ether was added 2.76 g. of lithium wire in small pieces over 1.5 hr. After addition of half of the metal an additional 20 ml. of ethanol was added. The ammonia was allowed to evaporate, the residue was neutralized with solid ammonium chloride, and the product was isolated with ether[6b] after the addition of 150 ml. of water. The semisolid residue was distilled affording 0.97 g., b.p. 100° (bath temp.) at 0.2 mm. Crystallization from pentane gave 0.43 g. (38%): m.p. 64–66.5°; $\lambda_{max}^{CCl_4}$ 5.83, 5.97 (C═C), 8.17 (C—O), 8.68, 9.00, 9.88, 14.91 μ; $\delta_{TMS}^{CCl_4}$ = 4.53 (C═C—H, singlet), 3.50 (O—CH_3, singlet), 2.58 p.p.m. (C═C—CH_2, singlet), in the ratio 1.8:6.0:7.9. The analytical sample, m.p. 69–69.5°, was obtained after several recrystallizations from hexane.

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.96; H, 8.39. Found: C, 74.9; H, 8.6.

When 46.8 g. of potassium was utilized in the reduction of 3.31 g. of **1** as described above, the crude crystalline residue could be directly recrystallized to give 2.44 g. (72%) of material, m.p. 68.5–69.5°.

B. **Using 32 G.-Atoms of Metal.**—Reduction of 1.95 g. of **1** in 160 ml. of 1:4 ether–ammonia containing 25 ml. of absolute ethanol with 12.0 g. of potassium as described above gave 1.64 g. (82%) of product, m.p. 66.5–69°, on repeated trituration of the crude crystalline material with pentane. The noncrystalline residues (0.13 g.) displayed λ_{max}^{EtOH} 235 mμ (ε 1100; mol. wt. 188) and 280 (300; mol. wt. 162), indicating less than 0.1% recovery of starting material and formation of methoxytetralin **2** in about 1% yield.[3]

Repetition of this experiment using 2.13 g. of lithium afforded 1.52 g. (76%) of material, m.p. 66.5–69°. The noncrystalline material (0.28 g.) displayed λ_{max}^{EtOH} 235 mμ (ε 1330; mol. wt. 188) and 280 (660; mol. wt. 162), indicating less than 0.2% recovery of starting material and formation of methoxytetralin **2** in about 5% yield.

1(9)-Octal-2,7-dione (**8**)—A solution containing 11.7 g. of bisenol ether **4** in 100 ml. of ethyl acetate; 45 ml. of ethanol, and 30 ml. of 10% aqueous hydrochloric acid was refluxed under nitrogen[6c] for 1.2 hr. The cooled solution was diluted with 200 ml. of water and the product was isolated with ethyl acetate[6b] affording 5.4 g. (54%) of yellow solid: m.p. 170–172.5° after recrystallization from ethyl acetate; $\lambda_{max}^{CHCl_3}$ 5.82 (ketone CO), 6.00 (conj. ketone CO), 6.22 μ (conj. C═C); λ_{max}^{KBr} 2.9–3.7 (OH), 6.27 (conj. CO), 6.52 (conj. C═C),[7] 8.53 (C—O), 7.42, 7.84, 10.87, 11.04, 11.39 μ. An additional recrystallization from ethyl acetate gave the analytical sample, m.p. 174–176°.

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37; neut. equiv., 164. Found: C, 73.2; H, 7.5; neut. equiv., 160.

The peak at 385 mμ in the ultraviolet spectrum of enol **5** (Table II) was used to obtain the concentration of anion **6** which, in turn, was used to calculate the pK_a. A value of 6.6 was thus obtained for **5** in 95% ethanol (2.6 × 10^{-5} *M* solution).

Extraction with aqueous sodium bicarbonate removed 96% of **5** from solution in ethyl acetate. Extraction with water under identical conditions removed only 8% of **5**. Acidification of the sodium bicarbonate extracts with acetic acid gave an essentially quantitative recovery of **5**.

7-Methoxy-2,3,4,4a,5,6-hexahydro-2H-naphthalenone (**7**).—A solution of 1.14 g. of enol **5** in 6 ml. of 10% aqueous sodium hydroxide and 3 ml. of water was treated with 3 ml. of dimethyl sulfate.[8] After 5 min., an additional 5 ml. of 10% aqueous sodium hydroxide was added and the solution was stirred for 1 hr. The reaction mixture was diluted with 20 ml. of water and the product was isolated with ethyl acetate[6b] affording 0.48 g. (39%) of waxy solid: b.p. 130° (bath temp.) at 0.2 mm.; λ_{max}^{KBr} 6.07 (conj. ketone CO), 6.21, 6.32 (conj. C═C), 8.50 (C—O), 7.21, 7.50, 7.90, 7.98, 8.28, 11.32 μ. The analytical sample, m.p. 94–95°, was obtained by recrystallization from heptane.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.0; H, 7.9.

Acidification of the aqueous alkaline portion of the reaction mixture with acetic acid afforded 0.63 g. (55% recovery) of enol **5**, m.p. 167–172°, which was isolated with ethyl acetate.[6b]

Acknowledgment.—We thank the Public Health Service (R.G. AI-04965) and the National Science Foundation for support of this work. The A-60 spectrometer was purchased with funds awarded Northwestern University by the National Science Foundation.

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[7] R. H. Lenhard and S. Bernstein [*J. Am. Chem. Soc.*, **78**, 989 (1956)] report 2.90, 3.19, 5.87, 6.25 and 6.47 μ for 3.5-pregnadiene-3,21-diol-7,20-dione.

[8] The procedure of J. Cornforth and R. Robinson [*J. Chem. Soc.*, 1855 (1959)].

Pyrolysis of 2-Acetoxy-2-(3-oxobutyl)cyclohexane-1,3-dione

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Received November 18, 1964

Pyrolysis of 2-acetoxy-2-(3-oxobutyl)cyclohexane-1,3-dione[1] (I) over a Pyrex glass packed column in a recycling apparatus[2] at 350° and 0.5 mm. affords 2-(3-oxobutyl)-Δ^2-cyclopentenone (II) in 70% yield. The other products of this remarkably efficient thermal ring contraction are acetic acid (79% yield), identified by infrared spectrum, v.p.c. retention time, and conversion to piperazonium diacetate,[3] and carbon monoxide, identified by v.p.c. retention time.

The 2-(3-oxobutyl)-Δ^2-cyclopentenone (II), b.p. 81–82° (0.1 mm.), had λ_{max} 5.85–5.88 and 6.10 μ, λ_{max}^{EtOH} 227 mμ (ε 12,400), $\delta_{TMS}^{CS_2}$ = 2.02 (3H) and 7.22 p.p.m. (1H), and formed (at room temperature) a monosemicarbazone, m.p. 180–182° dec. Upon hydrogenation over palladium on carbon, II was converted exclusively to 2-(3-oxobutyl)cyclopentanone[4] (III), which yielded a bissemicarbazone, m.p. 228–229° (lit.[4] m.p. 229°). Cyclization of III with pyrrolidine and acetic acid afforded 5,6,7,8-tetrahydroindanone-5[5] (IV) in 71% yield. The IV thus obtained, and its semicarbazone and 2,4-dinitrophenylhydrazone derivatives, were identical with authentic samples.[5]

The alternate structure V for the pyrolysis product can be ruled out for the following reasons. The expected ultraviolet absorption maximum for II in ethanol is 227 mμ[6]; for V it is 242 mμ.[7] The n.m.r. spectrum shows no peaks between 2.65 and 7.22 p.p.m.; the absorption due to the side-chain methylene protons of V should be found at *ca.* 3.1 p.p.m.[8] Treatment of

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[1] T. A. Spencer, K. K. Schmiegel, and K. L. Williamson, *J. Am. Chem. Soc.*, **85**, 3785 (1963).

[2] K. L. Williamson, R. T. Keller, G. S. Fonken, J. Szmuszkovicz, and W. S. Johnson, *J. Org. Chem.*, **27**, 1612 (1962).

[3] C. B. Pollard, D. E. Adelson, and J. P. Bain, *J. Am. Chem. Soc.*, **56**, 1759 (1934).

[4] N. S. Gill, K. B. James, F. Lions, and K. T. Potts, *ibid.*, **74**, 4923 (1952).

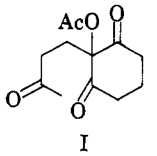
[5] G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *ibid.*, **85**, 207 (1963). We wish to thank Professor Stork for kindly providing us with a sample of IV.

[6] (a) Calculated according to the tabulation of L. M. Fieser and M. Fieser ["Steroids," Reinhold Publishing Corp., New York, N. Y., 1959, p. 19], including the 10-mμ hypsochromic shift noted for cyclopentenones by A. E. Gillam and E. S. Stern ["Electronic Absorption Spectroscopy," Arnold Publishers Ltd., London, 1954, p. 96]; (b) M. F. Ansell and S. S. Brown [*J. Chem. Soc.*, 2955 (1958)] report λ_{max} 226 mμ (ε 8300) for 2-methylcyclopentenone.

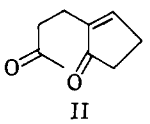
[7] H. S. French and L. Wiley [*J. Am. Chem. Soc.*, **71**, 3702 (1949)] discuss the ultraviolet spectra of exocyclically α,β-unsaturated cyclopentanones.

[8] See, for example, spectrum no. 545 in "NMR Spectra Catalog," Vol. 2, Varian Associates, Palo Alto, Calif., 1963.

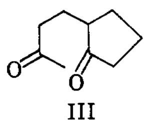
the pyrolysis product with base failed to produce 5-indanol (VI).



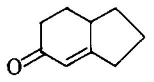
I



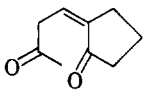
II



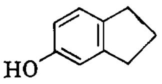
III



IV



V



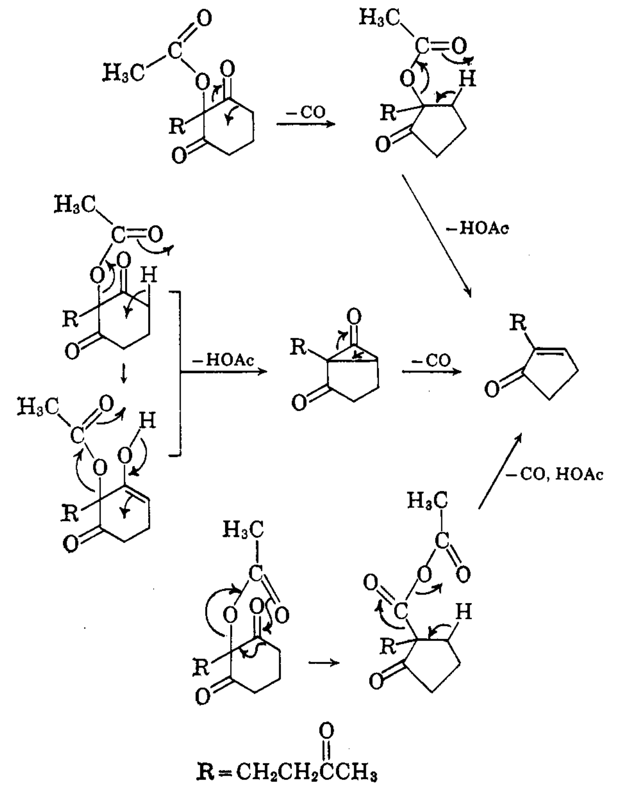
VI

Several aspects of this reaction are noteworthy. First, the reaction is a very clean one. No significant amount of product other than II, acetic acid, and carbon monoxide was obtained.[9] Second, this profound rearrangement occurs at a convenient rate at a moderate temperature. Indeed, simply heating I in air at 300° affords a distillate composed about equally of I and II, plus a large dark residue. Third, use of carbon packing in the pyrolysis column impaired the procedure; a lower yield of II was obtained and, in addition, some methyl vinyl ketone was produced. This behavior contrasts with the conversion of 2-acetoxycyclohexanone to cyclopentene which was reported[2] to be the *result* of the presence of carbon in the pyrolysis column during preparations of Δ^2-cyclohexenone.[10]

The conversion of I to II is analogous to this conversion of 2-acetoxycyclohexanone to cyclopentene, but the high yield, the survival intact of reactive substituents, and the lack of necessity for carbon catalysis make the present reaction novel. The reasons for the difference in the necessity for the presence of carbon are, like all factors related to the mechanism, obscure at present, but it can be pointed out that the 2-alkyl-2-acetoxycyclohexane-1,3-dione system would be more susceptible to homolytic cleavage leading to radical species which could react to give II by three distinct paths, which are summarized in Scheme I.

Studies have been initiated of the pyrolysis of substances which, it is hoped, will help to elucidate the actual course of this reaction and serve to delimit its synthetic potential.

SCHEME I



Experimental

Analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. Melting points were taken either in an open capillary or on a micro hot stage; that of the analytical sample is corrected. Boiling points are uncorrected. Ultraviolet spectra were determined in 95% ethanol on a Bausch and Lomb Spectronic 505 spectrophotometer. Infrared spectra were determined on a Perkin-Elmer Model 21 spectrophotometer. The n.m.r. spectrum was determined on a Varian A-60 instrument. Vapor phase chromatography was done on a Wilkens A-90-P2 chromatograph.

2-(3-Oxobutyl)-Δ^2-cyclopentenone (II).—The pyrolysis apparatus used has been depicted by Williamson, *et al.*[2] In the present work, the system was built with 14 20 ₮ joints, a pyrolysis column 12 mm. in diameter, and a fractionating column (Vigreux) 25 cm. long. Each column was wrapped with commercial heating tape and then asbestos tape. The temperature of each column was determined by a thermocouple attached to a pyrometer. The pyrolysis column was packed with Pyrex Raschig rings. Two Dry Ice–acetone traps were placed in sequence between the receiver and the vacuum pump.

A 50-ml. pyrolysis flask was charged with 20.52 g. (0.0855 mole) of 2-acetoxy-2-(3-oxobutyl)cyclohexane-1,3-dione (I),[1] m.p. 73–74° (when recrystallized from ether, I melts higher than the previously reported[1] 68–69°). The apparatus was assembled and evacuated to 0.1 mm., with a capillary bleed of nitrogen, and the flask was immersed in an oil bath at 215°. The pyrolysis column was maintained at 350° and the fractionating column at 60°. Material with b.p. 104–115° (0.1–0.5 mm.) was collected over a 5-hr. period. As the rate of distillation slowed, the bath temperature was raised to 260° and a yellow distillate, b.p. 116–140° (0.5–1.0 mm.), was collected as a separate fraction over about 1 hr. The first fraction weighed 8.35 g.; the second, 1.95 g. In the first trap was 3.82 g.; in the second, 0.23 g. The pot residue weighed 2.23 g. and the apparatus washings weighed 1.72 g. The total weight recovered thus was 18.30 g., or 101% of the theoretical amount expected if an equivalent of carbon monoxide were eliminated.

Redistillation of the product from fraction 1 afforded II: b.p. 81–82° (0.1 mm); $\lambda_{\max}^{\mathrm{EtOH}}$ 227 mμ (ε 12,400); $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.85–5.88 and 6.10 μ; $\delta_{\mathrm{TMS}}^{\mathrm{CS_2}}$ 2.02 (3H) and 7.22 p.p.m. (1H). V.p.c. analysis of this material on a silicone SE-30 column at 170° gave only one sharp peak.

Anal. Calcd. for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 71.49; H, 7.95.

At room temperature II formed a monosemicarbazone which, after recrystallization from methanol, had m.p. 180–182° dec. and strong ultraviolet absorption at 227 mμ only. Hence the side-chain carbonyl had been derivatized.

Anal. Calcd. for $C_{10}H_{15}N_3O_2$: C, 57.40; H, 7.23; N, 20.08. Found: C, 57.36; H, 7.24; N, 19.98.

At steam-bath temperature II afforded a semicarbazone derivative, m.p. 231–232°, which repeatedly gave analytical results indicating a composition intermediate between mono- and bis-semicarbazone derivatives.

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(9) Mechanical holdup in the pyrolysis system probably limited the yield of II to 70%, and larger scale runs should give higher isolable yields.

(10) The possibility that cyclopentene was being formed by decarbonylation of cyclohexenone in the pyrolysis of 2-acetoxycyclohexanone was considered by Williamson, *et. al.*,[2] but pyrolysis of cyclohexenone gave no cyclopentene. In the present case such a pathway, involving initial 1,2-elimination of acetic acid, is structurally impossible unless isomerization of V to II were occurring, which is very much less likely than isomerization of the double bond of V into conjugation with the side-chain carbonyl.

The 8.35-g. product fraction had $\lambda_{\max}^{\mathrm{EtOH}}$ 227 mμ with ϵ 11,300 (based on II), indicating that this material was 91% II. However, v.p.c. analysis showed only one peak. A small shoulder at 280 mμ, possibly due to 6-hydroxy-1-tetralone,[1] was the only indication of the possible nature of a contaminant. The 1.95-g. product fraction had $\lambda_{\max}^{\mathrm{EtOH}}$ 227 mμ with ϵ 9600 (based on II) and thus was 77% pure. Therefore, the yield of II, based on these ultraviolet spectra, was 70%.

V.p.c. analysis and an infrared spectrum of the 3.82 g. of material in the first trap indicated that it was essentially pure acetic acid. This trap material gave a 90% yield of piperazonium 1,4-diacetate, m.p. 208–209°,[3] which was identical with a sample prepared from known acetic acid. On the basis of its odor, the 0.23 g. in trap 2 was considered to be acetic acid, making the total yield 4.05 g. (79%).

In another pyrolysis experiment, the effluent vapors were collected over mercury and analyzed on a 5A Molecular Sieve column at 100°.[11] Carbon monoxide was found as the only gas present (other than oxygen and nitrogen) by comparison of its retention time to that of a known sample.

When the glass packing of the pyrolysis column was evenly interspersed with a total of 1 g. of 6–14-mesh activated charcoal and the pyrolysis of I was conducted under the same general conditions described above, there was obtained only 25% of II (by ultraviolet spectral analysis of a yellow distillate equivalent in weight to 41% of II). The material in both traps 1 and 2 had the characteristic odor of methyl vinyl ketone (as well as that of acetic acid). Decomposition of the material in the pyrolysis flask to a dark tar was more rapid when the carbon was present.

2-(3-Oxobutyl)cyclopentanone (III).—To 1.795 g. (7.48×10^{-3} mole) of II in 35 ml. of ethyl acetate was added 0.6 g. of 10% palladium on carbon and the mixture was hydrogenated at atmospheric pressure and room temperature for 30 min. The mixture was filtered and the filtrate was evaporated to give 1.803 g. of an oil which had $\lambda_{\max}$ 5.75 and 5.84 μ and showed one sharp peak upon v.p.c. analysis. This oil afforded a bissemicarbazone derivative which melted at 228–229° (lit.[4] m.p. 229°).

5,6,7,8-Tetrahydroindanone-5 (IV).—A mixture of 1.00 g. (6.5×10^{-3} mole) of hydrogenation product III and 0.6 ml. (7×10^{-3} mole) of pyrrolidine in 50 ml. of benzene was refluxed for 8 hr. A solution of 1.6 ml. of acetic acid, 1.6 ml. of water, and 0.9 g. of sodium acetate was then added and heating was continued for an additional 4 hr. Separation of the layers, extraction of the aqueous layer with benzene, and washing the combined extracts with 3 *M* hydrochloric acid and then saturated sodium bicarbonate solution gave, after removal of the benzene, a dark oil which was clarified by quick chromatography on acid-washed alumina to afford 0.63 g. (71%) of oil which had an infrared spectrum identical with that of a known sample of IV.[5] The material prepared from II *via* III had $\lambda_{\max}^{\mathrm{EtOH}}$ 236 mμ (ϵ 13,400), lit.[5] $\lambda_{\max}^{\mathrm{EtOH}}$ 233 mμ (ϵ 12,700), and formed a 2,4-dinitrophenylhydrazone, m.p. 197–198° (from methanol–chloroform), and a semicarbazone, m.p. 230–231° (from 1-butanol). The authentic sample of IV formed a 2,4-dinitrophenyhydrazone, m.p. 197–199°, and a semicarbazone, m.p. 230–231° (lit.[4] m.p. 214–219°). The respective mixture melting points were undepressed.

Treatment of II with either pyrrolidine and acetic acid in refluxing benzene or with a solution of sodium hydroxide in methanol yielded products which gave no spectral indication of containing any phenolic material, such as VI. These products were not characterized further, but a strong ultraviolet absorption maximum at 343 mμ in the product from the pyrrolidine–acetic acid treatment can tentatively be ascribed to the conjugated pyrrolidine enamine derived from the $\alpha,\beta,\gamma,\delta$-unsaturated ketone which would be formed by aldol cyclization–dehydration of II.

Acknowledgment.—This investigation was supported in part by Public Health Service Research Grant AM-05014. S. W. B. was a National Science Foundation Undergraduate Research Participant, 1963–1964. The authors are grateful to Professor K. L. Williamson for determining and discussing the n.m.r. spectrum.

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(11) G. Kyryacos and C. E. Boord, *Anal. Chem.*, **29**, 787 (1957).

Steric Requirements at Phosphorus in the Wittig Reaction

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Received October 19, 1964

The stereospecificity of the Wittig reaction of stable or quasi-stable ylids has been explained in terms of preferential formation and decomposition of the betaine from which the *trans* olefin is derived.[1] It has been reported[2] that tricyclohexylphosphoranes, in their reaction with aldehydes, yield the *trans* olefins as exclusive products and that carbethoxymethylenetributylphosphorane gives 95% of *trans*-ethyl cinnamate in its reaction with benzaldehyde.[1] The limited amount of data available suggests that trialkylphosphoranes react with aldehydes in a more stereospecific manner than do their triarylphosphorane counterparts and this phenomenon has been explained by the ability of the alkyl groups (which are more electron donating than phenyl) to retard decomposition of the betaine to olefin and phosphine oxide.[1,2]

In connection with some other work, the Wittig reaction of a series of ylids of type I, in which the size of the groups bound to phosphorus was varied systematically, has been studied.

$$R_3P{=}CHCO_2C_2H_5$$

I

The aim of this work was to determine if an increase in the size of the groups around phosphorus would affect the *cis–trans* ratio of ethyl cinnamates derived from the reactions of I with benzaldehyde, reasoning that as the steric requirements of the alkyl groups became greater, they could conceivably outweigh the preferential formation and decomposition of the *trans*-betaine thereby resulting in a loss of stereospecificity.

Since the trialkylphosphoranes, in most cases, are nonisolable, the ylids were prepared and used *in situ* from the corresponding phosphonium salts. As the long-chain alkyl phosphonium bromides were oils, the tetraphenylborates were utilized in order to obtain crystalline derivatives. These were treated with sodium ethoxide in ethanol under nitrogen with subsequent addition of benzaldehyde.

The olefin ratio was determined by g.l.p.c. and Table I contains the product ratio data obtained from several of these ylids. In the two cases in which the phosponium bromides were solids (*n*-butyl and cyclohexyl), the product ratio data were compared with those obtained from the tetraphenylborates. In addition, effect of reaction temperature upon product ratios was studied in two cases and the product ratios obtained from two triarylphosphoranes were determined.

As is obvious from the data in Table I, none of the factors studied significantly alters the stereochemical outcome of the Wittig reaction of the ylids considered. With the exception of the trioctylphosphorane, the

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(1) (a) A. J. Speziale and D. E. Bissing, *J. Am. Chem. Soc.*, **85**, 1888 (1963); (b) A. J. Speziale and D. E. Bissing, *ibid.*, **85**, 3878 (1963).

(2) H. J. Bestmann and O. Kratzer, *Ber.*, **95**, 1894 (1962).