Chemistry of unsaturated arenetricarbonylchromium compounds
1. Reaction of (η^6-arene)tricarbonylchromium complexes of nitrones with methyl phenylpropiolate*

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The reactions of nitrones of the composition $(CO)_3CrC_6H_5CH{=}N^+(O^-)R$ (R = Me, Ph, or Bu^t) with substituted acetylene were studied. The reactions proceed with high regioselectivity and give 4-isoxazolines (yields 50—60%). The composition and structures of these products were characterized by physicochemical methods. The reactions also afford (η^6-benzaldehyde)tricarbonylchromium, coordinated Schiff bases, and azoxy derivatives as thermal decomposition products of the starting nitrones. The reactions of uncoordinated nitrones with methyl phenylpropiolate were also investigated. These reactions produce 4-isoxazolines along with cyclic substituted isoxazolinones.

Key words: nitrone, (η^6-arene)tricarbonylchromium, isoxazoline, 1,3-dipolar cycloaddition.

In recent years, studies aimed at the synthesis and characterization of unsaturated arenetricarbonylchromium complexes capable of being involved in various heterolytic, radical, and pericyclic reactions[1] have received much attention from researchers in the field of chemistry of organometallic compounds of transition metals. Pericyclic reactions are of most interest. In particular, 1,3-dipolar cycloaddition reactions are widely used in organic chemistry as an approach to the design of five-membered heterocyclic structures,[2—4] which are difficult to synthesize by other methods.

Earlier, we have shown[5,6] that the use of unsaturated (η^6-arene)tricarbonylchromium complexes as dipoles in 1,3-dipolar cycloaddition reactions results in the formation of isoxazolidines in good yields with high regio- and stereoselectivity. Continuing our studies, we performed a detailed investigation of reactions of three C,N-disubstituted nitrones and their arenetricarbonylchromium complexes with substituted alkyne, *viz.*, methyl phenylpropiolate. The resulting 4-isoxazolines are efficient systems for the synthesis of a large number of various organic derivatives (γ-amino alcohols, β-hydroxy ketones, and so on).[7]

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Results and Discussion

We used a series of free[8—10] (**1a—c**) and coordinated (**1d—f**) C,N-disubstituted nitrones having a *trans* configuration[6,9] as dipoles in the reactions under study. Compounds **1d—f** were synthesized by the condensation of (η^6-benzaldehyde)tricarbonylchromium[11,12] with the corresponding hydroxylamines. Methyl phenylpropiolate (**2**), which was prepared in several steps according to a known procedure,[13] served as a dipolarophile. Due to the presence of the ester group $—CO_2Me$ having electron-withdrawing properties, alkyne is a more reactive dipolarophile compared with unsubstituted acetylenes. Cycloaddition reactions were carried out in degassed sealed tubes in DMF or toluene according to Scheme 1.

The purity of 4-isoxazolines **3a—f** was tested by HPLC. The composition and structures of these compounds were established by UV, IR, and NMR spectroscopy, elemental analysis, and, in some cases, by X-ray diffraction. The characteristics of the synthesized compounds are given in the Experimental section.

The reactions of free nitrones **1a—c** with dipolarophile **2** afforded the expected 4-isoxazolines **3a—c**. The IR spectra of these compounds show vibrational bands characteristic of the compounds under study (see the Experimental section). The ^1H NMR spectroscopic data confirm the compositions of the synthesized 4-isoxazolines.

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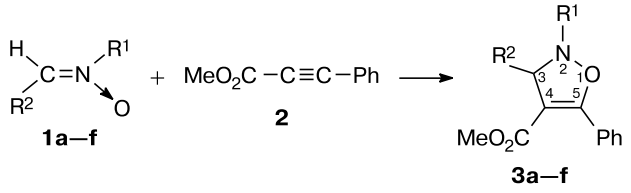
Scheme 1



Compound 1, 3	R^1	R^2	Compound 1,3	R^1	R^2
a	Me	Ph	**d**	Me	Ph[Cr(CO)$_3$]
b	Ph	Ph	**e**	Ph	Ph[Cr(CO)$_3$]
c	Bu^t	Ph	**f**	Bu^t	Ph[Cr(CO)$_3$]

For instance, the ^{1}H NMR spectrum of 4-isoxazoline **3a**, the reaction product of nitrone **1a** with methyl phenylpropiolate, shows signals of protons of two methyl groups at δ 3.02 (s, 3 H, NMe) and 3.67 (s, 3 H, CO_2Me), of two phenyl rings at δ 7.30—7.86 (m, 10 H, *o*-, *m*-, *p*-Ph), and a signal of the proton at the C(3) atom of the isoxazoline ring at δ 5.18 (s, 1 H, C(3)H). According to the results of earlier studies,[14] the reaction of nitrone **1a** with alkyne **2** affords exclusively one of the possible regioisomers, *viz.*, isomer **3a**, in which the ester group is attached to the C(4) atom of the ring, and the phenyl substituent is linked to the C(5) atom of the heterocyclic ring. We found that the reactions of other free nitrones (**1b**,**c**) with dipolarophile **2** also proceed with high regioselectivity and always give exclusively the C(5)-substituted product.

The formation of products **3d—f** with the retention of the chromium tricarbonyl group in the reactions of arenetricarbonylchromium complexes of nitrones **1d—f** with methyl phenylpropiolate (**2**) was established by IR spectroscopy (the presence of intense bands of degenerate carbonyl stretching vibrations in the region of 1850—2000 cm^{-1}), elemental analysis, ^{1}H NMR spectroscopy (signals of protons of the coordinated phenyl rings, see the Experimental section), and X-ray diffraction study of crystals of compound **3f** (Fig. 1, Table 1).

According to the X-ray diffraction data, the carbonyl groups in compound **3f** are in a staggered orientation with respect to the benzene ring. The Cr—η⁶-C and Cr—C(CO) distances are 2.199(2)—2.229(2) and 1.835(2)—1.853(2) Å, respectively. In the benzene ring, there is a significant C—C bond alternation (see Table 1). It should be noted that the CO groups are located under longer C—C bonds. The above-mentioned characteristics of the (η⁶-C_6H_5)-$Cr(CO)_3$ moiety in compound **3f** are similar to those in unsubstituted (η⁶-benzene)tricarbonylchromium.[15—17] Consequently, it can be suggested that the 2-*tert*-butyl-4-methylcarboxy-5-phenyl-4-isoxazoline moiety has no substantial electronic and steric effects on this part of the complex. In compound **3f**, the isoxazoline ring adopts an envelope conformation. The nitrogen atom deviates from

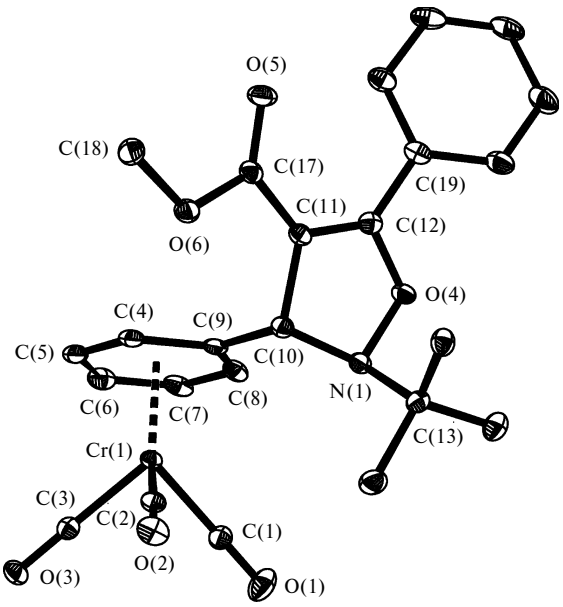


Fig. 1. Molecular structure of complex **3f** (hydrogen atoms are omitted for clarity).

the O(4)C(10)C(11)C(12) plane by 0.277 Å. The dihedral angle between the planes of the isoxazoline and phenyl moieties is 24.1°.

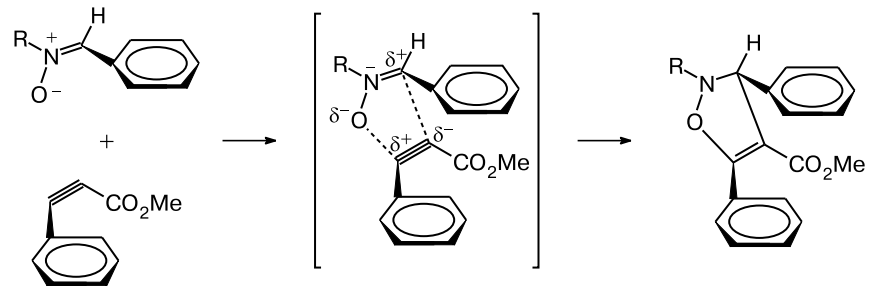
The X-ray diffraction data also confirm that the reaction of the asymmetrical dipole (nitrone) with the dipolarophile (methyl phenylpropiolate) affords a heterocycle containing the double bond, in which the —CO_2Me and phenyl groups are attached to the fourth and fifth carbon atoms, respectively, of the heterocyclic ring.

Therefore, the reactions of both free and coordinated nitrones result in the regiospecific formation of the corresponding 4-isoxazolines. This is indicative of the retention of high regioselectivity of the reaction in the case of

Table 1. Selected bond lengths (*d*) and bond angles (ω) in complex **3f**

Parameter	Value	Parameter	Value
Bond	*d*/Å	Bond	*d*/Å
N(1)—O(4)	1.483(2)	C(4)—C(5)	1.405(3)
C(10)—C(11)	1.521(3)	C(5)—C(6)	1.413(3)
C(11)—C(12)	1.350(3)	C(6)—C(7)	1.392(4)
N(1)—C(10)	1.478(3)	C(7)—C(8)	1.420(3)
Cr(1)—C(1)	1.853(2)	C(8)—C(9)	1.401(3)
Cr(1)—C(2)	1.838(2)	C(4)—C(9)	1.429(3)
Cr(1)—C(3)	1.835(2)		
Cr(1)—C(4)	2.199(2)	Angle	ω/deg
Cr(1)—C(5)	2.208(2)	C(12)—C(11)—C(10)	107.60(17)
Cr(1)—C(6)	2.206(2)	C(10)—N(1)—O(4)	104.32(13)
Cr(1)—C(7)	2.226(2)	C(12)—C(11)—C(10)	107.60(17)
Cr(1)—C(8)	2.230(2)	C(12)—O(4)—N(1)	108.51(14)
Cr(1)—C(9)	2.229(2)	C(11)—C(12)—O(4)	112.42(17)

Scheme 2

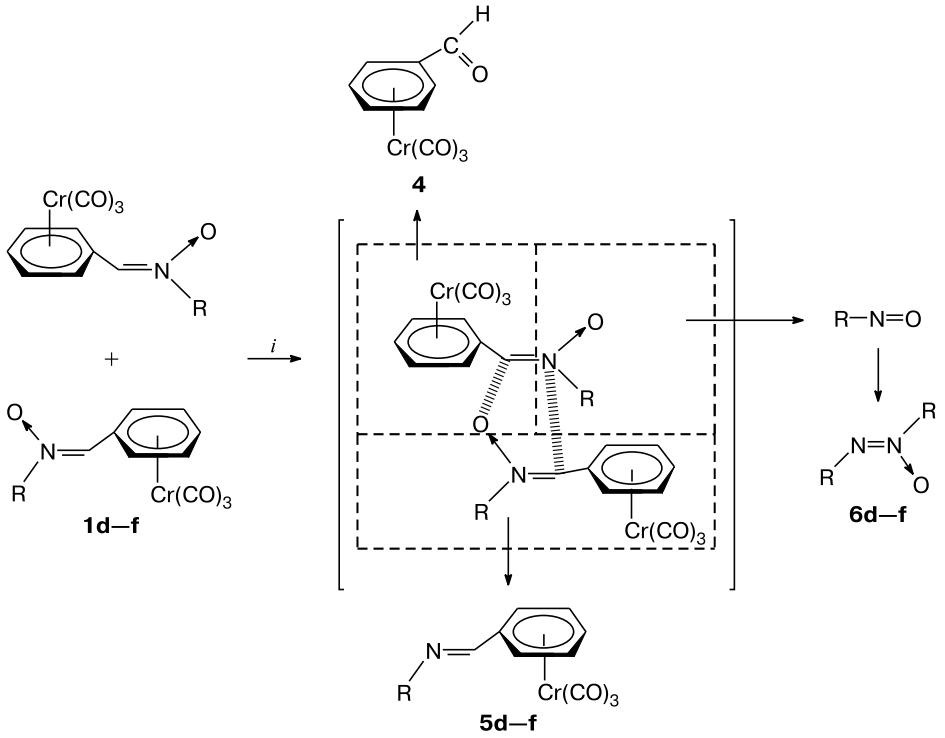


R = Me, Bu^t, Ph

nitrone molecules containing the chromium tricarbonyl group. The fact that the reactions under consideration afford only one of the two possible regioisomers can be explained in terms of the theory of charge distribution of interacting molecules[18] (Scheme 2).

Despite the fact that the target 4-isoxazolines were the major products in the final reaction mixtures, these compounds were not the only products of certain reactions under consideration. Some characteristic features of the cycloaddition were found with the use of both arenetricarbonylchromium complexes of nitrones and uncoordinated compounds. The detailed study of the reaction of each of complex nitrones **1d**—**f** with methyl phenylpropiolate (**2**) revealed the following three by-products: (η^6-benzaldehyde)tricarbonylchromium (**4**), the arenetricarbonylchromium complex of Schiff base (**5**), and the corresponding azoxy compound (**6**) (Scheme 3). We established that products **4**—**6** are formed as a result of the thermal rearrangement of coordinated nitrone **1d**—**f** competitive with the 1,3-dipolar cycloaddition. The reaction of *C*-[tricarbonyl(η^6-phenyl)chromium]-*N*-phenylnitrone (**1e**) at 80 °C in toluene was shown to give the following three new compounds: (η^6-benzaldehyde)tricarbonylchromium,[12] (η^6-benzylideneaniline)tricarbonylchromium,[19] and az-

Scheme 3



R = Me (**d**), Ph (**e**), Bu^t (**f**)

i. 80 °C, toluene.

oxybenzene.[20,21] Each of the three products was isolated, purified, and identified by HPLC, UV, IR, and NMR spectroscopy, as well as by mass spectrometry. In addition, all three compounds were prepared by the independent syntheses.[11,12,19,20] We found that the synthesized compounds are completely identical to the thermal rearrangement products of nitrone **1e**. Based on the analysis of the resulting compounds, it can be suggested that the reaction of complex nitrones under heating proceeds *via* the mechanism presented in Scheme 3: two nitrone molecules react to form the cyclic transition state followed by the formation of products **4** and **5** and a nitroso compound. Under the reaction conditions, the latter gives azoxy compound **6**.[21]

Interesting results were obtained also in the reaction of uncoordinated nitrones with dipolarophiles **2**. Thus, column chromatography of the reaction mixture obtained in the reaction of *C*-phenyl-*N*-*tert*-butylnitrone (**1c**) with methyl phenylpropiolate (**2**) gave 4-isoxazoline **3c** (yield 63%) along with a colorless crystalline compound (yield 10%, m.p. 96—97 °C) and a certain amount of acetophenone.[22] As was shown by IR and NMR spectroscopy and X-ray diffraction (Fig. 2, Table 2), the colorless crystalline compound is a five-membered heterocyclic compound containing the functional carbonyl group and the double bond between the carbon atoms C(2)—C(3) of the ring (see Fig. 2). This compound was identified as 2-*tert*-butyl-3-phenyl-3-isoxazolin-5-one. Selected bond lengths and bond angles in the structure of this compound are given in Table 2.

The observed products are by-products in the synthesis of 4-isoxazolines, which are, evidently, formed as a result of the process competitive with the cycloaddition. According to our suggestions, the acetylene-allene rearrangement of ester **2** (see Ref. 23) can take place in the system followed by the reaction of the resulting compound with nitrone according to Scheme 4. Alternative mechanisms of the formation of by-products can involve various thermal transformations of 4-isoxazolines.[14, 24—28]

To conclude, in the present study we synthesized and characterized new 4-isoxazoline derivatives with high regioselectivity. It was shown that arenetricarbonylchromium complexes of nitrones can undergo thermal rearrangements, and substituted isoxazolinones can be produced by the reaction of methyl phenylpropiolate with free nitrones.

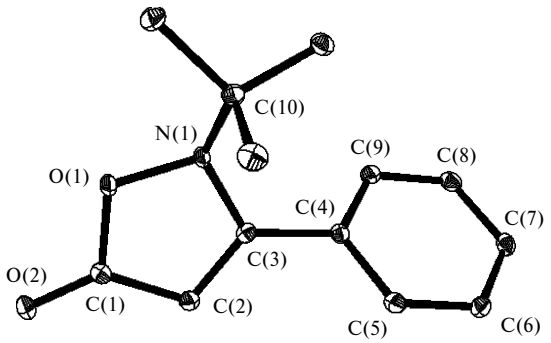


Fig. 2. Molecular structure of 2-*tert*-butyl-3-phenyl-3-isoxazolin-5-one (hydrogen atoms are omitted for clarity).

Table 2. Selected bond lengths (*d*) and bond angles (ω) in 2-*tert*-butyl-3-phenyl-3-isoxazolin-5-one

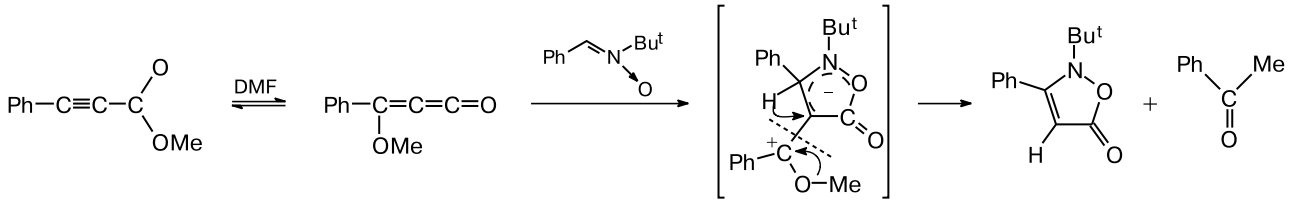
Bond	*d*/Å	Angle	ω/deg
O(1)—N(1)	1.4347(11)	C(1)—O(1)—N(1)	108.59(7)
O(1)—C(1)	1.3903(13)	C(3)—N(1)—O(1)	105.22(8)
C(1)—C(2)	1.4270(15)	C(2)—C(3)—N(1)	111.25(9)
C(2)—C(3)	1.3528(15)	C(3)—C(2)—C(1)	107.83(9)
N(1)—C(3)	1.3874(13)	O(1)—C(1)—C(2)	106.75(9)
C(1)—O(2)	1.2181(13)		

Experimental

All solvents were distilled over sodium metal under atmospheric pressure.[29] *N*-Phenyl- and *N*-*tert*-butylhydroxylamines were prepared by the reduction of the corresponding nitro compounds.[8,30] *N*-Methylhydroxylamine hydrochloride purchased from Sigma-Aldrich was used for the synthesis of *C*-phenyl-*N*-methylnitrone (**1a**). Benzaldehyde and triethyl formate were purified by the distillation under reduced pressure; the reaction of these compounds afforded benzaldehyde diethylacetal.[11] The reaction of the latter with chromium hexacarbonyl gave (η⁶-benzaldehyde diethylacetal)tricarbonylchromium, the hydrolysis of which afforded (η⁶-benzaldehyde)tricarbonylchromium.[12] C,N-Disubstituted nitrones (**1a—f**) were prepared by the condensation of the corresponding hydroxylamine derivatives with benzaldehyde[8—10] or (η⁶-benzaldehyde)tricarbonylchromium.[6,9] Methyl phenylpropiolate (**2**) was synthesized from ethyl cinnamate in several steps according to the known procedure.[13]

The products were isolated and purified by column chromatography on ACROS silica gel (0.035—0.070 mm) under an argon

Scheme 4



atmosphere. HPLC was performed on a Knauer Smartline 5000 chromatograph equipped with a S 2600 UV diode array detector and a Diasfer-110-C16 column (5 μm, 4.6×250 mm) using a 84 : 16 acetonitrile—water mixture as the eluent. The UV spectra of the eluates were recorded in the 200—500 nm region. The IR spectra were measured on an Infralum FT-801 instrument in the 480—4600 cm^{-1} region in a suspension with KBr. The ^1H NMR spectra were recorded on an Agilent DD2 NMR 400NB spectrometer operating at 400 MHz with the use of acetone-d_6 as the solvent.

(η^6-Arene)tricarbonylchromium complexes of nitrones and 4-isoxazolines were isolated under an argon atmosphere.

Synthesis of free 4-isoxazolines 3a—c (general procedure). According to a procedure described earlier,[31] C,N-Disubstituted nitrone **1a**—**c** (2.6 mmol), methyl phenylpropiolate (**2**) (2.6 mmol), and DMF (5 mL) were placed in a 10 mL glass tube. The tube was degassed and vacuum sealed. The reaction mixture was heated on an oil bath at 85 °C. After heating, the tube was opened, and the solvent was distilled off *in vacuo*. The reaction products were isolated from the residue by column chromatography.

2-Methyl-4-methylcarboxy-3,5-diphenyl-4-isoxazoline (3a). The synthesis was performed according to the above-described procedure.[14,31] The reaction mixture was heated for 2 h. One fraction was isolated by column chromatography (the retention time in the HPLC chromatogram was 6.7 min), and the recrystallization of this substance from hexane afforded colorless crystals of compound **3a**. Yield 42%, m.p. 100—101 °C. Found (%): C, 73.20; H, 5.80; N, 4.57. $C_{18}H_{17}NO_3$. Calculated (%): C, 73.22; H, 5.76; N, 4.75. IR (KBr), ν/cm^{-1}: 3005, 2970, 2920 (ν(C—H)); 1714 (ν(C=O)); 1636 (ν(C=C)); 1598 (ν(C—C_{Ar})); 1435 (ν(C—C)); 1237, 1086 (ν(N—O, C—O)); 795, 745, 695 (ω(C_{Ar}—H)). ^1H NMR, δ: 3.02 and 3.67 (both s, 3 H each, NMe, CO_2Me); 5.18 (s, 1 H, C(3)H); 7.30—7.86 (m, 10 H, *o*-, *m*-, *p*-Ph).

4-Methylcarboxy-2,3,5-triphenyl-4-isoxazoline (3b). The synthesis was performed according to the above-described procedure. The reaction mixture was heated for 10 h. Two substances were isolated by column chromatography (the retention times in the HPLC chromatogram were 5.9 and 6.0 min). The substance with the retention time of 5.9 min was a viscous oily liquid (acetophenone).[22] The substance with the retention time of 6.0 min was recrystallized from hexane. Yellow crystalline compound **3b** was obtained. Yield 31%, m.p. 100—101 °C. Found (%): C, 76.98; H, 5.48; N, 3.83. $C_{23}H_{19}NO_3$. Calculated (%): C, 77.31; H, 5.32; N, 3.92. IR (KBr), ν/cm^{-1}: 3057, 2948, 2846 (ν(C—H)); 1731 (ν(C=O)); 1686 (ν(C=C)); 1598 (ν(C—C_{Ar})); 1484 (ν(C—C)); 1223, 1046 (ν(N—O, C—O)); 870, 746, 702 (ω(C_{Ar}—H)). ^1H NMR, δ: 3.67 (s, 3 H, CO_2Me); 5.96 (s, 1 H, C(3)H); 6.71—7.55 (m, 15 H, *o*-, *m*-, *p*-Ph).

Reaction of C,N-disubstituted nitrone 1c with dipolarophile 2. The reaction mixture was heated for 10 h. Three substances were isolated by column chromatography (the retention times in the HPLC chromatogram were 5.9, 6.0, and 9.6 min). The substance with the retention time of 5.9 min was a viscous oily liquid (acetophenone).[22] The substances with the retention times of 6.0 and 9.6 min were recrystallized from a 5 : 1 hexane—ethyl acetate mixture. 2-*tert*-Butyl-3-phenyl-3-isoxazolin-5-one and 2-*tert*-butyl-4-methylcarboxy-3,5-diphenyl-4-isoxazoline (**3c**) were isolated. Both products were colorless crystalline compounds.

2-*tert*-Butyl-3-phenyl-3-isoxazolin-5-one. Yield 10%, m.p. 96—97 °C. Found (%): C, 71.50; H, 7.01; N, 6.47. $C_{13}H_{15}NO_2$. Calculated (%): C, 71.89; H, 6.91; N, 6.45. IR (KBr), ν/cm^{-1}: 1729 (ν(C=O)); 1635 (ν(C=C)); 1560 (ν(C—C_{Ar})); 1493 (ν(C—C)); 1245, 1095 (ν(N—O, C—O)); 775, 740, 705 (ω(C_{Ar}—H)). ^1H NMR, δ: 1.18 (s, 9 H, NBu^t); 5.44 (s, 1 H,C<u>H</u>Ph); 7.39—7.64 (m, 5 H, *o*-, *m*-, *p*-Ph).

2-*tert*-Butyl-4-methylcarboxy-3,5-diphenyl-4-isoxazoline (3c). Yield 63%, m.p. 62—63 °C. Found (%): C, 74.39; H, 6.87; N, 4.13. $C_{21}H_{23}NO_3$. Calculated (%): C, 74.78; H, 6.82; N, 4.15. IR (KBr), ν/cm^{-1}: 3065, 3035, 2973 (ν(C—H)); 1711 (ν(C=O)); 1635 (ν(C=C)); 1577 (ν(C—C_{Ar})); 1493 (ν(C—C)); 1245, 1095 (ν(N—O, C—O)); 775, 740, 705 (ω(C_{Ar}—H)). ^1H NMR, δ: 1.24 (s, 9 H, NBu^t); 3.50 (s, 3 H, CO_2Me); 5.58 (s, 1 H, C(3)H); 7.21—7.91 (m, 10 H, *o*-, *m*-, *p*-Ph).

Synthesis of (η^6-arene)tricarbonylchromium complexes of 4-isoxazolines 3d—f (general procedure). C,N-Disubstituted nitrone **1d**—**f** (0.74 mmol), dipolarophile **2** (0.74 mmol), and toluene (5 mL) were placed in a 10 mL glass tube. The tube was degassed and vacuum sealed. The reaction mixture was heated on an oil bath at 80 °C for 35 h. After heating, the tube was opened, and the solvent was distilled off *in vacuo*. The HPLC chromatogram of the reaction mixture showed four peaks, one of which corresponded to 4-isoxazoline; the other three, to rearrangement products of the corresponding (η^6-arene)tricarbonylchromium complex of nitrone. Two substances were isolated from the residue by column chromatography. The recrystallization of these substances from a hexane—ethyl acetate (diethyl ether) mixture afforded crystalline compounds. One of them was (η^6-benzaldehyde)tricarbonylchromium,[6,9] and the other was the corresponding (η^6-arene)tricarbonylchromium complex with 4-isoxazoline **3d**—**f**.

3-[Tricarbonyl(η^6-phenyl)chromium]-2-methyl-4-methylcarboxy-5-phenyl-4-isoxazoline (3d). Yellow crystals. Yield 50%, m.p. 125—126 °C. Found (%): C, 58.12; H, 4.18; N, 3.20. $C_{21}H_{17}CrNO_6$. Calculated (%): C, 58.47; H, 3.94; N, 3.25. IR (KBr), ν/cm^{-1}: 2953, 2918, 2851 (ν(C—H)); 1971, 1916, 1871 (ν(C≡O)); 1693 (ν(C=O)); 1630 (ν(C=C)); 1226, 1099 (ν(N—O, C—O)); 800, 753, 658 (ω(C_{Ar}—H)). ^1H NMR, δ: 3.07 and 3.67 (both s, 3 H each, NMe, CO_2Me); 4.94 (s, 1 H, C(3)H); 5.52—5.68 (m, 3 H, *m*-, *p*-C(3)PhCr); 5.75—5.96 (m, 2 H, *o*-C(3)PhCr); 7.37—7.62 (m, 3 H, *m*-, *p*-C(5)Ph); 7.84 (dd, 2 H, *o*-C(5)Ph, J = 8.2 Hz, J = 1.6 Hz).

3-[Tricarbonyl(η^6-phenyl)chromium]-4-methylcarboxy-2,5-diphenyl-4-isoxazoline (3e). Yellow crystals. Yield 55%, m.p. 136—137 °C. Found (%): C, 63.99; H, 4.10; N, 2.74. $C_{26}H_{19}CrNO_6$. Calculated (%): C, 63.29; H, 3.85; N, 2.84. IR (KBr), ν/cm^{-1}: 3090, 2919, 2851 (ν(C—H)); 1973, 1895, 1879 (ν(C≡O)); 1711 (ν(C=O)); 1624 (ν(C=C)); 1269, 1155 (ν(N—O, C—O)); 763, 662, 611 (ω(C_{Ar}—H)). ^1H NMR, δ: 3.64 (s, 3 H, CO_2Me); 5.68 (m, 2 H, *m*-C(3)PhCr); 5.78—5.89 (t, 1 H, *p*-C(3)PhCr, J = 8.0 Hz); 6.16 (dd, 2 H, *o*-C(3)PhCr, J = 7.0 Hz); 6.47 (s, 1 H, C(3)H); 7.09—7.17 (t, 1 H, *p*-NPh, J = 7.4 Hz); 7.18 (d, 2 H, *o*-NPh, J = 7.8 Hz); 7.35—7.43 (m, 2 H, *m*-NPh); 7.43—7.57 (m, 3 H, *m*-, *p*-C(5)Ph); 8.09 (d, 2 H, *o*-C(5)Ph, J = 7.0 Hz).

3-[Tricarbonyl(η^6-phenyl)chromium]-2-*tert*-butyl-4-methylcarboxy-5-phenyl-4-isoxazoline (3f). Yield 58%, m.p. 109—110 °C. Found (%): C, 60.07; H, 5.02; N, 2.96. $C_{24}H_{23}CrNO_6$. Calculated (%): C, 60.89; H, 4.86; N, 2.96. IR (KBr), ν/cm^{-1}: 2978, 2943, 2900 (ν(C—H)); 1961, 1882 (ν(C≡O)); 1688 (ν(C=O)); 1635 (ν(C=C)); 1235, 1100 (ν(N—O, C—O)); 690, 659, 625 (ω(C_{Ar}—H)). ^1H NMR, δ: 1.31 (s, 9 H, NBu^t); 3.67 (s, 3 H, CO_2Me); 5.28 (s, 1 H, C(3)H); 5.36—5.48 (m, 2 H, *m*-C(3)PhCr); 5.80 (t, 1 H, *p*-C(3)PhCr, J = 6.26 Hz); 6.02 (d, 1 H, *o*-C(3)PhCr, J = 6.7 Hz); 6.11 (d, 1 H, *o*-C(3)PhCr, J = 6.7 Hz); 7.44—7.61 (m, 3 H, *m*-, *p*-C(5)Ph); 7.85—7.96 (m, 2 H, *o*-C(5)Ph).

Thermal rearrangement of nitrones 1d—f. C,N-Disubstituted nitrone **1d**—**f** (0.74 mmol) and toluene (5 mL) were placed in a 10 mL glass tube. The tube was degassed and vacuum sealed. The reaction mixture was heated on an oil bath at 80 °C for 35 h. After heating, the solvent was distilled off *in vacuo*. The HPLC chromatogram of the reaction mixture showed three peaks corresponding to reaction products. In the case of nitrone **1e**, three substances were isolated by column chromatography from the residue, which was obtained after the distillation of the solvent. The recrystallization of these substances from a 4 : 1 hexane—ethyl acetate mixture afforded red crystals of (η⁶-benzaldehyde)-tricarbonylchromium,[6,9] orange crystals of (η⁶-benzylideneaniline)tricarbonylchromium,[19] and colorless crystals of azoxybenzene.[20,21]

X-ray diffraction study. Complex 3f. Crystals ($C_{24}H_{23}CrNO_6 \cdot 0.5Et_2O$, M = 510.49), triclinic, space group $P\bar{1}$, at 100 K: a = 9.4167(9) Å, b = 9.6938(10) Å, c = 13.9258(14) Å, α = 89.030(2)°, β = 86.830(2)°, γ = 78.077(2)°, V = 1241.9(2) Å^3, Z = 2, d_{calc} = 1.365 g cm^{-3}, μ = 5.04 cm^{-1}, F(000) 534, 2.15 < θ < 26.00°; were prepared by the crystallization from a 5 : 1 : 0.5 hexane—ethyl acetate—diethyl ether mixture. The intensities of 7473 reflections (4846 unique reflections, R_{int} = 0.0177) were measured on a Smart Apex diffractometer (graphite monochromator, λ(Mo-Kα) = 0.71073 Å). The final R factors are R_1 = 0.0656 ($I > 2\sigma(I)$), wR_2 = 0.1846 (the refinement based on F^2_{nkl} for all unique reflections), $S(F^2)$ = 1.092, ρ (max/min) = 1.920 / −0.772 e Å^{-3}.

2-*tert*-Butyl-3-phenyl-3-isoxazolin-5-one. Crystals ($C_{13}H_{15}NO_2$, M = 217.26), triclinic, space group $P\bar{1}$, at 100 K: a = 7.55264(12) Å, b = 8.32849(14) Å, c = 10.43754(15) Å, α = 67.5411(15)°, β = 69.9071(14)°, γ = 81.5091(14)°, V = 569.717(15) Å^3, Z = 2, d_{calc} = 1.266 g cm^{-3}, μ = 0.85 cm^{-1}, F(000) 232, 3.45 < θ < 26.00°; were prepared by the crystallization from a 5 : 1 hexane—ethyl acetate mixture. The intensities of 8304 reflections (2232 unique reflections, R_{int} = 0.0142) were measured on a Smart Apex diffractometer (graphite monochromator, λ(Mo-Kα) = 0.71073 Å). The final R factors are R_1 = 0.0333 ($I > 2\sigma(I)$), wR_2 = 0.0819 (the refinement based on F^2_{nkl} for all unique reflections), $S(F^2)$ = 1.071, ρ (max/min) = 0.231/ −0.200 e Å^{-3}.

Both structures were solved by direct methods and refined by the full-matrix least-squares method based on F^2_{hkl} with anisotropic displacement parameters for all nonhydrogen atoms. The hydrogen atoms were geometrically positioned and refined using a riding model. The absorption corrections were applied using the SADABS program.[32] All calculations were carried out using the SHELXTL program package.[33] The structures were deposited in the Cambridge Crystallographic Data Centre (CCDC 965364 and 965365).

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