Table II. Hyperfine Splitting Constants (G) and g Values of Substituted Phenylchloromethaniminoxyls (1) and 1-(2-Chlorophenyl)ethan-1-iminoxyl (2)

radical	Ar	a_N	a_{Cl}	a_{Ar}	g
1a	4-ClPh	29.02	1.40 (^{35}Cl), 1.16 (^{37}Cl)	0.65 (2 H)	2.0067
1b	Mes	29.50	1.77 (^{35}Cl), 1.48 (^{37}Cl)		
1c	Cl_2Mes	29.50	1.63 (^{35}Cl), 1.36 (^{37}Cl)		2.0063
1d[a,b]	2,4-Cl_2Ph	32.00	1.76[d]	2.15 (1 Cl)[d]	
2[a,c]	2-ClPh	33.50	1.40 (CH_3)	1.55 (1 Cl)[d]	2.0056

[a] Values measured in methylene chloride. [b] Reference 1. [c] Reference 4. [d] Mean for ^{35}Cl and ^{37}Cl.

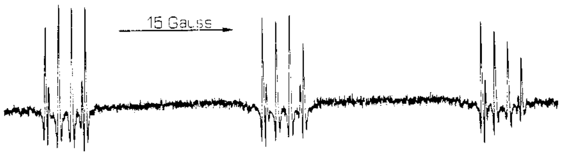

Figure 1. Second-derivative ESR spectrum of mesitylchloromethaniminoxyl (**1b**) recorded at room temperature.

by radicals **3a** and **3b**. By contrast, bulky X substituents destabilize the coplanar conformation and prevent the halogen nuclei from coupling with the unpaired electron. This repulsive effect is more important, as expected, in the ortho-disubstituted than in the monosubstituted derivatives. Actually, when the phenyl ring bears two ortho halogens, the hindrance exerted by the hydroxymethyl group is sufficient to induce significant deviations from coplanarity, as is demonstrated by the absence of chlorine splitting in radical **4c**. In ortho-monohalogenated aryl iminoxyls, this situation is found when X is the bulkier *tert*-butyl group (see radical **5**), while for X = CH_2OH the observed splitting of 1.10 G at chlorine indicates that the out of plane rotation of phenyl is not very large (radical **4d**). We may then conclude that the coupling at the ortho halogens in aryl iminoxyls is mainly determined by the size of the X group in the syn isomers, whereas it is always expected to be small in the anti isomers.

In the light of the above considerations, the value of 2.15 G for a_{Cl} (ortho) observed in the (2,4-dichlorophenyl)chloromethaniminoxyl **1d** (see Table II) is consistent with a syn configuration and a conformation about the Ar—C=N single bond where the chlorine is close to the iminoxy nitrogen and the phenyl ring slightly deviates from coplanarity.[10] On the other hand, we cannot find any plausible explanation for the magnitude of this splitting if the anti configuration is assumed. On the same basis, the a_{Cl} value of 1.55 G measured in 1-(2-chlorophenyl)ethan-1-iminoxyl (**2**) is also more consistent with the syn than with the anti configuration assigned by Norman and Gilbert.[4] It may be added that the *o*-chlorine splitting in radicals **4d**, **2**, and **1d** increases along the sequence $CH_2OH < CH_3 < Cl$ for the azomethine substituent, i.e., with decreasing the size of the X group in accord with expectations for the syn configuration. Similarly to the case of **2**, a reassignment may also be required for the radicals from *o*-fluoro-, *o*-bromo-, and *o*-iodoacetophenone oximes.[4]

Further, evidence in favor of the syn configuration of radicals **1** comes from the absence of the ca. 0.25-G splitting from the meta protons in mesitylchloromethaniminoxyl (**1b**). This splitting is usually observed in the anti isomers of the mesitylmethaniminoxyls.[8] The ESR spectrum of **1b**, reported in Figure 1, shows, in fact, well-resolved lines due to the isotopes ^{35}Cl and ^{37}Cl. Since the separation between the outer lines of the two quartets is only 0.15 G, any hyperfine splitting of the order of 0.2–0.3 G should be, if present, clearly observable.

Another indication is provided by the value of the coupling at the ortho protons in the (4-chlorophenyl)chloromethaniminoxyl (**1a**). The ESR spectrum of this radical consists at room temperature of three broad multiplets which, in our previous study,[1] we were not able to resolve. However, when the spectrum was recorded at lower temperature (ca. −40 °C), the resulting lines were relatively sharp, and all coupling could be determined. The ortho-proton splitting in **1a** is 0.65 G, a value which although rather unusual in iminoxyls supports the syn more than the anti configuration.[7]

In conclusion, the results now available uniformly favor the syn (*Z*) configuration for arylchloromethaniminoxy radicals (**1**), in contrast with the geometry previously proposed. A similar reassignment in favor of the *Z* configuration has been reported[11] by some of us for the precursors of radicals **1**, i.e., benzohydroxymoyl chlorides. Finally, our results also suggest that the configuration of 1-(2-halophenyl)ethan-1-iminoxyls[4] has to be reconsidered.

Experimental Section

Arylchloromethaniminoxy radicals (**1**) were generated by photolysis of solutions of the corresponding hydroxymoyl chlorides[12] in a 2:1 (by volume) mixture of *tert*-butylbenzene and di-*tert*-butyl peroxide. The same procedure was employed for the production of radicals **3** by starting from the corresponding substituted benzaldoximes. Radicals **4** and **5** were obtained in the same solvent by reaction of the proper benzonitrile oxides[12b,13] with photolytically generated hydroxymethyl (or $\cdot CD_2OD$) and *tert*-butyl radicals.[6]

A high-pressure 1-kW mercury lamp was used as UV source, and the temperature was controlled with standard accessories.

Acknowledgment. Financial support from CNR (Rome) is gratefully acknowledged by A.D. and G.F.P.

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[10] For a planar conformation one should in fact expect a_{Cl} (ortho) to be twice as large as it is in radical **3b**, i.e., 3.1 G.

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A Novel and Inexpensive Synthesis of Ethyl 4-Methyl-2,4-pentadienoate[1]

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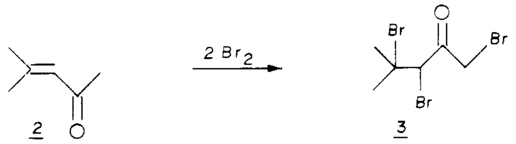
While investigating the reaction of 3,4-dibromo-4-methyl-2-pentanone with bases,[2] we encountered small amounts of ethyl 4-methyl-2,4-pentadienoate as a minor product in the reaction with sodium ethoxide in ethanol. Since pentadienoates have been used as intermediates in the syntheses of functionalized cyclic compounds, for example, through reactions with enamines,[3] maleic anhydride,[4] and ammonia,[5] and since the specific compound obtained has been prepared previously via the expensive modified Wittig procedure of reacting 2-methylacrolein with triethyl phosphonoacetate,[6] we felt it worth investigating the formation of the byproduct.

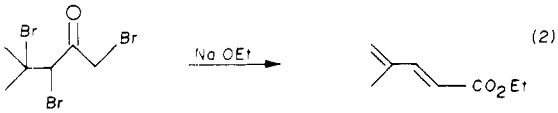
We initially suspected that the byproduct must have come from excess bromination of mesityl oxide which would produce tribromo ketones as an impurity in our dibromo ketone (3,4-dibromo-4-methyl-2-pentanone). Therefore we reacted the mesityl oxide (neat) with 2 mol of bromine and obtained a product with an NMR spectrum coherent with that expected for 1,3,4-tribromo-4-methyl-2-pentanone (eq 1), containing the 3,4-dibromo ketone[2] as a 10% impurity.



(1)

2 3

Reaction of the tribromo ketone with 3 equiv of sodium ethoxide (1 N in absolute ethanol) for 2 h at 0 °C led to the formation of ethyl *trans*-methyl-2,4-pentadienoate (88% according to gas chromatography) (eq 2). We were able to isolate the dienoate in 57% yield from the reaction mixture.



(2)

3 1

The reaction should occurr via a Favorskii rearrangement similar to that observed by us for 3,4-dibromo-4-methyl-2-pentanone[2] and by Wagner and Moore for 3,4-dibromo-3-methyl-2-pentanone.[7] It is probable that this reaction can be generalized and we are proceeding with our studies of it.

Experimental Section

NMR spectra were obtained by Antonio Ribeiro Jorge on a Varian XL-100 with chemical shifts expressed as values downfield from a tetramethylsilane internal standard. IR spectra were recorded with a Perkin-Elmer 467 spectrophotometer from liquid films between NaCl plates.

GLC was done on a Perkin-Elmer 900 instrument with an H_2 flame detector, using an aluminum column (1/8 in. × 10 ft) packed with 10% Carbowax 20M at a column temperature of 80 °C.

1,3,4-Tribromo-4-methyl-2-pentanone (3). In a 100-mL round-bottomed flask was placed 4.9 g (0.05 mol) of mesityl oxide and to the flask was attached an addition funnel with a pressure-equalizing sidearm, protected by a drying tube containing calcium chloride and containing bromine (16 g, 0.10 mol). The reaction vessel was immersed in an ice bath and the bromine was added dropwise over a period of 30 min. The resultant liquid exhibited the following spectrum: NMR (CCl_4) δ 2.0 (6 H, s), 4.2 (2 H, s), 5.1 (1 H, s), as well as an impurity peak corresponding to 3,4-dibromo-4-methyl-2-pentanone at δ 2.4 (7% of the area of the peak at δ 2.0). This product was used in the second reaction as quickly as possible because our own experience[2] and that of others[8,9] show that the α,β-dibromo ketones are highly unstable in contact with air.

Ethyl 4-Methyl-2,4-pentadienoate (1). A solution of 1 N sodium ethoxide was prepared by reacting sodium (3.45 g, 0.15 mol) with 150 mL of absolute ethanol in a 300-mL flask. To this solution was added 1,3,4-tribromo-4-methyl-2-pentanone (3; 16.9 g, 0.05 mol) dropwise in 10 min, while the reaction vessel was maintained in an ice bath and the mixture was subjected to magnetic stirring. The solution was stirred for 2 h and then added to ice water (200 mL), which was extracted with *n*-hexane (5 × 10 mL). The extract was dried over sodium sulfate and analyzed by GLC, showing 88% of the desired ester (the other 12% is the products observed in the analogous reaction of the dibromo ketone[2]).

The extract was stripped in the presence of crystals of *p*-hydroquinone and then distilled in a short-path head to yield 4.0 g (57%): bp 71-72 °C (17 mm) [lit.[6] 81-83 bp °C (17 mm)]; IR 1720, 1640, 1601, 970, 905 cm^{-1}; NMR ($CDCl_3$) δ 1.30 (3 H, t, J = 7 Hz), 1.86 (3 H, s), 4.20 (2 H, q, J = 7 Hz), 5.18 (2 H, br s), 5.75 (1 H, d, J = 13 Hz), 6.45 (1 H, d, J = 13 Hz) (agrees with the literature spectra[6]); mass spectrum (Varian CH 5-DF, 70 eV), m/e 140 (M^+), 67 (base), other peaks greater than 60% of base 95, 43, 41, and 39.

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Registry No. 1, 35227-70-4; 2, 141-79-7; 3, 74563-05-6.

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Decarboxylative Iodination: A Convenient Synthesis of Bridgehead Iodides

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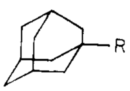
As part of a program of study of bridgehead-substituted derivatives of polycyclic hydrocarbons, we required the series of bridgehead iodides 1-6 (R = I). Of these, 1-3



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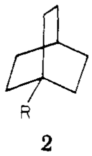

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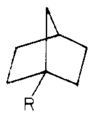

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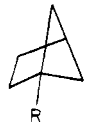

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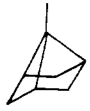

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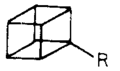

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have previously been synthesized, whereas 4-6 are, as yet, unknown.

1-Iodoadamantane[1-4] and 1-iodobicyclo[2.2.2]octane,[3,5,6]

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