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Light Induced Tritiation of Methyl Benzoate with Diethylamine-*N*-*t* and Triethylamine-Tritiated Water Mixture

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Synopsis. Methyl benzoate was tritiated at both nuclear and methyl positions on irradiation with diethylamine-*N*-*t* in benzene and with triethylamine–tritiated water in acetonitrile.

In a previous paper we demonstrated that irradiation of benzonitrile with diethylamine-*N*-*t* or a triethyl-amine–tritiated water mixture causes tritium uptake in the nucleus of benzonitrile, and proposed a mechanism involving the exciplex between benzonitrile and the amines.[1] In this paper we wish to report on our studies of methyl benzoate: irradiation of methyl benzoate with diethylamine-*N*-*t* and a triethylamine–tritiated water mixture, as well as 1-propanethiol-*S*-*t*,[2] brings about the incorporation of tritium not only in the nucleus but also in the methyl group of the ester.

Results and Discussion

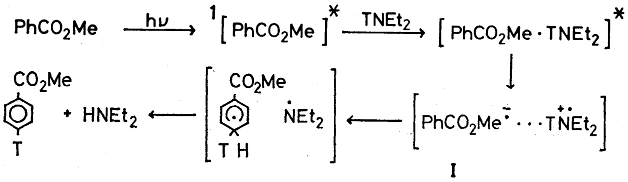
A mixture of methyl benzoate, benzene, and diethylamine-*N*-*t* was irradiated with a 1 kW high pressure mercury arc lamp for 30 h. The aromatic compounds were separated by fractional distillation and submitted to tritium assay. Methyl benzoate was degraded by the known procedures[3] in order to determine the tritium distribution. Light induced tritiation of methyl benzoate was also carried out with triethylamine and tritiated water in acetonitrile. Methyl benzoate was recovered and degraded in a similar way.

The rates of nuclear tritiation of methyl benzoate relative to benzene (k_N/k_B) and relative to the methyl group of the ester (k_N/k_M) and the tritium distribution in the nucleus of the ester are shown in Table 1. The relative rate, k_N/k_B, is high and the order of reactivity among the nuclear positions is *para*≫*ortho*>*meta* in the tritiation with both diethylamine-*N*-*t* and the mixture of triethylamine and tritiated water. These results are similar to those obtained for benzonitrile,[1] suggesting the following mechanism for the tritiation of methyl benzoate with diethylamine-*N*-*t*:

TABLE 1. LIGHT INDUCED TRITIATION OF METHYL BENZOATE

Triton donor	Tritium distribution (%)[a] *ortho*	*meta*	*para*	k_N/k_B[b]	k_N/k_M[c]
Diethylamine-*N*-*t*	17	1	82	183	12
Triethylamine and tritiated water	8	trace	92		4
1-Propanethiol-*S*-*t*	17[d]	1[d]	82[d]	421[d]	8[e]

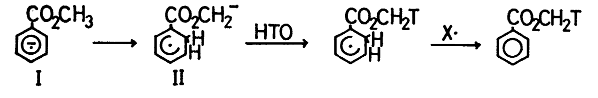
a) Average values of data obtained by duplicate runs. b) Rate (per C–H bond) of nuclear tritiation of methyl benzoate relative to benzene. c) Rate (per C–H bond) of nuclear tritiation relative to the methyl group. d) Data taken from Ref. 1. e) Unpublished data.



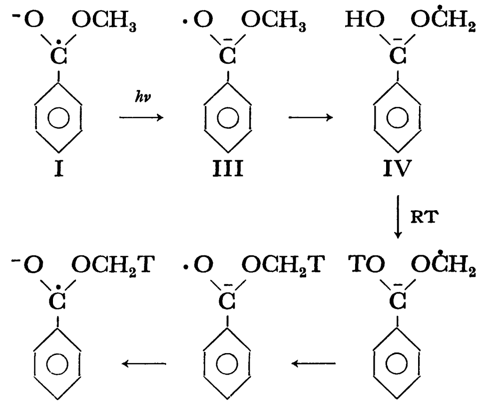
The singlet excited methyl benzoate forms an exciplex with the amine, which collapses to a radical cation and a radical anion (I). Triton transfer from the former to the latter produces a radical pair of a cyclohexadienyl radical and a diethylaminyl radical, which in turn disproportionates, leading to the tritiation of methyl benzoate. In the tritiation with triethylamine triton is transferred to the radical anion, I, from tritiated water.

In order to estimate the nature of the postulated radical anion, its charge density was calculated by the molecular orbital method using the CNDO/2 approximation.[4] The geometry of I was assumed to be planar with the benzene ring and the methyl group apart and was constructed by using the standard bond lengths and angles.[5] The results show that the charge on the *meta* carbons is slightly positive ($C_{meta}=+0.006$), while those on the *ortho* and *para* carbons are greatly negative ($C_{ortho}=-0.057$ and $C_{para}=-0.119$). Although the geometry used for the calculation was not optimized, the charge distribution pattern itself did not change seriously for small variant in the geometry. The similarity between the charge density and the tritium distribution pattern may be taken as indicating the intermediacy of the methyl benzoate radical anion, I, in the tritiation.

More remarkable is the methyl tritiation, of which specific mention must be made. The finding that no tritiation occurred at both methyl and nuclear positions on irradiation of methyl benzoate with tritiated water in the absence of triethylamine suggests that the methyl tritiation proceeds through the radical anion, I, or at least through the exciplex between methyl benzoate and the amines. The radical anion, I, might take intramolecularly a proton from the methyl group, producing a carbanion (II), which then undergoes a set of triton capture and protium loss, leading to methyl tritiation. If these reaction pathways were operating, the use of methyl-*t* benzoate as the starting ester would lead to the incorporation of tritium in the nucleus. Thus, a mixture of methyl-*t* benzoate, triethylamine, water, and acetonitrile was exposed to light from the 1 kW lamp for 30 h. For the recovered methyl benzoate, no incorporation was observed in the nucleus and the mechanism involving the proton (triton) transfer from the methyl group to the nucleus is improbable.



Under illumination the radical anion, I, might be excited to a higher electronic state represented by structure III. The excited radical anion, III, could intramolecularly abstract a hydrogen atom from the methyl group to afford another radical anion (IV), in which the proton on the hydroxy group would be exchangeable with tritons in the system. The resulting radical anion-*O-t* would decay to the starting radical anion, I, containing a triton at the methyl group.



Although no direct evidence was obtained for this mechanism, it is rationalized by the aforementioned circumstantial evidence; the tritiation with tritiated water proceeds only in the presence of triethylamine and the extent of the tritiation of the methyl group relative to that of the nucleus is not much affected by varying the triton donors. Accordingly, we suppose the above mechanism most probable.

Experimental

Materials. Benzene, triethylamine, and methyl benzoate were purified by distillation or vacuum distillation. Diethylamine-*N-t* was prepared by the method reported.[1] Methyl-*t* benzoate was prepared in the usual way from the reaction of methanol-*t* (1.72 g, 53.8 mmol, 51.5 mCi/mol) with benzoyl chloride (7.19 g, 51.2 mmol) in hexane (20 ml) in the presence of pyridine (4.5 ml), and distilled *in vacuo* (6.08 g, 87%, 43.5 mCi/mol, radiochemical yield: 71%).

*Tritiation of Methyl Benzoate with Diethylamine-*N-t. A mixture of diethylamine-*N-t* (1.18 g, 16.2 mmol, 2.19 Ci/mol), methyl benzoate (10.6 g, 77.7 mmol), and benzene (6.06 g, 77.7 mmol) was irradiated in a Pyrex tube under nitrogen for 30 h with a 1 kW high pressure mercury arc lamp. The reaction mixture was washed with 1 M sulfuric acid and water to remove the amine, and the aromatic compounds were separated by distillation. Benzene and methyl benzoate were further purified by fractional distillation and submitted to tritium assay (benzene, 3.64×10^{-3} mCi/mol; methyl benzoate, 0.581 mCi/mol). Methyl benzoate was hydrolyzed with a sodium hydroxide solution. Benzoic acid, isolated and purified by recrystallization, was submitted to tritium assay (0.554 mCi/mol).

Tritiation with Triethylamine and Tritiated Water. A solution of methyl benzoate (2.64 g, 19.4 mmol), triethylamine (1.46 g, 14.4 mmol), and tritiated water (2 ml, 111 mmol, 335 mCi/mol) in acetonitrile (10 ml) was irradiated in a Pyrex tube under argon for 30 h with a 1 kw lamp. Triethylamine, acetonitrile, and water were removed by distillation, and the residual methyl benzoate was washed with watre and fractionally distilled. Methyl benzoate purified and benzoic acid obtained by hydrolysis of the ester were submitted to tritium assay (methyl benzoate, 0.541 mCi/mol; benzoic acid, 0.477 mCi/mol).

Irradiation of Methyl Benzoate with Tritiated Water. A solution of methyl benzoate (5.28 g, 38.8 mmol) and tritiated water (4 ml, 222 mmol, 123 mCi/mol) in acetonitrile (20 ml) was irradiated for 30 h with a 1 kW lamp and treated in a similar way to that above mentioned. No tritium was found to be incorporated in methyl benzoate.

*Irradiation of Methyl-*t* Benzoate in the Presence of Triethylamine and Water.* A solution of methyl-*t* benzoate (7.92 g, 58.2 mmol, 3.63 mCi/mol), triethylamine (4.37 g, 43.2 mmol), and water (6 ml, 333 mmol) in acetonitrile (30 ml) was irradiated with a 1 kW lamp. No tritium was found to be incorporated in benzoic acid obtained after the usual work-up.

Degradation of benzoic acid for the determination of tritium distribution and tritium activity measurements were carried out as reported.[1]

References

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