A comparison of the entropies of activation for benzoin and α-hydroxyacetophenone further supports the chelate structure of the reaction intermediate. The presence of a single aryl group in structure I does not produce any appreciable steric interaction. If a second aryl group is present, however, considerable steric strain is introduced, resulting in the larger negative entropy of activation for benzoin.

Although the application of eq 2 for all of the α-ketols investigated has not been rigorously demonstrated, such an assumption seems justified by the general kinetic results obtained. In addition, the kinetic data have been interpreted in terms of steric hindrance to the formation of an intermediate chelate, but there should also be a corresponding effect on the enolization step. Thus, as the steric bulk around the enolizable proton increases, the ability of a base to attack the proton must decrease (*i.e.*, the rate of enolization decreases). In summary, therefore, a mechanism for the copper(II)-catalyzed oxidation of α-ketol in aqueous pyridine which involves an initial rate-determining proton removal from the α position of a copper(II)–ketol chelate is compatible with all of the available experimental evidence.

Experimental Section

Reagents.—Cupric acetate monohydrate (J. T. Baker, reagent grade), pyridine (Aldrich, reagent grade), and acetic acid (Du Pont, reagent grade) were used as obtained from commercial sources. Benzoin and 4,4′-dimethoxybenzoin (Matheson Coleman and Bell) were recrystallized several times from ethanol. The 3-hydroxy-2-butanone (Aldrich) was purified by the method of Marshall and Waters,[6] while 4-hydroxy-3-hexanone, 4-hydroxy-2,5-dimethyl-3-hexanone, and 4-hydroxy-2,2,5,5-tetramethyl-3-hexanone were prepared and purified by the method of Snell and McElvain.[12] The 2-hydroxycyclohexanone and 2-hydroxycyclopentanone were prepared and purified by the method of Schrapler and Ruhlmann.[13] In these last two reactions, the ester was slowly added through a Soxhlet extractor instead of the usual diluting head.

Kinetic Method.—Solutions of cupric acetate and the α-ketol were prepared in 50 mol % aqueous pyridine containing acetic acid to buffer the solutions. In the case of the less reactive systems, equal amounts of each solution were placed in a special Pyrex reaction cell which had previously been cooled to Dry Ice–acetone temperature. The reaction mixture was carefully degassed on a vacuum line by successive freezing and melting. The cell was sealed under vacuum (or under an atmosphere of purified nitrogen) and stored at the Dry Ice temperature until ready for use. The run was initiated by quickly bringing the reaction cell to the desired reaction temperature in a constant-temperature bath. At appropriate time intervals the cells were removed from the bath and placed in a thermostated cell compartment of a Beckman DU spectrophotometer. After the absorption of the reaction mixture was measured, the cell was returned to the bath. In the case of the more reactive reaction systems, the copper(II) solution was isolated from the ketol solution during the degassing using reaction cells similar to those described by Wiberg and Lepse.[14]

Registry No.—Copper, 7440-50-8.

(12) J. M. Snell and S. M. McElvain, "Organic Syntheses," Collect. Vol. II, A. H. Blatt, Ed., Wiley, New York, N. Y., 1943, p 114.
(13) U. Schrapler and K. Ruhlmann, *Chem. Ber.*, **97**, 1383 (1964).
(14) K. B. Wiberg and P. A. Lepse, *J. Amer. Chem. Soc.*, **86**, 2612 (1964)

Reactions of Polyarylated Carbinols. III.[1] Base-Catalyzed Rearrangement of 1,2,3,4,5-Pentaphenyl-2,4-cyclopentadien-1-ol[2]

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The base-catalyzed rearrangement of 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol (1) to 2,3,4,5,5-pentaphenyl-2-cyclopenten-1-one (4) has been observed and its mechanism has been investigated. This rearrangement has been found to occur with a wide variety of bases [sodium hydroxide, sodium carbonate, sodium bicarbonate, sodium amide, hexamethylphosphoramide (HMPA), and *N*,*N*-diethylformamide (*N*,*N*-DEF)], at various temperatures (173 and 95°), and after various reaction periods (3 and 8 hr). Mechanistic investigations established that the completely delocalized carbanion **7** is formed during the reaction and that 2,2,3,4,5-pentaphenyl-3-cyclopenten-1-one (**3**) is an intermediate in this rearrangement. It was further established that ketone **3** is the kinetically controlled product of this rearrangement while ketone **4** is the thermodynamically controlled product.

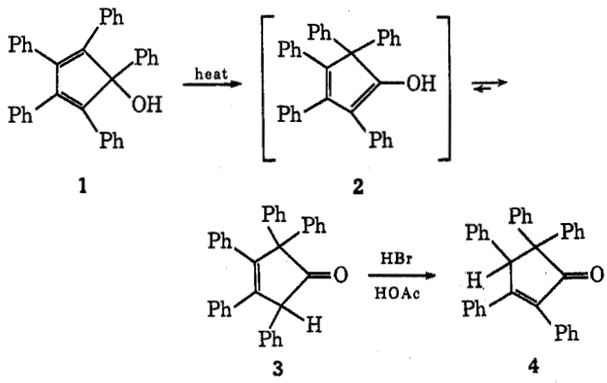
We have previously reported[1a] that 2,3,4,5,5-pentaphenyl-2-cyclopenten-1-one (**4**) could be prepared from 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol (**1**) *via* the following sequence of reactions: a thermally induced [1,5] sigmatropic phenyl rearrangement to give 2,2,3,4,5-pentaphenyl-3-cyclopenten-1-one (**3**), *via* the keto–enol tautomerization of the dienol intermediate **2**, followed by treatment of the ketone **3** with acid (HBr/HOAc) (Scheme I).

We now wish to report the direct base-catalyzed rearrangement of the dienol **1** to the ketone **4**. In addition to the interesting mechanistic aspects of this rearrangement, it also affords a simpler one-step preparative procedure for ketone **4** in greater yields than the preparative sequence represented in Scheme I.

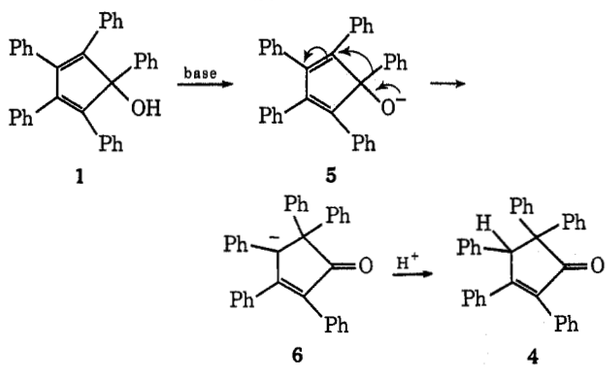
Initial treatment of dienol **1** with base followed by aqueous quench and work-up afforded only one product, ketone **4**. Based upon these results the initial mechanism postulated for this rearrangement involved formation of the alcoholate **5**, followed by phenyl migration to produce the enolate **6**, which was then protonated upon aqueous quenching to give the final product, ketone **4** (Scheme II). However, one objection to the above mechanism which arises is that ketone **4** is the only product obtained from this reaction. This objection arises because if the anion **6** is indeed formed it should not exist as a localized carbanion but as a com-

(1) For previous papers in this series see (a) A. K. Youssef and M. A. Ogliaruso, *J. Org. Chem.*, **37**, 2601 (1972); (b) *ibid.*, **38**, 487 (1973).
(2) Presented at the 24th Southeastern Regional Meeting of the American Chemical Society, Birmingham, Ala., Nov 3, 1972.
(3) Taken from the Ph.D. Thesis of A. K. Y. submitted to the faculty of the Department of Chemistry, VPI and SU, in partial fulfillment of the requirements for the Ph.D., July 8, 1972.

SCHEME I

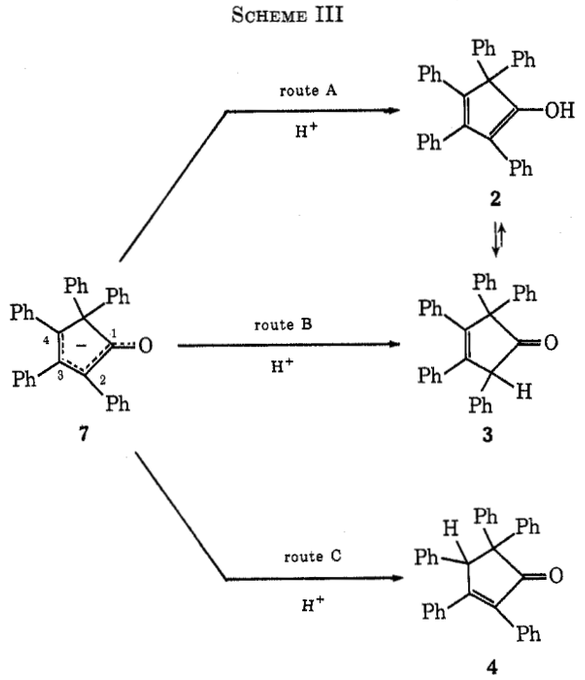


SCHEME II



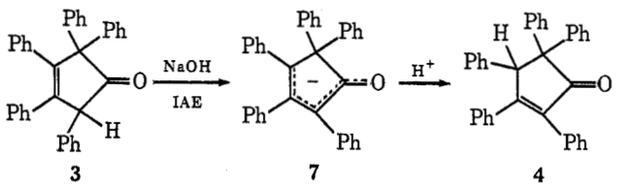
pletely delocalized carbanion, delocalized with the carbon–carbon double bond and the carbonyl group with which it is conjugated. Thus, as shown in Scheme IV, at least three resonance forms can be drawn for anion **6**, which are all best represented by the completely delocalized structure **7**. Subsequent protonation of anion **7** should then produce more than one product, since protonation could take place at three possible sites as shown below in Scheme III: at the

SCHEME III



oxygen atom (route A), at carbon 2 (route B), and at carbon 4 (route C).

Inspection of Scheme III shows that of the three possible products formed from the quench of anion **7**



only two products, ketone **3** and ketone **4**, should actually be obtained, since the enol **2** has previously[1a] been observed to tautomerize to ketone **3**. Since the only product obtained from the base-catalyzed rearrangement of dienol **1** is ketone **4**, we were led to the conclusion that possibly ketone **3** was an intermediate in this rearrangement, and that under the conditions of the reaction it reacted further to form ketone **4**. To test this hypothesis we treated ketone **3** separately under the same conditions used in the base-catalyzed rearrangement of the dienol **1**, and indeed ketone **3** was observed to isomerize in the presence of base exclusively and quantitatively to ketone **4**. In order to definitely establish ketone **3** as an intermediate it was necessary to examine the following conditions governing this base-catalyzed rearrangement: base strength, temperature, and reaction time or reflux period (Table I).

TABLE I

EFFECT OF BASE, TEMPERATURE, AND REFLUX PERIOD ON THE REARRANGEMENT OF 1,2,3,4,5-PENTAPHENYL-2,4-CYCLOPENTADIEN-1-OL (1) TO 2,3,4,5,5-PENTAPHENYL-2-CYCLOPENTEN-1-ONE (4)

Base–solvent	Temp, °C	Time, hr	Yield of 4, %
NaOH–IAE[h]	173	8	90
NaOH–IAE	95	8	10[a]
NaOH–IAE	50	20	0[b]
NaOH–IAE	23	20	0[b]
Na_2CO_3–IAE	173	7	86[c]
$NaHCO_3$–IAE	173	7	80[d]
$NaNH_2$–IAE	173	8	90
HMPA	173	3	88[e]
HMPA	95	3	10[f]
N,N-DEF	173	3	66[g]

[a] Also obtained were 84% **1** and 6% **3**. [b] Quantitative recovery of **1**. [c] Also obtained were 11% **1** and 3% **3**. [d] Also obtained were 13% **1** and 7% **3**. [e] Also obtained were 10% **1** and 2% **3**. [f] Also obtained were 87% **1** and 3% **3**. [g] Also obtained were 27% **1** and 7% **3**. [h] Isoamyl ether.

As can be seen from Table I, the rearrangement of dienol **1** to ketone **4** proceeds with weak as well as with strong bases, and also in cases where the solvent used can act as a base. The overall effect of the base strength observed on this rearrangement was only on the rate of production of ketone **4**. The decrease in the rate of production of ketone **4** at 95° in either IAE or HMPA is believed to be due to the fact that higher temperatures are required to facilitate the phenyl migration,[1b] which is the first step in this overall rearrangement.

The effect of the reflux period was investigated by adding the dienol **1** as a solid all at once to a mixture of IAE and sodium hydroxide at 173° and taking samples

by syringe at various times (Table II) which were subjected to both infrared and glpc analysis. The sample

TABLE II
THE ISOMERIZATION REACTION OF 1,2,3,4,5-PENTAPHENYL-2,4-CYCLOPENTADIEN-1-OL IN ISOAMYL ETHER WITH SODIUM HYDROXIDE

Reaction time, min	% ratio Dienol 1	Ketone 3	Ketone 4
15	89.9	10.1	0.0
45	86.9	13.1	0.0
75	78.1	16.1	5.8
90	71.6	21.0	7.4
110	67.5	22.5	10.0
135	63.3	24.9	11.8
150	60.0	25.7	14.3
180	53.7	24.2	22.1
240	38.6	20.2	41.2
315	21.3	11.2	67.5
380	14.7	7.9	77.4
440	6.8	4.0	89.2
470	0.0	0.0	100.0

taken after 10 min showed only two products in the ir with peaks at 3500 and 1760 cm^{-1} corresponding to the dienol **1** and ketone **3**, respectively. This was borne out by glpc analysis which also showed only two peaks corresponding to the same compounds. However, analysis of all samples taken after 60 min and up to 455 min showed three distinct compounds to be present with peaks in the ir at 3500, 1760, and 1720 cm^{-1}, corresponding to the dienol **1**, ketone **3**, and ketone **4**, respectively. Analysis of these samples by glpc also showed three distinct peaks corresponding to the same three compounds. Using fractional crystallization techniques it was possible to isolate ketone **3** in pure form from each of these intermediate samples. Samples taken after 455 min all showed only one peak in both the ir and glpc, corresponding to ketone **4**. Plotting the ratio of the products obtained from glpc analysis *vs.* time (Figure 1) shows clearly that ketone **3** is produced during the reaction and that it then slowly disappears with increased reaction time.

Based upon the information obtained from this investigation the mechanism proposed for the base-catalyzed rearrangement of dienol **1** is shown in Scheme IV. One consideration which should be mentioned is that the electron density is not equally distributed at the various sites in anion **7**, but according to Pariser–Parr–Pople SCF π calculations the electron density should be distributed in the following order: O (1.58 e) > C_2 (1.32 e) > C_4 (1.27 e), placing the largest electron density on oxygen. Thus, owing to the differences in the distribution of the electron densities, one might expect to obtain ketone **3** as the major product of this reaction because protonation of the anion **7** should take place at the more electron-dense sites, oxygen, which produces enol **2** which tautomerizes to ketone **3**, and C_2, which produces ketone **3** directly, while ketone **4** is formed in only minor amounts from protonation at the least electron-dense site C_4. This would be the course of the reaction if anion **7** were being internally protonated and the products thus formed were unreactive. Figure 1 shows that this is indeed exactly the situation which occurs in the early stages of the reaction. This mechanism suggests that ketone **3** is the

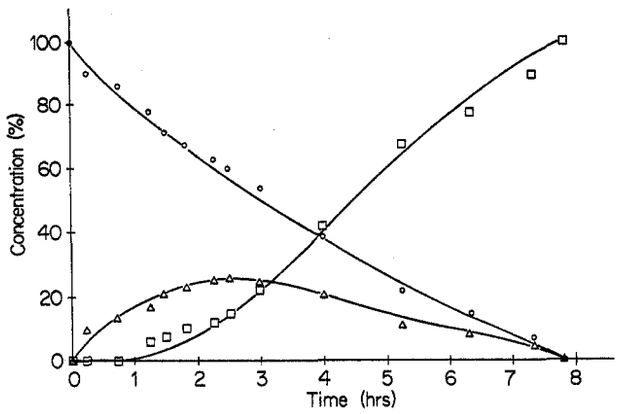
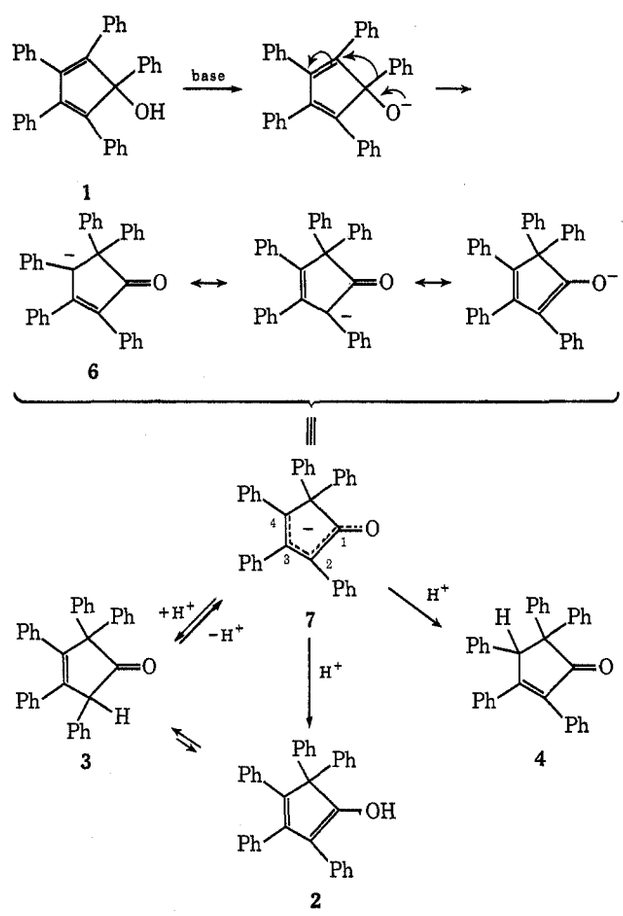


Figure 1.—Variation with time of the concentration of dienol **1**, ketone **3**, and ketone **4** at 173° in isoamyl ether with sodium hydroxide: ○, dienol **1**; △, ketone **3**; □, ketone **4**.

SCHEME IV



kinetically controlled product and ketone **4** the thermodynamically controlled product of this reaction.

There are three possible sources for internal protonation: the water formed from the reaction of the sodium hydroxide with the dienol **1**, the unreacted dienol **1** itself, and ketone **3** formed in the initial stages of the reaction. It appears that the water formed is not an important source of protons for the initial protonation process, because the minute amount of water formed could not survive long enough in the reaction medium owing to the high reaction temperature (173°), but that both the starting dienol **1** and the initially formed ketone **3** are the main sources of protons for the inter-

nal protonation process. To verify that the water formed does not play an important role in the protonation process, we investigated in detail the reaction of the dienol **1** with one of the bases previously mentioned, sodium amide. Treatment of the dienol **1** with a catalytic amount of sodium amide produced a small amount of anion **7** and ammonia. Following the path of this reaction by glpc analysis and comparing the results obtained with the reaction profile of the dienol **1** and sodium hydroxide gave exactly the same results with respect to the products produced and the intermediate observed; the absence of water did not in any way affect the product distribution. These observations also rule out the possibility of an external quenching mechanism taking place when the samples were removed from the reaction vessel and added to water, because, if external quenching were responsible for the formation of the products and there was no internal quenching of anion **7**, then the product distribution obtained should not be time dependent and the product ratio of ketone **3** to ketone **4** would be constant and time independent. This is contrary to what has been observed and thus the mechanism proposed in Scheme IV appears to be the most appropriate.

Experimental Section

Rearrangement of 1,2,3,4,5-Pentaphenyl-2,4-cyclopentadien-1-ol (1) to 2,3,4,5,5-Pentaphenyl-2-cyclopenten-1-one (4). I. In Isoamyl Ether (IAE) with Sodium Hydroxide. A. At 173°.—Into a 100-ml three-necked round-bottomed flask equipped with a reflux condenser and a magnetic stirrer was placed 50 ml of isoamyl ether and 3.0 g (75 mmol) of solid sodium hydroxide and the mixture was heated to the boiling point of the ether (173°). At this point 3.0 g (6.5 mmol) of 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol (**1**)[1a,4] was added as a solid all at once. The resulting mixture was refluxed for 8 hr, cooled to room temperature, and then poured into 100 ml of water. The organic layer was separated, washed several times with water, and dried over anhydrous magnesium sulfate and the solvent was removed under vacuum to afford a viscous yellow oil, which was crystallized from a mixture of benzene–petroleum ether (bp 30–60°) to give 2.7 g (5.8 mmol, 90%) of pale yellow crystals of 2,3,4,5,5-pentaphenyl-2-cyclopenten-1-one (**4**), mp 169–170° (lit.[1a,5] mp 169–170°). The ir,[5] uv,[5] and nmr[1a] spectral data for this compound agreed with the literature data.

The above experiment was repeated for glpc analysis using the same amount of material and essentially the same experimental set-up except that the flask was also equipped with a serum cap. Samples of 2 ml each were taken at various times (Table II) by inserting a hypodermic syringe through the serum cap. The samples thus removed were placed in separate containers and cooled by means of an ice–water bath. After all the required samples were collected, glpc analysis was carried out using a Bendix Model 2600 gas chromatograph and a Bendix Model 1200 recorder. The glpc was equipped with a 3 ft × 0.25 in. column packed with 3% QF-1 on Chromosorb W (H. P., mesh 100/120) support. Operating conditions were as follows: temperature of inlet, 210°; detector, 255°; injector, 255°; column, 210°; and a He carrier gas flow rate of 80 ml/min. Retention time of the dienol **1** was 6 min 15 sec; of the ketone **3**, 13 min 45 sec; and of the ketone **4**, 15 min 45 sec. Analysis of the peak areas observed were determined by triangulation[6] and the per cent composition represented by these peak areas was then calculated (Table II) and plotted on the same graph *vs.* time (Figure 1). Qualitative infrared analysis of each sample was also performed and for the sample taken after 10 min only two products were observed to be present, the dienol **1** with a hydroxyl peak at 3500 cm^{-1} and ketone **3** with a carbonyl peak at 1760 cm^{-1}. Analysis of all samples taken after 60 min and up to 455 min showed three distinct products to be present, the dienol **1** (hydroxyl peak at 3500 cm^{-1}), ketone **3** (carbonyl peak at 1760 cm^{-1}), and ketone **4** (carbonyl peak at 1720 cm^{-1}). Fractional crystallization techniques using varying mixtures of benzene–petroleum ether allowed separation and isolation of both ketone **3** and ketone **4** from each of these intermediate samples. The physical and spectral data for ketone **3** agreed with the literature.[1a] Analysis of samples taken after 455 min showed only one peak to be present in both the ir and glpc corresponding to ketone **4**. Crystallization of these samples from benzene–petroleum ether afforded 90–96% of ketone **4**, the deviation from 100% probably owing to losses during crystallization and isolation.

B. At Room Temperature (23°).—The above experiment was repeated using the same amount of material and the same experimental set-up except that the temperature used was room temperature. Analysis by both ir and glpc of samples taken in 2-hr intervals over a 20-hr period showed only the dienol **1** to be present. Work-up of the mixture after 20 hr afforded only recovered dienol **1** (99%).

C. At 50°.—Again the above experiment was repeated for 20 hr except that the temperature used was thermostatically maintained at 50 ± 1° by means of a constant-temperature oil bath. The results obtained were exactly the same as those described in B above except that work-up after 20 hr afforded a quantitative recovery of dienol **1**.

D. At 95°.—The above experiment was repeated for 8 hr, this time at a thermostatically controlled temperature of 95 ± 1°. Analysis by ir of the samples taken at 0.5-hr intervals during the 8-hr reaction period showed the presence of three distinct compounds after 1.5 hr, with peaks corresponding to dienol **1** (hydroxyl, 3500 cm^{-1}), ketone **3** (carbonyl, 1760 cm^{-1}),[1a,5,7] and ketone **4** (carbonyl, 1720 cm^{-1}).[1a,5] The composition of this mixture changed very slowly and continuously until after 8 hr glpc analysis still showed three compounds to be present, dienol **1** (84%), ketone **3** (6%), and ketone **4** (10%).

II. In Hexamethylphosphoramide (HMPA). A. At 173°.—Into a 100-ml, three-necked, round-bottomed flask equipped with a reflux condenser and a magnetic stirrer was placed 50 ml of HMPA, bp 90° (3 mm), which was heated to 173 ± 1° by a thermostatically controlled constant-temperature oil bath. At this temperature 1.8 g (3.9 mmol) of dienol **1** was added as a solid all at once, and the mixture was heated for 3 hr, cooled to room temperature, and poured into 100 ml of water. The aqueous solution was extracted twice with benzene, and the benzene solutions were combined, washed with water, dried over anhydrous magnesium sulfate, and concentrated to essential dryness on the rotoevaporator. The viscous yellow oil which resulted was taken up in carbon tetrachloride. A small sample of this solution was removed for glpc analysis while the rest was chromatographed on Woelm acid alumina using carbon tetrachloride as eluent. The first band which separated was collected, concentrated, and crystallized from benzene–petroleum ether, affording 1.5 g (3.2 mmol, 82%) of pale yellow crystals of ketone **4**, mp 169–170°. Further elution of the column with carbon tetrachloride, chloroform, and acetone followed by concentration and work-up did not afford any other organic material. Analysis of the sample removed from the carbon tetrachloride solution by glpc analysis showed 88% of ketone **4**, 10% of dienol **1**, and 2% of ketone **3** to be present.

B. At 95°.—The above experiment was repeated for 3 hr using a temperature of 95 ± 1° (thermostatically controlled) followed by work-up and chromatography. The first band eluted gave 10% of ketone **4**, while continued elution with carbon tetrachloride afforded a second band which upon concentration and crystallization from petroleum ether gave 87% of starting dienol **1**. Analysis by glpc of a sample removed before work-up showed 87% of dienol **1**, 10% of ketone **4**, and 3% of ketone **3**.

III. In *N,N*-Diethylformamide (*N,N*-DEF).—Using the same amount of dienol **1** as reported in IIA above, this experiment was performed as described above for 3 hr using 50 ml of *N,N*-DEF (bp 177–178°) thermostatically controlled at 173°. The product mixture was worked up and chromatographed as described in IIA to give 66% of ketone **4** and 27% of starting dienol **1**. Glpc analysis of a sample removed before work-up showed 27% of dienol **1**, 66% of ketone **4**, and 7% of ketone **3**.

IV. Using Sodium Carbonate and Bicarbonate.—Into a 100-ml, three-necked, round-bottomed flask equipped with a reflux

(4) K. Ziegler and B. Schnell, *Justus Liebigs Ann. Chem.*, **445**, 266 (1925).
(5) C. Dufraisse, G. Rio, and A. Ranjon, *C. R. Acad. Sci.*, **253**, 2441 (1961).
(6) As described in H. M. McNair and E. J. Bonelli, "Basic Gas Chromatography," Varian Associates, Palo Alto, Calif., 1969, p 154.
(7) R. Breslow and H. W. Chang, *J. Amer. Chem. Soc.*, **83**, 3727 (1961).

condenser and a magnetic stirrer was placed 50 ml of IAE and 2.0 g (19 mmol) of anhydrous sodium carbonate, and the mixture was heated to 173°. At this point 2.0 g (4.3 mmol) of dienol **1** was added as a solid all at once and the resulting mixture was heated at 173° for 7 hr. After this time a small sample was removed, worked up as previously described, and then chromatographed on Woelm acid alumina using carbon tetrachloride as eluent. The first band which was eluted afforded 1.7 g (3.7 mmol, 86%) of ketone **4**, while the second band gave 0.2 g (0.43 mmol, 10%) of recovered unreacted dienol **1**. Glpc analysis of the sample removed showed 10.4% of dienol **1**, 86.2% of ketone **4**, and 3.4% of ketone **3** to be present.

Repeating the above experiment but using sodium bicarbonate as the base afforded after work-up 1.6 g (3.4 mmol, 80%) of ketone **4** and 0.2 g (0.52 mmol, 12%) of dienol **1**. Glpc analysis of the sample removed showed 12.7% of dienol **1**, 80.5% of ketone **4**, and 6.8% of ketone **3**.

V. Using Sodium Amide.—Into a 100-ml, three-necked, round-bottomed flask equipped with a reflux condenser, a magnetic stirrer, a nitrogen inlet tube, and a serum cap was placed 40 ml of IAE which was heated to 173°. At this point a mixture of 0.008 g (0.2 mmol) of sodium amide and 1.0 g (2.2 mmol) of dienol **1** was added all at once. (Caution! This experiment should only be performed on a small scale and the stirring should be stopped until after the addition. Ammonia is liberated very vigorously at this temperature.) Samples of 1 ml each were taken at various times by inserting a hypodermic syringe through the serum cap. These samples were analyzed exactly the same as described in IA. Comparison of the glpc results obtained for these samples with the results obtained in IA showed them to be identical.

Rearrangement of 2,2,3,4,5-Pentaphenyl-3-cyclopenten-1-one (3) to 2,3,4,5,5-Pentaphenyl-2-cyclopenten-1-one (4) in Isoamyl Ether with Sodium Hydroxide.—Into a 100-ml, one-neck, round-bottomed flask equipped with a reflux condenser and a magnetic stirrer was placed 50 ml of IAE and 1.0 g (25 mmol) of sodium hydroxide and the mixture was heated to the boiling point of IAE (173°). At this temperature, 1.0 g (2.1 mmol) of ketone **3**[1a,b] was added as a solid all at once. The heterogeneous mixture was heated for 6 hr, cooled to room temperature, and poured into 100 ml of cold water, and the organic layer was separated, washed several times with 100-ml portions of water, and dried over anhydrous magnesium sulfate. Concentration of this dried solution under vacuum gave a viscous yellow oil which was crystallized from 50 ml of a mixture of benzene–petroleum ether to give a quantitative yield (1.0 g, 2.1 mmol) of pale yellow crystals of ketone **4**, mp 169–170° (lit.[1a,b] mp 169–170°).

Registry No.—**1**, 2137-74-8; **3**, 34759-47-2; **4**, 34759-48-3.

Acknowledgment.—We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Fluorinated Bicyclics. I. Exo-Cis-Bromination of Fluorinated Norbornenes[1]

BRUCE E. SMART

Contribution No. 1984 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

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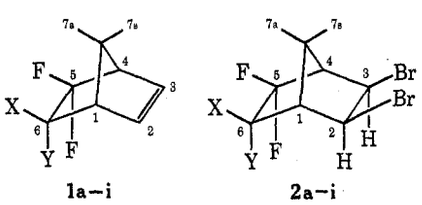
A number of fluorinated norbornenes **1a–h** brominate stereospecifically by a purely radical pathway in methylene dichloride or carbon tetrachloride at 25° to afford exclusively exo-cis dibromides **2a–h**. The radical bromination of 5,5-difluoro-6-*exo*-fluoro-2-norbornene (**1i**) affords a 2.1:1.9 mixture of exo-cis dibromide **2i** and trans dibromide **9**. These results suggest that the stereochemistry of the reaction is directed by endo fluorine substituents. Bromination of 5,5,6,6-tetracyano-2-norbornene (**13**) and *endo-cis*-5,6-dichloro-2-norbornene (**14**) is similarly stereospecific. The nmr spectra of the trifluoronorbornenes **1h** and **1i** and the dibromides **2**, along with dehydrobromination results, are discussed.

The reaction of bicyclo[2.2.1]-2-heptene (norbornene) with molecular bromine in CH_2Cl_2 at 25° readily affords a plethora of rearrangement products characteristic of reactions involving norbornyl cation intermediates.[2] It was therefore surprising to find 5,5,6,6-tetrafluoro-2-norbornene (**1a**) inert under these conditions, although bromination readily takes place under radical conditions (illumination) to afford exclusively *exo-cis*-2,3-dibromo-5,5,6,6-tetrafluoronorbornane (**2a**). A number of fluorinated norbornenes have been prepared and brominated to further investigate the scope of this reaction.



1a–i **2a–i**

a, X = Y = F
b, X = Y = CF_3
c, X = Y = Cl
d, X = CF_3; Y = F
e, X = F; Y = CF_3
f, X = CF_2Cl; Y = Cl
g, X = Cl; Y = CF_2Cl
h, X = H; Y = F
i, X = F; Y = H

Results

Norbornene Syntheses.—The norbornenes **1a–i** are readily prepared from the cycloaddition of the appropriate fluoro olefin and cyclopentadiene. The cycloaddition of cyclopentadiene and hexafluoropropene has been reported, although no description of the isomeric product mixture was presented.[3] At 155° for 72 hr a 53:47 mixture of **1d,e** (by nmr) was obtained. The structure of the respective isomers could not be unambiguously assigned by nmr. These derivatives

(1) Presented in part at the 164th National Meeting of the American Chemical Society, New York, N. Y., Aug 1972.

(2) (a) D. R. Marshall, J. R. Robinson, *et al.*, *Can. J. Chem.*, **49**, 885 (1971); (b) H. Kwart and L. A. Kaplan, *J. Amer. Chem. Soc.*, **76**, 4072 (1954).

(3) H. P. Braendlin, *et al.*, *J. Amer. Chem. Soc.*, **84**, 2112 (1962).