grade) and the alcohol (obtained in the later fractions) was distilled under vacuum yielding 17.8 g (47% recovery) of colorless, viscous oil, bp 107° (1.8 mm). Redistillation of a portion of the product yielded an analytical sample of the bromo alcohol: bp 107° (1.8 mm); ir (CCl_4) 3300 and 1655 cm^{-1}; nmr (CCl_4) δ 1.1–2.2 (m, 10), 4.36 (s [superimposed on a broad m], 2), and 5.86 ppm (d, 1, J = 7.0 Hz).

Anal. Calcd for $C_8H_{13}BrO$: C, 46.85; H, 6.39; Br, 38.96. Found: C, 46.89; H, 6.61; Br, 38.92.

Treatment of the alcohol with Jones–Weedon oxidant[62] gave 3-bromo-2-cycloocten-1-one which underwent isomerization to the β,γ olefinic ketone on distillation at reduced pressure.[61] Distillation (evaporative-still) at <0.1 mm afforded nearly pure 3-bromo-2-cycloocten-1-one [nmr (CCl_4) δ 6.34 (s, 1)] which contained about 5% of minor impurities by nmr analysis.

2,4-Diphenyl-1,4-pentadienyl Methyl Sulfoxide (12) or 2,4-Dienyl Isomer (11). Method A. By Catalytic Hydrogenation of 2a. A suspension of 10% palladium on charcoal (0.5 g) in absolute ethanol (15 ml) was prereduced under hydrogen, and a solution of **2a** (0.73 g, 0.0026 mol) in ethanol (35 ml) was added to the suspension of the prereduced catalyst. The reduction was stopped after uptake of 1 mol equiv of hydrogen had occurred. The catalyst was removed by filtration and the ethanol evaporated under vacuum, leaving 0.76 g of pale green crystalline solid which was recrystallized from methanol, giving 0.30 g (41%) of **12** (or **11**) as long white needles, mp 117.2–118.2°. An analytical sample had mp 119.2–119.7°; ir ($CHCl_3$) 1492, 1445, 1415, 1405, 1397, 1220, 1130, 910, and 698 cm^{-1}; uv max (MeOH) 252 nm (ϵ 29,700); nmr ($CDCl_3$) δ 2.37 (s, 3), an AB pattern (J = 13 Hz) centered at δ 3.73 and 4.21, 5.51 (t, 1, J = 1.1 Hz), 5.72 (s [br], 1), 6.82 (s [br], 1), and 7.10–7.69 ppm (m, 10).

Anal. Calcd for $C_{18}H_{18}OS$: C, 76.57; H, 6.43; S, 11.33. Found: C, 76.55; H, 6.41; S, 11.33.

Method B. By Reduction of 2a with Zinc in Acetic Acid. A solution of **2a** (4.20 g, 0.015 mol) in glacial acetic acid (30 ml) was added to a suspension of zinc dust (1.96 g, 0.026 g-atom) in glacial acetic acid (20 ml). The reaction mixture was stirred at room temperature for 1.0 hr, $CHCl_3$ was added, and the mixture was filtered. The filtrate was washed with H_2O and saturated $NaHCO_3$ and NaCl solutions, and dried ($MgSO_4$). Evaporation of the solvent under vacuum at room temperature gave 3.88 g (92%) of a pale yellow crystalline solid; recrystallization from $CHCl_3$–petroleum ether yielded 2.94 g (70%) of **12** (or **11**) as long white needles: mp 118.7–121.2°. A second crop amounted to 0.45 g (11%) of a mixture of the starting material and the reduction product.

Acknowledgments. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their support of this program. We also thank Messrs. Jack E. Martinelli and Edward A. Weiss for large-scale preparations of several starting materials and certain of the experimental data.

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(61) *Cf.* N. Heap and G. Whitham, *J. Chem. Soc. B*, 164 (1966).

Synthesis of Cyclobutenone

J. B. Sieja

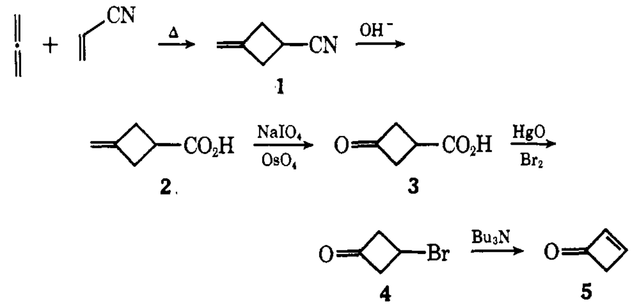
Contribution No. 1741 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898. *Received September 21, 1970*

Abstract: Cyclobutenone was prepared from 3-bromo- and 3-chlorocyclobutanone, which were synthesized by independent routes from allene and ketene, respectively.

Cyclobutenone (**5**) has thus far escaped isolation,[1] although numerous examples of substituted cyclobutenones have been reported. We wish to report the synthesis and isolation of **5**, which was obtained by two independent routes, both converging to a 3-halocyclobutanone as the immediate precursor.

3-Bromocyclobutanone. Cyclobutenone was first prepared as shown in Scheme I. Compounds **1**, **2**, and **3** were prepared according to literature methods.[2,3] The precursor **4** was prepared by a modification[4] of the Hunsdiecker reaction. The structure of **4** was proved by spectral and elemental analyses (see Experimental Section). A limitation of Scheme I is the conversion of **2** to **3**, because crude **3** is obtained as a black, water-soluble solid which is difficult to purify. Ozonolysis of **2** would probably be preferable on a small scale.

Scheme I



3-Chlorocyclobutanone. A preferable route to **5** (Scheme II) resulted from our work on the thermal cycloaddition of ketene to vinyl ethers,[5] where **6** was easily prepared in large quantities. Treatment of **6** with carbonyl fluoride[6] gave **7** in quantitative yield. This was converted to **8**, which liberated **9** on hydrolysis. The intermediacy of **8** is based on two facts: (1) glpc showed **9** to be absent in the crude reaction mixture be-

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(1) A. C. Cope, S. F. Schaeren, and E. R. Trumbull, *J. Amer. Chem. Soc.*, **76**, 1096 (1954); E. Vogel and K. Hasse, *Justus Liebigs Ann. Chem.*, **615**, 22 (1958); E. F. Silversmith, Y. Kithara, and J. D. Roberts, *J. Amer. Chem. Soc.*, **80**, 4088 (1958).

(2) H. N. Cripps, J. K. Williams, and W. H. Sharkey, *ibid.*, **81**, 2723 (1959).

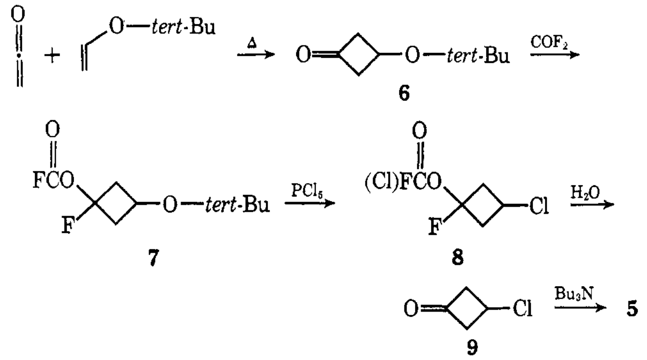
(3) J. D. Roberts and F. F. Caserio, *ibid.*, **80**, 5837 (1958).

(4) S. J. Cristol and C. W. Firth, Jr., *J. Org. Chem.*, **26**, 280 (1961).

(5) J. B. Sieja, *J. Amer. Chem. Soc.*, **93**, 130 (1971).

(6) F. S. Fawcett, C. W. Tullock, and D. D. Coffman, *ibid.*, **84**, 4275 (1962).

Scheme II



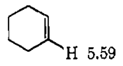
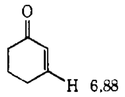
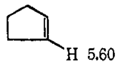
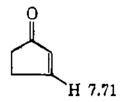
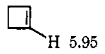
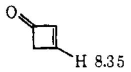
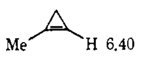
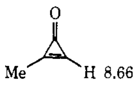
fore hydrolysis, and (2) bubbles of carbon dioxide were liberated on hydrolysis of the crude reaction mixture, which was subsequently shown to contain **9**. Interestingly, **8** was stable to prolonged treatment with boron trifluororide, phosphorus pentachloride, and phosphorus oxychloride even though analogous fluoroformates are converted to geminal difluorides by acidic reagents.[6]

Cyclobutenone. Compounds **4** and **9** were converted to **5** with tri-*n*-butylamine. In the case of **4**, diethyl Carbitol was used as solvent, but it was later found that with **9** no solvent was necessary. A high-boiling base is preferred because **5** is isolated by volatilization from the crude reaction mixture. In a neat state **5** polymerized quite rapidly, and samples that were stored at −78° formed significant quantities of polymer overnight. With increased purity and more careful handling (liquid nitrogen storage), storage life of **5** should be increased significantly. No attempts were made by us to treat **5** with other materials, but it probably can be formed and reacted *in situ* conveniently, or alternatively can be volatilized directly into the reaction medium.

Structural Proof for Cyclobutenone. Conclusive structural proof for **5** lies in its mass spectrum which shows the parent peak at *m/e* 68 (69% relative intensity), $[CH_2{=}C{=}O]^+$ at *m/e* 42 (13% relative intensity), $[C_3H_3]^+$ at *m/e* 39 (base peak), $[C_2H_2]$ at *m/e* 26 (9% relative intensity). The infrared spectrum is consistent with **5**, with bands at 3.23 (=CH), 3.35, 3.38 (CH_2), 5.58 (C=O), and 6.54 μ (C=C). The ultraviolet spectrum (isooctane), also consistent with **5**, has bands at 213 and 320 nm with relative intensities of 279:1. The extinction coefficients were not measured because of difficulties caused by polymerization. The nmr spectrum of **5** consists of a singlet at δ 3.29 (2 H, CH_2, width at half-height 2.5 cps), doublet centered at δ 6.17 (1 H, α-H, J = 2.5 cps), and multiplet at δ 8.35 (1 H, β-H).

The methylene hydrogens of **5** resonate at a frequency not unusual for the system $=CCH_2C(=O)-$,[7a] and the α-hydrogen appears at a frequency common to this system.[7b] The β-hydrogen of **5**, however, appears at an unusually low field when compared to the β-hydrogens of **10** and **11** (Table I). In this series, only the "β"-hydrogen of **12** appears at a field somewhat lower than δ 8.35. This might be expected because of the direct attachment of the "β"-carbon to the carbonyl carbon, and because of the known high polarizability of the carbonyl of cyclopropenones and the possibility of some ring current.[8] If one compares the $\Delta\delta$ from the alkene to the corresponding alkenone, one sees that the change is greatest for the four-membered ring. Since the ultraviolet spectrum suggests no abnormal polarization effects for **5** (2-cyclopentenone shows λ_{max} 218 nm), we ascribe the relatively low-field absorption of the β-hydrogen of **5** to its unique geometric position with respect to the magnetically anisotropic α,β-unsaturated system.

Table I[a]

A (δ)	B (δ)	$\Delta\delta$ A → B (ppm)
	 **10**	1.29
	 **11**	2.11
	 **5**	2.40
	 **12**	2.26

[a] See ref 7.

Experimental Section

All hydrogen nmr spectra were recorded at 60 MHz using tetramethylsilane as internal standard. All fluorine nmr spectra were recorded at 56.4 MHz and are reported as parts per million upfield from trichlorofluoromethane as internal standard.

3-Bromocyclobutanone (4). To a solution of 234 g (1.46 mol) of bromine in 2 l. of carbon tetrachloride at 70° was added an intimate mixture of 84 g (0.737 mol) of 3-oxocyclobutanecarboxylic acid and 123 g (0.567 mol) of red mercuric oxide over 30 min. A second batch of 84 g of 3-oxocyclobutanecarboxylic acid and 123 g of mercuric oxide was then mixed and added over the next 30 min. The solids were added in two batches because the mixture became rather sticky and difficult to add if allowed to stand for more than 30 min. About 24 l. of carbon dioxide was evolved during the addition, and heating was continued for a few minutes after addition until the solution was colorless. Solids were filtered off and solvent was removed at 30° (140 mm) up to a pot temperature of 45°. The pressure was then gradually reduced to about 10 mm, and the residue was distilled at 22–25° (0.5–0.25 mm). The last traces of product were removed at a pot temperature of 60° to give 95–100 g (45%) of **4**: n^{25}D 1.5026; ir (neat) 5.59, 7.32, 8.10, 9.20, 11.90 μ; nmr (neat) δ 4.46–4.87 (m, 1 H, methine), 3.12–4.10 (m, 4 H, CH_2); mass spectrum *m/e* 69 (26% relative intensity) $[M - Br]^+$, 79 (1.5% relative intensity) $[Br]^+$, 106 (3.0% relative intensity) $[CH_2CHBr]^+$, 120 (0.3% relative intensity) $[CH_2CHBrCH_2]^+$, 41 (base peak) $[CH_2{=}CHCH_2]^+$.

Anal. Calcd for C_4H_5OBr: C, 32.24; H, 3.38; Br, 53.64. Found: C, 31.89; H, 3.55; Br, 53.57.

1-Fluoro-3-*tert*-butoxycyclobutyl Fluoroformate (7). 3-*tert*-Butoxycyclobutanone (57 g, 0.4 mol), 4 ml of dimethylformamide, and 65 g (0.94 mol) of carbonyl fluoride were heated at 50° in a stainless steel pressure vessel for 12 hr. The material was quickly distilled into a cold trap (−78°) at reduced pressure to give 77.5 g (93%) of **7**: bp 32° (2 mm); ir (neat) 3.37, 5.38 (s, OCOF), 5.92 (m, impurity), 7.10, 7.20, 7.34, 7.75, 7.88, 8.23, 8.35, 8.73, 8.83, 9.35, 10.14, 11.16, 12.89, 13.18 μ; nmr (neat) δ 1.13 (s, 9 H, CH_3),

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(7) (a) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press Ltd., London, 1969, p 182; (b) p 188.

(8) R. Breslow and L. J. Altman, *J. Amer. Chem. Soc.*, **88**, 504 (1966).

2.0–3.3 (m, 4 H, CH_2), 3.75–4.5 (m, 1 H, methine); ^{19}F nmr 14.9 ppm (s, isomer 1, area 170, COF), 13.5 ppm (s, isomer 2, area 106, COF), 111 ppm (m, isomer 1, area 170, CF), 94 ppm (m, isomer 2, area 106, CF). Glpc analysis also suggests the presence of both cis and trans isomers.

3-Chlorocyclobutanone (9). 1-Fluoro-3-*tert*-butoxycyclobutyl fluoroformate (200 g, 0.96 mol) was quickly added to 350 g (1.68 mol) of phosphorus pentachloride. The temperature of the mixture reached 57°, and additional heat was applied until the mixture began to reflux (85°). During the heating period, two 2.5-ml portions of boron trifluoride ethereate were added, and during the reflux period (1 hr), four 0.5-ml portions were added. Starting material had been consumed at this point (glpc), and the mixture was cooled and poured onto ice. When the temperature of the hydrolysis mixture reached 15°, bubbles of carbon dioxide were evolved. The water was extracted with ether, which was then washed with water. Removal of solvent and distillation gave 12.5 g of **9** of about 80% purity, and 28 g of **9** of about 95% purity (~35% yield): bp 66° (47 mm); $n^{25}D$ 1.4626; ir (neat) 3.32, 3.38, 5.54 μ; nmr (neat) δ 4.50–4.92 (m, 1 H, methine), 3.0–4.0 (m, 4 H, CH_2); mass spectrum *m/e* 104 (5.5% relative intensity) $[M]^+$, 76 (21% relative intensity) $[CH_2CHClCH_2]^+$, 62 (8.5% relative intensity) $[CH_2CHCl]^+$, 42 (base peak) $[CH_2CO]^+$, 39 (48% relative intensity) [cyclopropenium ion].

Cyclobutenone (5) from 3-Chlorocyclobutanone (9). To 40 ml (0.17 mol) of tri-*n*-butylamine at 25° was added 12.3 g (0.12 mol) of **9** over 25 min. After 10 additional min volatile material was removed into a cold trap (−78°) at 0.2 mm. The material in the trap was then pumped into a second cold trap at 15 mm, allowing the first trap to come to 25°. This gave 5 ml (~5 g, 0.07 mol, 62%) of **5**.

Cyclobutenone (5) from 3-Bromocyclobutanone (4). To a solution of 14.9 g (0.1 mol) of **4** in 100 ml of diethyl Carbitol was added at 0° over 1 hr a solution of 23 ml (0.097 mol) of tri-*n*-butylamine in 80 ml of diethyl Carbitol. The mixture was stirred at 0° for 0.5 hr and then warmed to 25° over 1 hr. The volatile material was pumped into a cold trap (−78°) for 2 hr at 0.3 mm. The materal in the trap was then pumped into a second cold trap at 15 mm, allowing the first trap to come to 25°. The **5** in the second trap weighed 4.0 g (0.058 mol, 58%).

Synthesis and Interconversion of Some Shift Isomeric Polyene–*Tetrahapto*iron Tricarbonyl Complexes

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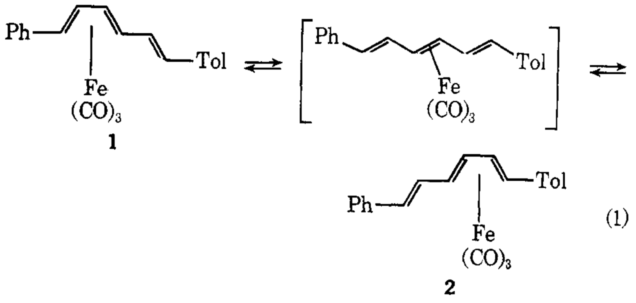
Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin.

Received November 3, 1969

Abstract: A series of *tetrahapto*iron tricarbonyl complexes of 1,6-disubstituted hexatrienes and 1,8-disubstituted octatetraenes has been synthesized. The mechanism of interconversion of shift isomers of these complexes has been studied. Electronic effects on equilibria are small. Electronic effects on rates are somewhat larger. The interconversion of the three shift isomers of 1-phenyl-8-tolyloctatetraeneiron tricarbonyl was studied.

Several years ago we[1] reported a study of the interconversion of the two shift isomers **1** and **2** of 1-phenyl-6-tolyl-1,3,5-hexatrieneiron tricarbonyl (eq 1). It was found that these two open-chain analogs of cyclooctatetraeneiron tricarbonyl[2] did in fact interconvert with one another but that the rate of interconversion was orders of magnitude less than in the case of the cyclooctatetraene complex. The mechanism proposed for the interconversion of **1** and **2** was as shown—a kinetically first-order rate-determining formation of a coordinatively unsaturated iron intermediate followed by collapse of this with formation of the other shift isomer. In addition to satisfying our experimental data, this picture is consistent with the great difference in rate between the cyclic and acyclic cases. The cyclic complexes possess the possibility of the metals' moving in concert with valence tautomerism of the ligand, thus leading to reestablishment of the original bonding picture with minimal intermediate structural changes (a "single jump"). The acyclic cases on the other hand lack the ability for valence tautomerization and must pass the iron a greater distance (a "double jump") along the chain before the original type of structure is reestablished.



The aim of the work now reported was to test the principal prediction of the above stepwise mechanism, that movement of an iron tricarbonyl residue from one end of a complexed octatetraene to the other *via* double jumps must of necessity proceed *via* the intermediate complex with the iron in the middle of the octatetraene (eq 2). In the course of testing this prediction we have prepared a number of shift isomers[3] of polyene–iron tricarbonyl complexes and have been able to examine the effect of the electronic nature of the terminal substituents on both the position and their rate of attainment of equilibrium. Our conclusions, as discussed below, are that (1) there is a relatively small effect of the electronic nature of the terminal substituents on the position of equilibrium, (2) substituents exhibit a somewhat greater effect on the rate of interconversion of

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[1] H. W. Whitlock and Y. N. Chuah, *J. Amer. Chem. Soc.*, **87**, 3606 (1965).

[2] A large variety of fluxional organometallic complexes has been reviewed recently by F.A. Cotton, *Accounts Chem. Res.*, **1**, 257 (1968).

[3] "Shift" isomers as used here are polyene–iron tricarbonyl complexes that differ by virtue of the site of attachment of the iron tricarbonyl group to the polyene (*e.g.*, **1** and **2**; **3**, **4**, and **5**).