and phenol were assayed by calibration against a weighed mixture on a 9-ft. Carbowax 20M packed column at 190°.

In general, the errors are probably large in the case of the runs in which a minor product was formed to the extent of 5% or less. These results are probably good to only ±1%.

The infrared and n.m.r. spectra of the pure esters were checked against these runs also and found to be essentially identical in all cases.

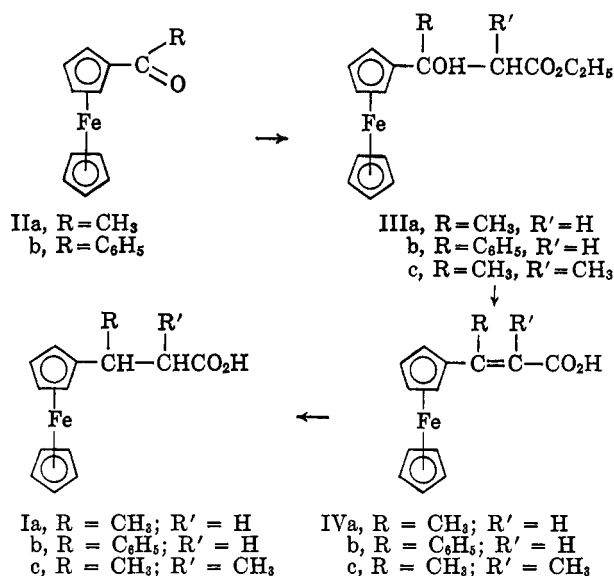# The Cyclization of Some β-Ferrocenylpropionic Acids

J. W. HUFFMAN AND R. L. ASBURY[1]

Department of Chemistry and Geology,
Clemson University, Clemson, South Carolina 29631

It has been found that cyclization of a variety of β-ferrocenylpropionic acids under Friedel–Crafts gives rise to heteroannularly substituted ("bridged") ketones,[2] rather than the homoannular indanone analogs. Although there are a few examples where a heavily substituted ferrocenylpropionic acid derivative gives the homoannular ketone,[2d,3] there appears to be little known about the effect of substitution in the propionic acid side chain upon the course of these cyclizations. It was initially felt that by suitable modifications of the alkyl portion of the molecule it might be possible to obtain acids which would undergo cyclization to give significant quantities of the homoannular products.[4] In addition, it was felt that such a study would give some insight into the steric factors governing the course of these cyclizations.

The acids chosen for this work were β-methyl- (Ia), β-phenyl- (Ib), and α,β-dimethyl-β-ferrocenyl propionic acids (Ic). Acids Ia and Ic were prepared from acetylferrocene[5] (IIa) in four steps. Reaction of the ketone with ethyl bromoacetate or ethyl α-bromopropionate under standard Reformatsky conditions gave the hydroxy esters IIIa and IIIc, respectively. Dehydration with toluenesulfonic acid in benzene followed by saponification gave the unsaturated acids IVa and IVc. Although ferrocenylcrotonic acid (IVa) was obtained as a crystalline solid, the α-methylcrotonic acid (IVc) could not be solidified and may well be a mixture of stereoisomers. β-Ferrocenylcinnamic acid (IVb) was prepared from benzoylferrocene[6] (IIb) by a similar sequence of reactions. The substituted β-ferrocenylpropionic acids were readily obtained from the unsaturated compounds by hydrogenation. Although β-ferrocenylbutyric and β-ferrocenyldihydro-

IIa, R = CH₃
b, R = C₆H₅

IIIa, R = CH₃, R' = H
b, R = C₆H₅, R' = H
c, R = CH₃, R' = CH₃

Ia, R = CH₃; R' = H
b, R = C₆H₅; R' = H
c, R = CH₃; R' = CH₃

IVa, R = CH₃; R' = H
b, R = C₆H₅; R' = H
c, R = CH₃; R' = CH₃

cinnamic acids were solids, the α,β-dimethyl acid Ic was an oil, presumably a mixture of the erythro and threo isomers.

Cyclization of β-ferrocenylbutyric acid by either polyphosphoric acid or trifluoroacetic anhydride gave a single, crystalline ketone in yields of 32 and 75%, respectively. This compound was a monomer of formula $C_{14}H_{14}FeO$ and showed infrared absorption at 6.06 μ and no high-intensity ultraviolet maximum above 230 mμ. These data are all consistent with the published spectra of 1,1'-(α-ketotrimethylene)ferrocene[2e,7] (Vd), and when coupled with the absence of in-

Va, R = CH₃; R' = H
b, R = C₆H₅; R' = H
c, R = CH₃; R' = CH₃
d, R = H; R' = H
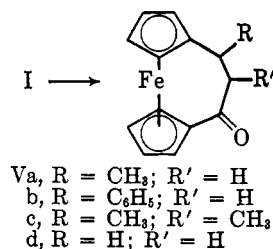
frared bands at 9 and 10 μ[8] indicate that this compound is 1,1'-(α-keto-α'-methyltrimethylene)ferrocene (Va). The cyclization products of ferrocenylhydrocinnamic acid (Ib) and the α,β-dimethyl acid Ic also had properties consistent with bridged structures Vb and Vc. It is thus apparent that, at least in the relatively simple substituted ferrocenylpropionic acid derivatives studied, the intramolecular Friedel–Crafts reaction gives heteroannular cyclization.

Experimental Section[9]

β-Ferrocenylcrotonic Acid.—To a mixture of 5.00 g. (2.19 × 10⁻² mole) of acetylferrocene in 150 ml. of anhydrous benzene, and 65.38 g. of metallic zinc (previously activated by treatment with 5% hydrochloric acid, successive washings with water,

(1) Abstracted from the Ph.D. Thesis of R. L. Asbury, Clemson University, Jan. 1965.

(2) (a) K. L. Rinehart and R. J. Curby, J. Am. Chem. Soc., 79, 3290 (1957); (b) K. Schlögl and H. Seiler, Tetrahedron Letters, No. 7, 4 (1960); (c) M. Rosenblum, A. K. Banarjee, N. Danieli, R. W. Fish, and V. Schlatter, J. Am. Chem. Soc., 85, 316 (1963); (d) K. L. Rinehart, D. E. Bublitz, and D. H. Gustafson, ibid., 85, 970 (1963); (e) K. L. Rinehart, R. J. Curby, D. H. Gustafson, H. G. Harrison, R. E. Bozak, and D. E. Bublitz, ibid., 84, 3263 (1962); (f) E. A. Hill and J. H. Richards, ibid., 83, 4216 (1961).

(3) D. E. Bublitz and K. C. Rinehart, Tetrahedron Letters, 827 (1964).

(4) While this work was in progress, it was reported (ref. 2c) that α,α-dimethyl-β-ferrocenylpropionic acid does in fact give both homoannular and heteroannular ketones on cyclization with trifluoroacetic anhydride.

(5) P. J. Graham, R. V. Linsey, G. N. Parshall, M. L. Peterson, and G. M. Whitman, J. Am. Chem. Soc., 79, 3416 (1957).

(6) N. Weliky and E. S. Gould, ibid., 79, 2742 (1957).

(7) Although Rinehart, et al.,²ᵉ report the carbonyl band of Vd at 5.95 μ, their spectrum was determined in carbon disulfide solution, while ours were run as Nujol mulls. The carbonyl absorption of Vd in Nujol appears at 6.02 μ (R. L. Asbury, Ph.D. Thesis, Clemson University, 1965).

(8) M. Rosenblum and R. B. Woodward, J. Am. Chem. Soc., 80, 5443 (1958).

(9) All melting points were taken on a Hershberg melting point apparatus and are uncorrected. Infrared spectra were recorded as liquid films or as Nujol mulls using a Perkin-Elmer Model 137 spectrophotometer. Microanalyses were carried out by either Galbraith Laboratories, Knoxville, Tenn., or Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

acetone, and anhydrous ether, and drying *in vacuo*) was added 10 ml. of ethyl bromoacetate. This mixture was stirred vigorously while the reaction was initiated by heating the bottom of the vessel with an open flame. The remaining ethyl bromoacetate was added at a rate to maintain gentle reflux. A total volume of 56.5 ml. (5.11 × 10⁻¹ mole) of halo ester was introduced into the reaction mixture, which was then stirred at reflux for 2.5 hr. After stirring for an additional 1.5 hr. at room temperature, the mixture was poured into a solution of 10% acetic acid, and the aqueous phase was drawn off and extracted with two portions of benzene. The organic portions were combined, washed with 10% ammonium hydroxide, 10% hydrochloric acid, and water, and dried.

To the previously dried organic extracts was added 100 mg. of *p*-toluenesulfonic acid, and the solution was heated at reflux under a constant water separator until no more water was produced. Subsequent washing with water, drying, and removing of the solvent at reduced pressure afforded 11.76 g. of unsaturated ester as a brown oil showing infrared maxima at 5.85 and 6.24 μ.

The crude unsaturated ester was heated at reflux for 4 hr. in a solution of 100 ml. of 10% potassium hydroxide and 20 ml. of 95% ethanol. The ethanol was removed and the remaining aqueous solution was cooled to room temperature and extracted with three portions of benzene. The basic aqueous solution was filtered through Celite and acidified with concentrated hydrochloric acid. The product, 4.63 g. (78%), was obtained as an orange-brown powder, m.p. 121–124°, infrared maxima at 6.03 and 6.27 μ. Three recrystallizations from ether provided the analytical sample as deep red plates, m.p. 158–160° dec.

Anal. Calcd. for C₁₄H₁₄FeO₂: C, 62.27; H, 5.22. Found: C, 62.49; H, 5.36.

β-Ferrocenylbutyric Acid.—Hydrogenation of a solution of 0.17 g. (6.30 × 10⁻⁴ mole) of β-ferrocenylcrotonic acid in 70 ml. of glacial acetic acid in the presence of 0.04 g. of platinum oxide was carried out at 50 p.s.i. and room temperature for 22 hr. After filtration to remove the spent catalyst, the solution was concentrated at reduced pressure, diluted with water, and extracted with several portions of ether. The ethereal extracts were combined, washed thoroughly with water, and dried. Filtration of the solution through Norit, concentration, and dilution with hexane afforded 0.14 g. (82%) of acid, m.p. 107–109°, infrared maximum at 5.89 μ. Two successive recrystallizations from hexane gave 0.12 g. of acid as orange platelets, m.p. 111–113°.

Anal. Calcd. for C₁₄H₁₆FeO₂: C, 61.79; H, 5.93. Found: C, 61.87; H, 5.95.

1,1′-(α-Keto-α′-methyltrimethylene)ferrocene. A.—To 20.00 g. of polyphosphoric acid was added 500 mg. (1.84 × 10⁻³ mole) of β-ferrocenylbutyric acid, and the mixture was stirred at steam-bath temperature until homogeneous and then allowed to stand at room temperature for 36 hr. The dark brown solution was poured into ice–water and the resulting suspension was extracted with four portions of ether. The organic portions were combined, washed with water, extracted with saturated sodium bicarbonate, washed successively with water, 10% hydrochloric acid, and water, and dried. Removal of the solvent at reduced pressure gave 0.31 g. of crude neutral material which was chromatographed on Merck acid-washed alumina to give 150 g. (32%) of the desired ketone from the benzene fraction. The crude product was sublimed at 80–85° *in vacuo* and then recrystallized from ether–pentane to give 0.11 g. of orange needles, m.p. 99–101°, infrared maximum at 6.06 μ (carbonyl), ultraviolet maxima at 273 mμ (ε 2910) and 338 mμ (ε 462).

Anal. Calcd. for C₁₄H₁₄FeO: C, 66.18; H, 5.55; mol. wt., 254. Found: C, 66.37; H, 5.64; mol. wt., 272.

Acidification of the sodium bicarbonate extracts with concentrated hydrochloric acid gave 0.03 g. of unreacted acid.

B.—To a stirred solution of 200 mg. (7.36 × 10⁻⁴ mole) of β-ferrocenylbutyric acid in 18 ml. of carbon tetrachloride was added 10 ml. of trifluoroacetic anhydride. The system was immediately flushed with nitrogen and stirred at room temperature in an atmosphere of nitrogen for 4.25 hr.

The brown solution was poured into saturated sodium bicarbonate solution and the organic layer was separated. After extracting the aqueous solution with chloroform, the organic portions were combined, washed with water, 5% hydrochloric acid, and water, and dried.

Chromatography of the crude neutral material on Bio-Rad Ag-7 neutral alumina and elution with benzene–ether (1:1) afforded 0.14 g. (75%) of ketone which solidified upon standing at room temperature. Sublimation at 75–85° and 0.2 mm. and recrystallization from ether–hexane gave 0.130 g. of material, m.p. 102–103°.

Ethyl β-Ferrocenylcinnamate.—In a manner analogous to the preparation of β-ferrocenylcrotonic acid, 2.89 g. (93%) of the desired α,β-unsaturated ester was obtained from 2.50 g. (8.64 × 10⁻³ mole) of benzoylferrocene and 11.30 ml. (1.02 × 10⁻¹ mole) of ethyl α-bromoacetate in the presence of 10 g. of zinc. The product was converted to the corresponding acid, β-ferrocenylcinnamic acid, which recrystallized from ether as deep purple platelets: m.p. 172–175.5°; infrared maxima at 6.05, 6.24, and 6.31 μ.

Anal. Calcd. for C₁₉H₁₆FeO₂: C, 68.70; H, 4.86. Found: C, 68.93; H, 5.04.

β-Ferrocenyldihydrocinnamic Acid.—A solution of 2.45 g. (6.81 × 10⁻³ mole) of ethyl β-ferrocenylcinnamate in 200 ml. of 95% ethyl alcohol was hydrogenated at 50 p.s.i. and room temperature for 18 hr., using 0.2 g. of platinum oxide. After removing the spent catalyst, the solvent was removed at reduced pressure to give 2.01 g. (82%) of clear orange oil.

The crude ester was heated at reflux for 4 hr. in 50 ml. of 10% potassium hydroxide and 30 ml. of 95% ethyl alcohol. Acidification with concentrated hydrochloric acid afforded 1.80 g. (97%) of product as a bright yellow powder, m.p. 150.0–153.5° (dec). Three recrystallizations from ether gave 1.19 g. of saturated acid as yellow needles, m.p. 159–160° dec., infrared maxima at 5.89 and 6.25 μ.

Anal. Calcd. for C₁₉H₁₈FeO₂: C, 68.28; H, 5.43. Found: C, 68.31; H, 5.67.

1,1′-(α-Keto-α′-phenyltrimethylene)ferrocene.—To 16 g. of polyphosphoric acid, which had been previously heated to 65° on a water bath, was added 0.98 g. (2.93 × 10⁻³ mole) of β-ferrocenyldihydrocinnamic acid. The resulting mixture was stirred for 20 min. at a temperature of 60–70° at which point the dark brown homogeneous mixture was allowed to stand at room temperature for 52 hr.

The reaction mixture was poured into water, and the aqueous suspension was extracted twice with chloroform. The organic portions were combined, washed with water, 10% sodium carbonate, and then successively water, 10% hydrochloric acid, and water, and dried. Removal of the solvent at reduced pressure gave 1.21 g. of neutral material as an orange-brown semisolid.

The crude neutral material was chromatographed on Merck acid-washed alumina to give 0.19 g. (21%) of ketone from the benzene–ether (1:1) fraction. Two recrystallizations from ether gave 0.16 g. of product as fluffy orange needles, m.p. 183–186° dec., infrared maxima at 6.05 and 6.26 μ, ultraviolet maximum at 269 mμ (ε 4910).

Anal. Calcd. for C₁₉H₁₆FeO: C, 72.17; H, 5.10; mol. wt., 316. Found: C, 71.96; H, 5.32; mol. wt., 310.

The ether fraction from the chromatogram afforded 0.01 g. of a ferrocene derivative, which exhibited multiple absorption in the carbonyl region of the infrared spectrum as well as absorption near 9 and 10 μ. The chloroform–methanol fractions gave 0.57 g. of intractable material, while acidification of the original sodium carbonate extracts gave 0.03 g. of uncyclized acid.

α,β-Dimethyl-β-ferrocenylpropionic Acid.—In the previously described manner, 5.00 g. (2.19 × 10⁻² mole) of acetylferrocene in 150 ml. of dry benzene was treated with 10 ml. (7.71 × 10⁻² mole) of ethyl α-bromopropionate in the presence of 14.3 g. of activated zinc. The deep purple product was chromatographed on Merck reagent grade alumina to give 7.74 g. of oily red crystals, which from the infrared spectrum was a mixture of the hydroxy and unsaturated esters.

The successive procedures of dehydration (azeotropic distillation), saponification, and hydrogenation (50 p.s.i., Adams catalyst) gave 3.05 g. (49%) the desired acid as a clear orange oil showing an infrared maximum at 5.91 μ. Repeated attempts to crystallize failed; however it was homogeneous by thin layer chromatography on silica gel G.

1,1′-(α-Keto-α′,β-dimethyltrimethylene)ferrocene.—A solution of 0.370 g. (1.29 × 10⁻³ mole) of α,β-dimethyl-β-ferrocenylpropionic acid and 10 ml. of trifluoroacetic anhydride in 25 ml. of carbon tetrachloride was stirred at room temperature for 4.5 hr. in an atmosphere of helium. The resulting dark brown solution was cautiously poured into 10% sodium carbonate, and the organic and aqueous phases were separated. The basic solu-

tion was extracted twice with chloroform, and the organic portions were combined, washed with 5% hydrochloric acid, water, and dried. Removal of the solvent at reduced pressure gave 0.360 g. of red oil. Chromatography on acid-washed alumina afforded 0.140 g. (41%) of ketone as a clear orange oil which crystallized upon standing at room temperature from the hexane–benzene (1:1) fraction. The ketone was purified by recrystallization from hexane to give red leaflets, m.p. 120–121°, infrared maximum at 6.00 μ, ultraviolet maxima at 272 $m\mu$ (ϵ 3140) and 337 $m\mu$ (ϵ 1012).

Anal. Calcd. for $C_{15}H_{16}FeO$: C, 67.19; H, 6.02; mol. wt., 268. Found: C, 67.02; H, 6.06; mol. wt., 275.

Preparation of Vinyl Chloroformate by the Gas Phase Decomposition of Ethylene Glycol Bis(chloroformate)[1]

LIENG-HUANG LEE

*Polymer and Chemicals Research Laboratory,
The Dow Chemical Company, Midland, Michigan*

The decomposition of simple alkyl chloroformates has been studied. Lewis and Herndon[2-4] have further established the decomposition to be one example of the S_Ni mechanism. The S_Ni mechanism was defined as a one-step unimolecular mechanism passing through a cyclic transition state.

The decomposition of ethylene glycol bis(chloroformate) has not been studied. Küng[5] discovered that by pyrolyzing ethylene glycol bis(chloroformate), vinyl chloroformate (CH_2=CHOCOCl) was obtained together with other products. These products generally contained 2-chloroethyl chloroformate, 1-chloroethyl chloroformate, 1,2-dichloroethane, 1,1-dichloroethane, and vinyl chloride. The yield of the desired product, vinyl chloroformate, was generally low. Vinyl chloroformate could be an important starting material for the synthesis of other vinyl monomers[6] if this compound can be made in better yield. The purposes of this study were, therefore, to understand the mechanism of the thermal degradation of ethylene glycol bis(chloroformate) and improve the yield of vinyl chloroformate. The decomposition products were analyzed with vapor phase chromatography. The relationship between the primary and the secondary decomposition products is discussed.

Experimental Section

Decomposition of Ethylene Glycol Bis(chloroformate).— The pyrolysis apparatus was similar to those used for the ester pyrolysis described elsewhere.[7] The vertical pyrolysis tube was made of Vycor (18.5 × 1 in.) and placed in the center of a cylin-

drical heater. The dropping funnel (500 ml.) was equipped with a side arm and a Teflon adjustable stopcock. The funnel was connected to the top portion of the vertical tube with a ball joint. The bottom of the vertical tube was connected to a receiver (250 ml.) placed in a dewar flask containing an acetone Dry Ice mixture. The side-arm outlet of the receiver was connected to a second receiver. The gases were scrubbed using two gas-scrubbing bottles containing 10% NaOH solution. It should be noted that the temperature was measured on the thermocouple inserted in the heater. The temperature on the wall of the tube was 10–20° higher than the heater temperature.

Prior to the addition of ethylene glycol bis(chloroformate) [Columbia Southern Chemical Corp., b.p. 188° (725 mm.)], the system was flushed with nitrogen through the side arm of the dropping funnel. During the pyrolysis, the nitrogen stream was kept at a rate of 6–8 cc./min. After the pyrolysis was completed, the pyrolysate mixture was distilled or analyzed with the Perkin-Elmer vapor phase chromatography unit. The v.p.c. analyses results are shown in Table I. The low boilers were run at 50° with a helium flow rate of 40 cc./min. The retention times of various compounds are as follows: vinyl chloride, 2.6 min.; 1,1-dichloroethane, 9.3 min.; vinyl chloroformate, 10.2 min.; and 1,2-dichloroethane, 15.9 min. The high and low boilers were run at 100° with a helium flow rate of 150 cc./min. The retention times of various compounds are as follows: vinyl chloride, 0.6 min.; vinyl chloroformate and 1,1-dichloroethane, 1.5 min.; 1,2-dichloroethane, 2.1 min.; an unidentified compound, presumably 1-chloroethyl chloroformate, 3.9 min.; 2-chloroethyl chloroformate, 7.3 min.; and ethylene glycol bis(chloroformate), 26.5 min. Except for 1-chloroethyl chloroformate, the positions of these peaks were checked with those of the known compounds. It should be noted that, owing to some unknown factors in the pyrolysis, the reproducibility of the results was not satisfactory.

The distillation of the pyrolysate was conducted in two steps. The first step was to fractionate the low-boiling fractions under atmospheric pressure with a Todd distillation column, Model A (approximately 60 plates). 1,1-Dichloroethane, b.p. 57–58° (lit.[8] b.p. 57.3°), was separated first. Vinyl chloroformate, $n^{25}D$ 1.4090, d^{25} 1.1597, b.p. 67–69° [lit.[5] b.p. 68–69° (735 mm.)], was then obtained. Without the use of the fractionating column, the first two compounds and 1,2-dichloroethane, b.p. 83–84° (lit.[8] b.p. 83.4–83.7°), were extremely difficult to separate. The identity of both 1,1-dichloroethane and 1,2-dichloroethane was checked by comparing them with the authentic samples. The structure of vinyl chloroformate was confirmed by infrared analysis. The spectrum (Figure 1) shows the C–H stretching band at 3100 cm.$^{-1}$, the CH_2 stretching band at 2960 and 2870 cm.$^{-1}$, and the C=O stretching at 1780 cm.$^{-1}$. The presence of the vinyl group is demonstrated by the C=C stretching band at 1640 cm.$^{-1}$ and the out-of-plane CH deformation at 940 (CH_2 twisting) and 910 cm.$^{-1}$ (CH_2 wagging).

It should be noted that the spectrum is considerably different from that of the starting material, ethylene glycol bis(chloroformate). The CH_2 stretching band is at 2970 cm.$^{-1}$, and the CH_2 deformation band is at 1460 cm.$^{-1}$. Since there are two symmetric C–O–C bonds in ethylene glycol bis(chloroformate), the C–O–C absorption yields a doublet: 1220 and 1188 cm.$^{-1}$. In the case of vinyl chloroformate, only one C–O–C band was found at 1150 cm.$^{-1}$.

The second step of distillation was conducted under vacuum. Most of the distillate was 2-chloroethyl chloroformate, b.p. 89–90° (76 mm.) [lit.[5] b.p. 89–90° (76 mm.), 61–63° (21 mm.)]. The infrared spectrum of this compound is shown in Figure 2. It should be noted that, in this case, the C–O–C is at 1180 cm.$^{-1}$. The spectrum of this compound is identical with that of the pure compound obtained from Eastman Kodak. It was reported originally by the inventor that there was a considerable amount of 1-chloroethyl chloroformate, b.p. 57–59° (76 mm.). We did not obtain a sufficient quantity of this compound, therefore, there was no spectrum made for this compound.

In order to study the source of vinyl chloroformate, we conducted two separate studies. The first study was to pyrolyze 2-chloroethyl chloroformate in the same apparatus. We did not obtain vinyl chloroformate. The decomposition products were 1,2 dichloroethane and vinyl chloride. When we pyrolyzed

(1) This paper was presented before the Division of Polymer Chemistry, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964.

(2) E. S. Lewis and W. C. Herndon, *J. Am. Chem. Soc.*, **83**, 1955 (1961).

(3) E. S. Lewis, W. C. Herndon, and D. C. Duffey, *ibid.*, **83**, 1959 (1961).

(4) E. S. Lewis and W. C. Herndon, *ibid.*, **83**, 1961 (1961).

(5) F. E. Küng, U. S. Patent 2,377,085 (1945).

(6) F. Strain and F. E. Küng, U. S. Patent 2,384,143 (1945).

(7) W. J. Bailey and H. R. Golden, *J. Am. Chem. Soc.*, **75**, 4780 (1953).

(8) "Handbook of Chemistry and Physics," The Chemical Rubber Publishing Co., Cleveland, Ohio.