

FREE RADICALS ORIGINATED FROM ISATOGEN DERIVATIVES

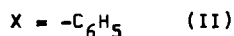
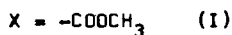
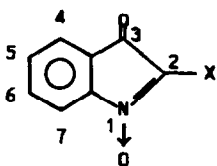
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(Received 18 July 1966)

By heating at the b.p. solutions of 2-carbomethoxy-(I) and 2-phenyl-isatogen (II) in oxygen-free toluene, xylene and mesitylene, the formation of free radicals with a life of several months was observed by E.S.R. spectroscopy.



The amount of radical produced was found to be related to the temperature at which the solution was heated: the most intense signals are thus observed in mesitylene solution (b.p. = 165°C). By operating under the same conditions in aprotic solvents (CCl₄, C₂Cl₄), no spin resonance signals were detected, an indication that hydrogen transfer is involved.

The spectra of compounds I (see fig. 1) and II are substan-

tially identical: thus it appears that the unpaired electron is not delocalized on $-\text{COOCH}_3$ and $-\text{C}_6\text{H}_5$. The analysis of the spectrum is given in table 1: the assignments were checked by investigating ESR-spectra of benzo-substituted phenyl-isatogens (1) and by comparing the calculated (see fig. 1) with the observed

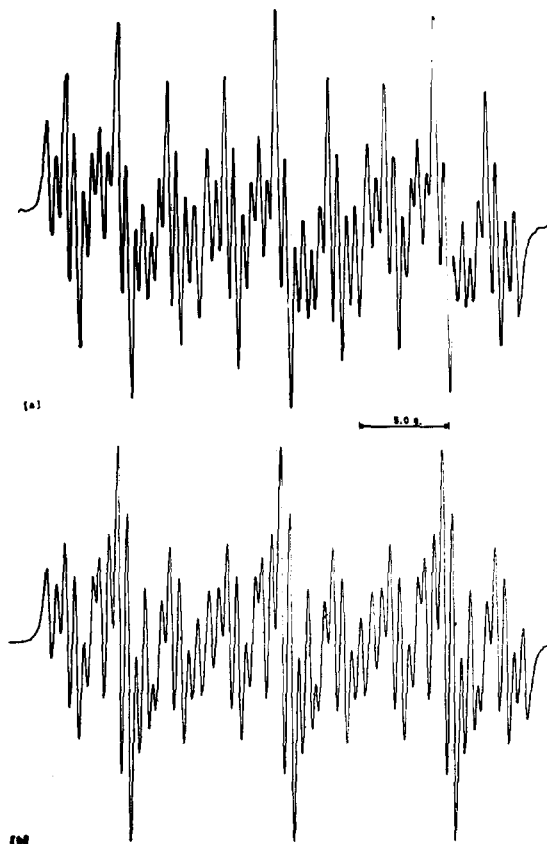


FIG. 1

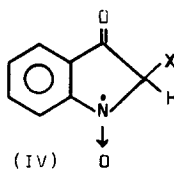
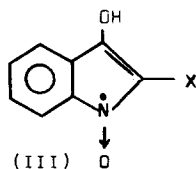
Observed (a) and calculated (b) spectrum
of compound I in mesitylene solution

spectrum. (x)

Three main groups of peaks, each containing 18 bands (intensity ratio 1:1:1) are observed and attributed to the coupling with N^{14} . The structure of each multiplet is interpreted as originated by the coupling of the unpaired electron with the two sets of equivalent protons H_5, H_7 and H_4, H_6 . The latter couple exhibit a smaller coupling constant (see table 1) than the former (H_5, H_7) and thus the charge distribution of the unpaired electron is higher for H_5, H_7 .

The spectrum shows also a further splitting of about 0.5 gauss which is attributed to the coupling with an hydrogen not originally present in molecules I and II. This constitute strong evidence for postulating that the free radicals, thermally generated from isatogens, arise by proton transfer from the solvent. The radical produced by the latter is not detected since it is expected to have a short lifetime (3).

Of two structures (III, IV) that can be attributed to the radicals III seems at present the most likely.



Further work is in progress to assign unambiguously the structure of the radicals.

TABLE 1

Coupling constants a in the ESR spectra of compounds I,II

	a_N	$a_5=a_7$	$a_4=a_6$	a_H (proton transferred from solvent)
X = $-\text{COOCH}_3$	8.96	2.90	1.00	0.52
X = $-\text{C}_6\text{H}_5$	9.24	2.97	1.05	0.48

* For the bands a Laurentzian shape was assumed (2) with a 0.28 gauss half-width; the calculations were performed with a digital computer provided with a plotter.

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- 3) R.L.Ward: J.Chem.Phys. 38, 2588 (1963).