Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.41; H, 6.35.

4-Oxo-6,6-dimethyl-4,5,6,7-tetrahydrocoumaran (11d).—Spectra were identical with that reported by Ichikawa, *et al.*[12]

Preparation of 1,1-Diacetylcyclopropane (12e).—To a solution of 3.00 g (30 mmol) of acetylacetone in 200 ml of anhydrous ether was added 1 equiv of K^+O^--*tert*-Bu. The reaction mixture was stirred for 2 hr, 11.10 g (30 mmol) of vinyltriphenylphosphonium bromide added, and the mixture stirred overnight. The solid was filtered and washed with 200 ml of ether. The solid was transferred to a Soxhlet and extracted with benzene for 24 hr. The benzene solution was concentrated *in vacuo* and the residue dissolved in ether. The ether solution was refluxed overnight with 5 ml of CH_3I. The white methyltriphenylphosphonium iodide was filtered. The ether filtrate was concentrated *in vacuo* and distilled to give 650 mg of **12e**.[11]

Preparation of 1-Acetyl-1-carbethoxycyclopropane (12d).—To a solution of 2.60 g (0.02 mol) of ethyl acetoacetate in 300 ml of anhydrous ether was added 2.26 g (0.02 mol) of K^+O^--*tert*-Bu. The reaction mixture was stirred at room temperature for 1 hr. To the white flocculent solid was added 7.38 g of vinyltriphenylphosphonium bromide, and the reaction mixture stirred for an additional 2 hr. The yellow solid was filtered and washed with 200 ml of anhydrous Et_2O. The yellow solid was placed in a Soxhlet extractor and extracted with toluene for 24 hr. The yellow toluene solution was concentrated *in vacuo* and the residue dissolved in 100 ml of ether and refluxed overnight with 5 ml of CH_3I. The white methyltriphenylphosphonium iodide was filtered, 4.96 g; melting point and spectra were identical with that of an authentic sample. The ether filtrate was concentrated *in vacuo* and distilled to give 1.84 g (58%) of **12d**; vpc retention time and spectra were identical with those of an authentic sample prepared by the method of Perkin.[15]

General Procedure for the Base-Catalyzed Rearrangement of Cyclopropanes.—In a sealed nmr tube was placed 80 mol % of cyclopropane and 20 mol % of triphenylphosphine or triethylamine. The tube was heated in a silicone oil bath at 200 ± 5°. The reaction was monitored by nmr for the appearance of 4,5-dihydrofuran and the disappearance of cyclopropane. The yield was determined by nmr and then checked by vpc upon completion of the reaction. All cyclopropane samples were heated at 200° without base present for the same period of time to determine whether or not the furan arose by a thermal pathway. None of the cyclopropanes showed any change after the heating period.

2-Phenyl-3-carbethoxy-4,5-dihydrofuran (11b).—Spectra and vpc retention time were identical with those of a previous sample of **11b**.

2-Methyl-3-benzoyl-4,5-dihydrofuran (11c) and 2-Phenyl-3-acetyl-4,5-dihydrofuran (11c').—Spectra and vpc retention time were identical with those of a previous sample of **11c** and **11c'**.

2-Methyl-3-acetyl-4,5-dihydrofuran (11e): ν^{neat} 1660 (m, >=O), 1230 cm^{-1} (s, COC); nmr ($CDCl_3$) 2.21 (s, 6, $COCH_3$ and $CH_3C(O)$=), 2.93 (t, 2, J = 10.0 Hz, OCH_2CH_2), 4.40 (t, 2, J = 10.0 Hz, OCH_2CH_2); mass spectrum m/e 126.

Anal. Calcd for $C_7H_{10}O_2$: C, 66.64; H, 7.99. Found: C, 66.56; H, 7.94.

2-Methyl-3-carbethoxy-4,5-dihydrofuran (11f): ν^{neat} 1700 (s, α,β-unsaturated >=O), 1650 (s, >=O), 1200 cm^{-1} (s, COC); nmr ($CDCl_3$) 1.23 (t, 3, J = 7.0 Hz, OCH_2CH_3), 2.18 (t, 3, J = 1.2 Hz, CH_3), 2.81 (t, 2, J = 10.0 Hz, OCH_2CH_2, 4.18 (q, 2, J = 7.0 Hz, OCH_2CH_3), 4.33 (t, 2, J = 10.0 Hz, OCH_2-CH_2); mass spectrum m/e 156.

Anal. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.71. Found: C, 61.86; H, 7.63.

Registry No.—**4a**, 28638-64-4; **4b**, 28638-65-5; **4c**, 28638-66-6; **4d**, 28638-67-7; **4e**, 28638-68-8; **4f**, 28638-69-9; **4g**, 28638-70-2; **6a**, 28638-71-3; **6b**, 28638-72-4; **6c**, 28638-73-5; **9b**, 28638-74-6; **9c**, 28638-75-7; **9d**, 28638-76-8; **10a**, 28638-77-9; **10d**, 28638-78-0; **11a**, 28638-79-1; **11c**, 28638-80-4; **11c'**, 28638-81-5; **11e**, 5831-64-1; **11f**, 2986-03-0; **12c**, 5186-09-4.

Acknowledgment.—The authors wish to gratefully acknowledge the support of Public Health Service Grant CA-11000-06.

(15) T. R. Marshall and W. H. Perkin, *J. Chem. Soc.*, **59**, 880 (1891).

Double-Bond Migration in 1-Methyl-4-(carbethoxymethylene)phosphorinane[1]

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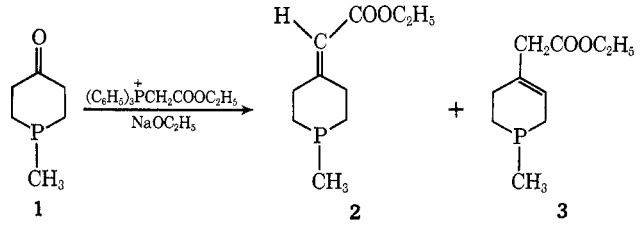
Received October 5, 1970

The product from the Wittig reaction of 1-methyl-4-phosphorinanone with carbethoxymethylenephosphorane was unexpectedly a mixture of 1-methyl-4-(carbethoxymethylene)phosphorinane (**2**) and 1-methyl-4-carbethoxymethyl-1,2,5,6-tetrahydrophosphorin (**3**). However, reaction of the ketone with the carbanion of triethylphosphonoacetate gave only **2**. This compound was found to be readily isomerized to **3** under basic or thermal conditions, accounting for the formation of the isomer mixture in the Wittig procedure. The same conditions were without effect on ethyl cyclohexylideneacetate, although the thermal treatment did cause extensive rearrangement of *N*-methyl-4-(carbethoxymethylene)piperidine. The pronounced tendency for the phosphine and the amine to rearrange was attributed to intramolecular catalysis of enolization by the basic centers.

One of the valuable features of the Wittig olefin synthesis is the specificity with which the product is obtained; isomer formation is not known to occur in this process. However, we found that 1-methyl-4-phosphorinanone (**1**), on reaction with the phosphorane prepared *in situ* from carbethoxymethyltriphenylphosphonium bromide and sodium ethoxide, gave an unsaturated product consisting of almost equal amounts of two isomers, **2** and **3**. This observation prompted an investigation of the factors responsible for the formation of isomer **3** and a comparison of the behavior of ketone **1** with that of cyclohexanone and of *N*-methyl-4-piperidone in this reaction.



1 **2** **3**

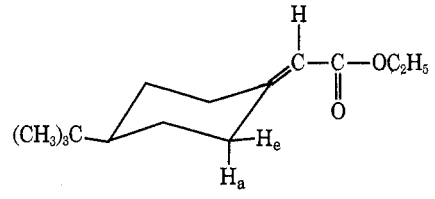
The study was facilitated by the obtention of pure **2** in 55% yield when the ketone was reacted with the carbanion of triethylphosphonoacetate.[2] The structure of the product was easily established by its spectral features. The uv spectrum was that of an α,β-unsaturated

(1) Supported by Public Health Service Research Grant CA-05507 from the National Cancer Institute.

(2) W. S. Wadsworth, Jr., and W. D. Emmons, *J. Amer. Chem. Soc.*, **83**, 1733 (1961). This reagent is preferred for introducing the carbethoxymethylene group into cyclic ketones.[3]

(3) (a) S. Sugasawa and H. Matsuo, *Chem. Pharm. Bull.*, **8**, 819 (1960); (b) S. Trippett and D. W. Walker, *Chem. Ind. (London)*, 990 (1961).

ester ($\lambda_{max}^{ethanol}$ 210 mμ, ε 13,700), as was the ir spectrum ($\nu_{C=O}$ 1716 and intense $\nu_{C=C}$ at 1645 cm^{-1}). The nmr spectrum, which confirmed the assignment, was of special interest in that the two allylic CH_2 groups had quite different chemical shifts (δ 3.15 and 2.24 ppm). This is due to the anisotropic effect of the carbonyl group, deshielding that CH_2 which is cis to it. That *both* protons of the cis CH_2 are affected is significant, for in the related cyclohexylidene derivatives **4**[4] and **5**,[5]



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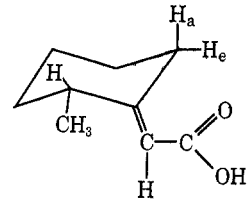

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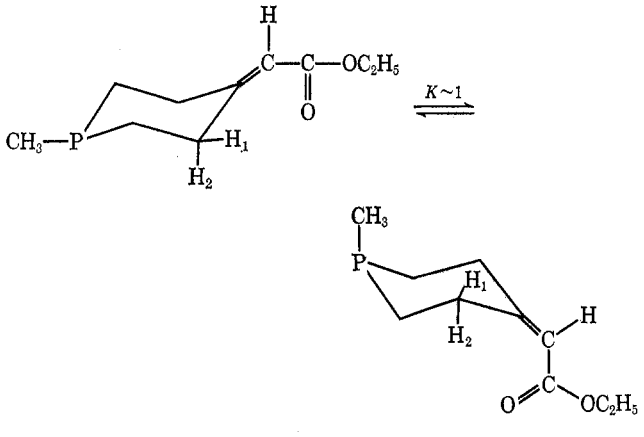
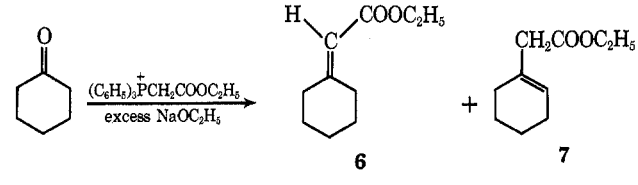
only the cis proton in the equatorial position is deshielded by carbonyl (to roughly the same extent seen in **2**). The different behavior for **2** can be related to the failure of the CH_3 group on phosphorus, which is configurationally stable, to exert a preference for the equatorial over the axial position.[6] The conformational equilibrium is not biased and permits no distinction between the equatorial and axial protons at the allylic position with regard to the deshielding effect of the carbonyl group.



The presence of **3** in the product from the reaction of **1** with carbethoxymethylenephosphorane (either preformed or generated *in situ*) was evident from the gas chromatogram, as well as from the ir spectrum which showed a second C=O band at higher frequency (1738 cm^{-1}). Isomer **3** gave a different nmr spectrum, possessing a singlet (δ 2.88, broad) attributable to CH_2 exo to the ring. The rearrangement was then found to have occurred during the distillation, for gas chromatography showed that at the conclusion of the reaction prior to this step only **2** was present.

That compound **2** was thermally unstable relative to **3** was established by heating pure **2** for 5 hr at 170° whereupon an isomer mixture of 86% **3**–14% **2** resulted. No change occurred on further heating. Base also caused rearrangement; holding an ethanolic solution of **2** (0.5 *M*) and sodium ethoxide (8×10^{-3} *M*) at 35° gave after 13 days a 1:1 isomer mixture, while after 64 days the mixture consisted of 86% **3**–14% **2**. Traces of base remaining in the crude product to be distilled, in combination with high pot temperatures, could therefore bring about the rearrangement observed in the purification of the Wittig product. That the phosphonate carbanion procedure gave a pure product may be due to the routine inclusion in this procedure of a water-washing step, which would have removed residual base prior to the distillation. While the difference between the two procedures was not further investigated, it is clear that the phosphonate carbanion method is preferred for the synthesis of **2**, giving a higher yield of pure product.

In a classical study of many years ago,[7] the tendency of cyclohexylidene esters (*e.g.*, **6**) to undergo base-catalyzed rearrangement was established. Nevertheless, cyclohexanone has been reported to form **6** in the Wittig reaction without the production of isomer[2,3] and we have confirmed this. However, when a small excess of sodium ethoxide (10%) was intentionally used to generate the phosphorane, the product both before and after distillation contained about 30% isomer **7**.



6 **7**

Its presence was readily detected by gas chromatography and by ir spectroscopy ($\nu_{C=O}$ 1739 cm^{-1}). That the cyclohexylidene system was nevertheless much less prone to rearrange than was the phosphine analog **2** was noted from the failure of the same thermal or basic treatment so destructive to **2** to have any effect on **6**.

The nitrogen counterpart **8** of phosphine **2** was obtained free of isomer by the phosphonate carbanion method applied to *N*-methyl-4-piperidone. It was characterized by spectral features similar to those useful for **2**, including the specific deshielding by carbonyl of the allylic CH_2 cis to it. While **8** was unaffected by the basic treatment causing phosphine **2** to rearrange, it did undergo thermal rearrangement, providing a mixture of 75% **9**–25% **8** after 5 hr at 170°.

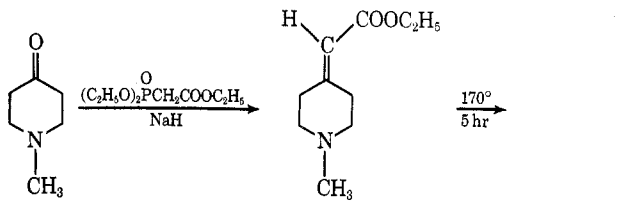
Apparently, the presence of similarly located basic atoms is the common feature in phosphine **2** and amine **8** leading to their rapid rearrangement under conditions not affecting their carbocyclic counterpart **6**. The rearrangment is associated with the tendency for the resonance-stabilized enolate ion to form, by loss of a proton at the allylic position. That those compounds with a basic center rearrange so rapidly suggests the

(4) H. O. House, W. L. Respess, and G. M. Whitesides, *J. Org. Chem.*, **31**, 3128 (1966).

(5) H. Hauth, D. Stauffacher, P. Niklaus, and A. Melera, *Helv. Chim. Acta*, **48**, 1087 (1965).

(6) H. E. Shook, Jr., and L. D. Quin, *J. Amer. Chem. Soc.*, **89**, 1841 (1967); to be treated more fully in a forthcoming paper (L. D. Quin and J. H. Somers).

(7) G. A. R. Kon and R. P. Linstead, *J. Chem. Soc.*, 1269 (1929); G. A. R. Kon, R. P. Linstead, and G. W. R. Maclennan, *ibid.*, 2454 (1932).



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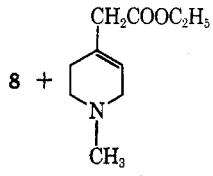

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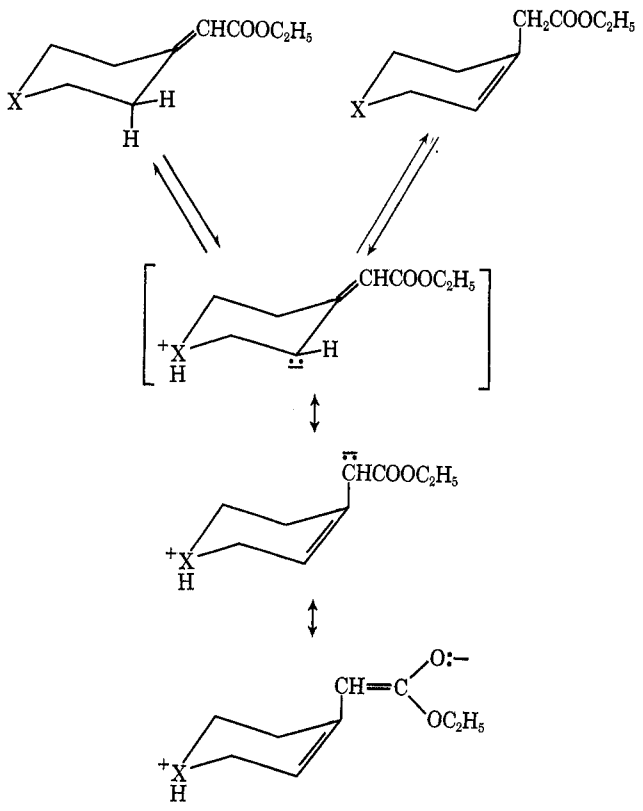
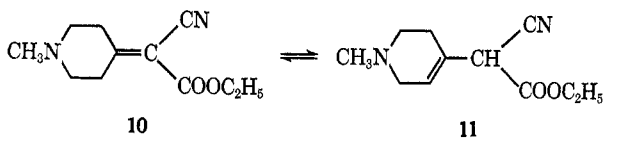
participation of this center in the enolization. This may be expressed by the intramolecular proton transfer process shown below.



X = CH_3N or CH_3P

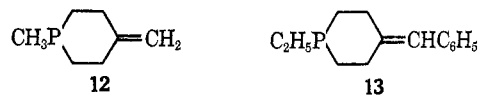
Mention is made of such intramolecular catalysis of enolization to explain the pronounced tendency of compound **10** to rearrange to **11**,[8] a property absent in



10 11

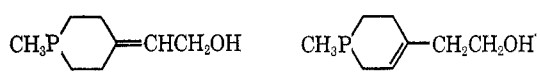
the carboxyclic analog.[9] The greater stability of compounds **3** and **9**, with the double bond endo, than of their isomers with the exo double bond (**2** and **8**, respectively), is not unexpected, based on the numerous observations of the same phenomenon for cyclohexane derivatives.[7,10] The novel feature of the present study is the more pronounced tendency of the phosphine system to undergo the rearrangement, leading to the unusual result of the formation of an isomer mixture in a Wittig product.[11]

Two other Wittig reaction were performed with 4-phosphorinanones without the formation of isomerized material. With methylenetriphenylphosphorane, ketone **1** gave the expected product **12**, while 1-ethyl-4-phosphorinanone gave only **13** with benzylidenetriphenylphosphorane. The allylic protons of **13** appeared as a 4-H broad multiplet; the phenyl group did not cause their differentiation as the carbonyl did in **2**. While the rearrangement would be expected to be slow with these compounds lacking the capability of forming the resonance-stabilized enolate, another factor needs also to be considered. Phosphorane generation in each case requires the use of stronger base (*n*-butyllithium) than the sodium ethoxide used for generating the more stable carbethoxymethylene ylide. Following each condensation, the reaction mixture was washed with water, thus removing residual base which might promote rearrangement during product distillation. These experiments suggest that the problem of isomer formation in Wittig reactions of phosphorinanones may be limited to special cases and may be solved by use of modified isolation procedures or of the phosphonate carbanion method.



12 13

In one attempted Wittig preparation of **2**, a product containing only 10% of this isomer (with 90% **3**) was obtained. This mixture was subjected to lithium aluminum hydride reduction to form a mixture of unsaturated alcohols **14** and **15**, used in previously reported work.[12] The reduction proceeded in good yield with retention of the starting isomer ratio.



14 15

Experimental Section

All operations involving phosphines were conducted in a nitrogen atmosphere. 1-Methyl-4-phosphorinanone (**1**) was prepared as described previously.[6] 1,2-Dimethoxyethane was distilled over sodium hydride; ethanol was digested with calcium oxide and then subjected to azeotropic distillation with benzene. Ir spectra were obtained with Perkin-Elmer 137 or 237 spectrophotometers, uv spectra with a Beckman DB-G spectrophotometer, and nmr spectra with a Varian A-60 spectrometer. Nmr chemical shifts are relative to tetramethylsilane as internal standard. Gas chromatography (gc) was performed with a Varian-Aerograph Model 202-1B instrument, using a 5 ft by 0.25

(8) S. M. McElvain and R. E. Lyle, *J. Amer. Chem. Soc.*, **72**, 384 (1950).

(9) E. Vargha and I. Mester, *Stud. Univ. Babes-Bolyai, Ser. Chem.*, 127 (1962); *Chem. Abstr.*, **61**, 2983 (1964).

(10) For recent discussions, see P. Coppens, E. Gil-Av, J. Herling, and J. Shabtai, *J. Amer. Chem. Soc.*, **87**, 4111 (1965); N. L. Allinger, J. A. Hirsch, M. A. Miller, and I. J. Tyminski, *ibid.*, **90**, 5773 (1968).

(11) This appears not to be an isolated instance of intramolecular participation of tertiary phosphorus in enolization, as we have observed other effects explicable on the same basis. Thus, in connection with another study to be reported in full elsewhere, we have found that ketone **1** can be extensively deuterated at the 3,5 positions merely by exposing it to a dioxane–D_2O mixture at room temperature. 4-Methylcyclohexanone was not deuterated in this medium: L. D. Quin and J. J. Breen, unpublished results.

(12) L. D. Quin and H. E. Shook, Jr., *J. Org. Chem.*, **32**, 1604 (1967).

in. stainless steel column packed with 20% SE-30 on 60–80 mesh acid-washed Chromosorb W. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Synthesis of 1-Methyl-4-(carbethoxymethylene)phosphorinane (2).—The carbanion of triethylphosphonoacetate (6.4 g, 0.0285 mol) was prepared by adding it to a suspension of 1.15 g (0.0285 mol) of sodium hydride (56.9% dispersion) in 60 ml of 1,2-dimethoxyethane. The temperature was kept below 20° during the addition (45 min), following which the mixture was stirred at room temperature for 1 hr. To this solution was added 4.0 g (0.0285 mol) of 1-methyl-4-phosphorinanone (1) over a 20-min period, maintaining the temperature below 30°. The mixture was stirred additionally for 30 min, during which time a viscous semisolid precipitated. The entire mixture was taken up in excess water and the solution extracted with three 250-ml portions of ether. The extracts, after drying over magnesium sulfate, were stripped of solvent on a rotary evaporator, and the residue was distilled to give 3.7 g (55%) of **2** at 58–59° (0.03 mm), pure by gc: uv $\lambda_{max}^{95\%\ EtOH}$ 210 mμ (ε 13,700); ir (neat), $\nu_{C=O}$ 1716 (strong), $\nu_{C=C}$ 1645 cm^{-1} (moderately strong); nmr ($CDCl_3$) δ 5.69 (broad s, 1, C=CH), 4.12 (q, 2, J = 7 Hz, OCH_2CH_3), 3.15 (m, 2, *cis*-$EtO_2CC{=}C{-}CH_2$), 2.24 (m, 2, *trans*-$EtO_2CC{=}C{-}CH_2$), 1.4–3.4 (m, 2, ring CH_2), 1.12 (t, 3, J = 7 Hz, OCH_2CH_3), 0.90 ppm (d, **3**, J_{PCH} = 3.5 Hz, PCH_3).

Anal. Calcd for $C_{10}H_{17}PO_2$: C, 59.98; H, 8.55; P, 15.46. Found: C, 59.73; H, 8.53; P, 15.62.

Reaction of Carbethoxymethylenetriphenylphosphorane with 1-Methyl-4-phosphorinanone (1).—The phosphorane was prepared from 17.0 g (0.040 mol) of carbethoxymethyltriphenylphosphonium bromide and a solution of 0.81 g (0.0356 g-atom) of sodium in 80 ml of ethanol. After being stirred for 1 hr at room temperature, the solution was treated with 5.0 g (0.0356 mol) of **1** and the mixture was stirred for 7 days at room temperature, conditions found useful for reactions with cyclic ketones.[3a] Periodic and final analysis by gc showed the presence of **2** as the only significant product. Solvent was then removed on a rotary evaporator, and the residual oil taken up in 60 ml of ether. After refrigeration overnight, triphenylphosphine oxide precipitated and was removed by filtration. Solvent was stripped and the residue again analyzed by gc, revealing only **2** as the major product. Distillation then gave 1.05 g (15%) of product at 88–90° (1.5 mm), shown by gc to contain 45% **3**–55% **2**. The ir spectrum contained a second $\nu_{C=C}$ for **3** at 1738 cm^{-1}.

A higher yield of the isomer mixture was obtained using preformed carbethoxymethylenetriphenylphosphorane. A solution of 12.5 g (0.0358 mol) of the phosphorane in 80 ml of ethanol was treated with 5.0 g (0.0356 mol) of ketone **1** and the solution stirred for 7 days at room temperature. Work-up as before gave 2.2 g (31%) of product distilling at 63–65° (0.03 mm), consisting of 37% **3**–63% **2**. Gc monitoring again revealed the presence of no **3** prior to the distillation.

Base Catalysis of Rearrangement of 1-Methyl-4-(carbethoxymethylene)phosphorinane (2).—To a 5-ml volumetric flask was added 0.5005 g (0.0025 mol) of **2** and 1 ml of 0.040 *M* ethanolic sodium ethoxide. The mixture was diluted to the mark with ethanol and placed in a constant temperature bath at 35°. The solution was analyzed periodically by gc. After 13 days, the solution contained equal amounts of **2** and **3**, and after 64 days 84% **3**–16% **2**.

Thermal Rearrangement of 2.—In each of several capillary tubes was placed 10 μl of **2**. These were sealed and placed in an oil bath at 170 ± 1°. Periodically, a tube was withdrawn and chilled, and its contents were analyzed by gc. After 5 hr, a mixture of 86% **3**–14% **2** had been reached and was unchanged in samples heated several additional hours.

A 1:5 mixture of **2** and **3** (2.65 g) was held in a 150° bath for 36 hr. The material was distilled, but only 0.51 g was obtained, bp 86° (0.45 mm), since extensive decomposition had occurred. Gc showed the product to be 93% **3**–7% **2**. The purity was sufficient to make spectral measurements for **3**: uv $\lambda_{max}^{95\%\ EtOH}$ 206 mμ (ε 4500); ir (neat) $\nu_{C=O}$ 1736, $\nu_{C=C}$ 1653 (weak) cm^{-1}; nmr ($CDCl_3$) δ 5.59 (s, 2, C=CH), 4.08 (q, 2, J = 7 Hz, OCH_2CH_3), 2.88 (broad s, 2, CH_2COOR), 1.3–2.5 (m, 6, ring protons), 1.16 (t, 3, J = 7 Hz, OCH_2CH_3), 0.89 ppm (d, 3, J_{PCH} = 3.5 Hz, PCH_3).

Ethyl Cyclohexylideneacetate (6).—The carbanion from triethylphosphonoacetate (11.2 g, 0.05 mol) was prepared as described previously and treated with 4.9 g (0.05 mol) of cyclohexanone. The same work-up procedure was used, and the product (4.7 g, 56%) distilled at 34.5–35° (0.11 mm) [lit.[2] bp 89–90° (10 mm)]. No isomer **7** was indicated by gc: uv $\lambda_{max}^{95\%\ EtOH}$ 221 mμ (ε 13,300) [lit.[3] 219 mμ (ε 13,500)]; ir (neat) $\nu_{C=O}$ 1720 (strong), $\nu_{C=C}$ 1650 (moderately strong); nmr (neat) δ 5.62 (broad s, 1, C=CH), 4.16 (q, 2, J = 7 Hz, OCH_2CH_3), 2.84 (m, 2, *cis*-$EtO_2CC{=}C{-}CH_2$), 2.18 (m, 2, *trans*-$EtO_2CC{=}C{-}CH_2$), 1.45–2.85 (m, 4, other ring methylenes), 1.28 ppm (t, 3, J = 7 Hz, OCH_2CH_3).

6 was also prepared in 33% yield from preformed carbethoxymethylenetriphenylphosphorane (17.4 g, 0.05 mol) and cyclohexanone (4.9 g, 0.05 mol) in ethanol (100 ml) for 7 days at room temperature. Triphenylphosphine oxide was precipitated from the residue left from solvent stripping by adding ether and refrigerating. The distilled product (2.8 g) was free of **7** by gc and had properties identical with those of the above sample.

When the phosphorane was generated *in situ* as in the reaction with ketone **1**, a 40% yield of **6**, free of **7**, was obtained. With an excess of sodium ethoxide (0.055 mol) to the phosphonium salt (0.05 mol) and cyclohexanone (0.05 mol), the product, prior to stripping ethanol solvent, was shown by gc to contain 28% **7**–72% **6**. After work-up as before, the final product contained 30% **7**–70% **6**. The ir spectrum had $\nu_{C=O}$ for **6** at 1718 and for **7** at 1739 cm^{-1}.

Attempted Rearrangement of Ethyl Cyclohexylideneacetate (6).—Conditions for base-catalyzed and thermal rearrangement used for **2** were applied to **6**. Gc revealed the presence of no isomer **7** after 64 days in base, or after 5 hr at 170°.

***N*-Methyl-4-(carbethoxymethylene)piperidine (8).**—Following the procedure already described, triethylphosphonoacetate (11.2 g, 0.05 mol) was converted to its carbanion and reacted with 5.65 g (0.05 mol) of *N*-methyl-4-piperidone. The product (6.3 g, 68%) had bp 44–45° (0.05 mm) and gc revealed no isomer to be present: uv $\lambda_{max}^{95\%\ EtOH}$ 215 mμ (ε 13,900); ir (neat) $\nu_{C=O}$ 1718, $\nu_{C=C}$ 1655 cm^{-1}, both strong; nmr ($CDCl_3$) δ 5.65 (broad s, 1, C=CH), 4.14 (q, 2, J = 7 Hz, OCH_2CH_3), 3.04 (m, 2, *cis*-$EtO_2CC{=}C{-}CH_2$), 2.17–3.69 (m, 4, ring CH_2 including allylic CH_2 trans to COOEt), 2.27 (s, 3, NCH_3), 1.25 ppm (t, 3, J = 7 Hz, OCH_2CH_3).

Anal. Calcd for $C_{10}H_{17}NO_2$: C, 65.54; H, 9.35; N, 7.64. Found: C, 65.30; H, 9.44; N, 7.68.

Preparation of **8** *via* the Wittig method, using *in situ* ylide generation, gave a 50% yield, with no isomer present.

Rearrangement of *N*-Methyl-4-(carbethoxymethylene)piperidine (8).—The technique used for thermal rearrangement of **2** was followed. After 5 hr at 170°, the composition, 25% **8**–75% **9**, had been reached. The basic conditions used for rearranging **2** were without effect on **8** after 64 days.

1-Methyl-4-methylenephosphorinane (12).—To a solution of 0.030 mol of *n*-butyllithium (19.2 ml of 1.6 *M* hexane solution) in 100 ml of anhydrous ether was added 10.7 g (0.030 mol) of methyltriphenylphosphonium bromide over a period of 10 min. The mixture was stirred for 5 hr at room temperature; some yellow solid precipitated. To the mixture was added 2.88 g (0.022 mol) of 1-methyl-4-phosphorinanone (1) in 100 ml of ether. Heat of the reaction caused the ether to reflux. The mixture was held at reflux for 17 hr. A fine precipitate that formed was removed by filtration on Whatman No. 41 paper. The residue was washed with ether. The filtrate was extracted with water; after four 100-ml washes, the water extract was neutral. The ether wash of the solid and the ether layer from the water extraction were combined, dried over magnesium sulfate, and stripped of ether. The residue was distilled, yielding 1.22 g (43%) at 30–40° (5 mm): ir (neat) $\nu_{C=C}$ 1645, $\sigma_{=CH_2}$ 890 cm^{-1}; nmr (neat) δ 4.51 (s, 2, $=CH_2$), 1.2–2.6 (m, 8, ring CH_2 groups), 1.02 ppm (d, 3, J_{PCH} = 3 Hz, PCH_3).

The methiodide, prepared in ether and recrystallized from ethanol, had mp 262.5–264°.

Anal. Calcd for $C_8H_{16}IP$: C, 35.57; H, 5.97; P, 11.47. Found: C, 35.51; H, 6.00; P, 11.52.

1-Ethyl-4-benzylidenephosphorinane (13).—A procedure similar to that used for preparing **12** was employed, consisting of reaction of 0.04 mol of *n*-butyllithium, 13.3 g (0.04 mol) of benzyltriphenylphosphonium bromide, and 4.3 g (0.03 mol) of 1-ethyl-4-phosphorinanone. Distillation gave 3.0 g (46%) of **14**, bp 120–121° (0.5 mm), having a single gc peak; nmr spectrum ($CDCl_3$) δ 7.2 (s, 5, C_6H_5), 6.3 (s, 1, C=CH), 2.2–2.8 (m, 4, allylic CH_2 groups), 0.8–2.0 ppm (m, 9, other ring CH_2 groups and CH_3CH_2).

Anal. Calcd for $C_{14}H_{19}P$: C, 77.02; H, 8.77; P, 14.19. Found: C, 77.27; H, 8.92; P, 14.05.

1-Methyl-4-(2-hydroxyethylidene)phosphorinane (14) and 1-Methyl-4-(2-hydroxyethyl)-1,2,5,6-tetrahydrophosphorin (15).—To a suspension of lithium aluminum hydride (11.4 g, 0.3 mol)

in 300 ml of anhydrous ether was added 23.1 g (0.155 mol) of a mixture of the esters **2** and **3** (1:9) in 100 ml of anhydrous ether. During the 1-hr addition, the mixture was cooled with an ice bath. After refluxing for 3 hr, excess hydride was destroyed by the addition of wet ether (100 ml) and then water (200 ml). The mixture was then stirred for 1 hr. A 5% sodium sulfate solution (400 ml) was added, and the aqueous phase was separated from the organic layer. The aqueous phase was extracted with two 300-ml portions of ether. Removal of the solvent on a rotary evaporator and vacuum distillation of the residue gave 16.3 g (90.0%) of a mixture of alcohols **14** and **15**, bp 90–94° (0.4 mm). On redistillation, a cut with bp 88° (0.35 mm) was taken for analysis: ir (neat) ν_{OH} 3350 (broad, strong), $\nu_{C=C}$ 1670 cm^{-1}; nmr (CD_3COCD_3) δ 5.3–5.7 (m, C=CH), 4.07 (d, J = 7 Hz, C=CHCH_2OH), 3.2–4.2 (m, CH_2CH_2OH and OH), 1.2–2.5 (m, ring CH_2), 0.95 ppm (d, J_{PCH} = 3.0 Hz, PCH_3). Addition of D_2O simplified the 3.2–4.2 multiplet to a triplet (J = 7 Hz) for CH_2CH_2OH; from the area of this and the C=CH-CH_2OH signal, the composition of the mixture was 12% **14**–88% **15**.

Anal. Calcd for $C_8H_{15}OP$: C, 60.74; H, 9.56; P, 19.58. Found: C, 60.74; H, 9.65; P, 19.33.

Registry No.—**1**, 16327-48-3; **2**, 28399-79-3; **3**, 28399-80-6; **6**, 1552-92-7; **8**, 28399-82-8; **12**, 28399-83-9; **12** methiodide, 28399-85-1; **13**, 28399-84-0; **14**, 28405-55-2; **15**, 16469-47-9.

Ferrocene Studies. XIX.[1a] Synthesis of 1,2-Terferrocene[1b,c]

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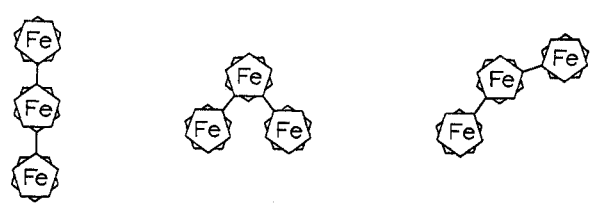
An unequivocal route of synthesis of 1,2-terferrocene (**2**) has been developed. Cyclocondensation of ferrocil (**9**) and acetone was accomplished in 79% yield to give 3,4-diferrocenyl-4-hydroxy-2-cyclopenten-1-one (**10**), which was reduced to 3,4-diferrocenyl-2-cyclopenten-1-one (**11**) by the action of titanium(III) chloride in 95% yield. The cyclopentenone was converted to the corresponding diferrocenylcyclopentenol (**12**). The latter compound proved to be rather sensitive to most reaction conditions, but its dehydration was eventually effected in acceptable yield. The resulting diene was shown to be a single substance, 1,2-diferrocenyl-1,3-cyclopentadiene (**4**). It was converted to its aromatic anion by treatment with *n*-butyllithium, and the former allowed to react with iron(II) chloride in the presence of cyclopentadienyl anion. While ferrocene itself was the major product of the reaction, 1,2-terferrocene also resulted in small yield. The title compound, which is an orange crystalline substance, was characterized by the usual set of spectral data.

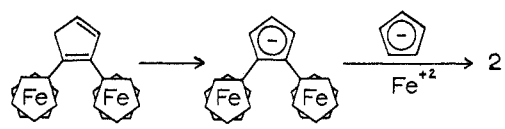
Despite an increasing interest in systems containing directly bonded ferrocene nuclei,[2] only one of the three constitutionally isomeric possibilities for assembly of three ferrocene nuclei (**1**, **2**, and **3**) has heretofore been



1 2 3

synthesized. 1,1′-Terferrocene (**1**) was obtained *via* construction of the central ferrocene nucleus[3] and *via* direct coupling[4] of ferrocene nuclei, but no unequivocal synthesis of either of the two remaining isomeric terferrocenes (**2** and **3**) has been previously reported. Synthesis of 1,2-terferrocene (**2**), however, has been accomplished in this laboratory, and we now report on that work.

Our synthesis scheme pivoted on an unequivocal preparation of 1,2-diferrocenylcyclopentadiene (**4**).[5] In this way structural ambiguity as regards disposition of the two ferrocenyl groups on the central ferrocene nucleus would be avoided. Formation of the central ferrocene nucleus, *via* complexing of **4** and cyclopentadiene (both as anions) about the central iron atom, was projected as the final step. This plan proved to be successful, although the final ferrocene-forming step occurred in disappointingly low yield.



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Our initial approach toward development of a synthesis of **4** lay in attempts to effect intramolecular pinacol formation of the dione **5**, followed by didehydration of the pinacol (**6**). We were, however, unsuccessful in all attempts to achieve this goal. While the majority of these experiments led only to recovery of the starting dione, electrolytic reduction, a technique that worked well with benzophenone to give benzopinacol,[6] appeared promising in that the red color characteristic of **5** was discharged. However, the product of electrolytic reduction (yellow) underwent decomposition (dark brown) during every attempt to isolate it.

Weliky and Gould[7] found that benzoylferrocene was converted to its pinacol with methylmagnesium bro-

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(1) (a) Previous paper: S. I. Goldberg, W. D. Bailey, and M. L. McGregor, *J. Org. Chem.*, **36**, 761 (1971); (b) Abstracts, 19th Southeastern Regional Meeting of the American Chemical Society, Atlanta, Ga., Nov 1967, No. 309; (c) taken in part from the doctoral dissertation submitted by J. G. B. to the Graduate School of the University of South Carolina, July 1967, in partial fulfillment of the requirements for the Ph.D. Degree; (d) Fellow of the National Science Foundation, 1963–1964, and holder of the C. Jules Seideman Memorial Fellowship, 1965–1966, established by Columbia Organic Chemicals Co., Inc.

(2) See D. E. Bublitz and K. L. Rinehart, Jr., *Org. React.*, **17**, 1 (1969), and M. D. Rausch, *Chem. Commun.*, 502 (1970), for accounts of, and references to, much of the work in this area.

(3) K. L. Rinehart, Jr., D. G. Ries, and P. A. Kittle, 149th National Meeting of the American Chemical Society, Denver, Colo., Jan 1964, Abstracts, P-23.

(4) A. N. Nesmeyanov, V. N. Drozd, V. A. Sazonova, V. I. Romanenko, A. K. Prokofev, and L. A. Nikonova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 667 (1963).

(5) Obviously, any combination of the three possible double bond isomers was acceptable. In actual fact, however, only **4** was obtained.

(6) S. Swann, S. W. Briggs, V. C. Neklutin, and A. T. Jerome, *Trans. Electrochem. Soc.*, **80**, 163 (1941).

(7) N. Weliky and E. S. Gould, *J. Amer. Chem. Soc.*, **79**, 2742 (1957).