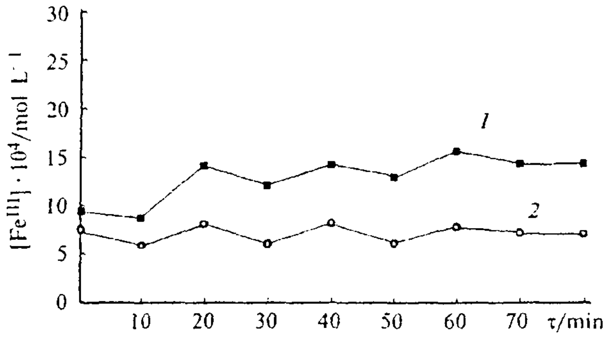

**Fig. 2.** Kinetic curves for the variation of the $Fe^{III}$ concentration in solutions sonicated under $N_2$: (*1*) [HCl] = 12 mol L$^{-1}$; (*2*) [HCl] = 8 mol L$^{-1}$

It is known[3] that $N_2$ molecules participate in sonochemical reactions, which result ultimately in the fixing of nitrogen as the products of its oxidation or hydrogenation; these species, in turn, are able to oxidize $Fe^{II}$ or to reduce $Fe^{III}$. The pattern of the curves presented in Fig. 2 indicates that the initial stage of the process yields mainly reducing agents; for example, these could be active species such as H, NH, and $NH_2$ and some chloro-substituted ammonia derivatives able to rapidly reduce $Fe^{III}$. However, the generation of reducing agents by the ultrasonic field does not suffice to make up for their consumption in the reaction with $Fe^{III}$ and other products of sonolysis; finally, oxidants are accumulated in the solution and the direction of the process is reversed. Once a particular concentration of the oxidative species has been attained, the rate of their interaction with $Fe^{II}$ becomes higher than the rate of their generation. After that, consumption of the oxidants starts and their concentration decreases to some critical value at which the process returns to the initial point. The oscillations in the system are damped due to the decrease in the concentration of $N_2$ in the solution upon its chemical transformations and ultrasonic degassing of the solutions. Apparently, the oscillation process in this system is possible only provided that $[Fe^{II}] >> [Fe^{III}]$.

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## References

1. M. V. Nikonov, Y. Fuji, and V. P. Shilov, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 1555 [*Russ. Chem. Bull.*, 1997, **46**, 1489 (Engl. Transl.)].
2. M. A. Margulis, *Zh. Fiz. Khim.*, 1986, **60**, 1 [*Russ. J. Phys. Chem.*, 1986, **60** (Engl. Transl.)].
3. M. A. Margulis, *Zvukokhimicheskie reaktsii i sonolyumines-tsentsiya* [*Sonochemical Reactions and Sonoluminescence*], Nauka, Moscow, 1986, 286 pp. (in Russian).

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# Reaction of fullerene $C_{60}$ with diazoacetylcymanthrene: the first $C_{60}$ derivative containing a manganese π-complex

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The synthesis of fullerene derivatives containing an organometallic fragment in an addend is of interest, first of all, from the viewpoint of intramolecular charge transfer. Earlier,[1] we obtained a tricarbonylarenechromium derivative (in the form of a mixture of methanofullerene and fulleroid) by the reaction of $C_{60}$ with a monochromium tricarbonyl complex of diphenyldiazomethane. The present publication reports the synthesis of a fullerene derivative containing a cymanthrenyl fragment (tricarbonylcyclopentadienylmanganese, Cym) by a similar reaction from diazoacetylcymanthrene (**1**)[2] (Scheme 1).

The reaction of $C_{60}$ with an equimolar amount of diazo ketone **1** in boiling toluene for 14 h affords a low-polar product **2** ($R_f$ = 0.8, yield 8%, 20% with respect to the consumed $C_{60}$, 1 : 2 toluene—hexane as the eluent) and a more polar compound **3** ($R_f$ = 0.4, yield 8.5%, 22% with respect to the consumed $C_{60}$). The degree of conversion of $C_{60}$ is 37%. The products were isolated from the reaction mixture by chromatography on $SiO_2$ (100/160 μm): product **2** was eluted following the recovered $C_{60}$ with a 1 : 4 toluene—hexane mixture, and product **3** was eluted with a 1 : 1 toluene—hexane mixture. IR spectra ($CHCl_3$) suggest the presence of an

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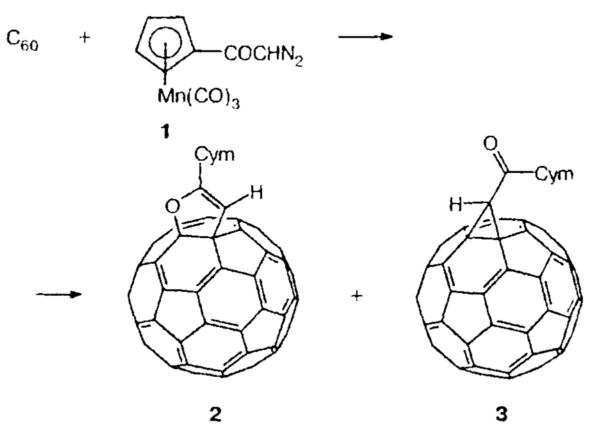
**Scheme 1**



$Mn(CO)_3$ group in both products: 1950 and 2028 cm$^{-1}$ (**2**), 1955, 1965, and 2035 cm$^{-1}$ (**3**). In addition, the IR spectrum of adduct **3** exhibits a peak of the ketone CO group at 1690 cm$^{-1}$, which is absent in the spectrum of **2**. $^1$H NMR spectra ($CS_2$) each contain two triplets characteristic of the α- and β-protons of monosubstituted cymanthrene: δ 5.44 and 4.98 for **2** and δ 5.90 and 5.03 for **3**. In addition, the $^1$H NMR spectrum of compound **2** contains a singlet at δ 6.26, while that of compound **3** contains a singlet at δ 5.00. The mass spectra of **2** and **3** show peaks with *m/z* 880 [$M^+ - 3$ CO], which is characteristic of cymanthrene fragmentation. The electronic absorption spectra of products **2** and **3** exhibit absorption maxima at 430 and 699 nm, which correspond to a 6,6-monoadduct. Hence, the structures of methanofullerene and isomeric dihydrofuranofullerene may be assigned to adducts **3** and **2**, respectively. In our case, no fulleroid product (5,6-adducts) was detected. Dihydrofuran derivatives, along with methanofullerenes, are also formed in reactions of $C_{60}$ with diazo ketones containing no organometallic substituent.[3]

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## References

1. M. N. Nefedova and V. I. Sokolov, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 780 [*Russ. Chem. Bull.*, 1995, **44**, 761 (Engl. Transl.)].
2. E. Cuingnet and Y. Dhedin-Dubois, *Compt. Rend.*, 1969, **269C**, 1216.
3. H. J. Bestmann and C. Moll, *Synlett*, 1996, 729.

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# (Benzamidomethyl)dimethylsilanol hydrochloride. Oxonium structure and intra- and intermolecular coordination interactions

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Recently,[1,2] we published some preliminary data on the synthesis and structure of the first representatives of monosubstituted amides of the general formula $RC(O)NHCH_2SiMe_2X$ (R = Alk, Ar; X = Hal) in which not only the amide oxygen atom but also the NH hydrogen atom can be involved in coordination. Such compounds are promising as model subjects for studying competitive intra- and intermolecular coordination. The formation of an O→Si intramolecular coordination bond is typical of *N*-silylmethyl derivatives of amides and related compounds containing, at least, one sufficiently electronegative Si-substituent.[3] Ordinary monosubstituted amides usually form intermolecular coordination bonds.[4]

In a continuation of these investigations, we studied the structure of a crystalline specimen of benzamidomethylsilanol hydrochloride by X-ray diffraction analysis. The starting compound for the preparation of the latter was disiloxane (**1**),[2] whose reaction with thionyl

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