Formation of Di-*t*-butyl Polyoxides in the Reaction of *t*-Butyl Hydroperoxide with Iodosobenzene and Iodosobenzene Diacetate in Methylene Chloride and in Diethyl Ether at −80 to +5° [1]

Nicholas A. Milas and Bozo Plesnicar[2]

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received February 10, 1968*

Abstract: The reaction of *t*-butyl hydroperoxide with iodosobenzene diacetate and iodosobenzene in methylene chloride and in diethyl ether has been studied quantitatively at −80 to +5°. The results seem to indicate that at −80° *t*-butylperoxy radicals are formed and couple in equilibrium to form di-*t*-butyl tetroxide without the evolution of oxygen. At −75 to −65° the tetroxide decomposes to di-*t*-butyl trioxide as deduced from the amount of oxygen produced. The trioxide seems to be in equilibrium with *t*-butoxy and *t*-butylperoxy radicals and, as the temperature rises, the former abstract hydrogen atoms to form *t*-butyl alcohol while the latter couple and undergo a secondary decomposition at −45° to give oxygen and di-*t*-butyl trioxide. When the trioxide is generated at −75° in ethyl ether the *t*-butoxy radicals abstract hydrogen atoms from the solvent and the ether radicals formed trap the *t*-butylperoxy radicals and produce α-*t*-butylperoxyethylether in almost quantitative yields. The structure of this ether peroxide was confirmed by an independent synthesis. A mechanism was proposed of all the reactions studied.

Our interest in di-*t*-alkyl trioxides[3] and tetroxides[4] led us long ago to examine other reactions in which this class of organic polyoxides is possible. One of these is the reaction at −80 to +5° of iodosobenzene and iodosobenzene diacetate in methylene chloride and in diethyl ether. We have found that in all reactions in the two solvents at −80° there was no observable gas evolution, even after vigorous magnetic stirring in dry nitrogen for 2 hr. However, there was a definite separation of iodobenzene as detected by infrared measurements. In both solvents at −75 to −65° a vigorous evolution of oxygen took place and the first step of the reaction (disappearance of iodosobenzene and iodosobenzene diacetate and cessation of gas evolution) was complete within 1 hr. With iodosobenzene and iodosobenzene diacetate in methylene chloride a secondary but less vigorous evolution of oxygen occurred at −45 to +5°, while in diethyl ether there was no secondary evolution of oxygen at any temperature above −65°.

Table I. Reaction of Iodosobenzene Diacetate with *t*-Butyl Hydroperoxide in Methylene Chloride at −80 to +5° [a]

	IBDA:TBHP,	TBA, mmol		DTBP, mmol		IB, mmol		O_2,[c] cm³		O_2,[d] cm³	
Expt	mmol	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
1[b]	11:22	19.2	17.0	1.38	1.90	11	...	123	105	123	92
2	11:22	19.2	17.3	1.38	1.76	11	9.5	123	115	123	78
3	11:22	19.2	16.7	1.38	1.78	11	10.7	123	154	123	45
4	5.5:22	19.2	18.9	1.38	0.91	5.5	...	123	92	123	110

[a] IBDA = iodosobenzene diacetate, DTBP = di-*t*-butyl peroxide, TBHP = *t*-butyl hydroperoxide, IB = iodobenzene, TBA = *t*-butyl alcohol. [b] 0.5 hr at −80°. [c] −75 to −68°. [d] −45 to +5°.

Table II. Reaction of Iodosobenzene with *t*-Butyl Hydroperoxide in Methylene Chloride at −80 to +10° [a]

	IDBvTBHP,	TBA, mmol		DTBP, mmol		IB, mmol		O_2,[b] cm³		O_2,[c] cm³	
Expt	mmol	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
5	11:22	19.2	15.3	1.38	2.3	11	9.2	123	126	123	110
6	11:22	19.2	14.7	1.38	2.1	11	...	123	133	123	101
7	5.5:22	19.2	18.7	1.38	1.38	5.5	...	123	119	123	128

[a] IDB = iodosobenzene; see Table I for other abbreviations. [b] −75 to −65°. [c] −40 to +10°.

With the exception of acetic acid and water which were not estimated quantitatively, the products formed in seven representative experiments from the over-all reactions using iodosobenzene diacetate and iodosobenzene in methylene chloride were: *t*-butyl alcohol, di-*t*-butyl peroxide, iodobenzene, and oxygen, but no acetone or carbon dioxide. These are listed in Tables I and II. The equations used for the various steps of the reactions from which the calculations were made are shown in Schemes I and II.

In the experiments in which ethyl ether was used as the solvent, the reaction steps both with iodosobenzene diacetate and iodosobenzene were somewhat different,

---

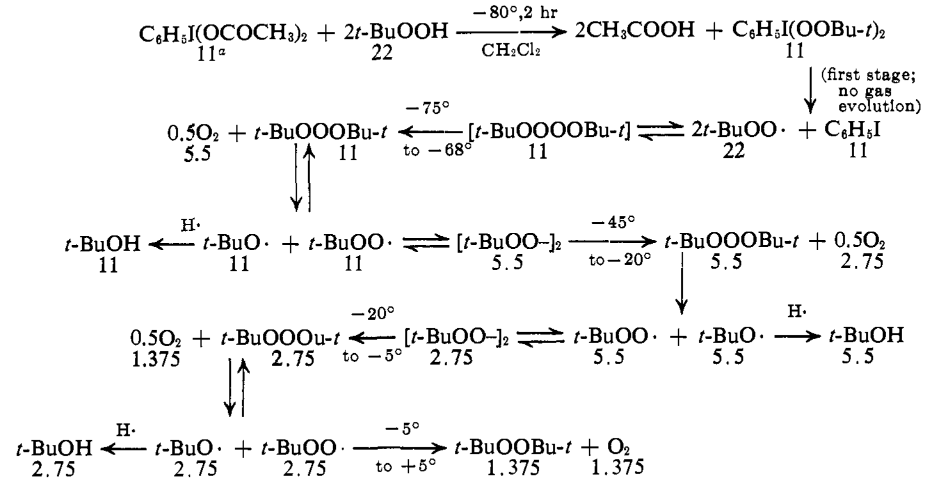
[1] Paper XLIII on organic peroxides; presented before the International Symposium on the Chemistry of Organic Peroxides, Berlin-Adlershof, Sept 1967.

[2] Postdoctoral Research Associate (1966–1967) on leave from the University of Ljubljana, Yugoslavia.

[3] N. A. Milas and G. G. Arzoumanidis, *Chem. Ind.* (London), 66 (1966).

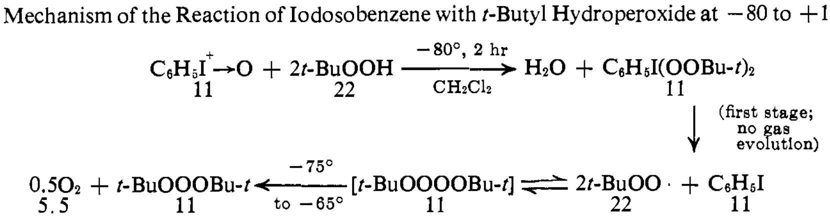
[4] N. A. Milas and S. M. Djokic, *ibid.*, 405 (1962); *J. Am. Chem. Soc.*, **84**, 3098 (1962).

Scheme I. Proposed Mechanism of the Reaction of Iodosobenzene Diacetate with *t*-Butyl Hydroperoxide at −80 to +5° in Methylene Chloride



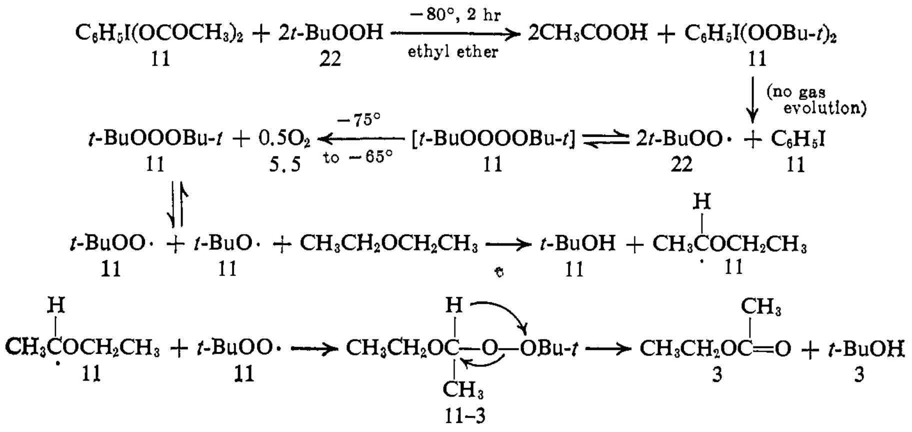
[a] Numbers signify millimoles used and calculated after each step.

Scheme II. Proposed Mechanism of the Reaction of Iodosobenzene with *t*-Butyl Hydroperoxide at −80 to +10° in Methylene Chloride[a]



[a] The remaining steps are the same as in Scheme I.

Scheme III. Proposed Mechanism of the Reaction of Iodosobenzene Diacetate with *t*-Butyl Hydroperoxide in Diethyl Ether at −80 to +5°



since there was no secondary oxygen evolution at any temperature above −65°. The quantitative results obtained in this solvent are listed in Table III, and the equations from which the calculations were made are illustrated in Scheme III. The calculations with iodosobenzene were similar, so that they are not repeated.

Discussion

Preliminary experiments showed the reaction of *t*-butyl hydroperoxide with either iodosobenzene diacetate or iodosobenzene at −80° in methylene chloride or ethyl ether to be rather slow so that reproducible measurements could be obtained only when prolonged contact of the reactants, usually 2 hr with magnetic stirring in nitrogen, was allowed to take place. The bis-*t*-butylperoxyiodosobenzene which is formed initially is not expected to be stable due to the magnetic field effect of the heavy iodine atom[5] which would tend to expel the *t*-butylperoxy radicals which couple in a solvent cage at −80° to form di-*t*-butyl tetroxide. It is now generally conceded[4–8] that at moderate low temperatures di-*t*-butyl tetroxide may exist in a solvent cage in equilibrium with *t*-butylperoxy radicals and decompose at higher temperatures to di-*t*-butyl trioxide and oxygen.

In the pure state, di-*t*-butyl trioxide should be stable

---

(5) J. E. Leffler, R. D. Faulkner, and C. C. Petropoulos, *J. Am. Chem. Soc.*, **80**, 5345 (1958).

(6) A. Factor, C. A. Russell, and T. G. Traylor, *ibid.*, **87**, 3692 (1965).

(7) J. R. Thomas, *ibid.*, **87**, 3935 (1965).

(8) P. D. Bartlett and P. Günther, *ibid.*, **88**, 3288 (1966).

Table III. Reaction of Iodosobenzene Diacetate and Iodosobenzene with *t*-Butyl Hydroperoxide in Diethyl Ether at −80 to +5° [a]

Expt	Complex, mmol	$\text{TBA} + \text{TBA}_t$, mmol Calcd	Found	MPA + EA, mmol Calcd	Found	IB, mmol Calcd	Found	O_2,[b] cm^3 Calcd	Found	O_2,[c] cm^3 Found
8	11:22[d]	11 + 3	14	11	7 + 3	11	9.1	123	79	0
9	11:22[e]	11 + 3	13.1	11	7.5 + 2.4	11	...	123	72	0

[a] TBA_t = *t*-butyl alcohol from the partial decomposition of MPA, EA = ethyl acetate, MPA = α-*t*-butylperoxyethyl ether. [b] −75 to −65°. [c] −45 to +5°. [d] IBDA:TBHP. [e] IDB:TBHP.

at a wide range of temperatures between −75 and −5°,[9] although recently ditrifluoromethyl trioxide was shown to have a half-life at 25° of 65 weeks![10,11] In methylene chloride or ethyl ether, di-*t*-butyl trioxide seems to exist in equilibrium with *t*-butoxy and *t*-butylperoxy radicals. Of the two radicals the *t*-butoxy is the least stable and more reactive and could abstract hydrogen atoms to give *t*-butyl alcohol.[12,13] As the concentration of these radicals decreases, that of the more stable *t*-butylperoxy radicals[14] increases and simultaneously that of the solvent-caged coupled *t*-butylperoxy radicals. When the temperature reached in the neighborhood of −45°, the coupled *t*-butylperoxy radicals begin to decompose to di-*t*-butyl trioxide and oxygen. This process is repeated until a temperature is reached at which the coupled radicals decompose to a more stable di-*t*-butyl peroxide and oxygen and the radical reactions terminate.

That the secondary evolution of oxygen at temperatures above −45° does not come from the decomposition of di-*t*-butyl triooxide is amply supported by our measurements which show low yields of di-*t*-butyl peroxide and high yields of *t*-butyl alcohol. Moreover, the isolation from ethyl ether of α-*t*-butylperoxy ethyl ether provides additional support to this view.[15] Since there was no secondary evolution of oxygen when the reaction was performed in ether, it is reasonable to assume that the *t*-butylperoxy radicals, the precursors of the coupled di-*t*-butyl tetroxide and the evolution of oxygen, were used up to produce α-*t*-butylperoxyethyl ether which was obtained in nearly quantitative yields if the ethyl acetate isolated were considered as part of the original α-*t*-butylperoxyethyl ether. Furthermore, di-*t*-butyl trioxide is structurally related to molozonides which are not known to decompose to give oxygen and dialkyl peroxides; instead they undergo homolytic or heterolytic rearrangements, depending upon the temperature, solvents, etc.

It must be mentioned here that at higher initial temperatures, 30 ± 1°, the reaction of *t*-butyl hydroperoxide with iodosobenzene diacetate seems to follow a different course. The reaction is highly exothermic and, in addition to the products isolated from the low-temperature reactions, acetone, carbon dioxide, methane, and ethane were also isolated in substantial yields. This reaction is not well understood at present and further work is being done to clarify it.

Experimental Section

General. The *t*-butyl hydroperoxide used in this research was obtained from Lucidol Division of Wallace and Tiernan, Inc. and was further purified by low-pressure fractionation and the fraction boiling at 36–37° (18 mm) collected and analyzed iodometrically; purity, 99.8%. The iodosobenzene diacetate was prepared from iodobenzene and peracetic acid (40%, Food Machinery Corp.) by the method of Sharefkin and Saltzman[16] and was purified every time before use from a 4:1 mixture of acetic acid and acetic anhydride (3 ml/g) and dried overnight in a vacuum desiccator over P_2O_5, mp 159–160° (Fisher-Johns melting point apparatus) (lit.[16] mp 158–159°). Iodometric titrations showed it to be 99.5% pure and good enough for our measurements. Iodosobenzene was prepared from iodosobenzene diacetate by hydrolysis.[17] The yellow product obtained was dried overnight in a vacuum desiccator over calcium chloride, mp 209–212° dec (lit.[17] mp 210° dec). Iodometric titration showed this product to be over 99.5% pure. Owing to its tendency to disproportionate, the iodosobenzene was prepared freshly before each experiment. The methylene chloride was dried and distilled over calcium chloride. Reagent ether was distilled over sodium and stored over sodium wire.

All vpc measurements of liquid products were made at 60° on a Perkin-Elmer vapor fractometer Model 154 using a column 2 m long and 0.25 in. in diameter packed with diisodecyl phthalate. Each liquid component was collected and identified by comparing its ir spectrum with that of an authentic sample. The gaseous products were collected in burets and analyzed using an Orsat apparatus. In order to make the proper correction for gas expansion, the reaction vessel was calibrated between −80 and +10°.

Iodosobenzene Diacetate (Typical Run). Iodosobenzene diacetate (3.54 g, 11 mmol) was dissolved in 40 ml of methylene chloride and the solution cooled over dry nitrogen at −80°. To it was then added slowly in the course of 20 min with vigorous magnetic stirring a precooled (−80°) solution of 10 ml of methylene chloride containing 1.97 g (22 mmol) of *t*-butyl hydroperoxide. Stirring was continued for 2 hr with no gas evolution. An infrared spectrum of the reaction mixture was taken at this time and revealed the presence of strong peaks of iodobenzene and acetic acid as compared with the infrared spectra of authentic samples.

The temperature of the reaction mixture was then allowed to rise slowly and, when it reached −75°, a vigorous evolution of oxygen began and did not stop until the temperature reached −68°. No further gas was evolved until the temperature reached −45° when a secondary evolution of oxygen took place at a much lower rate than the initial evolution and continued until the temperature reached +5°. The gaseous and liquid products were then analyzed; the results for each run are tabulated in Table I.

Since iodosobenzene was insoluble in methylene chloride at low temperatures, it was suspended rather than dissolved in the solvent; otherwise the experiments were carried out in the same manner as those with iodosobenzene diacetate.

Reaction of *t*-Butyl Hydroperoxide at −80 to +5° with Iodosobenzene Diacetate and Iodosobenzene in Diethyl Ether. Since *t*-butoxy radicals are known to abstract hydrogen atoms from ethers,[18] it was anticipated that if di-*t*-butyl trioxide were generated in ethyl ether at low temperatures from the decomposition of di-*t*-butyl tetroxide, the solvent would trap the more stable *t*-butylperoxy radicals and the trapped molecules could be isolated. A preliminary experiment was therefore performed with the purpose of isolating and identifying the trapped molecules. To a suspension of 7.08 g (22 mmol) of iodosobenzene diacetate in 50 ml of diethyl ether cooled to −80° over dry nitrogen was added with magnetic stirring in the course of 30 min 10 ml of a precooled

---

(9) S. W. Benson, *J. Am. Chem. Soc.*, **86**, 3922 (1964).

(10) L. R. Anderson and W. B. Fox, *ibid.*, **89**, 4313 (1967).

(11) P. G. Thompson, *ibid.*, **89**, 4316 (1967).

(12) P. Gray and A. Williams, *Chem. Rev.*, **59**, 239 (1959).

(13) P. Gray, R. Shaw, and J. J. C. Thynne, *Progr. Reaction Kinetics*, **4**, 63 (1967).

(14) J. C. W. Chien and C. R. Boss, *J. Am. Chem. Soc.*, **89**, 571 (1967).

(15) *Cf.* M. S. Kharasch. A. Fono, W. Nudenberg, and B. Bischof, *J. Org. Chem.*, 17, 212 (1952).

(16) J. G. Sharefkin and H. Saltzman, *Org. Syn.*, **43**, 62 (1963).

(17) H. Saltzman and J. G. Sharefkin, *ibid.*, **43**, 60 (1963).

(18) R. L. Huang and S. Singh, *J. Chem. Soc.*, 891 (1958).

ethyl ether solution containing 3.96 g (44 mmol) of *t*-butyl hydroperoxide. Stirring was continued at −80° for an additional hour. No gas was evolved until the temperature was allowed to rise to −75°, when evolution of oxygen began and did not stop until the temperature reached −65°. No additional evolution of gas took place above −65°, and the temperature was allowed to rise to +5°. A vpc and an infrared investigation of the products formed in this reaction revealed the presence of *t*-butyl alcohol, acetic acid, iodobenzene, ethyl acetate, traces of unreacted *t*-butyl hydroperoxide, and an appreciable amount of a substituted *t*-butyl peroxide, the vpc and infrared spectrum of which were different from those of di-*t*-butyl peroxide.

In order to isolate this peroxide, the ether solution was shaken with 5% potassium hydroxide solution, dried with magnesium sulfate, and filtered. The ether was then removed by distillation, the residue fractionated under reduced pressure, and the fraction boiling at 34–34.5° (7 mm) collected and analyzed; $n^{11}\text{D}$ 1.3977.

Anal. Calcd for $C_8H_{18}O_3$: C, 59.25; H, 11.11; (O), 9.88 Found: C, 59.40; H, 11.20; (O), 10.20, 9.68 (HI method at 60°).

This peroxide has a characteristic odor and fails to react with KI solution in acetic acid. Even HI gives low values at room temperature. It gives a single peak on the vapor phase chromatogram with retention time of 27 min as compared to that of *t*-butyl hydroperoxide of 24 min at 60° with helium pressure on the column at 18 psi. The infrared spectrum showed the following bands in cm^{-1}: 2980 vs, 2925 s, 2900 s, 2870 ms, 1475 ms, 1455 ms, 1440 ms, 1375 s, 1360 vs, 1340 w, 1320 m, 1255 w, 1240 m, 1195 vs, 1160 m, 1150 vs broad, 1075 s, 1040 m, 1025 w, 940 s, 925 w, 895 vw, 865 vs, 840 w, and 750 w.

Synthesis of α-*t*-Butylperoxyethyl Ether. Since it was suspected that if one hydrogen atom had been abstracted from ethyl ether by the *t*-butoxy radical, the resulting ethyl ether radical would trap the *t*-butylperoxy radicals to form α-*t*-butylperoxyethylether. It was necessary therefore to synthesize this peroxide by an independent route and show that its properties are identical with those of the peroxide obtained in our free-radical reaction.

The synthesis was accomplished by the following procedure. Acetaldehyde diethyl acetal (8.1 g, 0.05 mol) was mixed with 4.5 g (0.05 mol) of *t*-butyl hydroperoxide. To this mixture was then added three drops of methanesulfonic acid. The reaction became exothermic and had to be cooled with ice. After 3 hr at 0°, the reaction mixture was extracted with three 20-ml portions of ethyl ether. The combined ethyl ether extracts were shaken with 20 ml of 5% potassium hydroxide solution, dried with magnesium sulfate, and filtered. The ether was removed by distillation, the residue fractionated under reduced pressure, and the fraction boiling at 35° (8 mm) collected and analyzed; yield 3.4 g (43%); $n^{19}\text{D}$ 1.3976.

Anal. Calcd for $C_8H_{18}O_3$: (O), 9.88. Found: (O), 9.80 (HI method at 60°).

The vpc and infrared spectra of this peroxide were identical with those of α-*t*-butylperoxyethyl ether isolated from our free-radical reaction. This peroxide has also been synthesized in low yields by Rieche and Bischoff[19] using a somewhat different procedure than the one given above.

In experiment 8 the reaction of iodosobenzene diacetate (11 mmol) with *t*-butyl hydroperoxide (22 mmol) at −80° in ethyl ether was carried out in the same way as the experiment described above except that the reaction was kept at −80° for 2 hr before it was allowed to warm up to −75° and both the oxygen evolved and the liquid products formed, with the exception of acetic acid, were determined quantitatively; the results are listed in Table III.

In experiment 9 the reaction of *t*-butyl hydroperoxide (22 mmol) with iodosobenzene (11 mmol) suspended in ethyl ether at −80° was carried out in the same manner as in experiment 8. The gaseous and liquid products, with the exception of water which was detected in the vapor phase chromatogram and by the copper sulfate test, were determined quantitatively; the results are listed in Table III.

Acknowledgment. The authors wish to thank Dr. Nagy for the combustion analyses, Dr. Paul G. Arapakos for assistance in some preliminary experiments, and the Industrial Fund of the Institute for financial support of this investigation.

---

[19] A. Rieche and C. Bischoff, *Chem. Ber.*, **94**, 2457 (1961).

Communications to the Editor

Oligomerization Catalysts. II. Spectroscopic Examination of Bis(cyclooctatetraene)iron

Sir:

A new type of valence tautomerism, characterized by simultaneous intra- and internuclear electronic and conformational rearrangements, has been found in bis(cyclooctatetraene)iron, $(\text{COT})_2\text{Fe}^0$ (**1**).

This complex, recently described by us,[1] selectively catalyzes the oligomerization of butadiene and the codimerization of butadiene and ethylene to *cis*-1,4-hexadiene. Now we report the first results of spectroscopic examinations, which confirm the assigned structure and elucidate both the conformation of the COT rings and the type of their bonding to iron.

On the basis of our first results,[1] we had excluded for both COT rings the tub conformation, characteristic of $(\text{COT})\text{Ni}^0$, as well as the planar conformation of a dianion, found in $(\text{COT})_3\text{Ti}_2^{\text{II}}$. Moreover, on the basis of a supposed rare gas configuration of the iron, which requires the donation of ten π electrons from the COT rings to the iron, one might expect that the two ligands are differently coordinated to the metal.

The nmr spectrum at room temperature showed only one single peak, indicating equivalence of all protons. In order to reveal a supposed temperature-dependent valence tautomerism, we carried out a nmr examination at various temperatures. The spectra were run (Varian HA, 100 Mc) between −10 and −84° (TMS internal standard), using deuterated toluene as solvent (Figure 1). The spectrum at −10° still exhibits one peak at τ 5.00. Down to −35° this signal broadens and, below the coalescence temperature (between −35 and −45°), it begins to split off. At −84° we observe four signals at τ 4.60, 4.91, 5.42, and 5.50. (The doublet at τ 5.46 and 5.55 (J = 9 cps) is centered at τ 5.50.) The relative intensities of the four signals are 1:5:1:1. Spin-decoupling experiments were carried out at all the above positions and at τ 5.02. A decoupling was observed only by irradiating at this last position: the τ 4.60 signal (presumably a multiplet) sharpens markedly and the τ 5.50 doublet becomes a singlet (Figure 1). This proves that the τ 4.91 signal is composite and results from the superposition of a

---

[1] A. Carbonaro, A. Greco, and G. Dall'Asta, *Tetrahedron Lett.*, **22**, 2037 (1967).