

ylidenetriphenylphosphorane gave the ethyl ester of IIa, mp 299–302° dec; $\lambda_{\max}^{\text{EtOH}}$ 303 m μ (ϵ 17,875); $\lambda_{\text{sh}}^{\text{EtOH}}$ 270 m μ (ϵ 9400); nmr (DMSO- d_6) δ 1.20 (t, 3 H, $J = 7$ Hz), 2.28 (s, 3 H), 4.13 (q, 2 H, $J = 7$ Hz), 7.13 (d of d, 2 H, $J = 16$ Hz), 11.27 (s, 2 H, exchangeable). Alkaline hydrolysis of the ester followed by acidification gave an acid which was identical with the eight-carbon acid from sparsomycin as judged by infrared, ultraviolet, and nmr spectra and by tlc in three solvent systems.

Heating a mixture of sparsomycin, water, and Raney nickel under reflux resulted in isolation of 2 mol of methane per mol of sparsomycin and a compound (IIb) having the molecular formula $C_{11}H_{17}N_3O_4$ (established by high resolution mass spectrometry) and melting at 231° dec. Alkaline hydrolysis of IIb followed by acidification gave another eight-carbon acid (IIc) which appeared to be the analog of IIa in which the *trans*-olefin system is reduced. The physical properties of IIc are mp 302–304° dec; $\lambda_{\max}^{\text{H}_2\text{O}}$ 266 m μ (ϵ 8237); ν_{\max} 3050, 1720, 1630, 1530, 1375, 1340, 1280, 1210, 1175, 870, 815, 792, and 725 cm^{-1} ; nmr (DMSO- d_6) δ 2.08 (s, 3 H), 2.26–2.60 (m, 4 H), 10.63 (s, 1 H), 10.91 (s, 1 H); mass (m/e) 198.0646. The product was identified as 5-(β -carboxyethyl)-6-methyluracil (IIc) by comparison with an authentic sample synthesized by the procedure of Johnson and Heyl⁴ for the carboxymethyl analog.

Freeze drying of the filtrate from IIc followed by treatment of the residue with benzoyl chloride in pyridine on the steam bath gave a compound which was purified by chromatography on silica gel using chloroform as the eluting agent. The compound, mp 87–89°, $[\alpha]_D -61.4^\circ$ (c 1, CHCl_3), had a molecular formula of $C_{24}H_{21}NO_4$ established by high-resolution mass spectroscopy. The ir spectrum had no bands in the NH–OH region but had bands at 1720, 1660, 1595, and 1575 cm^{-1} . The synthetic tribenzoyl derivative of *L*-2-aminopropanol, mp 90–92°, $[\alpha]_D +63.2^\circ$ (c 2, CHCl_3), nmr (CDCl_3), δ 1.59 (d, 3 H), 4.50–5.60 (m, 3 H), 7.0–8.0 (m, 15 H), mass (m/e) 387.1495, had an ir spectrum superimposable on that of the benzoyl derivative from sparsomycin. The two compounds also had identical R_f values (0.75) in tlc on silica using chloroform–methanol (95:5). These results establish that *D*-2-aminopropanol was formed by hydrolysis of IIb. The absence of a basic group in sparsomycin indicates that *D*-2-aminopropanol and IIc must be combined by an amide linkage to give a compound having the structure indicated in expression IIb. The nmr spectrum of sparsomycin shows two signals for methyl groups, both of them being singlets. Consequently it is apparent that the methyl group of *D*-2-aminopropanol is not present as such in sparsomycin as its nmr would contain a doublet for a CH_3C in such case. From this it seems that the atoms of sparsomycin removed by Raney nickel treatment must be attached at the carbon atom which becomes the methyl group of *D*-2-aminopropanol after desulfurization and hydrolysis. Such a hypothesis, in view of the molecular formula of sparsomycin, suggests that a $\text{C}_2\text{H}_5\text{S}_2\text{O}$ moiety is attached through a sulfur atom with the carbon–sulfur bond being cleaved by Raney nickel.

The nmr spectrum of sparsomycin indicates the presence of three methylene groups. One of these groups generates a doublet of doublets (δ 3.85 and 4.02) which

(4) T. B. Johnson and F. W. Heyl, *Am. Chem. J.*, **38**, 659 (1907).

must arise from a methylene having no adjacent hydrogen. A second methylene group is represented by a complex AB pattern (of an ABX system) and must be the methylene of the hydroxymethyl group as the signal shifts downfield on acylation. Another AB complex centered at δ 3.14 necessarily arises from the methylene group attached to sulfur which methylene group becomes the methyl group of *D*-2-aminopropanol. The value of the chemical shift is such that the sulfur atom must be oxidized either to sulfoxide or sulfone.⁵ Of the nmr signals representing methyl groups, the one with a chemical shift of δ 2.30 must be a CH_3S group as the chemical shift is appropriate for such a system,⁵ and this methyl group appears substantially downfield after treatment of sparsomycin with sodium periodate or hydrogen peroxide. There, then, remains a methylene group which must separate the two sulfur atoms. The AB pattern already mentioned no doubt arises from such a group. A combination of the above groups leads to the view that the moiety $\text{CH}_3\text{SCH}_2\text{SO}$ is present in sparsomycin and is removed by Raney nickel treatment. Evolution of 2 mol of methane is to be expected from this fragment.

The combination of the above data points to I as the structure of sparsomycin.

Acknowledgments. We wish to express our gratitude to Dr. Marvin Grostic for his invaluable assistance with the mass spectra.

(5) F. A. Bovey, "Nmr Data Tables for Organic Compounds," Vol. 1, Interscience Publishers, New York, N. Y., 1967, pp 152, 217–219.

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Isotopic Exchange Induced by Excitation of the Iodine–Iodobenzene Charge-Transfer Complex

Sir:

The photochemical isotopic exchange between radioactive iodine and iodoaromatic compounds has been the subject of several investigations.^{1–3} The experimental observations were discussed in terms of two possible mechanisms, involving initiation *via* photodissociation of either iodine ($\text{I}_2 \xrightarrow{h\nu} 2\text{I}$ followed by $\text{I} + \text{I}^*\text{I} \rightarrow \text{I}^* + \text{I}_2$ and $\text{PhI} + \text{I}^* \rightarrow \text{PhI}^* + \text{I}$) or the iodoaromatics ($\text{PhI} \xrightarrow{h\nu} \text{Ph} + \text{I}$ followed by $\text{Ph} + \text{I}^* \rightarrow \text{PhI}^*$ or $\text{Ph} + \text{I}^*\text{I} \rightarrow \text{PhI}^* + \text{I}$).⁴ However, no attempts have been made to carry out critical tests of such schemes. It is the purpose of the present communication to report experimental evidence indicating that, in iodine–iodobenzene methylcyclohexane solutions, the photochemical exchange is not induced by excitation of either I_2 or PhI , but rather by light absorption within the charge transfer (CT) band of the $\text{PhI} \cdot \text{I}_2$ complex. The results bear not only on the mechanism of isotopic exchange in iodoaromatic systems, but also on the chemical consequences of light absorption within CT bands, a problem which, in spite of the extensive

(1) R. M. Noyes, *J. Amer. Chem. Soc.*, **70**, 2614 (1948).

(2) R. M. Noyes and D. J. Sibbett, *ibid.*, **75**, 767 (1953).

(3) M. Anbar and R. Rein, *Chem. Ind. (London)*, 1524 (1963).

(4) R. K. Sharma and N. Kharasch, *Angew. Chem. Intern. Ed. Engl.*, **7**, 36 (1968).

data available on organic CT complexes,⁵ has only recently gained attention.^{6,7}

Deaerated solutions of iodobenzene in cyclohexane and methylcyclohexane containing radioactive iodine (¹³¹I), with or without I₂ carrier, were exposed to irradiation from a medium-pressure Hg lamp. Excitation wavelengths were controlled by means of solution, interference, or Corning glass filters. The amount of ¹³¹I incorporated in the aromatic material was determined by extraction of unreacted iodine using an alkaline thiosulfate solution and counting the radioactivity of the organic phase in an ionization chamber (mediac dose calibrator, Nuclear-Chicago). No iodoaromatic by-products were detected, even after prolonged irradiations (at 365 nm), as indicated by uv spectroscopy and gas chromatography.

Deaerated solutions of 0.1–0.2 M iodobenzene, 3–5 × 10⁻³ M iodine, and 1.5–3 × 10⁻⁸ M ¹³¹I in methylcyclohexane were first exposed to unfiltered light from the Hg source. In all cases high exchange yields were observed. However, when a 3-73 Corning glass filter (transmitting above 410 nm) was introduced for a selective excitation of the 520-nm iodine band, no exchange was detected even after prolonged irradiations. Since light absorption by the I₂ visible band is well known to lead to dissociation, it may be concluded that iodine atoms as such do not lead to efficient exchange.

Excitation of the same I₂-PhI system by means of the isolated 365, 334, and 313 nm mercury lines resulted in significant exchange. However, the interpretation of such data was complicated by the overlap between the iodobenzene absorption and the CT band of the PhI·I₂ complex,^{8,9} which prevented their separate (selective) excitation. We have, therefore, faced the problem of discriminating between photochemical effects due to excitation of PhI and those due to light absorption by the complex. Assuming that the percentage of isotopic exchange (*P*) is proportional to the number of light quanta (*I_x*) absorbed by species *x* (where *x* is either PhI or PhI·I₂), one may write

$$P = KI_x \quad (1)$$

where *K* is a constant. The light fraction (α_x) absorbed by *x* is

$$\alpha_x = [(OD)_x / (OD)_T] (\alpha_T) \quad (2)$$

where α_T and $(OD)_T$ are the total light fraction absorbed by the solution and total optical density, respectively. One therefore obtains for exchange initiation *via* light absorption by species *x*

$$P = KI_0 \alpha_x = KI_0 (OD)_x [\alpha_T / (OD)_T] \quad (3)$$

where *I₀* is the number of quanta falling on the solution. Assuming that *K* is independent of the exciting light wavelength, the "relative exchange yield" $P / I_0 [\alpha_T / (OD)_T]$ is expected to be proportional at each wave-

(5) For reviews see: (a) S. P. McGlynn, *Chem. Rev.*, **58**, 1113 (1958); (b) G. Briegleb, "Elektronen-Donator-Acceptor Komplexe," Springer-Verlag, Heidelberg, 1961; (c) R. S. Mulliken and W. B. Person, *Ann. Rev. Phys. Chem.*, **13**, 107 (1962); (d) E. M. Kosower, "Progress in Physical Organic Chemistry," Vol. 3, Interscience Publishers, New York, N. Y., 1961, pp 81–163.

(6) A. M. Halpern and K. Weiss, *J. Phys. Chem.*, **72**, 3863 (1968).

(7) R. Potashnik, C. R. Goldschmidt, and M. Ottolenghi, *ibid.*, **73**, 3170 (1969).

(8) J. Ferguson and T. Iredale, *J. Chem. Soc.*, 2959 (1953).

(9) G. Jungähnel, "Theory and Structure of Complex Compounds," Pergamon Press, New York, N. Y., 1964, pp 697–707.

length to $(OD)_x$ and, at a constant concentration, it should also be proportional to the extinction coefficient of the species initiating the exchange. The results of this treatment are presented in Table I, clearly favoring the CT complex as initiator of the reaction.

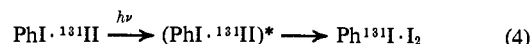
Table I. Wavelength Dependence of the ¹³¹I Exchange Reaction between Iodine and Iodobenzene (3 × 10⁻² M) in Deaerated Methylcyclohexane Solutions

Excitation wave-length, nm	Relative exchange yields ^a		Relative extinction coefficients	
	Carrier-free	With 10 ⁻⁴ M I ₂ carrier	PhI ^b	CT band of PhI·I ₂ ^c
365	1.0 ± 0.1	1.0 ± 0.1	1.0 ± 0.1	1.0 ± 0.1
334	5.5 ± 0.5	3.9 ± 0.4	16 ± 2	4.6 ± 0.5
313	7.3 ± 0.7	5.2 ± 0.5	46 ± 5	6.1 ± 0.6

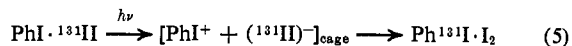
^a All values were obtained from initial slopes of per cent exchange vs. irradiation time plots. They have been normalized to the light intensity of the source, and divided by $\alpha_T / (OD)_T$. The values at 365 nm were arbitrarily set equal to 1. ^b Measured in 0.1–1 M PhI solutions in methylcyclohexane (see also ref 8). ^c Measured in a 0.18 M PhI, 4 × 10⁻³ M I₂ solution in methylcyclohexane. The 365, 334, and 313 nm Hg lines are distributed on both sides of the CT band, peaking in methylcyclohexane at 316 nm.

The data of Table I should also be considered in conjunction with an additional set of experiments in which we have measured the quantum yields (γ_d) of the deiodination process¹⁰ at 365, 334, and 313 nm. The experiments, carried out in 0.07–0.3 M iodobenzene solution in air-saturated cyclohexane, yielded a constant value of $\gamma_d = 0.23 \pm 0.02$ at all three wavelengths. In view of the above discussion and of the data in Table I it becomes apparent that the exchange quantum yields (γ_e), calculated by assuming initiation *via* excitation of PhI, are markedly wavelength dependent, in contrast to the wavelength independence of the deiodination process. This may be considered as a definite indication against an exchange process induced by the primary dissociation: $\text{PhI} \xrightarrow{h\nu} \text{Ph} + \text{I}$, which is the one responsible for deiodination.⁴ Supporting the same argument is the fact that exchange yields in air saturated solutions (with $\sim 10^{-3}$ M I₂ carrier) were found to be identical with those observed in corresponding deaerated systems. In view of the marked effect of O₂ on the deiodination yields (*via* scavenging of Ph radicals),⁴ this observation is inconsistent with a mechanism where exchange is initiated by dissociation of PhI. Initiation *via* some other path involving excitation of PhI is unlikely in view of the resulting wavelength dependence of the yields, while assumption of exchange initiation, *via* the CT absorption, results in wavelength-independent yields.

The detailed mechanism of exchange following excitation of the CT complex is still an open question. At present it is impossible to discriminate between a simple excited state scrambling

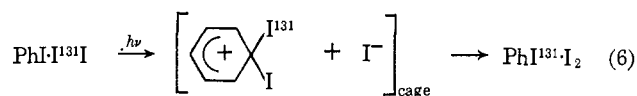


or ionic recombinations such as



(10) E. Olaerts and J. C. Jungers, *Discuss. Faraday Soc.*, **2**, 222 (1947).

or



When the exchange quantum yield is calculated according to any of the above equations, 4, 5, or 6, taking into account the inner light filter effect of nonactive complexes ($\text{PhI}\cdot\text{I}_2$) and of PhI , the value $\gamma_e = 0.01 \pm 0.003$ is obtained (with $\sim 10^{-3} M \text{I}_2$).

Preliminary observations indicate that similar reactions take place in the closely related $\text{Ph}^{131}\text{I}/\text{Br}_2$ and $\text{CH}_3(\text{C}_6\text{H}_4)\text{I}/^{131}\text{I}$ systems, but not with $\text{PhCl}/^{131}\text{I}$. Further work is in progress to elucidate the detailed CT exchange mechanism.

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Photolysis of $9\alpha,10\alpha$ - and $9\beta,10\beta$ -Oxidoestr-4-en-3-ones¹

Sir:

We wish to report the results of the photolyses of $9\alpha,10\alpha$ -oxido-17 β -hydroxy- (1), $9\alpha,10\alpha$ -oxido-17 β -acetoxy- (2), and $9\beta,10\beta$ -oxido-17 β -acetoxyster-4-en-3-ones (5) which resulted in the selective synthesis of the novel 8(9 \rightarrow 10)*abeo*-10 α - (from 1 and 2) as well as the 8(9 \rightarrow 10)*abeo*- and 11(9 \rightarrow 10)*abeo*-10 α -steroid nuclei (from 5).^{2,3}

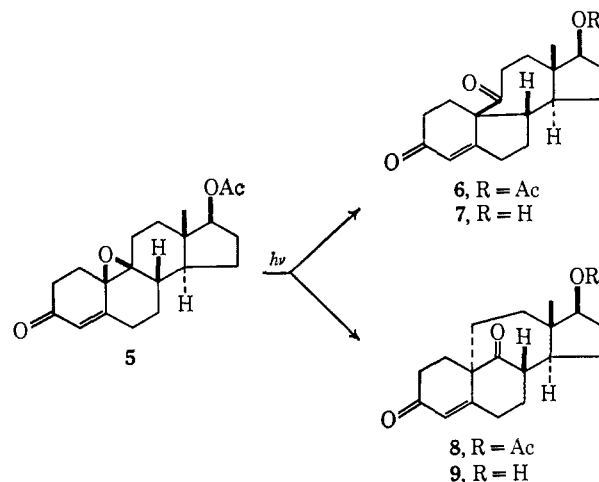
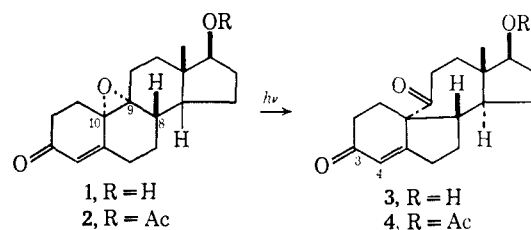
Irradiation of 1 with 2537-Å ultraviolet light in *t*-butyl alcohol gave in 70% yield a new α,β -unsaturated ketone (3) having the following properties: mp 215–216°; $[\alpha]_D -222^\circ$ (*c* 1.15, CHCl_3); ir (CHCl_3) ν_{CO} 1660, 1685 cm^{-1} ; uv (EtOH) λ_{max} 236 $\text{m}\mu$ (ϵ 13,350); nmr (CDCl_3) δ 0.90 (s, CH_3 -18), 5.72 (broadened s, CH-4).^{4a} Of the two ketone bands in the infrared, the band at 1660

(1) Part LVII of the E.T.H. series on Photochemical Reactions; for part LVI see S. Domb, G. Bozzato, J. A. Saboz, and K. Schaffner, *Helv. Chim. Acta*, **52**, in press. The photochemical results have been summarized in part by O. J.: Plenary Lecture, VIth International Symposium on the Chemistry of Natural Products, Mexico, April 1969; cf. O. Jeger and K. Schaffner, *Pure Appl. Chem.*, in press.

(2) (a) For a comprehensive review of epoxyketone photochemistry, see A. Padwa in "Organic Photochemistry," O. L. Chapman, Ed., Vol. I, Marcel Dekker, New York, N. Y., 1967, p 91; (b) H. Wehrli, C. Lehmann, P. Keller, J.-J. Bonet, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **49**, 2218 (1966); (c) O. Jeger, K. Schaffner, and H. Wehrli, *Pure Appl. Chem.*, **9**, 555 (1964).

(3) (a) For the preparation of 1 and 2, see E. Farkas and J. M. Owen, *J. Med. Chem.*, **9**, 510 (1966). (b) The preparation of $9\beta,10\beta$ -epoxide 5 will be described in a full paper.

(4) (a) A Rayonet chamber photochemical reactor (Southern New England Ultraviolet Co., Middletown, Conn.) equipped with 16-R.P.R. 2537-Å lamps was employed as the light source, using a quartz vessel and a stream of oxygen-free nitrogen at 40°; (b) irradiation by an NK 6/20 2537-Å lamp (Quarzlampen GmbH., Hanau) placed in a central quartz immersion well, with magnetic stirring at ca. 20°; (c) irradiation by a Q 81 high-pressure mercury lamp (Quarzlampen GmbH., Hanau) placed in a central Pyrex immersion well which was cooled by circulating an aqueous potassium hydrogen phthalate solution (wavelength cut-off at 3100 Å) through an outer jacket of 1-cm width, with magnetic stirring at ca. 20°.



cm^{-1} (in CHCl_3) was readily assigned to the A-ring Δ^4 -en-3-one chromophore on the basis of its nmr and uv properties. Moreover, this photoproduct was readily converted to a monoketal and a monoenol acetate, each retaining the 1685- cm^{-1} carbonyl band.⁵ The latter carbonyl group was unaffected by attempted reduction of the ethylene ketal of 3 with lithium aluminum tri-*t*-butoxyhydride. These data suggest that the newly generated carbonyl function is considerably hindered.

Photoisomerization of 2 with 2537 Å in dioxane furnished in 80% yield of reacted starting material the product 4, mp 181–182°, $[\alpha]_D -204^\circ$ (*c* 0.5, CHCl_3),^{4b} which on hydrolysis gave compound 3. The reaction $2 \rightarrow 4$ could also be effected on selective excitation of the $n \rightarrow \pi^*$ absorption band, both in dioxane and in benzene solutions.^{4c}

Irradiation of the $9\beta,10\beta$ -epoxyenone 5 with 2537-Å light in dioxane and in *t*-butyl alcohol gave a ca. 3:1 mixture of the two isomers 6 and 8. Both compounds were obtained in amorphous form. 6 [ir (CHCl_3) ν_{CO} 1670, 1695, 1730 cm^{-1} ; uv (EtOH) λ_{max} 240 nm (ϵ ca. 10,000); nmr (CDCl_3) δ 0.87 (s, CH_3 -18), 5.95 (broadened s, CH-4)] formed a crystalline compound, 7, on hydrolysis of the acetate function [mp 205–206°; $[\alpha]_D +104^\circ$ (*c* 0.41, CHCl_3); ir (CHCl_3) ν_{CO} 1670, 1690, ν_{OH} 3610 cm^{-1} ; uv (EtOH) λ_{max} 237 $\text{m}\mu$ (ϵ ca. 10,000)]. Compound 8 exhibited the following spectral data: ir (CHCl_3) $\nu_{\text{C}=\text{C}}$ 1615, ν_{CO} 1670, 1715–1735 (broad), (CCl_4) ν_{COC} 1240, $\nu_{\text{C}=\text{C}}$ 1618, ν_{CO} 1680, 1712, 1740 cm^{-1} ; uv (EtOH) max 242 $\text{m}\mu$ (ϵ ca. 10,000); nmr (CDCl_3) δ 0.90 (s, CH_3 -18), 5.91 (broadened s, CH-4). Alkaline hydrolysis of 8 gave the amorphous 17-hydroxy derivative 9 [ir (CHCl_3) $\nu_{\text{C}=\text{C}}$ 1615, ν_{CO} 1668, 1710, ν_{OH} 3590 cm^{-1} ; uv (EtOH) λ_{max} 243 $\text{m}\mu$ (ϵ ca. 10,000)].

(5) (a) B. E. Edwards and P. N. Rao, *J. Org. Chem.*, **31**, 324 (1966); the enolacetate of the photoproduct 3 had a uv absorption at 236 $\text{m}\mu$ (ϵ 15,500) and an nmr spectrum typical of a $\Delta^3,5$ -diene structure; (b) exchange dioxolanation methods are extensively reviewed by J. Keana in "Steroid Reactions," C. Djerrassi, Ed., Holden-Day, San Francisco, Calif., 1963, p 1.