effect in these and other solvolyses reactions becomes more prominent as the water percentage of alcohol-water solutions is increased.[16] It also is prominent in "80%" acetone. This is to be expected, on the basis that solvation of the electron-deficient ring of the transition state should tend to become more important, and hence more sensitive to steric shielding, as the water content of the solvent is increased.[17,25] It is interesting to note that as the alcohol percentage is decreased, the heats of activation tend to increase slightly, rather than decrease (Tables I, II and III). Thus the general increase in rate accompanying a decrease in alcohol percentage is due to an increase in the entropy of activation. Both the increase in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ with increasing water content of the ethanol-water solvents may be a reflection of the fact that those solvent molecules that participate in solvating the highly polar transition state (perhaps preferentially water molecules) are in the ground state more tightly associated with neighboring solvent molecules in the more aqueous solvent mixture. The lower rates in "80%" acetone (Table IV) are mainly due to a less favorable, more negative, entropy of activation. Perhaps this means that solvent association is less rigid in this medium.

Acknowledgment.—The authors wish to express their appreciation to the Office of Ordnance Research, United States Army, for partial support of this research.

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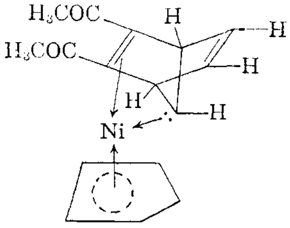
[25] The Baker–Nathan effect in the principal electronic transition energies of *p* alkylnitrobenzenes and acetophenones is found only in polar basic solvents and is more prominent in water than in various alcohols.[13]

COMMUNICATIONS TO THE EDITOR

THE SYNTHESIS OF [2,3-BIS-(METHOXYCARBONYL)-2π,5-NORBORNADIEN-7-YL](π-CYCLOPENTADIENYL) NICKEL(II)[1]

Sir:

A new class of nickel complexes has been discovered as a result of the reaction of dicyclopentadienylnickel with dimethyl acetylenedicarboxylate. In a previous communication[2] it was reported that acetylene reacted with dicyclopentadienylnickel to form the binuclear nickel complex bis-(cyclopentadienylnickel)-acetylene. Recently, it has been found that substitution of electron withdrawing groups about the acetylenic bond altered the electronic distribution about the bond to such an extent that binuclear nickel complexes were not formed as major products of reaction with dicyclopentadienylnickel. Thus, when dimethylacetylene dicarboxylate was contacted with dicyclopentadienylnickel a bright orange-red air stable solid, m.p. 84°, was isolated which possessed an elemental composition and a molecular weight indicative of a simple bimolecular coupling of the two reactants. On the basis of its diamagnetism,[3] n.m.r. data and degradative studies, structure I is proposed for the new complex.



I

The complex was prepared by contacting a solution of 2.0 g. (0.011 mole) of dicyclopentadienylnickel with 1.5 g. (0.011 mole) of dimethyl acetylenedicarboxylate in 25 ml. of tetrahydrofuran at room temperature for 65 hours under a protective atmosphere of pure nitrogen. The solvent was removed under reduced pressure at room temperature and the residue was relieved of 0.6 g. of unreacted dicyclopentadienylnickel by sublimation at 40° and 0.02 mm. The remaining residue was extracted with hot low boiling petroleum ether and the orange extracts were filtered. Concentration of the filtrate caused the crystallization of 1.7 g. of a dark red solid which was purified by recrystallizations from methanol and low boiling petroleum ether to yield an orange red solid, m.p. 84° (calcd. for $C_{16}H_{16}O_4Ni$: C, 58.1; H, 4.87; Ni, 17.7; mol. wt., 331. Found: C, 57.9; H, 4.88; Ni, 17.4; mol. wt., 326. The yield of product based on consumed dicyclopentadienylnickel was 68%.

Hydrogenation of the complex in ethanol over platinum at atmospheric pressure and room temperature caused complete decomposition to metallic nickel, cyclopentane and dimethyl *endo-cis*-2,3-norbornanedicarboxylate, m.p. 55°. Calcd. for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60; found: C, 62.3; H, 7.55. The organic fragments were isolated in yields of 70 and 60%, respectively. The identity of cyclopentane was established by comparing it with an authentic sample with vapor phase chromatographic and mass spectrometric techniques. An authentic sample of dimethyl-*cis-endo*-2,3-norbornanedicarboxylate was prepared by a Diels–Alder addition of dimethyl acetylenedicarboxylate and cyclopentadiene and then reduction over platinum. The degradative sample and the synthesized material were identical, having superimposable infrared spectra and identical melting points separately or mixed. The above results indi-

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[1] Presented before the 138th meeting of the American Chemical Society, New York, N. Y., Sept., 1960.

[2] M. Dubeck, *J. Am. Chem. Soc.*, **82**, 502 (1960).

[3] I am indebted to Dr. Stanley Kirschner, Wayne State University, for the magnetic susceptibility measurements.

cated that when dimethyl acetylenedicarboxylate reacted with dicyclopentadienyl nickel it did so in a typical Diels–Alder manner with one of the cyclopentadienyl rings leaving the remaining one intact. Supporting evidence for this type of addition was obtained from a study of the n.m.r. spectrum of the complex which revealed a single signal at −5.24 p.p.m. relative to tetramethylsilane and with an intensity signifying five equivalent hydrogens in the molecule. The entire n.m.r. spectrum consisted of signals at −6.55, −5.24, −3.7 and −2.18 p.p.m., with relative intensities in the ratio of 2:5:8:1, respectively. The triplet at −6.55 was assigned to the two free olefinic protons shown in Structure I. The group of bands at −3.7 was concluded to be a superposition of a singlet from the six methoxy hydrogens over a partially visible multiplet from the two tertiary type hydrogens. The small triplet at −2.18 p.p.m. was assigned to the lone hydrogen bonded to the carbon possessing a free pair of electrons bonded to nickel.

Complex I represents an example of a non-conjugated olefin electron pair system bonded to a metal. A most notable feature of the structure is that the double bond bonded to nickel arises from the incoming reagent, dimethylacetylene dicarboxylate, and not from the cyclopentadienyl ring originally bonded to nickel. The extension of this reaction to other acetylenes together with a more detailed discussion of the structure will be set forth in a future publication.

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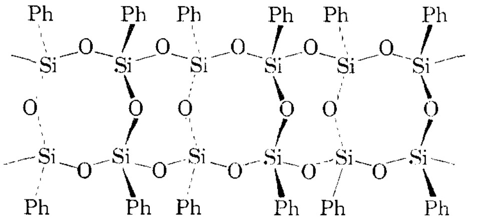
RECEIVED SEPTEMBER 20, 1960

DOUBLE CHAIN POLYMERS OF PHENYLSILSESQUIOXANE

Sir:

We wish to report the synthesis of high molecular weight soluble polymers from a trifunctional monomer, along with evidence that they possess a stereoregular double chain structure. These polymers contain phenylsilsesquioxane (*i.e.*, "phenyl-T" or $C_6H_5SiO_{3/2}$) units joined together to form syndiotactic chains which are joined in turn through *cis*-fusion at each unit to give a "ladder" like linear network structure:



Soluble low polymers of phenylsilsesquioxane have been prepared by equilibrating the condensation products of phenylsilanetriol in a suitable solvent, such as toluene, xylene, or diglyme.[1] Thus, refluxing a mixture of the hydrolysate of phenyltrichlorosilane with 0.1% KOH and an equal weight of toluene through a distilling trap arranged for water separation for 16 hours, cooling, filtering off the small amounts of crystalline phenyl-T_8 and phenyl-T_{12} formed, and precipitating the product into ligroin or methanol resulted in approximately 99.9% condensation of the silanol and gave a polymer analyzing correctly for $(C_6H_5SiO_{3/2})_x$. We observed no tendency toward gelation in any such equilibration where enough solvent was present to give a liquid mixture. The polymer obtained, ($[\eta]$ = 0.12 dl./g. in benzene, $\bar{M}_n$ = 14,000, $\bar{M}_w$ = 26,000) showed a "most probable" molecular weight distribution, rather than the very broad distribution expected for a branched polymer and observed for methylsilsesquioxane copolymers.[2] Fractionation gave a little additional T_{12} and a series of polymer fractions which showed the steep, linear log $[\eta]$ *vs.* log $\bar{M}_w$ relation ($a = 0.92$) characteristic of linear, nearly rigid rod polymers, rather than the very low slope $[\eta]$ *vs.* $\bar{M}_w$ relations observed for micromicrogels.[2]

The soluble phenyl-T polymers prepared by Sprung and Guenther[3] *via* the base-catalyzed hydrolysis of phenyltriethoxysilane resemble the above materials in their infrared spectra and X-ray diffraction patterns, but are of somewhat higher molecular weight ($[\eta]$ = 0.14–0.26 dl./g.) and somewhat narrower molecular weight distribution.

Soluble polymers of much higher molecular weight have been obtained by equilibrating phenyltrichlorosilane hydrolysate, phenyl-T_{12}, or the above soluble low polymers with an alkaline rearrangement catalyst in the presence of lesser (*e.g.*, 5–30%) quantities of suitable solvents.[1] For example, a mixture of 0.50 g. of phenyltrichlorosilane hydrolysate, 0.5 mg. of KOH, 0.5 g. of benzene, and 0.13 g. of Dowtherm A was heated for one hour at 250° in a loosely stoppered test-tube. The resulting tough, frothy mass was dissolved in benzene, neutralized with acetic acid, and precipitated into a large excess of methanol to give 0.33 g. of high polymer, $[\eta]$ = 4.0 dl./g., $\bar{M}_w = 4.1 \times 10^6$. However, curvature in the $[\eta]$-$\bar{M}_w$ relations indicated that some branching was present in such specimens where $\bar{M}_w > 2 \times 10^5$.

None of the phenylsilsesquioxane polymers obtained could be melted upon heating, but they did dissolve in benzene, tetrahydrofuran, and methylene chloride, and films of the higher polymers could be oriented by stretching in benzene vapor. The X-ray diffraction patterns of the crude polymerization products, the reprecipitated dry polymers, and of the oriented films indicated that all such polymer specimens were poorly crystallized (7–8 distinct reflections observed, none very sharp). Evidently, the direction of the polymerization process is not controlled by the formation of an extended crystalline phase.

The X-ray data (repeating distance 5.0 ± 0.5 Å., mean interchain spacing 12.5Å., whence four monomer units per repeating chain segment), detailed analyses of the ν_a(Si–O–Si) skeletal chain vibrational spectrum in the 1040–1160 cm.$^{-1}$ region of the infrared, and determinations of end

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[1] General Electric Company, Belgian Patent 586,783, May 16, 1960.

[2] F. P. Price, S. G. Martin and J. P. Bianchi, *J. Polymer Sci.*, **22**, 41 (1956).

[3] M. M. Sprung and F. O. Guenther, *ibid.*, **28**, 17 (1958).