3-Benzoyl-3-(R-1-pyridino)-1,1,2-tricyano-2-propenides-1 (IVa) and (IVb). A sample of 2 mmoles TCE was added to a mixture of 4 mmoles salt (Ia) or (Ib), 3 mmoles $Et_3N$, and 3 ml methanol at 0°C. The mixture was stirred for 0.5 h at 0°C and left for 1 h. The precipitate was removed, washed with water and methanol, and recrystallized from acetonitrile (Table 1).

1,1-Dicyano-3-carbamoyl-3-(3-methyl-1-pyridino)-2-propenide-1 (V). A mixture of 10 mmoles salt (IId), 10 mmoles (IIIb), and 10 mmoles $Et_3N$ in 15 ml methanol was heated to 50-55°C and then stirred at 20°C for 5 h. The precipitate was separated and washed with water and methanol (Table 1).

1-Carbamoylmethyl-2-(2,3-dicyano-2-propen-1-ylidene)-1,2-dihydropyridine (VI) was obtained by analogy to (V) (Table 1).

1-(4-Bromophenyl)-2-imino-4-methylthio-5-(1-pyridino)pyrimidin-6-olate (VII). A mixture of 3 mmoles salt (Ie), 3 mmoles (IIIc), and 3 mmoles $Et_3N$ in 10 ml ethanol was heated to reflux, cooled, and maintained for 120 h at -4°C. The precipitate was separated and washed with ethanol and hexane (Table 1).

1-Phenacylpyridinium Tricyanoethylenolate (VIII). A mixture of 2 mmoles salt (Ia) and 2 mmoles TCE in 2 ml methanol was stirred for 1 h and left overnight to evaporate at ~20°C. Then, 2 ml water was added. The precipitate was separated, washed with water, propanol, and hexane, and recrystallized from water (Table 1).

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# PREPARATION OF SILYL DERIVATIVES OF UNSATURATED CARBOCYCLIC COMPOUNDS BY THE DIELS-ALDER REACTION OF 1,2-DIMETHYLENECYCLOBUTANE AND VINYLSILANES

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The Diels–Alder reactions of 1,2-dimethylenecyclobutane with vinyltrichlorosilane and vinylmethyldichlorosilane give the corresponding trichlorosilyl and methyldichlorosilyl derivatives of cyclobutene. Methylation of these derivatives gave 4-trimethylsilylbicyclo[4.2.0]oct-1-ene, which underwent thermal isomerization to 4-trimethylsilyl-1,2-dimethylcyclohexane.

The highly reactive structure of 1,2-dimethylenecyclobutane (1,2-DMCB) holds great interest in organic synthesis, especially in the preparation of cyclic monomers. This hydrocarbon, which is a product of the thermal dimerization of allene (type 2 + 2 cycloaddition) has been recently become more available [1, 2]. Nevertheless, the synthetic possibilities for 1,2-DMCB have not been sufficiently studied.

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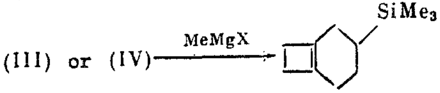
In the present work, we studied the Diels-Alder reaction of 1,2-DMCB with vinylchloro(organyl)silanes. Vinyltrichlorosilane (I) and vinylmethyldichlorosilane (II), which have high activity in the Diels-Alder reaction with cyclopentadiene [3,4], served as the dienophiles. We have shown that the reaction with 1,2-DMCB in both cases proceeds by the usual course to give the corresponding silicon-containing bicycloolefins

(I), (II) (III), (IV)

$n = 0$ (I), (III); 1 (II), (IV).

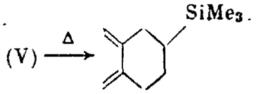
An excess of the vinylsilanes was used to achieve a greater conversion of 1,2-DMCB (3:1 mole ratios of (I) or (II) to 1,2-DMCB were employed). The reaction with (I) (n = 0) proceeds well at 90-97°C and is complete in 9-12 h as indicated by gas-liquid chromatographic analysis. The yield of (III) relative to 1,2-DMCB taken was 40-60%. The reaction of 1,2-DMCB with (II) proceeds with greater difficulty and no further change in the reaction mixture is noted only after heating at reflux for 40-50 h. The major reaction in both cases is accompanied by the formation of up to 10-35% condensation products. This is apparently a consequence of the presence of hydrogen chloride in the silyl chlorides, which may lead to cationic polymerization of 1,2-DMCB. Furthermore, 1,2-DMCB may also be consumed due to Diels-Alder self-condensation.

Products (III) and (IV) are stable and readily distilled in vacuum. The reaction of (III) or (IV) with $CH_3MgX$ gives (V).



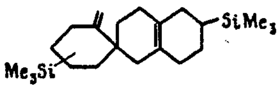
(V)

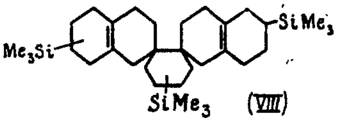
Cyclobutene derivatives are "cryptodienes" and readily isomerize upon heating to give the corresponding butadiene derivatives. In this case, (V) is converted to 4-trimethylsilyl-1,2-dimethylenecyclohexane (VI).



(VI)

This reaction begins to proceed at a significant rate only at 130°C. By heating in sealed tubes and periodically taking the PMR spectra, we established that the formation of (VI) at 136°C proceeds very slowly and is accompanied by thermal dimerization and oligomerization. The use of pentane or benzene as the solvent suppresses the bimolecular and oligomerization processes. The optimal conditions for this reaction involves heating (V) in five parts of a hydrocarbon solvent in a sealed, evacuated tube at 200°C for 25-35 min. The reaction course was monitored by PMR spectroscopy. The reaction was terminated after disappearance of the PMR signal for the allyl protons of the four-membered ring at about 2.5 ppm. The yield of (VI) was 70-80%. On the other hand, up to 15% products of the condensation of (VI) were obtained even under these conditions. The molecular mass of these condensation products (410) corresponds to a mixture of the dimer and trimer. The presence of bands at 890, 1640, 3075, and 1400 $cm^{-1}$ in the IR spectrum of this dimer-trimer mixture indicates terminal $CH_2$ groups with the double bond. The band at 1670 $cm^{-1}$ corresponding to C=C stretching vibrations indicates aprotic double bonds. Furthermore, these species have endocyclic $CH_2$ groups (1440 $cm^{-1}$), a $CH_2$–$CH_2$ fragment in the ring (730-750 $cm^{-1}$), isolated $CH_2$ groups in the ring (the band for rocking vibrations of the $CH_2$ group at 760 $cm^{-1}$), an Si–$CH_3$ bond (1250 $cm^{-1}$), and $(CH_3)_3Si$ group (deformation band at 840 and 850 $cm^{-1}$). All these findings indicate that the dimerization and trimerization of (VI) proceed through a Diels-Alder reaction, in which the exocyclic double bond acts as the dienophile to give dimer (VII) and trimer (VIII).


(VII)


(VIII)

Indeed, dimer (VII) was isolated as a pure compound upon the vacuum distillation of this dimer-trimer mixture. The mass spectrum of (VII) ($[M]^{+\cdot}$ with m/z 360) and a PMR signal for protons of the terminal double bond supports this assignment.

In conclusion, we should note that (VI) holds interest for anionic polymerization as a dienic monomer containing a trimethylsilyl group.

## EXPERIMENTAL

The IR spectra were taken on UR-20 and Perkin-Elmer 577 spectrometers. The PMR spectra were taken on Varian T-60 and Bruker MSL-300 spectrometers. The mass spectra were taken on an LKB-2091 mass spectrometer. The molecular masses of the condensation products were determined by measuring the heat effects of the condensation on a Knauer instrument.

A sample of 1,2-DMCB was isolated from the products of the thermal dimerization of allene and used after distillation. The content of 1,2-DMCB was >95%. Vinyltrichlorosilane (I) and vinylmethyldichlorosilane (II) were distilled prior to use.

Procedure of the Diels-Alder Reaction. A mixture of 1 mole 1,2-DMCB and 3 moles (I) or (II) was heated in a reactor equipped with a jacket, magnetic stirrer, and reflux condenser at 95-100°C. The reaction was terminated after gas-liquid chromatographic analysis of a probe showed the absence of 1,2-DMCB. Excess dienophile was distilled off and the residue was distilled in vacuum.

Product (III) was obtained in 44% yield, bp 87-89°C (1-1.5 mm), $n_D^{20}$ 1.5100, $d_4^{20}$ 1.2703. Mass spectrum, m/z (%): 240/242/244 $[M]^{+\cdot}$ (7.9/7.6/2.7), 212/214/216 $[M - C_2H_4]^{+\cdot}$ (1.4/1.5/0.5), 133/135/137 $[SiCl_3]^+$ (12.2/11.2/5.3), 108(9.3), 107 $[M - SiCl_3]^+$ (100), 105(15.2), 93(12.7), 92(7.4), 91(40), 80(21), 79 $[M - SiCl_3 - C_2H_4]^+$ (84), 78(8.4), 77(18.8), 67(11.3), 65(10.3), 63(5.1), 53(8.2), 52(9.1), 51(10.5), 50(5), 41(11.8), 40(7.1), 39(22).* m* 58.3 (107 → 79) Metastable transition $[M - SiCl_3]^+ - C_2H_4$.

PMR spectrum in $CCl_4$ (δ, ppm, TMS as standard): 1.31-2.34 m (1H, Si-H-C; 2H, $SiCCH_2CC=$; 2H, $SiCCCH_2C=$; 2H, $SiCCH_2C=$), 2.45 s (4H, $=CCH_2CH_2C=$).

Product (IV) was obtained in 23% yield, bp 54°C (0.03 mm), $n_D^{20}$ 1.4977. Mass spectrum, m/z (%) 220/222/224 $[M]^{+\cdot}$ (9/6.2/1), 192/194/196 $[M - C_2H_4]^+$. (3.8/2/0.7), 169/171 $[M - CH_3 - HCl]^+$ (3.6/1.1), 113/115/117 $[SiCl_2CH_3]^+$ (24.4/16.8/4), 108(8.8), 107 $[M-SiCl_2CH_3]^+$ (100), 106(6.4), 105(13.1), 93(20), 91(39.5), 80(21.6), 79 $[M - SiCl_2CH_3 - C_2H_4]^+$ (89.8), 78 (15.8), 77(16), 67(7), 65(9.4), 63(8.6), 53(8.5), 52(6.2), 51(8.9), 41(12), 40(5), 39(19.4), m* 58.2 (107 → 79) Metastable transition $[M - SiCl_2CH_3]^+ - C_2H_4$.

PMR spectrum in $CCl_4$ (δ, ppm, TMS as standard): 0.71 s (3H, $Si-CH_3$), 1.5-2.6 m (1H, Si-CH-C; 2H, $SiCCH_2CC=$; 2H, $SiCCCH_2C=$; 2H, $SiCCH_2C=$), 2.44 s (4H, $=CCH_2CH_2C=$).

Preparation of (V). A solution of 0.25 mole (I) in an equal volume of ether was added over about 2.5 h or a solution of 0.4 mole (II) in an equal volume of ether was added over about 3 h to a solution of 0.9 mole $CH_3MgX$ in ether. After 1 h, the mixture was heated at reflux for 4 h and the maximum amount of ether was distilled off. All of the organic phase was then condensed in vacuum into a trap cooled by liquid nitrogen. Vacuum distillation of the condensate gave (V) in ~85% yield, bp 69-71°C (4 mm), $n_D^{20}$ 1.4820, $d_4^{20}$ 0.8780. Mass spectrum, m/z (%) 180 $[M]^{+\cdot}$ (12.6), 165 $[M - CH_3]^+$ (9.4), 152 $[M - C_2H_4]^{+\cdot}$ (I), 137 $[M - C_3H_7]^+$ (3.6), 106(14.9), 91(7.3), 78(5), 73 $[Si(CH_3)_3]^+$ (100), 59(12.8), 45(9.2), 43(5), m* 113.7 (165 → 137) Metastable transition $[M - CH_3]^+ - C_2H_4$.

PMR spectrum in $CCl_4$ (δ, ppm, benzene as standard): 0.08 s (9H, $SiCH_3$), 0.93-2.17 m (1H, SiCH-C; 2H, $SiCCH_2CC=$; 2H, $=CCH_2CC$; 2H, $=CCH_2CSi$), 2.51 s (4H, $=CCH_2CH_2C=$).

Preparation of (VI). A PMR tube was filled with 0.7 ml of a solution containing a 1:5 mixture of (V) and benzene, evacuated, sealed, and heated at 200°C. The complete conversion of (V) as indicated by the disappearance of the PMR signal for the allylic protons of the four-membered ring required 25 min. Then, a similarly prepared reaction

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*Here and later uninformative peak intensities of less than 5% are not shown.

ampule containing 10 ml (V) and 50 ml benzene was heated at 200°C for 30 min. The ampul was opened and benzene was removed. The residue was distilled in vacuum. The yield of (VI) was 70%, bp 66°C (3.5 mm), $n_D^{20}$ 1.4794, $d_4^{20}$ 0.8650.

The mass spectra of (VI) and (V) were identical.

PMR spectrum in $CCl_4$ (δ, ppm, benzene as standard): 0.15 s (9H, $SiCH_3$), 1.0-2.85 m (1H, Si-CH-C; 4H, $CCH_2$; 2H, $=CCCH_2$), 4.64 and 4.89 d (4H, $CH_2=$).

Isolation of (VII). The combined still residues of four runs for the preparation of (VI) with 410 mean molecular mass were distilled in vacuum. Dimer (VII) with bp 132°C (0.5 mm) was isolated with average yield of about 7% per run. The mass spectrum of (VII) has a weak molecular ion peak at m/z 360, the peak for the ion corresponding to loss of a methyl group, and the peak for the trimethylsilyl group with m/z 73.

PMR spectrum in $CCl_4$ (δ, ppm, benzene as standard): 0.07 s (18H, $SiCH_3$), 0.95-2.3 m (2H, Si-CH-C; 10H, $CH_2C=$; 6H, $SiCCH_2$; 2H, $=CCCH_2CC=$), 4.59 br.s (2H, $CH_2=$).

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# TRIS(FLUOROALKOXY)METHYLPHOSPHONIUM SALTS IN THE SYNTHESIS OF METHYLPHOSPHORANES

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The reactions of phosphites containing electron-withdrawing fluoroalkyl groups with methyl triflate gave tris(fluoroalkoxy)methylphosphonium triflates, which react with alcohols to give either tetrakis(fluoroalkoxy)methylphosphoranes (in the case of fluoroalcohols) or alkylation products - ethers and bis(fluoroalkoxy)methylphosphonates (in the case of unsubstituted alcohols). The structures of the phosphonium salts and phosphoranes were supported by $^1H$ and $^{31}P$ NMR spectroscopy.

Quasiphosphonium salts are very strong alkylating agents [1]. Thus, the action of phosphonium triflates on alcohols readily gives ethers [2]. We have found that quasiphosphonium salts (Ia)-(Ic) obtained from fluoroalkyl phosphites (II) and methyl triflate react with phosphorus-containing alcohols in the presence of base to give methylphosphoranes (IIIa)-(IIIc).

$$\underset{\text{(IIa—c)}}{(R_FO)_3P} + MeOSO_2CF_3 \rightarrow \underset{\text{(Ia—c)}}{(R_FO)_3\overset{+}{P}-Me\ CF_3SO_3^-} \xrightarrow[-Et_3\overset{+}{N}HCF_3SO_3^-]{R_FOH,\ Et_3N} \underset{\text{(IIIa—c)}}{Me-P(OR_F)_4}.$$

$$R_F = CH_2CF_3\ (a),\ CH_2CF_2CHF_2\ (b),\ CH_2(CF_2)_3CHF_2\ (c).$$

Tetrafluoroalkoxymethylphosphoranes (IIIa)-(IIIc) are highly hygroscopic liquids, which may be distilled. The $^{31}P$ NMR spectra of these compounds have signals at from −48 to −49 ppm. The weaker alkylating capacity of quasiphosphonium salts (Ia)-(Ic) in comparison

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