spectrum showed both carbonyl and ester absorption. By the absence of absorption between 1600 and 1700 cm^{-1} and by the failure to give a purple color with alcoholic ferric chloride, the carbethoxy and ethoxybutenyl groups were shown to be on the same carbon.[16] Gas chromatographic purification and a final distillation[15] gave a colorless liquid, bp 132–133° (1 mm), n^{21}_{D} 1.4745.

Anal. Calcd for $C_{15}H_{24}O_4$: C, 67.16; H, 8.95. Found: C, 67.32; H, 8.97.

2-Carbethoxy-2-(4-ethoxy-2-butene-1-yl)cycloheptanone. A.—Addition of *trans*-1,4-dichloro-2-butene (0.396 mole) to a solution of 2-carbethoxycycloheptanone (0.396 mole) in ethanolic sodium ethoxide prepared from 18.2 g (0.792 g-atom) of sodium in 400 ml of ethanol produced 41.4 g of liquid, bp 143–170° (1.5 mm), n^{22}_{D} 1.4709. Redistillation gave a colorless liquid, bp 155° (1.5 mm), n^{23}_{D} 1.4728.

Anal. Calcd for $C_{16}H_{26}O_4$: C, 68.09; H, 9.23. Found: C, 68.40; H, 9.25.

B.—Addition of 1-chloro-4-ethoxy-2-butene to the sodium salt of 2-carbethoxycycloheptanone in 250 ml of ethyl alcohol, using 0.45 mole of each reactant, gave 37.0 g of liquid, bp 155–160° (2 mm), n^{23}_{D} 1.4732. Gas chromatographic purification and a final distillation[15] gave a colorless liquid, bp 142° (1 mm), n^{25}_{D} 1.4759. The infrared spectrum was identical with that of the product obtained by the 1,4-dichloro-2-butene reaction.

C.—Addition of 1-chloro-4-ethoxy-2-butene (0.0231 mole) to a solution of 2-carbethoxycycloheptanone (0.0231 mole) in 30 ml of *t*-amyl alcohol in which 0.51 g (0.0231 g-atom) of sodium had been dissolved produced 0.55 g of forerun, bp 140° (1 mm), 1.40 g of product, bp 145–160° (1 mm), n^{22}_{D} 1.4769, whose infrared spectrum was identical with that of the fraction above with bp 142° (1 mm), and 2.2 g of residue.

2-Carbethoxy-2-(4-ethoxy-2-butene-1-yl)cyclopentanone.—Reaction of 78 g (0.5 mole) of 2-carbethoxycyclopentanone with 67.3 g (0.5 mole) of 1-chloro-4-ethoxy-2-butene in the presence of sodium *t*-amylate gave 15.7 g of forerun, 33.0 g of a yellowish liquid, bp 130–200° (1 mm), n^{24}_{D} 1.4660, and 30 g of polymeric residue. Gas chromatographic purification[15] gave a colorless liquid, bp 123–125° (0.5 mm), n^{22}_{D} 1.4695.

Anal. Calcd for $C_{14}H_{22}O_4$: C, 66.14; H, 8.66. Found: C, 66.20; H, 8.55.

Treatment of Ethyl 1-Carbethoxy-2-oxocyclohexaneacetate with Sodium *t*-Amylate. A.—A solution of 0.92 (0.04 g-atom) of sodium in 108 ml (1.0 mole) of *t*-amyl alcohol, a 4% solution,[11] was treated with 20 g of ethyl 1-carbethoxy-2-oxocyclohexaneacetate. After it had been stirred at room temperature for 24 hr, the mixture was acidified, taken up in ether, washed with water, and dried. Distillation gave 18 g of liquid, bp 145° (1 mm), and 2 g of polymeric residue. Redistillation gave 13.0 g of colorless liquid, bp 125–130° (1 mm), n^{24}_{D} 1.4646, whose infrared spectrum was identical with that of the starting material.

B.—To a *t*-amylate solution prepared from 54 ml (0.5 mole) of *t*-amyl alcohol and 2.3 g (0.1 g-atom) of sodium, a 20% solution,[11] was added 22.6 g of ethyl 1-carbethoxy-2-oxocyclohexaneacetate. The mixture was refluxed for 8 hr and worked up as above. Distillation gave 11.0 g of crude material, bp 135–150° (1.5 mm), n^{25}_{D} 1.4725. These properties, the infrared spectrum, and the coloration of alcoholic ferric chloride established the structure as ethyl 3-carbethoxy-2-oxocyclohexaneacetate.

α-(δ-Valeric acid)-γ-vinyl-γ-valerolactone (IV).—Ethyl 6-carbethoxy-10-ethoxy-8-decenoate (II), 42 g, was refluxed overnight with 300 ml of 10% hydrochloric acid. The mixture was then cooled and taken up in ether. The ether solution was washed with water and then with sodium bicarbonate solution. The sodium bicarbonate solution was washed with ether and then acidified to give 10.6 g of a white solid.[17] Recrystallization from toluene gave a pure white solid melting at 94°.

Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.23; H, 7.60. Found: C, 62.26; H, 7.71.

Spiro[4.5]dec-2-en-6-ene.—A solution of 46 g (2.0 g-atoms) of sodium in 1 l. of *t*-amyl alcohol was evaporated to dryness and 1500 ml of toluene was added to the residue. A mixture of 125 g (1.0 mole) of *cis*-1,4-dichloro-2-butene[18] and 98 g (1.0 mole) of cyclohexanone was kept at a gentle reflux for 48 hr. After cooling, 200 ml of water and 400 ml of 10% hydrochloric acid were added and the mixture was separated, dried, and distilled to give 27 g of fraction 1, bp 60–72° (3 mm), n^{24}_{D} 1.4747; 20 g of fraction 2, bp 72–74° (3 mm), n^{24}_{D} 1.4939; 14 g of fraction 3, bp 74–85° (3 mm), n^{24}_{D} 1.4973; and 8 g of fraction 4, bp 100–110° (2 mm), n^{24}_{D} 1.5067. Fraction 5 consisted of polymeric residue. The second and third fractions were combined and separated from cyclohexylidenecyclohexanone contaminant by gas chromatography[15] to give a colorless liquid, bp 73° (2 mm), n^{25}_{D} 1.4951; 2,4-dinitrophenylhydrazone, mp 119–120°.

Anal. Calcd for $C_{10}H_{14}O$: C, 80.00; H, 9.33. Found: C, 79.82; H, 9.42.

Spiro[4.5]decan-6-one.—A solution of 9 g of spiro[4.5]dec-2-en-6-one in 90 ml of 95% alcohol was treated with 1.0 g of palladium-on-barium sulfate catalyst (Englehard) and placed in the Parr low-pressure hydrogenator. After 8 hr of shaking at room temperature, 96% of the theoretical amount of hydrogen had been absorbed, and the mixture was filtered and concentrated to give 7.5 g of liquid. Gas chromatographic purification[15] gave a colorless liquid, n^{21}_{D} 1.4870, whose 2,4-dinitrophenylhydrazone melted at 117–118° and showed no depression on mixture with the 2,4-dinitrophenylhydrazone of spiro[4.5]decan-6-one.[19]

Registry No.—II, 13958-65-1; III, 14002-05-2; IV, 13958-66-2; 1,4-dichloro-2-butene, 764-41-0; ethyl 5-carbethoxy-9-ethoxy-7-nonenoate, 13958-67-3; 2-carbethoxy-2-(4-ethoxy-2-butene-1-yl)cyclopentanone, 13958-68-4; 2-carbethoxy-2-(4-ethoxy-2-butene-1-yl)cyclopentanone, 13958-69-5; spiro[4.5]dec-2-en-6-one, 14054-26-3; 2,4-dinitrophenylhydrazone of spiro[4.5]dec-2-en-6-one, 13958-70-8.

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[16] The infrared spectra[12] and the ferric chloride test[11] were used to distinguish between ethyl 1-carbethoxy-2-oxocyclohexaneacetate and ethyl 3-carbethoxy-2-oxocyclohexaneacetate.

[17] When a sample of crude II was hydrolyzed, a crude IV and a bicarbonate-insoluble liquid, found to be III, were isolated. Heating the crude IV with quinoline gave a trace of Ic, thereby indicating the presence of Ib.

[18] When the *trans* isomer was used, the product was much more seriously contaminated with cyclohexylidenecyclohexanone.

[19] R. D. Sands and D. G. Botteron, *J. Org. Chem.*, **28**, 2690 (1963).

Reactions of Phenylmagnesium Bromide with Sterically Hindered Cyclobutanones.

III. The Mechanism of Grignard Addition to These Carbonyl Groups[1,2]

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The results presented here indicate that, in the addition of a Grignard to the carbonyl groups studied, the Grignard species containing the group to be added to the carbonyl carbon is not coordinated to the carbonyl oxygen.[2]

Sterically hindered cyclobutanones, such as I[3,4] and II,[5] undergo three types of reaction with Grignard reagents.[6] A methylmagnesium halide adds to the carbonyl group of I normally to produce a tertiary

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[1] (a) Presented in part at the Meeting of the Georgia Academy of Sciences, Statesboro, Ga., April 22, 1966, Abstracts p 70; (b) research supported by the Petroleum Research Fund administered by the American Chemical Society, Grant-1867-B.

[2] Paper II. R. D. Kimbrough and R. D. Hancock, *Chem. Ind.* (London), 1180 (1965).

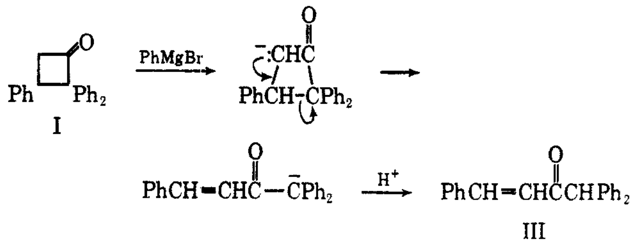
[3] H. Staudinger and E. Suter, *Ber.*, **53**, 1092 (1920).

[4] E. Bergmann and O. Blum-Bergmann, *J. Chem. Soc.*, 727 (1938).

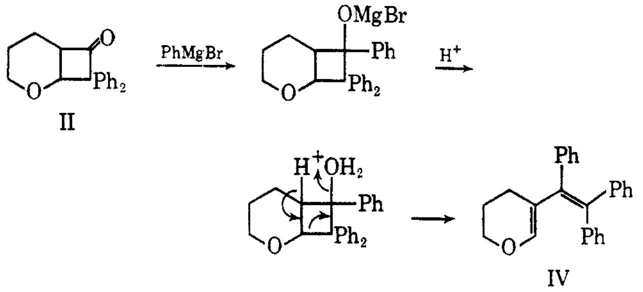
[5] C. D. Hurd and R. D. Kimbrough, *J. Am. Chem. Soc.*, **82**, 1373 (1960).

[6] R. D. Kimbrough, *J. Org. Chem.*, **28**, 3577 (1963).

alcohol.[7] The approach of the bulkier phenylmagnesium bromide to the carbonyl carbon is hindered by the two phenyl groups and the product is the α,β-unsaturated ketone, III.[7] Even though the carbonyl group of II is as hindered as I, phenylmagnesium bromide adds to the carbonyl carbon of II to give the yellow substituted diene, IV.[6] The present investigation is a study of the differences in reactivity between these two sterically hindered cyclobutanones.

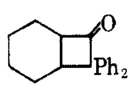


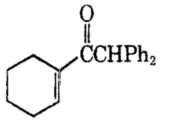
I
III

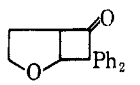


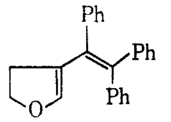
II
IV

The reaction of V[8] with phenylmagnesium bromide produced the α,β-unsaturated ketone, VI,[9] by the same pathway as I but not as II where the product was the yellow substituted diene, IV. Further, VII reacted with phenylmagnesium bromide to give the yellow substituted diene, VIII,[9] resulting from a reaction pathway like that for the formation of IV from II.


V

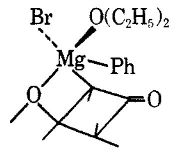

VI


VII


VIII

The cyclobutanones containing an ether oxygen, II and VII, give the yellow dienes, IV and VIII, and the cyclobutanones without this ether oxygen, I and V, give the α,β-unsaturated ketones, III and VI. The factor that decides the mode of reaction of phenylmagnesium bromide with these sterically hindered cyclobutanones seems to be the presence or absence of the ether oxygen.

The carbonyl groups of the cyclobutanones I, II, V, and VII are all so hindered that the solvated phenylmagnesium bromide, $PhMgBr \cdot 2C_2H_5OC_2H_5$,[10] cannot approach near enough to react. However, the ether oxygen on the cyclobutanone ring in II and VII may be able to replace an ether of the Grignard reagent, IX, thus allowing the phenyl group to come close enough to react.[11] In II and VII the approach of the Grignard to the carbonyl carbon is perhaps assisted by the ether oxygen. When this assistance is not available, in I and V, no reaction occurs at the carbonyl carbon.

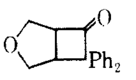

IX

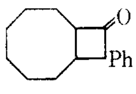
In the reaction of II and VII, the Grignard species which contains the phenyl group to be bonded to the carbonyl carbon is probably coordinated to the ether oxygen, as in IX, and, if that is the case, it cannot be coordinated to the carbonyl oxygen. If there is also a Grignard coordinated to the carbonyl oxygen, two Grignards are involved in the reaction.

Preparation of Cycloadducts of Diphenylketene.—For this investigation several cycloadducts of diphenylketene and cyclic olefins were prepared. The cycloaddition of diphenylketene to electron-rich olefins, such as conjugated dienes, α,β-unsaturated ethers, and thioethers, or vinyl esters, proceeds readily at room temperature to give the substituted cyclobutanones.[3,5,12–14] Cyclohexene requires 3 days in a sealed tube at 110° for cycloaddition to diphenylketene.[8] No other cycloaddition of diphenylketene to simple olefins has been reported.[14]

Diphenylketene was found to react with 2,3-dihydrofuran on mixing at room temperature to give VII in 58% yield.[9] Under these conditions no reaction occured between 2,5-dihydrofuran and diphenylketene, so that pure VII could be prepared from the crude mixture of the two isomeric dihydrofurans obtained on treatment of 2,5-dihydrofuran with potassium *t*-butoxide.[15]

Diphenylketene was found to add to 2,5-dihydrofuran and to cyclooctene at 100° over a period of several days to give the substituted cyclobutanones, X in 51% yield and XI in 74% yield, respectively.[9,16]


X


XI

Experimental Section

Analyses were by Galbraith Laboratories, Inc., Knoxville, Tenn. Melting points are uncorrected. Infrared spectra were recorded with a Perkin-Elmer 221 spectrometer. Nmr spectra were measured with a Varian A-60 spectrometer at 60 Mc using tetramethylsilane as an external standard. Chemical shifts are reported in τ values and relative intensities are given in parentheses.

Phenylmagnesium Bromide and V in Ether at 20°.—With V, the reaction conditions used for the conversion of II to IV[6]

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[7] H. Staudinger and A. Rheiner, *Helv. Chim. Acta*, **7**, 8 (1924).

[8] L. I. Smith, C. L. Agre, R. M. Leekley, and W. W. Prichard, *J. Am. Chem. Soc.*, **61**, 7 (1939).

[9] The structure assignments for VI, VII, VIII, X, and XI are consistent with the elementary analyses, the infrared spectra, and the nmr spectra.

[10] G. D. Stucky and R. E. Rundle, *J. Am. Chem. Soc.*, **85**, 1002 (1963); E. C. Ashby and F. Walker, *J. Organometal. Chem.* (Amsterdam), **7**, 17 (1967).

[11] A similar explanation can be made for a dimeric Grignard structure.

[12] H. Staudinger, *Ber.*, **40**, 1145 (1907).

[13] R. H. Hasek, P. G. Gott, and J. C. Martin, *J. Org. Chem.*, **29**, 1239 (1964).

[14] Extensive work on the cycloaddition of dialkylketenes to olefins has been reported by J. C. Martin and co-workers: J. C. Martin, P. G. Gott, V. W. Goodlet, and R. H. Hasek, *J. Org. Chem.*, **30**, 4175 (1965), and earlier papers.

[15] R. Paul, M. Fluchaire, and G. Collardeau, *Bull. Soc. Chim. France*, 668 (1950).

[16] The cycloaddition of 2,5-dihydrofuran and ethylisobutylketene at 180° in an autoclave has been reported.[13]

gave starting material in 90% recovery: mp 125–128° (lit.[8] mp 132–133°); mmp 129–131°.

Reaction of V with Phenylmagnesium Bromide in Tetrahydrofuran at 65°. Synthesis of 1-Cyclohexenyl Benzhydryl Ketone (VI).—The phenylmagnesium bromide from 10 g of bromobenzene and 5 g of magnesium in 50 ml of ether was decanted from excess magnesium. About half the ether was distilled off, 50 ml of dry tetrahydrofuran was added, and the solvent was distilled off until the boiling point reached 65°. A solution of 2.0 g of V in 15 ml of tetrahydrofuran was added. The mixture was refluxed for 20 hr. The brown reaction mixture was cooled in ice and 50 ml of water was added dropwise with swirling followed by 15 ml of concentrated hydrochloric acid. The resulting mixture was extracted three times with 20 ml of benzene. The combined benzene extracts were dried with $MgSO_4$ and evaporated. The solid residue was recrystallized from 30 ml of ethanol; yield, 1.2 g (60%); mp 124–126°; infrared spectrum (KBr) showed peaks at 6.03, 6.13, 6.89, 8.64, 13.44, and 14.28 μ; nmr (CS_2), τ singlet 2.85 (10), multiplet 3.08 (1), singlet 4.38 (1), doublet 7.80 and 8.45 (8).

Anal. Calcd for $C_{20}H_{20}O$: C, 86.9; H, 7.3. Found: C, 86.9; H, 7.4.

Reaction of VII with Phenylmagnesium Bromide. Synthesis of 4-Triphenylvinyl-2,3-dihydrofuran (VIII).—The ether solution of phenylmagnesium bromide from 10 ml of bromobenzene, 5 g of magnesium, and 50 ml of ether was decanted from the unreacted magnesium. A solution of 2 g of VII in 70 ml of ether was added dropwise at 20°. The mixture was kept at 20° for 3 days. To the stirred and cooled reaction mixture was added dropwise 15 ml of water and 15 ml of concentrated hydrochloric acid. The organic layer was separated and dried over $MgSO_4$. The solvent was evaporated and the semisolid residue crystallized on treatment with ethyl acetate. The yield of yellow crystals was 1.4 g (60%), mp 129–131°. Further recrystallization from ethyl acetate raised the melting point to 137–138°. The infrared (KBr) spectrum showed peaks at 6.27, 6.70, 6.93, 8.51, and 9.65 μ; nmr (CS_2), τ multiplet 2.9 (15), triplet, 4.1 (1), triplet 5.8 (2), sextuplet 7.1 (2).

Anal. Calcd for $C_{24}H_{20}O$: C, 88.8; H, 6.2. Found: C, 88.4; H, 6.2.

Synthesis of 2,3-Dihydrofuran.—The synthesis of 2,3-dihydrofuran was by a modification of the method of Paul.[15] A mixture of 22.5 g of a saturated solution of potassium *t*-butoxide in *t*-butyl alcohol and 17.3 g of 2,5-dihydrofuran was heated in a sealed tube at 165–175° for 6 hr. The reaction mixture was distilled through a 9-in. Vigreaux column and the fraction boiling at 51–61° was collected. This material could be used without further purification in the next experiment, the preparation of VII.

Synthesis of 6,6-Diphenyl-2-oxabicyclo[3.2.0]heptanone-7 (VII).—Diphenylketene[17] (2.0 g) was mixed with 4 ml of the above mixture of the two isomeric dihydrofurans. The reaction mixture became warm and the color faded. The mixture was cooled and a white solid formed. The solid was recrystallized from ethyl acetate–ethanol: yield, 1.6 g (58%); mp 124–126°;[18] infrared (KBr), 3.35, 3.48, 5.63, 8.07, and 9.20 μ; nmr (CS_2), τ multiplet 2.8 (10), doublet 4.8 (1), triplet 6.2 (2), triplet with fine structure 6.8 (1), multiplet 8.1 (2).

Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.8; H, 6.1. Found: C, 82.0; H, 6.1.

Synthesis of 6,6-Diphenyl-3-oxabicyclo[3.2.0]heptanone-7 (X).—A mixture of 6.7 g of diphenylketene[17] and 10 ml of 2,5-dihydrofuran was sealed in a glass tube under nitrogen. The tube was heated at 100° for 5 days, while the color faded to pale yellow. The tube was cooled in ice and the solid product was collected on a filter: yield, 4.6 g (51%); mp 123–124°[18] (the melting point was not raised on recrystallization from ethanol); infrared (KBr), 5.65, 6.70, 6.91, 8.75, 9.22, 9.40, and 11.08 μ; nmr (CS_2), τ multiplet 2.7 (10), multiplet 5.5–6.5 (6).

Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.8; H, 6.1. Found: C, 82.1; H, 6.2.

Synthesis of 9,9-Diphenylbicyclo[6.2.0]decanone-10 (XI).—A mixture of 5.4 g of diphenylketene[17] and 20 ml of cyclooctene was heated at 100° under nitrogen in a tightly stoppered container for 40 hr. The color faded to pale yellow. The excess cyclooctene was evaporated under vacuum and the residue crystallized on addition of ethanol. The solid product was recrystallized from ethanol: yield, 5.5 g (74%); mp 94–95°; infrared (KBr), 3.35, 3.44, 5.64, 6.64, 6.77, and 6.85 μ; nmr (CS_2), τ multiplet 2.7 (10), triplet 6.8 (2), singlet 8.6 (12).

Anal. Calcd for $C_{22}H_{24}O$: C, 86.8; H, 7.9. Found: C, 86.9; H, 8.1.

Registry No.—VI, 4173-56-2; VII, 14002-01-8; VIII, 13958-56-0; X, 14002-02-9; XI, 13958-57-1; phenylmagnesium bromide, 100-58-3.

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[17] L. I. Smith and H. H. Hoehn, *Org. Syn.*, **20**, 47 (1940).

[18] The melting point of a mixture of VII and X was 98–113°.

Hexahydro-1,3,5-trithia-6b-azacyclopenta[*c*,*d*]pentalene

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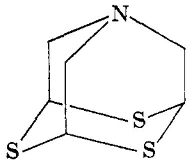
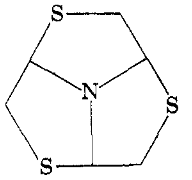
In 1955, Craig and co-workers reported[1] the isolation, as a by-product in the reaction of ammonium dithiocarbamate with chloroacetaldehyde hydrate, of a compound to which they assigned the adamantane structure I. The assignment was based upon elemental analysis and the infrared spectrum, which indicated the absence of NH or SH bonds and any multiple linkages. More recently, Thiel[2] has synthesized I by a relatively unambiguous route and found it to have properties different from those reported by Craig. Thiel was also able to obtain, from ammonia and mercaptoacetaldehyde, a second substance, seemingly identical with Craig's. Utilizing analysis and infrared spectra, he suggested structure II for this compound and submitted that it was this material which Craig had actually isolated.



I



II

Since these are isomeric compounds, and indeed, even give the same product, triethylamine, upon desulfurization with Raney nickel, the structure of II, and its identity with Craig's compound, have remained less than firmly established.

We have obtained a sample of Craig's *original* product,[3] and wish to report that its proton magnetic resonance spectrum confirms Thiel's assignment of structure II, the title compound. Spectra were run on approximately 1% w/v solutions of II in deuteriochloroform, benzene, and trifluoroacetic acid. The solutions in the first two solvents were maintained at 60° during observation to keep II in solution. Coupling constants were abstracted in each case by first-order analysis, and refined by hand computation. They are

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[1] D. Craig, J. J. Shipman, A. Hawthorne, and R. Fowler, *J. Am. Chem. Soc.*, **77**, 1283 (1955).

[2] M. Thiel, F. Asinger, K. Schmiedel, H. Petschik, R. Haberl, and O. Hromatka, *Monatsh. Chem.*, **91**, 473 (1960); M. Thiel, F. Asinger, and K. Schmiedel, *Ann.*, **61**, 121 (1958).

[3] Dr. Craig is deceased. We wish to thank the B. F. Goodrich Co., Brecksville, Ohio, for providing us with this sample.