Scheme 1

$$H_2C=C(CN)COOH \xrightarrow{PCl_5} H_2C=C(CN)C(O)CI$$

 $R = CH_2CH = CHCH_2$ (a), $CH_2C \equiv CCH_2$ (b)

¹H NMR (C_6D_6), δ : 4.2–4.3 (s, 4 H, OCH₂); 5.51 (s, 2 H, –CH=); 6.40 (s, 2 H, –CH=).

2-Butyne-1,4-diol bis(2-cyanoacrylate) (1b) was prepared under the same conditions in 45 % yield. M.p. 92–93 °C (*cf.* Ref. 1: 92–93 °C). ¹H NMR (C_6D_6), δ : 4.47 (s, 4 H, OCH₂); 5.52 (s, 2 H, -CH=); 6.44 (s, 2 H, -CH=).

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Synthesis of η^6 -tricarbonylchromium derivatives of diphenylmethanofullerene using an organometallic derivative of diazomethane

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Isomeric chromotricarbonyl derivatives of diphenylmethanofullerene and -fulleroid have been obtained by the reaction of C_{60} with benchrotrenyl(phenyl)diazomethane.

Key words: fullerenes, methanofullerene, fulleroids, arenechromiumtricarbonyls.

Combining fragments of fullerene and a metal π -complex in the same molecule may disclose some new interesting aspects of reactivity. Though the highly unsaturated structure of fullerenes allows different types of coordination with a metal,¹ only complexes with η^2 -coordination of fullerene, although twofold, are known so far.^{2,3} Our attempt at direct π -metallocarbonylation by refluxing C₆₀ with (NH₃)₃Cr(CO)₃ in decalin also failed to afford the η^6 -complex. But the common benzene rings of diphenylmethanofullerene are capable of

complexation under these conditions. This follows from the appearance of the absorption bands of the valent oscillations of C=O bond at 1910 and 1980 cm⁻¹ in the IR spectra of the reaction product, although the yield of the complex is very low. A modification of the Wudl reaction,⁴ *i.e.*, the interaction of C₆₀ with hitherto unknown (benchrotrenyl)phenyldiazomethane obtained by Scheme 1, appeared to be a far more convenient route for the introduction of the benchrotrenyl fragment into the fullerene molecule.

 $H_2C = C(CN)COO - R - OOC(CN)C = CH_2$ 1a,b



Benzophenone hydrazone was subjected to direct chromiumtricarbonylation. As a result, the mono- π -complex (1) of the hydrazone was obtained in 36 % yield and a LCr(CO)₅ type n-complex was formed as the by-product. Diazomethane 2 was used *in situ*.

Ċr(CO)₃

2

The interaction of C_{60} with an equimolar amount of 2 in toluene for 48—72 h at room temperature led to a mixture of compounds, which was chromatographed on SiO₂ to afford chromium-containing compound 3. The IR spectrum of 3 comprises the C=O absorption bands characteristic of Cr(CO)₃ at 1980 and 1910 cm⁻¹. The UV-VIS spectrum of 3 is close to the spectra of C_{60} and $C_{60} \cdot \text{CPh}_2$ (λ_{max} 248 and 257 nm, 280, 328, 540, and 605 nm, respectively) except that the maxima at 280 and 328 nm are slight (smoothed). The FAB-MS data point to the presence of the molecular ion $[M+1]^+$ at m/z 1023, which refers to the product of the addition of one $[Ph-C-PhCr(CO)_3]$ moiety to C_{60} and its further fragmentation as follows, m/z: $[M+1-3CO]^+$ 930 and $[M+1-Cr(CO)_3]^+$ 886, as well as 720 for $[C_{60}]^+$.

Reactions of C_{60} with diazomethanes are known to lead to the products of addition both at 6,6-fusions (methanofullerenes) and at 5,6-fusions (fulleroids) in different ratios. The fulleroids may convert into the more thermodynamically stable methanofullerenes when heated or otherwise treated. With asymmetrically substituted diazomethanes, two isomeric fulleroids may be formed in different ratios along with methanofullerene.⁵

The ¹H NMR spectra indicate that product **3** is a mixture of comparable amounts of two isomers (Fig. 1, *a*). In the region where the signals for the PhCr(CO)₃ fragment are present, two sets of signals for the *ortho*-, *meta*-, and *para*-protons are clearly displayed at δ 6.41, 5.03, and 5.48 and 5.82, 4.79, and 5.31, correspondingly (Fig. 1, *b*). The sets of signals are easily distinguished by their splitting character and relative intensity. In the area of the signals of the uncoordinated benzene ring there are three groups of multiplets at δ 7.05, 7.45, and 7.95. The ratio of the intensities of these signals allows



Fig. 1. ¹H NMR spectra of compounds 3 (*a*, *b*) and 4 (*c*). The area of the signals of the uncoordinated benzene ring protons is represented separately (*b*) (CS₂ solution, C₆D₆ as the external standard relative to TMS).



Fig. 2. Possible isomers of the molecule of 3.

one to consider them to be the result of the overlap of the signals for two groups of *ortho*-, *meta*-, and *para*protons $(o_1, m_1 + p_1 + o_2, and m_2 + p_2)$. The multiplets have a complex structure and their total intensity exceeds that of the signals present in the $\delta 4.5-6.5$ region by 30-50 %, so that we cannot entirely exclude the presence of some other isomer (see Fig. 1, *a*).

Treating 3 with iodine in toluene results in the removal of the $Cr(CO)_3$ fragment, and the ¹H NMR spectrum of the fullerene derivative (4) thus formed has no signals in the δ 4.5–6.5 region and has the same three benzene multiplets as the spectrum of 3 (see Fig. 1, c). Unlike the known data,⁵ refluxing 4 in toluene for 25 h did not cause its transformation into a single isomer. It is noteworthy that the interaction of equimolar amounts of C_{60} and Ph_2CN_2 in toluene affords an adduct whose ¹H NMR spectrum is identical to that of 4, except for some slight differences in the relative intensities of the multiplets.

The computer modelling demonstrates a strong steric hindrance in the molecule of 3 along with a considerable restriction of the conformational mobility around the Ph-C bond. Some additional non-equivalence in the molecule of 3 is possibly the cause of the differences in the spectra of 3 and 4 in the region near δ 8 (the signals of *ortho*-protons).

The facts presented allow one to consider **3** to be a mixture of two (of the three possible) isomeric monoadducts $C_{60} \cdot C(Ph)PhCr(CO)_3$ formed by addition at the 6,6- and 5,6-fusions of C_{60} (Fig. 2).

The interaction of C_{60} with a 2.5-fold excess of 1 leads to a more complex product mixture. Silica gel chromatography of this mixture affords, besides 3, three more Cr-containing fractions with absorption bands for C=O at 1910 and 1980 cm⁻¹ in their IR spectra. The ¹H NMR spectra of all of these compounds are close to the spectrum of 3, but are strongly broadened, as it would only be natural to expect in the spectra of mixtures of bis- and polyadducts.

Thus, we have demonstrated that diazomethane 2 with a benchrotrenyl substituent reacts with fullerene C_{60} as do CH_2N_2 or Ph_2CN_2 to afford adducts with different C_{60} —Cr ratios. The study of the adducts obtained is in progress.

Experimental

¹H NMR spectra were recorded on a Bruker WP-200 SY spectrometer at 200.13 MHz relative to TMS. IR spectra were obtained using an UR-20 instrument. UV spectra were recorded on a Specord UV-VIS spectrophotometer.

PhC(=NNH₂)[PhCr(CO)₃] (1). Benzophenone hydrazone (0.5 g, 2.5 mmol) and (NH₃)₃Cr(CO)₃ (0.5 g, 2.5 mmol) in absolute dioxane (0.5 mL) were refluxed for 1 h under argon. The reaction mixture was cooled and the insoluble black precipitate was filtered off through a small layer of silica gel. Dioxane was removed, and the residue was dissolved in benzene and chromatographed on a silica gel column using a 1 : 1 hexane-benzene mixture as the eluent. First NH₃Cr(CO)₅, then $Ph_2C=NNH_2 \cdot Cr(CO)_5$ [IR, v(CO)/cm⁻¹: 1920, 1940, 2070], and, finally, the main product 1 (0.31 g, 36 %) were eluted. Hydrazone 1 was purified by rechromatography on silica gel followed by crystallization from hexane to give 1 as yellow needles, m.p. 115-116.5 °C. Found (%): C, 57.91; H, 3.68; N, 8.30. C₁₆H₁₂CrN₂O₃. Calculated (%): C, 57.84; H, 3.64; N, 8.43. IR (C_6H_6) , $v(CO)/cm^{-1}$: 1910, 1980. ¹H NMR (C_6D_6) , δ : 7.64, 7.42, 7.0 (all m, 5 H, Ph); 6.07 (br.s, 2 H, NH₂); 5.33, 4.85, 4.35 (all m, 5 H, PhCr(CO)₃). MS (m/z): 332 [M]⁺, 304 [M⁺-CO], 276 [M⁺-2CO], 248 $[M^+-3CO], 196 [L]^+$

[PhCr(CO)₃]C(Ph)N₂ (2). MgSO₄ (0.24 g, 2 mmol) and MnO₂ (0.17 g, 2 mmol) were added to a solution of compound **1** (0.17 g, 0.5 mmol) in CH₂Cl₂ (5 mL) under argon, and the reaction mixture was stirred at room temperature until the disappearance of the starting **1** in TLC samples (~3 h); compound **2** thus formed was eluted much faster than **1**. The red solution was filtered, and the solvent was removed *in vacuo* without heating. In the IR spectrum of the residue (0.15 g), besides the bands for C=O at 1900 and 1970 cm⁻¹, an intense absorption at 2060 cm⁻¹, which is characteristic of diazocompounds, was registered. This product was used immediately with no further purification. On storage, **2** decomposed rather quickly to form the respective azine and a number of unidentified products.

Interaction of C_{60} with diazomethane 2. A. A toluene solution of 2 obtained from 1 (40 mg, 0.12 mmol) was added to a toluene solution of C_{60} (86 mg, 0.12 mmol) at room temperature under argon, and the mixture was left to stand for 72 h. Silica gel (~1/3 of the mixture volume) was then added to the mixture, and the solvent was removed *in vacuo*. The dry residue was placed onto a silica gel column. The unreacted C_{60} (37 mg, 43 %) was eluted with heptane. A toluenc—heptane mixture (2 : 1) was used to elute a violet compound with no chromium in it, which was identified to be the adduct $C_{60} \cdot CPh_2$ according to its ¹H NMR spectrum. This was followed by the elution of the main product **3** (30 mg, 25 % yield, 45 % based on C₆₀ reacted). The ¹H NMR data are reported in the above text and in Figs. 1, *a*, *b*.

B. The reaction mixture obtained after the interaction of C_{60} (50 mg, 0.07 mmol) with diazomethane 2 prepared from 1 (60 mg, 0.17 mmol) was subjected to chromatography on silica gel to afford small amounts of the unreacted C_{60} , adduct $C_{60} \cdot \text{CPh}_2$ (23 mg, 32 %), 3, and three more Cr-containing fullerenes.

Though the elemental analyses of the adducts are not always satisfactory for all of the elements, the presence or the absence of chromium is determined reliably enough by both X-ray-fluorescence and combustion analyses. For example, here is the analysis of one of the adducts obtained from the reaction with excess diazomethane **2**. Found (%): C, 78.07; H, 3.09; Cr, 9.16. $C_{108}H_{30}Cr_{3}O_{9}$. Calculated (%): C, 79.65; H, 1.84; Cr, 9.58.

Decomplexation of compound 3. A solution of iodine (20 mg) in toluene was added to a solution of 3 (20 mg) in toluene and stirred for 1 h. The solvent was removed *in vacuo*. The residue was washed with ether to remove the remaining

iodine and dried *in vacuo*. The ¹H NMR spectrum of product 4 is given in Fig. 1, c.

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An unusual pathway of the oxidation of diethyl ether by bismuth(v) derivatives

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Di(*tert*-butylperoxy)triphenylbismuth and the triphenylbismuth—*tert*-butyl hydroperoxide system transform diethyl ether into ethoxyacetic aldehyde. The latter undergoes further conversions under these reaction conditions to give the corresponding hydroxyperoxide, ethoxyacetic acid, and bismuth(III) acylates.

Key words: diethyl ether, ethoxyacetic aldehyde, triphenylbismuth, *tert*-butyl hydroperoxide, oxidation.

We have established previously that di(*tert*butylperoxy)triphenylbismuth (1) and the triphenylbismuth—*tert*-butyl hydroperoxide system are capable of direct ketonization of methylene groups in aliphatic¹ and alkylaromatic² hydrocarbons. We assume that ketonization occurs under the action of singlet oxygen, like in the oxidation of hydrocarbons by the aluminum tri(*tert*-butoxide)—hydroperoxide and *tert*-butylperoxydibutoxyaluminum—hydroperoxide systems.^{3,4}

The reaction of peroxide 1 or the $Ph_3Bi-Bu^{t}OOH$ oxidizing system (at 1 : 2, 1 : 3, or 1 : 4 reagent ratios) with diethyl ether at temperatures not exceeding 15 °C did not result in direct ketonization of the methylene groups. Instead, oxidation of the methyl group occurred.