Thus, vertical stabilization, in the gas phase, of the benzenonium ion by carbon–tin σ electrons can be readily observed by CIMS techniques and establishes this interaction as being of prime importance in electrophilic aromatic cleavage reactions of benzyltin compounds. To our knowledge this is the first example of carbon–metal σ–π conjugation being documented in the gas phase, as related to electrophilic reactions with aromatic compounds, and the results reported herein support previous spectroscopic techniques[2-4] as well as solvolysis studies[9] concerning the significance of this effect.

Experimental Section

The CIMS were obtained on a Finnigan 1015D instrument (isobutane at 0.5 torr) coupled to a System Industries Model 150 computer. The compounds, **1–10**, were introduced using the direct inlet technique and volatilized by slowly heating the probe (~100 °C). Compounds **1–4** and **8** were prepared according to literature ref 3a, 10, 11, 11, and 12, respectively, and were of analytical purity.

Compounds **5**, **6**, and **7** were prepared similarly from tribenzyltin chloride and the corresponding methyl, cyclopentyl, and phenyl Grignard reagents in diethyl ether and were purified by column chromatography (SiO_2 or Al_2O_3) using benzene as the eluent. Compound **5** (mp 47–49 °C) had a ^1H NMR spectrum (270 MHz, CCl_4, Me_4Si) with signals at 0.15 (CH_3Sn), 2.55 (CH_2Sn), and 6.80 and 7.46 ppm (aromatic) in the correct ratios; compound **6** (mp 66–69 °C; MeOH) had signals (60 MHz) at 1.1–1.8 (ring CH_2's), 2.20 (CH_2Sn), and 6.63 and 7.23 ppm (aromatic); compound **7** (thick oil) had signals (60 MHz) at 2.34 (CH_2Sn) and 6.63 and 7.20 ppm (aromatic). Compound **9** was prepared by the following procedure: diphenylethylmethyltin was reacted with hydrochloric acid in methanol to give phenylethylmethyltin chloride. Reaction of this compound with benzylmagnesium chloride gave **9** (bp 116–117 °C, 0.2 mm) in 77% yield. Compound **9** had signals at 0.18 (CH_3), 1.0 (CH_2CH_3), 1.15 (CH_2CH_3), and 7.0–7.38 ppm (aromatic). All new compounds (**5**, **6**, **7**, **9**) gave satisfactory C, H, and Sn analyses (±0.3%).

Acknowledgments. This study was supported in part by a grant from the National Institute of Environmental Health Sciences (P01 ES00049) and a grant from the Belgian Nationaal Fonds voor Wetenschappelijk Onderzoek (N.F.W.O.).

Registry No.—Tribenzyltin chloride, 3151-41-5; diphenylethylmethyltin, 17842-01-2; phenylethylmethyltin chloride, 68024-64-6; benzylmagnesium chloride, 6921-34-2.

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(8) In a recently submitted paper on the gas-phase electrophilic cleavage reactions of organotin compounds, the mechanism we proposed was challenged because our spectra lacked $[M + 1]^+$ ions. Additionally, the reviewers suggested that our results could be explained by electron-transfer reactions rather than by electrophilic reactions. It is obvious that electron-transfer reactions with the *tert*-butyl cation are not significant with the benzyltin compounds, since most of the compounds reported gave an observed $[M + 1]^+$ or $[M + 57]^+$ ion. This supports the assumption that the ionization potential of the *tert*-butyl cation is lower than the organotin compounds precluding electron transfer reactions [see ref 5b].

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Regio- and Stereospecific Acyl–Metal Insertion from $Fe(CO)_5$-Mediated Photolysis of (+)-α-Thujene[†]

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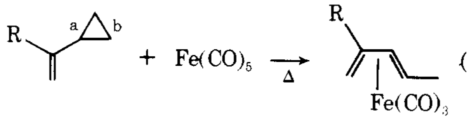
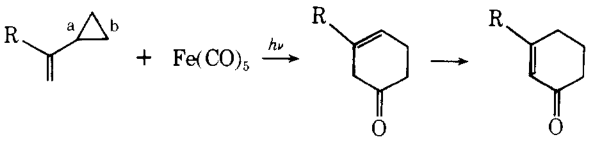
Received June 6, 1978

(+)-α-Thujene has been brought into reaction under photolytic conditions with $Fe(CO)_5$ and under thermal conditions with $Fe_3(CO)_{12}$. It was possible to isolate from both the thermal and the photochemical reaction an adduct resulting from ring opening and acyl-$Fe(CO)_3$ insertion to yield a complex accommodating both σ- and π-allyl components. The observed stereospecific and regiospecific rearrangement–insertion reaction is envisioned to arise from an orthogonal electrophilic attack of an $Fe(CO)_4$ species on the α-thujene from the side opposite to the cyclopropane ring. The photochemical reaction of (−)-umbellulone yielded an intractable heat-sensitive σ,π-allyl complex which readily ejects the metal to form (±)-umbellulone. Factors governing the course of this reaction are discussed.

Our previous studies of the reactions between iron carbonyl and systems in which cyclopropyl groups are conjugated with C–C π-electron units led to characterization of four distinctly different modes of rearrangement. The first one was the thermolysis of cyclopropylethylenes in presence of $Fe(CO)_5$ to form 1,3-dienes resulting from ring opening and a hydrogen shift (eq 1).[1] The second was the photochemical reaction, yielding cyclohexenones arising from rearrangement coupled with carbonyl insertion (eq 2).[2] We showed that the latter reaction is general for a number of cyclopropylethylenes and that it is quite sensitive to effects of substitution.[3]



(bond a scission) (1)



(2)

[†] Dedicated to Professor E. Havinga on the occasion of his 70th birthday.

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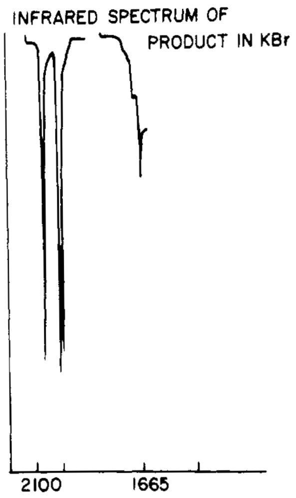
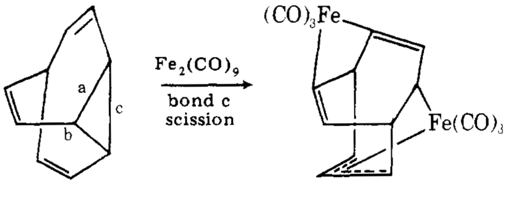


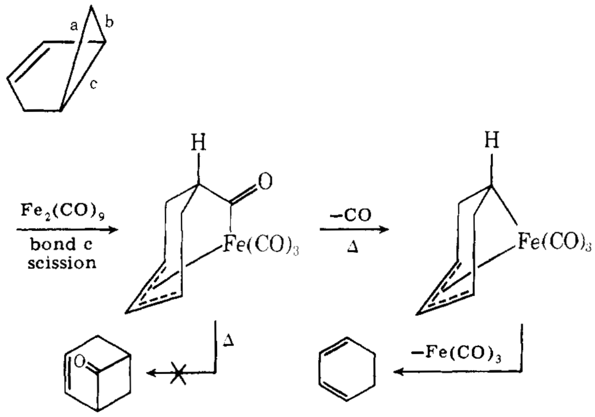
Figure 1. Infrared spectrum of III in KBr (frequencies in cm^{-1}).

The third mode relates to ring openings of polycyclic olefins containing cyclopropane to yield bicyclic complexes in which the metal makes use of a four-point attachment, accommodating the σ and π components (eq 3).[4]



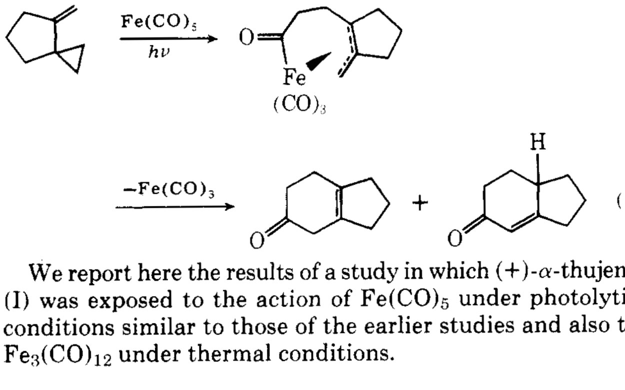
(3)

When the substrate was bicyclo[3.1.0]hex-2-ene the photochemical reaction with $Fe(CO)_5$ yielded an acyl–π-allyl complex.[5] The latter did not show tendency to produce the bicyclo ketone, but favored to lose carbonyl and $Fe(CO)_3$ to provide cyclohexadiene (eq 4).



(4)

Unlike bicyclo[3.1.0]hex-2-ene, the photochemical reaction of 4-methylenespiro[2.*x*]alkanes provides bicyclic enones in very good yields (eq 5).[6]



(5)

We report here the results of a study in which (+)-α-thujene (I) was exposed to the action of $Fe(CO)_5$ under photolytic conditions similar to those of the earlier studies and also to $Fe_3(CO)_{12}$ under thermal conditions.

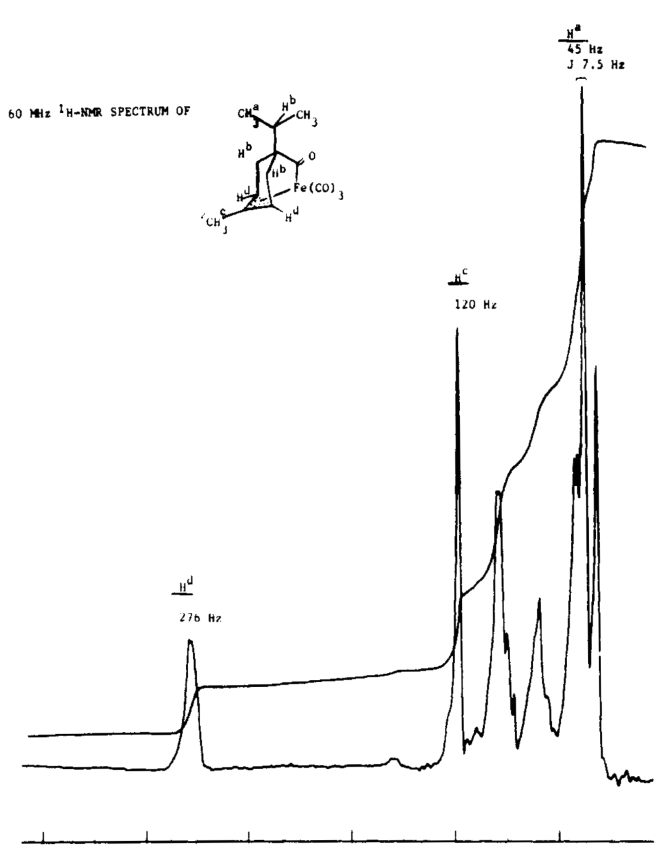


Figure 2. 60-MHz ^1H NMR spectrum of III in $CDCl_3$ (chemical shifts in hertz).

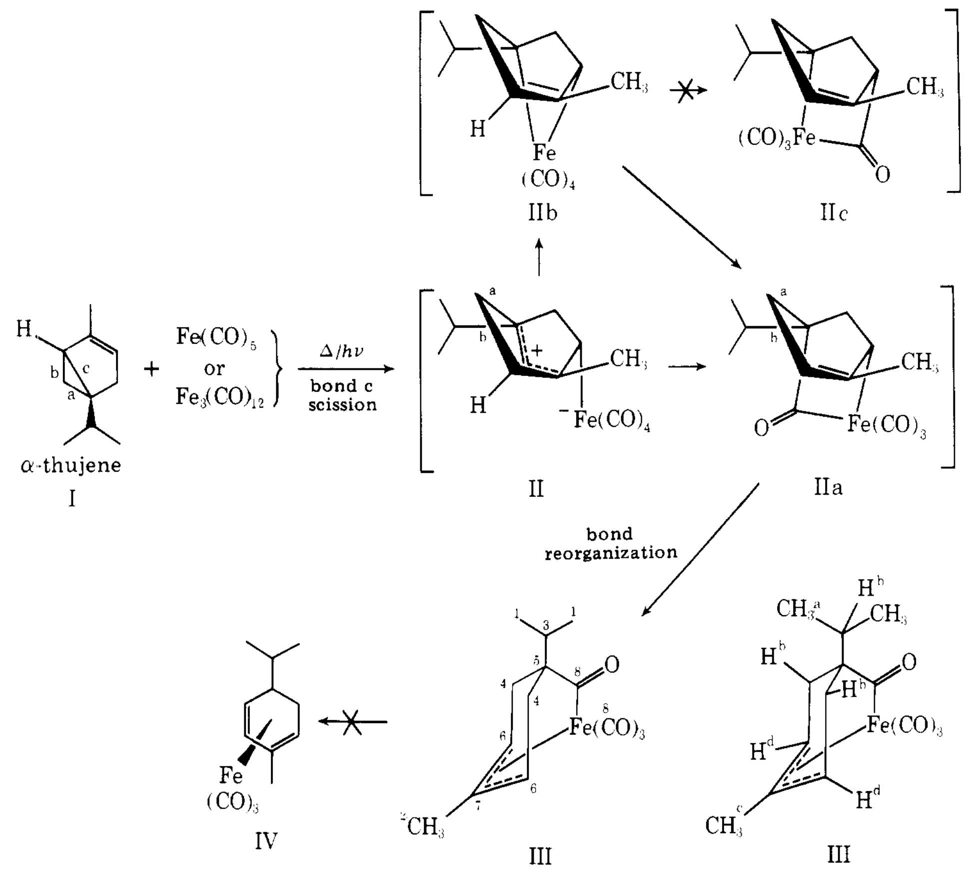
Results

When I (~0.007 M) and $Fe(CO)_5$ (0.014 M) were irradiated by a 125-W lamp in petroleum ether (40–60 °C) solution, the reaction went to completion within 1 h, and workup gave a mixture containing largely a product derived from incorporation of one α-thujene group into an organometallic species (eq 6). The only isolable product was optically inactive yellow compound which could be induced to crystallization. It analyzed as a $C_{10}H_{16}COFe(CO)_3$ complex and assigned the acyl–irontricarbonyl π-allyl structure III. This formulation was deduced from IR, ^1H NMR, ^{13}C NMR, and MS analyses of the reaction product.

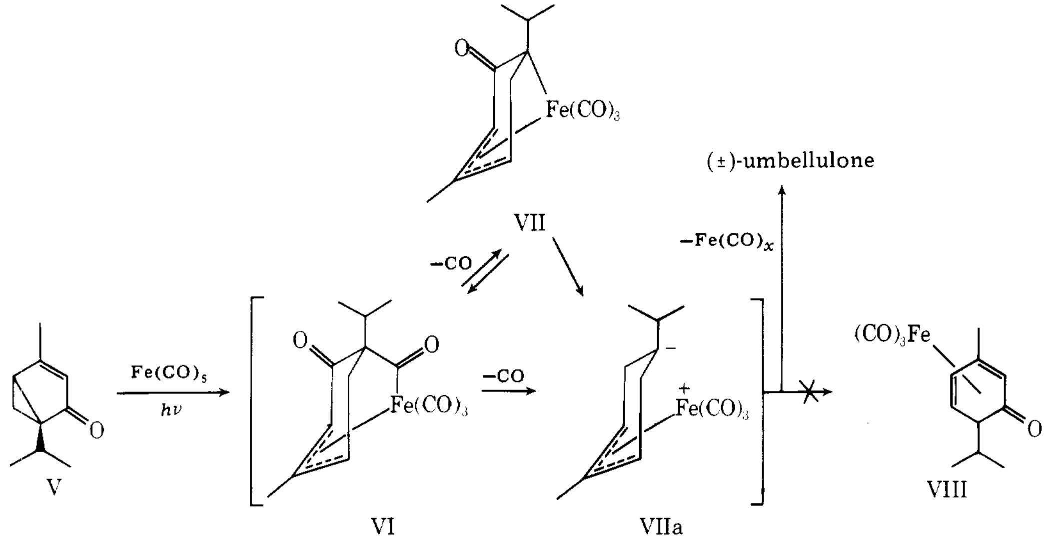
The IR spectrum of III (see Figure 1) exhibits three Fe–CO absorption bands at 2005, 2020, and 2080 cm^{-1} and one ketonic carbonyl band at 1665 cm^{-1}. Its 60-MHz (Figure 2) ^1H NMR spectrum in $CDCl_3$ indicates the complete disappearance of the cyclopropane signals at 14 Hz in the substrate and the appearance of a new triplet at 276 Hz (2 H) attributable to protons attached to π-allyl complex (H^d). The isopropyl protons (H^a) appear as a doublet at 45 Hz (J = 7.5 Hz), while the singlet (3 H) at 120 Hz is assigned to the methyl protons (H^c). The multiplet between 108 and 78 Hz (5 H) is assigned to the ring methylene and the methine protons (H^b).

The decoupled 15-MHz ^{13}C NMR spectrum of III exhibits eight signals (see Figure 3), ranging (in ppm) from 211.9 (carbonyl carbons, C^8) to 19.56 (isopropyl methyl carbons, C^1). The signals at 104.4 and 75.0 are assigned to the three π-allyl carbons, C^7 and C^6, respectively, and that at 74.8 to the bridgehead carbon (C^5). The resonances at 30.83, 30.3, and 27.33 are attributable to the corresponding methylene (C^4), methine (C^8), and methyl (C^2) carbons, in consonance with formulation III.

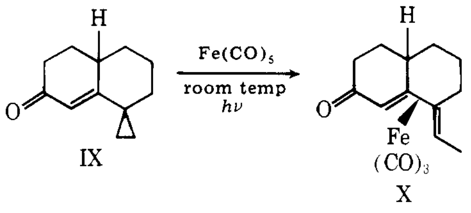
The 70-eV mass spectrum of III exhibits the molecular ion peak at *m/e* 304, and peaks at *m/e* 276 (M − CO), 248 (M − 2CO), 220 (M − 3CO), and 164 [M − $Fe(CO)_3$] arising from successive losses of CO and iron.[7]



(6)



(7)



(8)

The same product (III) was obtained when I (~0.007 M) was refluxed in benzene or in tetrahydrofuran with $Fe_3(CO)_{12}$ (0.014 M), and the minor products could not be isolated.

Thermal decomposition of III in boiling xylene was very slow. The decomposition products could not be isolated. On the other hand, solutions of III in petroleum ether (40–60 °C) or in diethyl ether tend to decompose on standing at room temperature (open to the air) to yield iron oxides mixed with an unidentifiable polymeric material. In contrast to the case of bicyclo[3.1.0]hex-2-ene (eq 4) we could not detect isomers of phellandrene (IV) in the decomposition mixture.

The photolysis of (−)-umbellulone (V) (~0.007 M) with $Fe(CO)_5$ (0.014 M) under similar conditions led to intractable mixture containing σ,π-bonded organometallic species presumably of structures VI and VII (eq 7). This was inferred from analysis of its IR spectrum (hexane) exhibiting absorptions at 2060, 2037, 2017, 1995, and 1983 cm^{-1} (Fe–CO) and between 1690 and 1660 cm^{-1} (ketones). Attempts toward

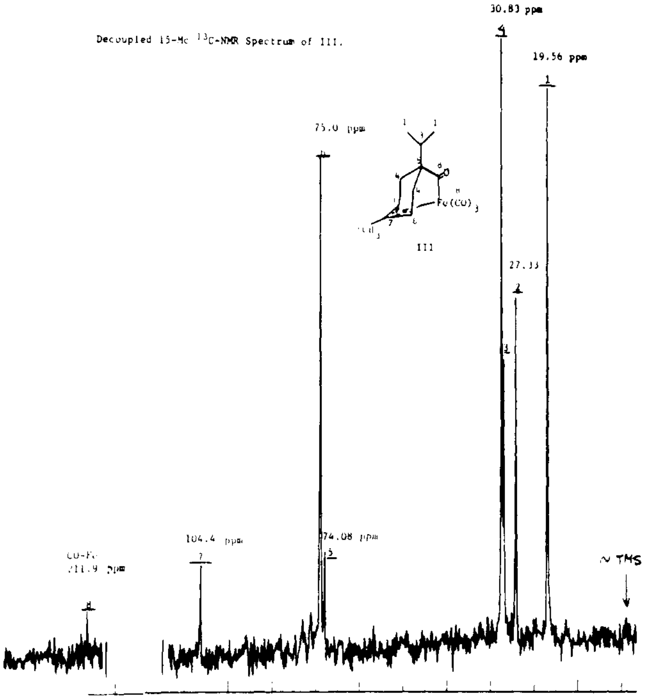
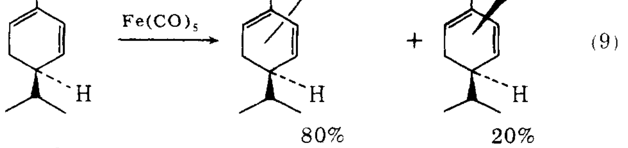


Figure 3. Decoupled 15-MHz ^{13}C NMR spectrum of III (chemical shifts in ppm).

separation between VI and VII failed. Repeated column chromatography brought about loss of the metal and regeneration of a racemic form of umbellulone [(±)-V]. It was not possible to detect diene–π-complex of structure VIII. The conversion of VI and VII into (±)-umbellulone rather than into a diene–π-complex is at variance to the behavior of 1,1-ethylene-7-keto-$\Delta^{8(9)}$-octalene (IX) which rearranged into the corresponding diene–π-complex (X) on photolysis in the presence of $Fe(CO)_5$ (eq 8).[6]

Discussion

The data presented here clearly indicates that under both the thermal and the photochemical conditions iron carbonyls are able to induce ring expansion of α-thujene by scission of bond c of the cyclopropane with the concomitant insertion of the CO–$Fe(CO)_3$ residue across the vinylcyclopropane conjugated system. In a typical manner the metal makes use of a four-point attachment, favoring generation of structure III because in this way the metal can accommodate sterically the σ and π components. Most striking is the ability of the iron carbonyl to distinguish between the two sides of α-thujene, which exist in an L-shaped conformation with the cyclopentene ring planar.[8] Equation 6 illustrates stereospecific attachment to the rear of the cyclopropane ring, orthogonal to the cyclopentene ring probably because this side is less hindered than the opposite one. In the following stage (II → IIa) the CO insertion is oriented toward the cyclopropane to the same side as the isopropyl group, undergoing bond reorganization to form III. The alternative mode of CO insertion (II → IIc) is precluded probably because it leads to an overcrowded arrangement. Indeed, eq 9 illustrates that the isopropyl group in α-phellandrene (XI) does not favor the attachment of $Fe(CO)_3$ to the same side as the substituent (XI → XIIB).[9]



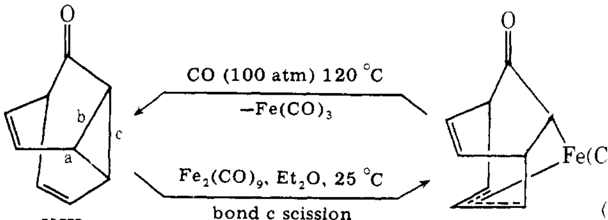
(9)

80% 20%

XI XIIa XIIb

This stands in contrast to the catalytic hydrogenation over platinum, and also to the hydroboration–oxidation of α-thujene, which takes place in an anti-Markownikoff sense exclusively from the side away from the cyclopropane ring.[10] On the other hand, addition reactions of I in the presence of acids proceed entirely in the opposite direction, leading invariably to ring-opened products in a stereospecific way following the Markownikoff sense.[11–14] Evidently, the attachment of CO–$Fe(CO)_3$ residue across the vinyl cyclopropane system in I closely parallels those electrophilic addition reactions.[15]

In contrast to $Fe(CO)_5$-induced racemization of V (eq 7), similar irradiation of V in the absence of $Fe(CO)_5$ did not produce its racemic form [(±)-V)] nor the starting (−)-umbellulone. Instead, it yielded a mixture comprising nonketonic products,[16] indicating that the metal plays an active role in the loss of optical activity most likely via sequence V → VI → VIIa → (±)-V. A precedent to that could be found in the generation of barbarolone (XIII) from a σ,π-allyl iron tricarbonyl precursor (XIV) (eq 10).[17]

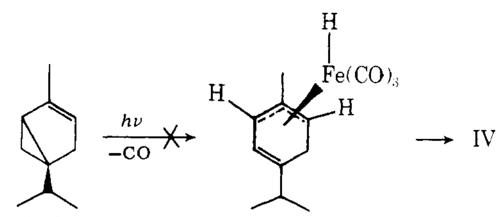


XIII XIV (10)

Apparently the carbonyl group in the ring systems confers considerable instability to the σ,π-allyl complexes VI and VII relative to III. They seek stability in reverting in a nonstereospecific fashion via VIIa to (±)-umbellulone.

Unlike IX, which affords X on photolysis with $Fe(CO)_5$ (eq 8) as a consequence of ring opening coupled with hydrogen migration, V is precluded to do so because the metal could approach the substrate only from the side opposite to the cyclopropane ring.

Mechanistically, the rearrangement–insertion reaction (I → III) could be envisioned to arise from an initial oxidative addition of $Fe(CO)_4$ to the double bond to yield a zwitterionic species[18] followed by CO insertion to yield intermediate IIa (not observed), which undergoes bond reorganization to give III. However, the I → IV interconversion should presumably involve the intermediacy of a hydro–iron carbonyl π-allyl species (XV), the formation of which is precluded on steric grounds, as explained above.[3]



α-thujene
I XV

Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. IR spectra were measured on a Perkin-Elmer 237 grating infrared spectrophotometer. Proton magnetic spectra were taken on a Bruker W-60H spectrometer ($CDCl_3$ solution, Me_4Si standard) and ^{13}C NMR spectra on the same Bruker instrument ($CDCl_3$ solution, Me_4Si standard). Mass spectra were measured on an MAT CH-5 spectrometer.

Elementary analyses were carried out at the Hebrew University Microanalytical Laboratory, Jerusalem, Israel.

Materials. (+)-(α)-Thujene, $[\alpha]^{25}{}_D$ +80.17°, and (−)-umbellulone, $[\alpha]^{25}{}_D$ −37°, were obtained from Dragoco, Gerberding and Co., GmbH, Holzminden, West Germany, and used without further purification. Pentacarbonyliron was obtained from the Badische Anilin und Sodafabrik, West Germany. Triiron dodecacarbonyl was prepared according to literature.[19]

Photochemical Reaction of (+)-α-Thujene (I) with $Fe(CO)_5$. Irradiation was carried out for 1 h under nitrogen in petroleum ether (40–60 °C) solution using a Philips HPK-125 lamp in a water-cooled quartz immersion vessel. Reaction solutions of 1 g of I and 2.7 g of $Fe(CO)_5$ in ~300 mL of solvent were employed. The product mixture was filtered through Celite and the solution evaporated on a rotary evaporator. The residue (1.0 g) was washed with cold ether and recrystallized from tetrahydrofuran. The light yellow crystals of III melted at 106–107 °C, yield 62%.

Anal. Calcd for $C_{14}H_{16}O_4Fe$: C, 55.2; H, 5.2. Found: C, 55.0; H, 5.0.

Thermal Reaction of I with $Fe_3(CO)_{12}$. Solutions of I (1 g, ~0.007 M) and $Fe_3(CO)_{12}$ (7.56 g, 0.014 M) were heated at reflux in benzene or tetrahydrofuran for 3 h under nitrogen. Workup of the product mixture was as described above for the photochemical reaction, yield of III 55%.

Photochemical Reaction of (−)-Umbellulone (V) with $Fe(CO)_5$. A solution of V (0.007 mol) was irradiated with $Fe(CO)_5$ (2.6 g) in petroleum ether (40–60 °C) for 6 h and the resulting green solution was chromatographed on a florisil column. The first eluted fraction contained a very labile organometallic species which could not be analyzed. The second eluted fraction contained the main product which comprised a mixture of VI and VII which could not be separated. On repeated TLC chromatographies the organometallic mixture decomposed to form (±)-umbellulone (85%).

Acknowledgments. The authors wish to thank the Badische Anilin und Sodafabrik for a generous gift of pentacarbonyliron, to the Dragoco, Gerberding and Co., GmbH, Holzminden, West Germany, for their generous gift of (+)-α-thujene, to Dr. Israel Ringel for his contribution on the ^1H NMR and ^{13}C NMR spectra, and to Dr. Rae Victor for highly valuable help and discussion.

Registry No.—I, 563-34-8; III, 68024-48-6; V, 546-78-1; VI, 68024-49-7; VII, 68024-50-0; $Fe(CO)_5$, 13463-40-6; $Fe_3(CO)_{12}$, 17685-52-8.

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Acetyldiarylamines by Arylation of Acetanilides. Some Applications and Limitations[1]

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Received August 7, 1978

The Goldberg reaction (the interaction of an aryl bromide and an acetanilide) is a convenient general method for preparing *N*-acetyldiarylamines, which can usually be readily hydrolyzed to the corresponding diarylamines. Aryl bromides containing two ortho substituents, however, give only low yields of *N*-acetyldiarylamines. These amides, furthermore, are relatively resistant to hydrolysis when they contain two or more ortho substituents. It has also been found that aryl chlorides (as well as bromides) may react under the conditions of the Goldberg reaction and, therefore, mixtures may be obtained when a chloro-substituted aryl bromide is allowed to react with an acetanilide.

Over seventy years ago Goldberg[2] noted that the condensation of an aryl bromide and an acetanilide in the presence of potassium carbonate and copper iodide yields an *N*-acetyldiarylamine and that hydrolysis of the amide thus obtained yields a diarylamine. Although the Goldberg procedure has been employed in a number of laboratories,[3] it has probably been overshadowed by other methods of preparing diarylamines, especially via the Chapman rearrangement and the Ullmann condensation.[4] The Ullmann condensation, however, is useful primarily for the preparation of diarylamines containing nitro or carboxy groups, while moisture-sensitive imidoyl chlorides are necessary precursors to the use of the Chapman rearrangement. In contrast, the Goldberg reaction usually gives high yields of stable, easily handled *N*-acetyldiarylamines from readily available substances. It should be emphasized, however, that the success of the Goldberg reaction does depend on the use of rigorously dried starting materials.

The yields of *N*-acetyldiarylamines obtained by the Goldberg reaction are not adversely affected by the presence of one *o*-methyl substituent in the aryl halide or of one or two *o*-methyl substituents in the acetanilide (cf. Scheme I). Thus, the usual reaction conditions gave the amides **1–4** in yields that ranged from 70–90%. Low yields of *N*-acetyldiarylamines were obtained, however, when the aryl halide possessed two *o*-methyl groups. Thus, the amides **5**, **6**, and **7** were obtained in yields of only 46, 18, and 14%, respectively, when 2-bromomesitylene was allowed to react with the appropriate acetanilides.

N-Acetyldiarylamines containing no ortho substituents (or only a single *o*-methyl group) are readily hydrolyzed by refluxing with 2 equiv of potassium hydroxide in ethanol for 2–3

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