Brief Communications

Photochemical reactions of some mono- and diketo derivatives of adamantane in various solvents

S. V. Rykov,[a]* *E. D. Skakovskii,*[b] *V. D. Oppengeim,*[a] *E. I. Bagrii,*[a] *and M. P. Filatova*[a]

[a]*A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences,*
29 Leninsky prosp., 117912 Moscow, Russian Federation.
Fax: +7 (095) 230 2224
[b]*Institute of Physical Organic Chemistry, Belarussian Academy of Sciences,*
13 ul. Surganova, 220603 Minsk, Belarus'

Adamantanes are photoactive in the presence of CCl_4 and $CDCl_3$. The mechanism of their photolysis, involving the formation of singlet or triplet excited donor-acceptor complexes has been suggested.

Key words: adamantanes, photolysis.

Adamantanes and their derivatives are of interest both for basic research and practical applications, in particular, for preparing compositions that transform light to coherent radio-frequency radiation (CRFR).[1] Photochemistry of adamantanes has been almost unstudied until recently.

In this work, photophysical and photochemical properties of adamantanes[1—8] containing photoactive substituents were studied by NMR. The adamantanes synthesized (**1**—**8**) have been identified by high-resolution ^1H and ^{13}C NMR spectroscopy.

Experimental

Adamantanone was prepared by the Geluk method.[2] Compounds **1**, **4**, and **8** were obtained from 4-oxo-1-adamantanecarboxylic acid and compound **5** was prepared from 2-oxa-3-oxohomoadamantane treated with 60 % sulfuric acid.[3] Compounds **2**, **3**, and **6** were synthesized by previously described procedures (see Refs. 4, 5, and 6, respectively).

Compounds prepared were purified by crystallization or sublimation. The structures of adamantanes **1**—**8** were confirmed by mass spectrometry and ^1H and ^{13}C NMR spectra.

Initial compounds and photolysis products were identified, and their purity and the purity of solvents were determined on a Bruker MSL-300 NMR spectrometer. The photoactivity of adamantanes were studied on a modified Tesla-BS-497 NMR spectrometer.[8] Irradiation was carried out directly in the probe of the spectrometer with total or filtered light from a DRSh-1000 high-pressure mercury lamp. IR radiation was eliminated by passing the light through a quartz vessel with parallel edge windows filled with distilled water (with addition of 3 wt. % of $CuSO_4$). Deuterated methanol, chloroform, and cyclohexane, CCl_4, hexachlorobutadiene, DMSO-d_6, D_2O, and CD_2Cl_2 were used as solvents. The purity of solvents was controlled by NMR, mass spectroscopy, and other spectral methods. Complexation of adamantanes was studied by ^1H NMR and UV spectroscopy on a Specord UV-VIS spectrometer.

Results and Discussions

Adamantanes **1**—**8** are photochemically stable at the light intensity $I \approx 10^{16}$ quantum s^{-1} in all solvents except CCl_4 and, in some cases, $CDCl_3$. No products of photolysis were found after irradiation for 3 h. Adaman-

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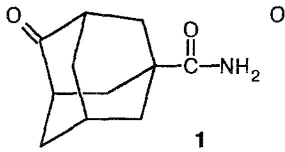

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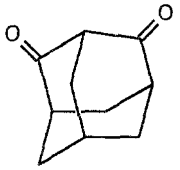

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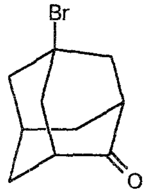

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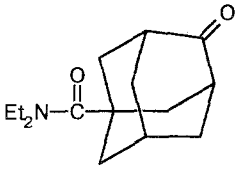

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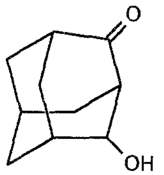

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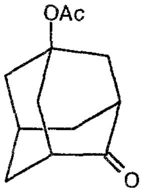

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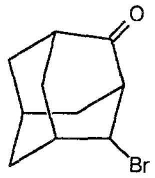

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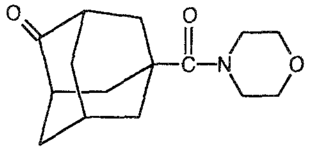

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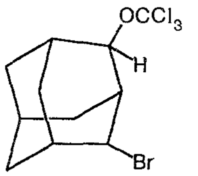
tanes **1—8** are photochemically active in solutions of CCl_4 and $CDCl_3$ or in the presence of CCl_4. The maximum quantum yield of photolysis products ($\varphi \approx 10^{-3}$) and the maximum chemically induced dynamic nuclear polarization (CIDNP) are observed in the case of compound **2**. Adamantanes **1** and **7** exhibit considerable photoactivity.

The character of the process, the yield of reaction products, and CIDNP effects depend on the $[CCl_4]_0/[Ad]_0$ ratio (Fig. 1), where [Ad] is the concentration of adamantane. In C_6D_{12}, DMSO-d_6, and CD_3OD in the presence of CCl_4, the CIDNP effect was observed only for a proton of $CHCl_3$. The sign of CIDNP depends on the nature of adamantane and its concentration. For example, when the concentration of compound **7** ([**7**]) is equal to 10^{-2} mol L^{-1}, the CIDNP sign is positive, while it is negative at [**7**] $\approx 10^{-4}$ mol L^{-1}. Compounds **9** and **10**, $CHCl_3$, CH_2Cl_2, and CCl_3—CCl_3 are the main reaction products.



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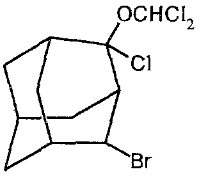

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Photodecomposition of adamantanes in the presence of CCl_4 is observed at $\lambda > 290$ nm, *i.e.*, in the region where their absorption is nearly absent. In this respect, adamantanes **1—8** behave similarly to acetone upon its photolysis in CCl_4 (see Ref. 9). It is likely that adamantanes studied in a CCl_4 solution or in the presence of CCl_4 form weak donor-acceptor complexes (DAC) Ad...CCl_4 that absorb in the long-wave region ($\lambda > 280$ nm). Irradiation of these complexes in CD_3OD may result in the electron transfer to form a radical ion pair (RIP), which eliminates HCl and is transformed to the radical pair leading to CIDNP effects.

The study of the interaction between diketoadamantane **2** and CCl_4 by UV spectroscopy has confirmed our suggestion that dissolution of compound **2** in CCl_4 results in the formation of a donor-acceptor complex. This is evidenced by the appearance of a new broad

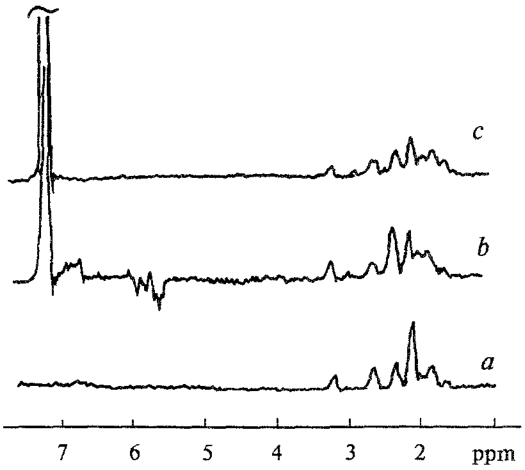

Fig. 1. Photolysis of diketoadamantane **2** in CCl_4 ([**2**] = 10^{-2} mol L^{-1}, 300 K): *a*, initial ^1H NMR spectrum; *b*, ^1H NMR spectrum during irradiation; *c*, ^1H NMR spectrum 5 s after switching off light (CIDNP of chloroform is retained due to a long duration of spin-lattice relaxation (T_{1n})).

absorption band with a maximum at 357 nm, whose intensity depends on the concentration of diketoadamantane. No DAC between adamantane **2** and the solvent were found in cyclohexane.

The variety of photolysis products at relatively high concentrations of adamantane in CCl_4 is caused by the photolysis of chloroadamantanes, which are accumulated in the reaction mixture. Depending on the concentration of CCl_4 and a type of an adamantane derivative, a RIP can be formed from singlet ([**8**] = 10^{-2} mol L^{-1}, positive CIDNP) or triplet ([**8**] = 10^{-4} mol L^{-1}, negative CIDNP) excited DAC. The sign of the integral CIDNP is determined by a type of the electron excited state of DAC which determines the multiplicity of the RIP formed from it.[7,9] Our attempts to choose conditions for preparing thin films of products of photolysis of adamantanes on the NMR tube surface and to observe effects of light conversion to CRFR[7] have not yet been successful.

The results considered make it possible to draw the conclusion that adamantanes are photostable in solutions with which they do not form DAC and are photoactive in the presence of CCl_4 and $CDCl_3$. It is likely that the primary reaction act is determined by the excitation of a weak DAC. Depending on the concentration of DAC and the type of adamantane, either singlet or triplet excited [Ad...CCl_4] complexes are photoactive.

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