.*, **94**, 8932 (1972); E. Negishi and H. C. Brown, *Synthesis*, 77 (1974); B. F. G. Johnson, J. Lewis, and D. J. Thompson, *Tetrahedron Lett.*, 3789 (1974); K. Ogura, M. Yamashita, S. Furukawa, M. Suzuki, and G. Tsuchihashi, *ibid.*, 2767 (1975). $3 + 2 \rightarrow 5$ type reactions: V. Bilinski and A. S. Dreiding, *Helv. Chim. Acta*, **55**, 1271 (1972), and references cited therein; P. L. Fuchs, *J. Am. Chem. Soc.*, **96**, 1607 (1974); Y. Ito, K. Nakayama, K. Yonezawa, and T. Saegusa, *J. Org. Chem.*, **39**, 3273 (1974); A. A. Schegolev, W. A. Smit, G. V. Roitburd, and V. F. Kucherov, *Tetrahedron Lett.*, 3373 (1974); I. Kawamoto, S. Muramatsu, and Y. Yura, *ibid.*, 4223 (1974). $1 + 6 \rightarrow 7$ type reactions: H. C. Brown and E. Negishi, *J. Am. Chem. Soc.*, **89**, 5477 (1967). $3 + 4 \rightarrow 7$ type reactions: J. Clabattori and G. A. Berchtold, *J. Org. Chem.*, **31**, 1336 (1966). $5 + 2 \rightarrow 7$ type reactions: A. R. Katritzky and Y. Takeuchi, *J. Am. Chem. Soc.*, **92**, 4134 (1970); *J. Chem. Soc. C*, 878 (1971).
- R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).
- J. Lascombe, P. Grange, and M.-L. Josien, *Bull. Soc. Chim. Fr.*, 773 (1957).
- R. Huisgen, R. Grashey, and J. Sauer, "The Chemistry of Alkenes", Vol. 1, S. Patai, Ed., Interscience, New York, N.Y., 1964, p 878.
- E. Koerner von Gustorf, Z. Pfajeer, and F. W. Grevels, *Z. Naturforsch.*, **26b**, 66 (1971).
- H. M. R. Hoffmann, K. E. Clemens, and R. H. Smithers, *J. Am. Chem. Soc.*, **94**, 3940 (1972).
- S. Itô, H. Ohtani, and S. Amiya, *Tetrahedron Lett.*, 1737 (1973).
- R. C. Cookson, M. J. Nye, and G. Subrahmanyam, *J. Chem. Soc. C*, 473 (1967).
- J. P. Zahra, J. Casanova, and B. Waegell, *Bull. Soc. Chim. Fr.*, 2247 (1974).
- Recently Vinter and Hoffmann performed a similar cyclocoupling reaction using zinc-copper couple on alumina as the reducing agent and obtained the cis diaxial compound **46** as the main product together with oily trans isomer **47** [J. G. Vinter and H. M. R. Hoffmann, *J. Am. Chem. Soc.*, **96**, 5466 (1974)]. They claimed without evidence that **47** obtained by us^{2b} is a mixture of chair and boat forms of **46** and **47**. However, we obtained **47** as the major product and analysis by NMR, GLC, and TLC revealed that the compound was indeed homogeneous.
- N. J. Turro, S. S. Edelson, J. R. Williams, T. R. Darling, and W. B. Hammond, *J. Am. Chem. Soc.*, **91**, 2283 (1969).
- The facile rearrangement of 2,2,8-trimethyl-8-azabicyclo[3.2.1]oct-6-en-3-one into the corresponding α -substituted pyrroles has been reported: N. J. Turro, S. S. Edelson, J. R. Williams, and T. R. Darling, *J. Am. Chem. Soc.*, **90**, 1926 (1968); N. J. Turro and S. S. Edelson, *ibid.*, **90**, 4499 (1968).
- L. A. Paquette, "Modern Heterocyclic Chemistry", R. Breslow, Ed., W. A. Benjamin, New York, N.Y., 1968, p 102; G. Marino, *Adv. Heterocycl. Chem.*, **13**, 263 (1971).
- S. Gronowitz, *Adv. Heterocycl. Chem.*, **1**, 43 (1963).
- R. Huisgen, R. Grashey, and J. Sauer, "The Chemistry of Alkenes", S. Patai, Ed., Interscience, New York, N.Y., 1964, p 894.
- General stabilizing effect of halogen attached to carbocation center: G. A. Olah and M. B. Comisarow, *J. Am. Chem. Soc.*, **91**, 2955 (1969). Stable perchloroallyl cation: R. West and P. T. Kwitowski, *ibid.*, **88**, 5280 (1966).
- H. M. R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **12**, 819 (1973), and references cited therein. See also R. Schmid and H. Schmid, *Helv. Chim. Acta*, **57**, 1883 (1974).
- Quite recently, Hoffmann also communicated a synthesis of **68** and **70** by the reduction of tetrabromoacetone with zinc-triethyl borate in the presence of furan: H. M. R. Hoffmann and M. N. Iqbal, *Tetrahedron Lett.*, 4487 (1975). The yield was only ~30%, however.
- Recently, some one-step syntheses of cycloheptatriene derivatives have been reported: R. E. Moerck and M. A. Battiste, *J. Chem. Soc., Chem. Commun.*, 1171 (1972); D. N. Reinhoudt, P. Smael, W. J. M. van Tilborg, and J. P. Visser, *Tetrahedron Lett.*, 3755 (1973).
- H. Takaya, Y. Hayakawa, S. Makino, and R. Noyori, *J. Am. Chem. Soc.*, following paper in this issue.
- Y. Hayakawa, Y. Baba, S. Makino, and R. Noyori, *J. Am. Chem. Soc.*, **100**, 1786 (1978).
- R. Noyori, T. Souchi, and Y. Hayakawa, *J. Org. Chem.*, **40**, 2681 (1975).
- C. Rappe, *Acta Chem. Scand.*, **16**, 2467 (1962).
- R. B. King, *Organomet. Synth.*, **1**, 93 (1965).
- C. F. H. Allen and A. Bell, "Organic Syntheses", Collect. Vol. III, Wiley, New York, N.Y., 1955, p 312.
- A. T. Blomquist and D. T. Longone, *J. Am. Chem. Soc.*, **79**, 3916 (1957).
- G. Wilkinson, "Organic Syntheses", Collect. Vol. IV, Wiley, New York, N.Y., 1963, p 476.
- G. S. Reddy, L. Mandell, and J. H. Goldstein, *J. Chem. Soc.*, 1414 (1963).
- R. M. Acheson and J. M. Vernon, *J. Chem. Soc.*, 457 (1961).
- E. LeGoff, *J. Org. Chem.*, **29**, 2048 (1964).
- A. E. Hill, G. Greenwood, and H. M. R. Hoffmann, *J. Am. Chem. Soc.*, **95**, 1338 (1973).
- N. A. LeBel and R. J. Maxwell, *J. Am. Chem. Soc.*, **91**, 2307 (1969).