establish that $FeCl^{2+}$ is produced in the reaction of $CoCl^{2+}$ with Fe^{2+} and that this reaction proceeds *via* an inner-sphere activated complex in which the chloride is bonded directly to both the cobalt and the iron.

It should be noted that the equilibrium constant for the reaction $Co^{3+} + Cl^- \rightleftharpoons CoCl^{2+}$ is about ten times larger than that for the $Fe^{3+} + Cl^- \rightleftharpoons FeCl^{2+}$ reaction.[7] Consequently, when the chloride is added to only the cobalt(III), the amount of $FeCl^{2+}$ produced in the $CoCl^{2+} + Fe^{2+}$ reaction is about forty times its final equilibrium concentration.

In order to minimize the extent of the reaction

$$2Co^{3+} + 2Cl^- \rightleftharpoons 2Co^{2+} + Cl_2$$
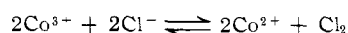
the cobalt(III) was generally added to the chloride solution immediately before the runs.[7] On the other hand, when the cobalt(III) chloride solution was allowed to age for about 15 min. prior to mixing it with the iron(II) solution, a reaction which produces $FeCl^{2+}$ at a rate intermediate between that of the $CoCl^{2+} + Fe^{2+}$ and $Fe^{3+} + Cl^-$ reactions could be detected. Apparently this reaction is the oxidation of Fe^{2+} by Cl_2. This was confirmed by mixing a solution of Cl_2 in 3.0 M $HClO_4$ containing 4.0×10^{-3} M (Cl^-) with a solution containing 1.0 M [Fe(II)] and 3.0 M ($HClO_4$); the formation of $FeCl^{2+}$ ($k \approx 50$ M^{-1} sec.$^{-1}$) and its subsequent dissociation were observed.

(7) T. J. Conocchioli, G. H. Nancollas, and N. Sutin, submitted to *Proc. Chem. Soc.*

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Tetrakis(trimethylsilyl)silane

Sir:

Since the first reported preparation of a branched chain organopolysilane,[1] several efforts have been made to synthesize tetrasilyl-substituted silanes.[1,2] Tris(triphenylsilyl)silane (4.4%) was obtained from the reaction of trichlorosilane with triphenylsilyllithium.[1] The attempted synthesis of tetrakis(triphenylsilyl)silane by the reaction of triphenylsilyllithium and silicon tetrachloride only afforded hexaphenyldisilane (72%) and a yellow oil.[1] We now report the preparation of tetrakis(trimethylsilyl)silane (I).

<p align="center">
SiMe₃
|
Me₃Si–Si–SiMe₃
|
SiMe₃
I
</p>
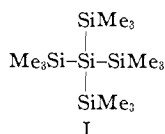
In a typical procedure, 94.18 g. (0.864 mole, 20% molar excess) of chlorotrimethylsilane was dissolved in 200 ml. of sodium-dried tetrahydrofuran, to which 15.13 g. (2.16 g.-atom, 50% g.-atom excess) of lithium wire was added. To this rapidly stirred mixture, 20 ml. of a solution of 30 g. (0.18 mole) of silicon tetrachloride dissolved in 150 ml. of sodium-dried tetrahydrofuran

(1) D. Wittenberg, M. V. George, and H. Gilman, *J. Am. Chem. Soc.*, **81**, 4812 (1959).

(2) G. Schwebke and P. K. Sen, unpublished studies.

was added at room temperature.[3] After stirring at room temperature for 4 hr., the reaction mixture became dark brown and heat was evolved. At this stage, dropwise addition of the silicon tetrachloride solution was continued. Upon completed addition, the mixture was stirred overnight at room temperature. Unreacted lithium metal, some salts, and a brown polymer[4] were separated by filtration of the reaction mixture prior to hydrolysis with 200 ml. of 15% hydrochloric acid. The organic layer was separated, dried over anhydrous sodium sulfate, and the organic solvents were distilled under reduced pressure. To the yellow semisolid residue was added a few milliliters of 95% ethanol. The solids were filtered from the ethanolic solution and purified by sublimation at 75° (0.01 mm.) giving 40.5 g. (70%) of I, m.p. 261–263.[5] Gas phase chromatography on a Dow Corning silicone grease column at 200° gave a single peak indicative of its purity. *Anal.* Calcd. for $C_{12}H_{36}Si_5$: C, 44.91; H, 11.31; mol. wt., 321. Found: C, 45.76; H, 11.22; mol. wt., 319 (by osmometry in benzene). The infrared spectrum of I showed no peaks indicative of Si–H, Si–OH, or Si–O–Si. N.m.r. exhibits a sharp singlet at τ 9.79, consistent with the highly symmetrical structure. Also, it is of interest that its high melting point[6] and ease of sublimation are presumably associated with its symmetry. Other related group IVB types are being investigated.

(3) Silicon tetrachloride reacts with refluxing tetrahydrofuran giving a mixture of chlorobutoxysilanes [M. Kratochvil and J. Frejka, *Chem. Listy*, **52**, 151 (1958); *Chem. Abstr.*, **52**, 16, 329e (1958)].

(4) Possibly mixtures of siloxanes.

(5) Melting points were taken in a sealed tube completely immersed in the heating unit of a Mel-Temp melting point apparatus.

(6) With the straight chain analogs of the type Me₃Si(SiMe₂)ₙSiMe₃, only n = 6, b.p. 194–198° (3 mm.), m.p. 60–61, and n = 8, b.p. 244° (3 mm.), m.p. 113–114°, are low melting solids; whereas n = 0 through 5 are liquids. [M. Kumada, private communication; also see M. Kumada and M. Ishikawa, *J. Organometal. Chem.*, **1**, 153 (1963)].

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## Conversion of Hexasubstituted Benzenes to Cyclohexadienones

Sir:

In a recent communication[1] the use of peroxytrifluoroacetic acid in the presence of boron fluoride to effect hydroxylation of aromatic hydrocarbons was reported. For example, mesitylene was converted to mesitol in good yield with efficient use of the peracid. In the oxidation of prehnitene (1) a cyclohexadienone (II) was isolated in small quantities, and its formation was attributed to attack by a positive species (here referred to, for simplicity, as OH^+), followed by methyl

(1) C. A. Buehler and H. Hart, *J. Am. Chem. Soc.*, **85**, 2177 (1963).

migration as shown
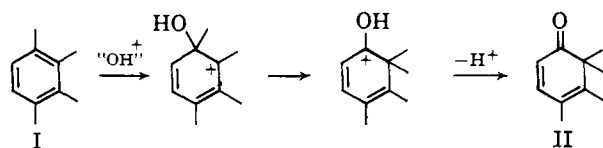
We have now studied the reaction of this reagent with hexaalkylbenzenes, where phenol production is impossible, but where alkyl migration should become important. This hope was fulfilled when hexamethylbenzene was converted at $0°$ in excellent yield to 2,3,4,-5,6,6-hexamethyl-2,4-cyclohexadienone (III), and hexaethylbenzene to the analogous hexaethylcyclohexadienone (IV), even at $-40°$.

III, R = CH₃
IV, R = C₂H₅
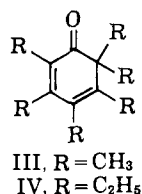
These cyclohexadienones, unlike less substituted analogs, are stable to dimerization, no change being detected after they had been allowed to stand neat, in the dark at room temperature, for 2 months.[2] However, reflux of an ether solution of III with maleic anhydride gave an adduct (V), m.p. 139.5–140.5°.

V
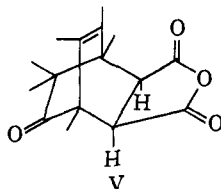
The structure of dienone III follows from its physical properties and reactions. Its infrared spectrum shows conjugated carbonyl absorption at 1642 cm.$^{-1}$ (CCl₄) or 1647 cm.$^{-1}$ (liquid film) and C=C absorption at 1567 cm.$^{-1}$ (liquid film).[3] III, which is a yellow oil, has a λ_{max}^{EtOH} 330 mμ (log ϵ 3.62), similar to that reported earlier[1] for II (λ_{max} 327 mμ, log ϵ 3.48), and devoid of the changes which one might predict for additional methyl substitution.[3] The n.m.r. spectrum of III consisted of three singlets at τ 8.89, 8.14, and 7.96 with relative areas 2:3:1, which are assigned, respectively, to the gem-dimethyl group at C-6, the three allylic methyls at C-3, C-4, and C-5, and the single methyl group on C-2, adjacent to the carbonyl.
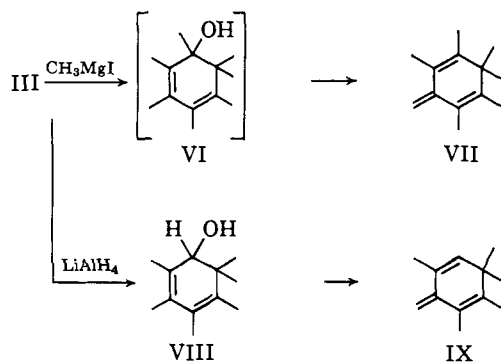
Reaction of III with methylmagnesium iodide in ether, followed by ammonium chloride work-up, failed to give alcohol VI, but led directly to triene VII in good yield. This triene, previously prepared by Doering, et al.,[4] was readily converted, in hydrochloric acid, to the heptamethylbenzenonium ion. Properties of VII and the carbonium ion obtained from

it by protonation are in reasonable agreement with those reported earlier.[4,5]

Dienone III was reduced with the expectation that the resulting alcohol VIII might, on protonation, be converted to hexamethylbenzene. Lithium aluminum hydride reduction of III followed by alkaline hydrolytic work-up led to an oil, which was presumed to be VIII, but on exposure to laboratory air the oil rapidly became cloudy and deposited water. The new product was shown to be triene IX. Its infrared spectrum (CCl₄) was very similar to that of VII, with a doublet at 1377 cm.$^{-1}$ (gem-dimethyl), conjugated C=C bonds at 1680, 1613, and 1560 cm.$^{-1}$, and a terminal methylene band at 862 cm.$^{-1}$. Its ultraviolet spectrum (isooctane) was superimposable on that of VII. Its n.m.r. spectrum had singlets at τ 8.93 (6 protons, gem-dimethyl), 8.19 and 8.16 (6 and 3 protons, respectively, allylic methyls), and at 4.57 (1 ring vinyl proton) and a multiplet at τ 5.14–5.19 (2 methylene protons). The formation of cross-conjugated rather than completely conjugated triene, even when one less methyl group is present, is noteworthy.

Although IX was formed by the dehydration of VIII, treatment of the triene, in ethanol, with a few drops of hydrochloric acid led to rather rapid rearrangement to hexamethylbenzene in moderate yield.

Extension of the use of this oxidizing reagent to other highly substituted aromatics, as well as to olefins of biogenetic interest, is in progress, and further study of the properties of these highly substituted dienones and trienes is planned

A procedure for the preparation of III follows: A solution of peroxytrifluoroacetic acid (0.06 mole, from 1.63 ml. of 90% H₂O₂ and 9.75 ml. of trifluoroacetic anhydride) in distilled methylene chloride was kept at $0°$ and added dropwise over 45 min. to a solution of 9.7 g. of hexamethylbenzene in 100 ml. of methylene chloride. The reaction mixture was maintained at $0°$ by external cooling, and BF₃ (0.06 mole) was passed into it during the addition. The mixture was stirred an extra 35 min., then water (30 ml.) was added, and the organic layer was washed with bicarbonate and water and dried. Evaporation gave a yellow oil mixed with a solid (unreacted hexamethylbenzene). The crude mixture, chromatographed on alumina, gave 1.54 g. (16%) of unchanged hexamethylbenzene, eluted with petroleum ether (b.p. 30–60°), and 8.33 g.

(2) Cf. D. Y. Curtin and R. R. Fraser, Chem. Ind. (London), 1358 (1957); K. Alder, F. H. Flock, and H. Lessenich, Ber., 90, 1709 (1957); D. Y. Curtin, R. J. Crawford, and M. Wilhelm, J. Am. Chem. Soc., 80, 1391 (1958); J. D. McClure, J. Org. Chem., 28, 69 (1963).

(3) These figures are slightly outside the usual range quoted for cyclohexadienones. The special features of this and other physical properties of hexasubstituted dienones will be discussed in a full paper.

(4) W. von E. Doering, M. Saunders, H. G. Boyton, H. W. Earhart, E. F. Wadley, W. R. Edwards, and G. Laber, Tetrahedron, 4, 178 (1958).

(5) The relative positions and areas of peaks in the n.m.r. spectra are identical, but earlier[4] τ-values are in appreciable error; our values agree with what might now be reasonably expected for the absolute band positions, in comparison with model compounds. The ultraviolet spectra agree well.

(93% based on converted starting material) of III, b.p. 87–90° (1.5 mm.).[6]

When 1.23 equiv. of peroxytrifluoracetic acid and BF_3 was used, an 88% yield of III was obtained and only 4% of unchanged hexamethylbenzene remained. When BF_3 was omitted, the conversion was only 70%, although the yield of III was 86%.

Acknowledgment.—We are grateful to the National Science Foundation (GP-71) for financial support of this work. A. J. W. also wishes to thank the United States Educational Commission in the United Kingdom for the award of a Fulbright Travel Grant.

(6) New compounds III, IV, V, and IX gave correct microanalyses.

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Heterocyclic Studies. XI.[1] The Tautomeric Structure of 3(5)-Methyl-4-phenylpyrazole

Sir:

It has long been recognized that unsymmetrical pyrazoles can exist in two tautomeric forms, 1 and 2. von Auwers[2] concluded from molecular refraction exaltations that the 3-phenyl tautomers (2, R = C_6H_5) predominated in 3(5)-phenylpyrazole and methyl 3(5)-phenylpyrazole-5(3)-carboxylate. This method was applicable only to 3(5)-arylpyrazoles, and little further work on the question of pyrazole tautomerism has been done.[3] The data presented below indicate that the tautomeric structure of 3(5)-substituted pyrazoles can be determined from n.m.r. measurements by the method used by Moore and Whittaker to establish the structure of tetrazole.[4]

A major problem in approaching the question of pyrazole tautomerism is the difficulty of obtaining N-alkyl pyrazole isomers of rigorously known structure.[5] We have now prepared 3- and 5-methyl-4-phenylpyrazole-1-acetic acids by conventional syntheses from 1-ethoxymethylene-1-phenylacetone and ethyl hydrazinoacetate, and also by alkylation of 3(5)-methyl-4-phenylpyrazole[7] with methyl bromoacetate: 3-methyl isomer (4), m.p. 212°, λ_{max}^{EtOH} 245 mμ, methyl ester, m.p.

(1) Paper X: J. A. Moore and L. J. Pandya, *J. Org. Chem.*, **29**, 336 (1964).

(2) K. von Auwers, *Ann.*, **508**, 51 (1933).

(3) A recent review has been presented by A. R. Katritzky and J. M. Lagowski, "Advances in Heterocyclic Chemistry," Vol. 2, Academic Press, New York, N. Y., 1963, p. 31.

(4) D. W. Moore and A. G. Whittaker, *J. Am. Chem. Soc.*, **82**, 5007 (1960).

(5) Structures were assigned to a number of isomeric pairs of N-alkyl pyrazoles, *e.g.*, 1,3- and 1,5-dimethylpyrazole (K. von Auwers and H. Hollmann, *Ber.*, **59**, 601, 1282 (1926)) on the basis of fairly complete chemical evidence, but reversal of the assignment for the dimethyl isomers has recently been suggested[6] on the basis of assumptions concerning the mechanism of condensation of methylhydrazine and β-keto acetals. If these later conclusions are valid, presumably many of the structural assignments made by von Auwers and others are open to question.

(6) D. M. Burness, *J. Org. Chem.*, **21**, 97 (1956).

(7) G. N. Walker and B. N. Weaver, *ibid.*, **26**, 4441 (1961).

60°; 5-methyl isomer (3), m.p. 212°, λ_{max}^{EtOH} 244 mμ, methyl ester, m.p. 91°.[8] A firm basis for the structural assignments is provided by the formation of the latter compound (5-methyl isomer) in 50% yield by alkaline hydrogen peroxide oxidation of the diazepinone 5.[9]
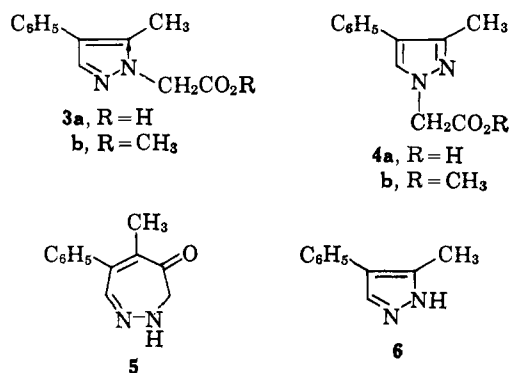
The proton n.m.r. spectra of the methyl esters 3b and 4b and of the unsubstituted pyrazole 6 were obtained in $CDCl_3$ solution (tetramethylsilane internal standard) with a Varian A-60 instrument. The spectra of 3b and 4b were obtained at solution concentrations of 2 and 8% (w./w.) and that of the less soluble pyrazole 6 at 1 and 4% concentrations. In contrast to the marked concentration dependence of the 2-proton peak in indole n.m.r. spectra,[10] the positions of all peaks, including that of the 3(5)-proton, in these pyrazole spectra were constant over a fourfold change in concentration within the reproducibility (± 1.0 c.p.s.) of the measurements.

The spectra of 3b and 4b contained single peaks corresponding to 3(5)-CH_3, -OCH_3, -NCH_2CO, C_6H_5, and 5(3)-H in the correct intensities; that of 6 had sharp peaks for 3(5)-CH_3, C_6H_5, and 5(3)-H. The -NH signal was a broadened peak at δ 11.50 p.p.m.; there was no multiplicity in any of the peaks. The peak positions for the 3- or 5-proton, 4-aryl protons, and 5- or 3-methyl protons are shown in Table I.

TABLE I

| Compound | Chemical shift, δ^a | | | Δ | |
	3- or 5-H	C_6H_5	5- or 3-CH_3	3(5)-H-C_6H_5	3(5)-H-CH_3
3b	7.62	7.33	2.30	0.29	5.32
4b	7.49	7.37	2.40	0.12	5.09
6	7.70	7.34	2.46	0.36	5.24

^{a} Average of three values, in p.p.m.

The differences in chemical shifts and spacing (Δ) of the 3- or 5-proton peaks and the phenyl and methyl peaks of 3b and 4b are evidently due, as in the case of 1H- and 2H-tetrazole isomers,[4] to the difference in double bond positions in the two isomers. Although the difference in chemical shifts of the ring protons (0.13 p.p.m.) in 3b and 4b is considerably less than that (0.6–0.8 p.p.m.) in the tetrazole case, and would be too small to permit assignment of the tautomeric structure of 6, comparison of the spacings (Δ) of this signal and those of the phenyl and methyl groups in 3b and 4b permits a tentative conclusion that the predominant tautomer of 6 possesses the same double bond system as 3b. It is hoped to test the validity of this conclusion when ad-

(8) All new compounds gave satisfactory analytical values.

(9) J. A. Moore and J. Binkert, *J. Am. Chem. Soc.*, **81**, 6029 (1959).

(10) M. G. Reinecke, H. W. Johnson, Jr., and J. F. Sebastian, *Chem. Ind.* (London), 151 (1964).