The details of the experimental method, calculations and a complete discussion of their bearing on the concepts of chemical bonding in ferrocene proposed and discussed by various workers[6,11-13] will be published elsewhere.

The author wishes to thank the Research Corporation and the Monsanto Chemical Co. for supporting this work.

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RECEIVED FEBRUARY 5, 1962

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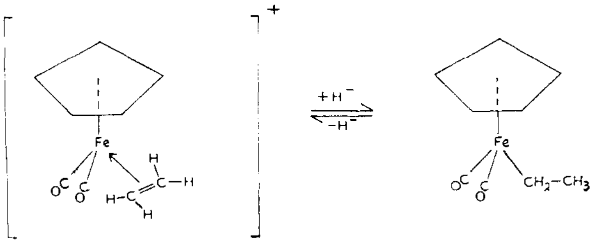
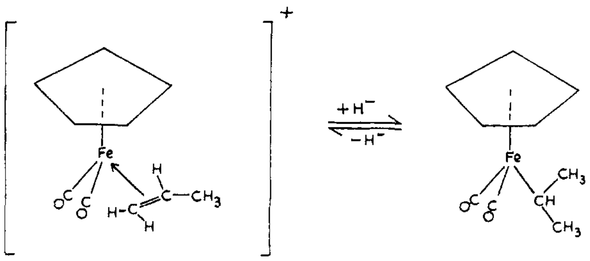
## HYDRIDE ADDITION TO SOME π-BONDED OLEFIN-IRON COMPLEXES

*Sir:*

We have noted previously the abstraction of a hydride ion from some σ-bonded iron–alkyl complexes.[1] We now report that this reaction is *reversible* and that reduction with sodium borohydride of tetrahydrofuran solutions of the cation perchlorates, $[\pi\text{-}C_5H_5Fe(CO)_2CH_2{=}CHR]^+ClO_4^-$ where R = H,Me,[1,2,3] forms σ-alkyl complexes. The cation (I), R = H, gives the ethyl complex (II) in good yields. The product was identified by comparison of the infrared and proton magnetic resonance spectra with those of a sample of the ethyl compound prepared as previously reported.[4] Reduction of the cation (III), R = Me, gives the isopropyl complex (IV) in high yield. The isopropyl complex was identified by the comparison of the spectra with those of characterized samples of the isopropyl and *n*-propyl complexes prepared by the reaction of the sodium salt, $Na^+[\pi\text{-}C_5H_5\text{-}Fe(CO)_2]^-$ with the propyl halides.[5] No *n*-propyl isomer was found in the reaction products. The major product of the reduction of the cation $[Mn(CO)_5.\text{propene}]^+$,[5] under similar conditions, was manganese carbonyl. When the reduction of the cation (III) was carried out in the presence of a large excess of 1-hexene and also of butadiene only the isopropyl complex (IV) was formed. It therefore seems reasonable that the reaction proceeds by an internal mechanism rather than by the prior formation of the hydride $\pi\text{-}C_5H_5Fe(CO)_2H$[6] and expulsion of the propene, followed by the addition of the Fe-H across the olefinic double bond. This latter reaction has been shown separately.[5] The reaction may proceed by hydride ion attack either on the metal, as suggested for the reduction of the related cobalticinium cation,[7] or on the cyclopentadienyl group, with transfer from the intermediate cyclopentadiene complex to the ethylenic group,[6] or directly on the ethylenic group.



I II



III IV

Since the propene cation (III) may be prepared readily from the *n*-propyl complex, $\pi\text{-}C_5H_5Fe\text{-}(CO)_2n\text{-propyl}$,[1] and its reduction gives high yields of the isopropyl complex (IV), the isomerization of the *n*-propyl to isopropyl may be understood as a simple, two-step hydride removal and addition process. This mechanism is very similar to that put forward recently for the isomerization of olefins on metal surfaces.[8] Also this reversible conversion of alkyl to olefin complexes very clearly bears a strong relationship to the intermediate steps postulated to occur in the hydroformylation, Fischer–Tropsch and related reactions.[8]

**Acknowledgments.**—We thank the International Nickel Company (Mond) Ltd. for a gift of iron carbonyl, the Ethyl Corporation for a gift of manganese carbonyl and the Hungarian Relief Fund for financial support to P.L.I.N.

(1) M. L. H. Green and P. L. I. Nagy, *Proc. Chem. Soc.*, in press.

(2) E. O. Fischer and K. Fichtel, *Chem. Ber.*, 1200 (1961).

(3) M. L. H. Green and P. L. I. Nagy, *Proc. Chem. Soc.*, 378 (1961).

(4) T. S. Piper and G. Wilkinson, *J. Inorg. and Nucl. Chem.*, **3**, 104 (1956).

(5) M. L. H. Green and P. L. I. Nagy, to be published.

(6) A. Davison, M. L. H. Green and G. Wilkinson, *J. Chem. Soc.*, 3172 (1961).

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(8) H. W. Sternberg and I. Wender, Int. Conf. Co-ordination Chem. London, 1959. Chem. Soc. Special Publ., No. 13, p. 35, and references therein.

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RECEIVED FEBRUARY 1, 1962

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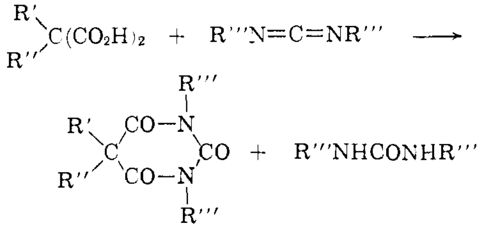
## A NEW SYNTHESIS OF BARBITURIC ACIDS

*Sir:*

We wish to report that the reaction of carbodiimides with substituted malonic acids leads to barbiturates in many instances. Thus, when malonic acid and two moles of N,N′-dicyclohexylcarbodiimide were brought together in tetrahydrofuran solution, an exothermic reaction ensued with the separation of crystalline N,N′-dicyclohexylurea. On filtering off the urea and evaporating the tetrahydrofuran solution, a colorless crystalline compound I, m.p. 200–201°, was obtained in 65% yield (based on the malonic acid). *Anal.* Calcd. for $C_{16}H_{24}N_2O_3$: C, 65.72; H, 8.27; N, 9.58. Found: C, 66.00; H, 8.19; N, 9.39.

Partly on the basis of n.m.r. and infrared spectra, the barbituric acid structure I was assigned to this compound. The correctness of this assignment was later proved by the synthesis of I by the action of malonyl chloride on N,N′-dicyclohexylurea.

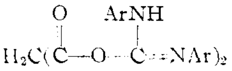


I, R′ = H, R″ = H, R‴ = $C_6H_{11}$
II, R′ = H, R″ = $C_6H_5CH_2$, R‴ = $C_6H_{11}$
III, R′ = Et, R″ = Et, R‴ = $C_6H_{11}$
IV, R′ = H, R″ = H, R‴ = *i*-Pr
V, R′ = Et, R″ = Et, R‴ = *p*-tolyl

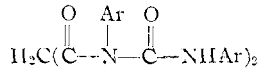
Substituted malonic acids led to substituted barbiturates on reaction with N,N′-dicyclohexylcarbodiimide and N,N′-diisopropylcarbodiimide. Some of the compounds prepared by this method are: II, m.p. 120–121°; III, m.p. 160–162°; IV, m.p. 128–129°.

Malonic acid and di-*p*-dimethylaminophenylcarbodiimide have been reported to react in pyridine medium to give a diacylurea but the fate of malonic acid on reaction with di-*p*-tolylcarbodiimide has not been established.[1] We found that the reaction of malonic acid with N,N′-di-*p*-tolylcarbodiimide in tetrahydrofuran solution afforded N,N′-di-*p*-tolylurea and a compound that melted at 141–142°, solidified at about 150° and remelted at 225–230°. *Anal.* Calcd. for $C_{33}H_{32}N_4O_4$: C, 72.24; H, 5.88; N, 10.21; mol. wt., 548.6. Found: C, 72.63; H, 5.68; N, 9.93; mol. wt., 570; $\lambda_{\max}^{\text{nujol}}$: 3.05–3.20μ (weak), 5.76μ (strong), 5.95μ (weak), 6.00μ (weak); n.m.r. peaks,[2] 7.68 (6H), 7.58 (6H), 6.77 (2H), 2.78 (center of multiple peak, 16H), −0.87 (2H).

On the basis of infrared and n.m.r. spectra, we prefer structure VI to the acylurea structure VII for this compound. On heating above the melting point, VI was converted into the di-*p*-toluidide of malonic acid. Analogous results were obtained on using ethylmalonic acid. When, however, diethylmalonic acid was allowed to react with N,N′-di-*p*-tolylcarbodiimide the barbiturate V, m.p. 168–168.5°, was formed readily.

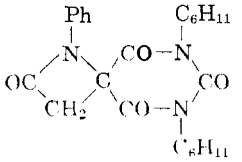

$$H_2C(\overset{\overset{O}{\|}}{C}-O-\overset{\overset{ArNH}{|}}{C}=NAr)_2$$

VI


$$H_2C(\overset{\overset{O}{\|}}{C}-\overset{\overset{Ar}{|}}{N}-\overset{\overset{O}{\|}}{C}-NHAr)_2$$

VII

The difference between aromatic and aliphatic carbodiimides in the reaction with malonic acid is striking. It is also remarkable that diethylmalonic acid yields a barbiturate on reaction with di-*p*-tolylcarbodiimide but ethylmalonic and malonic acids do not. The role of steric and electronic factors in these reactions is under investigation.



VIII

The usefulness of this novel reaction of carbodiimides was demonstrated by the synthesis of β-lactam-substituted spirobarbiturates [for example, VIII, m.p. 234–235°] which could not be prepared by the usual methods of barbituric acid synthesis.

We are thankful to J. Zuclich[3] and J. Pelosi[3] for valuable technical assistance and to Dr. E. R. Malinowski and R. S. Magee[3] for the n.m.r. spectra and their interpretation. This investigation was supported in part by a research grant (MY-3930) from the National Institute of Mental Health, U. S. Public Health Service, for which grateful acknowledgement is made.

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[1] F. Zetzsche and H. Lindlar, *Ber.*, **71**, 2095 (1938).

[2] Determined in dilute deuterated chloroform solution using tetramethylsilane as an internal standard. The first number indicates the τ value and the figure in parentheses denotes the number of equivalent protons under the peak.

[3] National Science Foundation undergraduate research participant.

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## COMPLEX FORMATION IN OLIGONUCLEOTIDES AND ITS APPLICATION TO THE SEPARATION OF POLYNUCLEOTIDES

*Sir:*

Recent studies[1] on oligonucleotides have shown that they are capable of complexing with themselves in buffered salt solutions. The complex formation appears to be of the "Watson-Crick" type and depends on the chain length, temperature and nature of the nucleotide bases present. For example, a mixture of thymidine dodecanucleotide,[2] $(pT)_{12}$ and 2 mole equivalents of deoxyadenosine hexanucleotide, d-$(pA)_6$ at 0° in 1 *M* NaCl, pH 7 displays an 11% decrease in optical density at 259 and 267 mμ. The complex melts over the range 4–30° with a melting point ($T_m$) at *ca.* 16°. A mixture of $(pT)_6$ and d-$(pA)_6$, however, shows no significant hypochromicity under these conditions.

These results suggested the possibility of devising a polynucleotide-cellulose column which would separate polynucleotides not only on the basis of their nucleotide composition, but also by virtue of their nucleotide sequence. A column of cellulose on which polynucleotide chains had been incorporated by bonding at one end of the chains, was expected to be the most efficient, as this type of column should allow maximum interaction with the polynucleotides to be separated.

Thymidine 5′-phosphate (2 mmole) in dry pyridine (3 ml.) was mixed with dicyclohexylcarbodiimide (4 mmole) and shaken with glass balls for 5 days. The mixture was added to dry cellulose (5 g.) dicyclohexylcarbodiimide (2 g.) in pyridine (50 ml.) and shaken for 5 days. The filtered cellulose was washed with pyridine and allowed to stand in aqueous pyridine overnight and then washed with ethanol and water. Analysis of the combined washings showed an incorporation of the nucleotide of more than 50%. The cellulose prepared in this way was expected to contain chains of thymidine polynucleotides (of up to *ca.*

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[1] P. T. Gilham, unpublished.

[2] For preparation of oligonucleotides see H. G. Khorana and J. P. Vizsolyi, *J. Am. Chem. Soc.*, **83**, 675 (1961); R. K. Ralph and H. G. Khorana, *ibid.*, **83**, 2926 (1961).