of the contact of the sensitizer film and the primary acceptor and, thus, increase the quantum yield of the photochemical reaction.

CONCLUSIONS

A proposal was made for a photosensitive electrode with a bilaminar film consisting of $PXV-PSS_2$ and $[(C_{17}H_{35})_2Dipy]Ru(Dipy)_2^{2^+}$ deposited on a conducting base. Its use in a photoelectrochemical cell permits electron transport from EDTA in one half-cell through the bilaminar film and external circuit to $Fe(CN)_6^{3^-}$ in the other half-cell.

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FRAGMENTATION OF 16α , 17α -CYCLOBUTENOPREGNANE

A. V. Kamernitskii, V. N. Ignatov, I. S. Levina, and L. E. Kulikova

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In our previous work [1], we showed that the strained double bond in the additional ring of $pregna-D_4'-pentaranes$ such as (I) is highly reactive and, in particular, may undergo Diels-Alder condensation. A study of a catalytic variant of this reaction for (I) and 2,3-dimethylbutadiene revealed a reduction in the yield of the desired cycloadduct, an increase in reaction time, and the unexpected formation of increasing amounts of pregnenolone acetate (III) [1]. In the present work, we examined this reductive fragmentation of (I) under various conditions and attempted to explain this phenomenon (Scheme).



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$\mathbf{R} = \mathbf{H}(\mathbf{II}), \ (\mathbf{IX}); \ \mathbf{Ac}(\mathbf{III}), \ (\mathbf{X}).$

The formation of (III) is related to the decomposition of cyclobuteneketone (I) by the action of FeCl_3 used as a catalyst for the Diels-Alder reaction [1]. Indeed, treatment of (I) with 0.5-1.5 mole eq. FeCl_3 or Et_2O · BF₃ in CH₂Cl₂ at about 20°C gives ketoacetate (III) in yields up to 60%. This acetate product was characterized spectrally and by direct comparison with an authentic sample.

This reductive fragmentation is also found under mild conditions upon the reaction of (I) with alkaline H_2O_2 . In this case, in contrast to the reaction with Lewis acids, which is accompanied by considerable tar formation, the yield of (III) after acetylation of the intermediate alcohol (II) was 78%. Finally, approximately the same overall yield of the fragmentation products of ketol (II) and related glycols (IX), which were converted in all cases to acetates (III) and (X), was found in the reduction of (I) by lithium in ammonia at $-45^{\circ}C$.

These results may be explained assuming loss of a C_2H_2 fragment from the initial molecule in all cases examined with formation of the stabilized enolate carbanion (IV). This species may be obtained from (I) by a previously undescribed decomposition of the peroxy anions (V) and (VI), of which (V) may form as a result of intramolecular reaction of the hydroperoxy anion with the strained C = C bond of the cyclobutene ring. The preparation of a mixture of (II) and (IX) by the action of lithium in ammonia may be explained through intermediate radical-anions (VII) and (VIII). On the other hand, the formation of pregnenolone (III) by the action of equimolar amounts of Lewis acid likely proceeds through the decomposition of an intermediate complex of the steroid with this Lewis acid.

EXPERIMENTAL

The melting points were obtained on a Koefler block. The IR spectra were taken on a UR-10 spectrometer in KBr. The PMR spectra were obtained on a Tesla BS-497 spectrometer in CDCl₃ from TMS. Thinlayer chromatography was carried out on L brand $(5-40 \mu)$ silica gel microplates. Column chromatography was carried out on L brand (200-250 mesh) iron-free silica gel.

Fragmentation of Cyclobutenoketone (I) by the Action of Lewis Acids. A solution of 110 mg (I) and 60 mg FeCl₃ in 8 ml CH₂Cl₂ was left at 20°C for 1 h and then the dark cerise reaction mass was diluted with CH₂Cl₂, washed with water, and dried with MgSO₄. After removal of the solvent, the residue was subjected to chromatography on 20 g silica gel. Elution with 95:5 petroleum ether –ether gave 58 mg (58%) pregnenolone acetate (III) with mp 142–146°C (from ether –hexane) [2]. IR spectrum (ν , cm⁻¹): 1705, 1735. PMR spectrum (δ , ppm): 0.55 s (3H, 18–Me), 0.95 s (3H, 19–Me), 1.92 s (3H, 3–OAc), 2.02 s (3H, 21–Me), 4.47 m (1H, HC³), 5.30 m (1H, HC⁶).

A solution of 0.2 g (I) and 1 ml $\text{Et}_2\text{O}\cdot\text{BF}_3$ in 9 ml CH_2Cl_2 was left at 20°C for 2 h and then treated as in the previous experiment to yield 80 mg (43%) (III), which was identical in its melting point, IR and PMR spectra to an authentic sample.

Fragmentation of (I) by the Action of Alkaline H_2O_2 . A solution of 0.38 g (I) in 33 ml methanol, 17 ml 4 N NaOH and 24 ml 30% H_2O_2 was left for 24 h at 5°C. The reaction mass was then poured onto ice. The precipitated powder was filtered off, washed with water, dried in the air, and crystallized from acetone -hexane to yield 0.25 g (78%) pregnenolone (II), mp 196-198°C [2], IR spectrum (ν , cm⁻¹): 1695, 3400. PMR spectrum (δ , ppm): 0.60 s (3H, 18-Me), 0.97 s (3H, 19-Me), 2.07 s (3H, 21-Me), 3.48 m (1H, HC³), 5.30 m (1H, HC⁶).

Acetate (III) prepared by the standard procedure with 1:1 acetic anhydride -pyridine at 20°C over 10 h was identical in its melting point, IR and PMR spectra to an authentic sample.

<u>Fragmentation of (I) in a Solution of Lithium in Ammonia</u>. A solution of 0.39 g (I) and 0.15 ml t-BuOH in 5 ml THF was added to a vigorously stirred solution of 90 mg Li in 50 ml ammonia at -45° C under argon. After 25 min, the reaction mass was decomposed by excess NH₄Cl. The ammonia was evaporated and the residue was washed with water and extracted with ether. The usual work-up of the extract gave 0.40 g of a product mixture

which was acetylated under the conditions described above. Subsequent standard treatment of the acetylation products gave 0.45 g of a substance which was subjected to chromatography on 40 g silica gel. Elution with 98:2 petroleum ether – ether gave 0.12 g (30%) of an oily mixture of acetates (X). Crystallization from ether – hexane gave 80 mg (X) with mp 128–140°C [2]. IR spectrum (ν , cm⁻¹): 1240–1260, 1735. PMR spectrum (δ , ppm): 0.70 s (3H, 18–Me), 1.03 s (3H, 19–Me), 1.24 (3H, 21–Me, J = 6.3 Hz), 2.01 s and 2.04 s (6H, 3– and 20–OAc), 4.60 m (1H, HC³), 4.94 m (1H, HC²⁰), 5.38 m (1H, HC⁶).

Further elution with 96:4 petroleum ether – ether gave 0.16 g (44%) (III), which was identical to an authentic sample.

CONCLUSIONS

An unusual fragmentation was discovered and studied for 16α , 17α -cyclobutenopregnenolone leading to pregnenolone. A possible mechanism was discussed for this transformation.

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¹²⁷I NQR SPECTRA OF CARBORANE-CONTAINING

COMPOUNDS OF POLYCOORDINATED IODINE

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G. K. Semin, S. I. Gushchin,S. A. Petukhov, V. V. Grushin,T. P. Tolstaya, and I. N. Lisichkina

Despite the current interest in polycoordinated iodine compounds, the NQR spectra of these compounds have not been studied adequately. Table 1 gives the ¹²⁷I NQR spectra of electroneutral PhICl₂ derivatives with intermolecular coordination in the solid state and ionic compounds including compounds with interionic coordination.

The central iodine atom in PhICl₂ compounds which form intermolecular coordination complexes with bridging bonds through the chlorine atoms is located at the center of the field of a nucleus whose distortion depends on R and is seen in sharp changes in the asymmetry parameter (η) and the quadrupole coupling constant (e^2Qq_{ZZ}). The change in e^2Qq_{ZZ} is opposite to that for η , i.e., the change in e^2Qq_{ZZ} occurs in the series ICl₄⁺ > ICl₃ > PhICl₂ > Ph₂I⁺ > PhCBI⁺ (CB = carboranyl), while the asymmetry parameter increases in the same series (see Table 1). In mixed ionic compounds PhCBI⁺X⁻, e^2Qq_{ZZ} is lower than in the diphenyliodonium compound while the asymmetry parameter η is much greater. The following behavior is found for e^2Qq_{ZZ} is carboranyl compounds PhCBI⁺BF⁻₄: meta > para > ortho. The asymmetry parameter, depending on the site of addition and type of carborane system, varies in a different sequence: ortho > meta > para. All the experimental data indicate that distortion of the coordination environment in the carborane derivatives is greater than in the corresponding phenyl derivatives (9-m-CBICl > PhICl₂; PhCBIX > Ph₂IX).

EXPERIMENTAL

The spectra for the $\nu(1/2-3/2)$ and $\nu(3/2-5/2)$ transition were taken on an incoherent pulse spectrometer in the frequency range from 300 to 900 MHz [2].

CONCLUSIONS

A considerable increase in the quadrupole coupling constants (e^2Qq_{ZZ}) and significant decrease in the asym metry parameter η is found in carborane-containing CBICl₂ and PhCBIX compounds in comparison with the corresponding phenyl and diphenyl derivatives.

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No.11, pp.2622-2623, November, 1984. Original article submitted January 31, 1984.