

TABLE I

Eu(II)-Eu(III) EXCHANGE RATES AT 39.4°, $\mu = 2.0$						
Total Eu(II) + Eu(III) concn., <i>f</i>	Eu(II) concn., <i>f</i>	Eu(III) concn., <i>f</i>	H ⁺ concn., <i>f</i>	Cl ⁻ concn., <i>f</i>	Half- time, min- utes	k moles ⁻² ·l ⁻¹ · min. ⁻¹
0.0653	0.0244	0.0409	1.00	1.86	53	0.108
.0894	.0258	.0636	1.00	1.82	40	.107
.1055	.0683	.0372	1.00	1.84	33	.108
.0677	1.00	.716	132	.108
.0630	0.30	1.87	58	.102

The europium used was of 99.9% purity and was loaned to us by Mrs. Ethel Terry McCoy to whom we express our sincere gratitude. We thank Professor Don M. Yost and Dr. David L. Douglas of the California Institute of Technology for the Eu¹⁵² activity.

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ON *p*-AMINOTROPOLONE

Sir:

Very recently, Dewar¹ not only reported a molecular orbital calculation² of tropolone (I, X = H) but also predicted that *p*-aminotropolone (II, X = NH₂), which should be obtainable by the reduction of its azo-compound, may show interesting pharmacological properties as a precursor *in vivo* of *p*-aminobenzoic acid.

We have already reported on the syntheses of I³ (independent of other three laboratories⁴), α -aminohinokitiol,⁵ *i.e.*, *p*-amino-*m*-isopropyltropolone (III), *o*-bromo-*p*-aminotropolone⁶ (IV) and other various derivatives^{3,6} of I. We have also recently synthesized II, a brief account of which is given here.

Catalytic reduction of phenylazotropolone³ (m.p. 161–161.5°; *anal.* Calcd. for C₁₃H₁₀N₂O₂: N, 12.39. Found: N, 12.58) or *p*-tolylazotropolone³ (m.p. 202.5–203°; *anal.* Calcd. for C₁₄H₁₂N₂O₂: N, 11.66. Found: N, 11.42) with Adams catalyst, or their reduction with sodium hydrosulfite, yields yellow scaly crystals (II), m.p. 177–177.5°. *Anal.* Calcd. for C₇H₇O₂N: C, 61.32; H, 5.14; N, 10.21. Found: C, 61.09; H, 5.32; N, 10.02; yield, 30–40%. II is also obtained by the similar methods from *p*-nitrosotropolone⁷ (X = NO), charring at 180° (*Anal.* Calcd. for C₇H₅O₂N: N, 9.27. Found: N, 9.10) in better yield (70–80%). II is

(1) M. J. S. Dewar, *Nature*, **166**, 790 (1950).

(2) Similar calculation and measurement of dipole moments of I and its related compounds have already been reported; Y. Kurita, T. Nozoe and M. Kubo, *J. Chem. Soc. Japan*, **71**, 543 (1950); *Bull. Chem. Soc. Japan*, in press.

(3) T. Nozoe, S. Seto, Y. Kitahara, M. Kunori and Y. Nakayama, *Proc. Japan Acad.*, **26**, (7) 38 (1950); presented at the Annual Meeting of the Chemical Society of Japan in Kyoto, April 2, 1950.

(4) W. von E. Doering and L. H. Knox, *This Journal*, **72**, 2305 (1950); J. W. Cook and A. R. Gibb, *Chemistry & Industry*, 427 (1950); R. D. Haworth and J. D. Hobson, *ibid.*, 441 (1950).

(5) T. Nozoe and E. Sebe, *Proc. Japan Acad.*, **26**, (9) 45 (1950); T. Nozoe, S. Ebine, S. Itô and A. Konishi, *ibid.*, **27**, 10 (1951).

(6) T. Nozoe, Y. Kitahara, K. Yamane and A. Yoshikoshi, *ibid.*, **27**, 18 (1951); T. Nozoe, S. Seto, T. Ikemi and T. Arai, *ibid.*, **27**, 24 (1951).

(7) T. Nozoe and S. Seto, to be published soon.

amphoteric and its chemical behaviors are closely analogous to III and IV. Copper complex salt: greenish yellow microcrystals. Picrate: yellow scaly crystals, m.p. 225–226° (dec.); *anal.* Calcd. for C₁₃H₁₀O₉N₄: N, 15.30. Found: N, 15.42. Diacetate: colorless scaly crystals, m.p. 180.5–181°; *anal.* Calcd. for C₁₁H₁₁O₄N: N, 6.33. Found: N, 6.02.

Application of the Sandmeyer reaction to II yields the following halogen compounds. *p*-Bromotropolone (V, X = Br); m.p. 189–190°, alone or in admixture with β -bromotropolone,⁸ obtained as a by-product during the synthesis of I and the position of its bromine atom was later established to be at para,⁶ so that the amino group in II is also clearly in the para position. *p*-Chlorotropolone: orange needles, m.p. 147–149°. *p*-Iodotropolone: orange needles, m.p. 169–170°.

Details of the results of our studies will be reported shortly. The effects of I, II, and some of their allied compounds on Yoshida sarcoma have already been published.⁸

We are deeply indebted to Dr. R. Majima (Emeritus Professor of this University) for his unflinching encouragement and to the Ministry of Education of Japan for the financial support.

(8) S. Katsura, K. Satô, K. Akaishi, T. Nozoe, *et al.*, *Proc. Japan Acad.*, **27**, 31, 36 (1951).

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ON A NEW TYPE OF AROMATIZATION BY THE DIAZOTIZATION OF *o*-AMINOTROPOLONE DERIVATIVES

Sir:

Tropolone and its allied compounds, the tropoloids, possess a fair degree of aromatic properties in spite of the unsaturated, seven-membered ring structure. On the other hand, it has also been established that these compounds, when heated with highly concentrated alkalis, undergo benzylic rearrangement to carboxylic acids of benzenoid series. According to Raistrick¹ and Dewar,² tropolones can be taken as precursors, *in vivo*, of natural benzenoid carboxylic acids, and recently Robinson³ has also discussed on the assumption of a biogenetic relation between the tropolones and various alkaloids or anthocyanines. These certainly seem attractive suggestions but they must be confirmed by future experimental evidence. In this connection, studies on the aromatization of tropoloid series become of great significance.

Previously, we had encountered a notable fact that when *o'*,*p*-dinitro-*m*-isopropyltropolone is heated with 50% aqueous ethanol for ten minutes at 100°, or with absolute methanol, ethanol or isopropyl alcohol at 50–60° for a few minutes, it undergoes rearrangement to form *o'*,*p*-dinitro-*m*-cuminic acid or its respective esters quantitatively.⁴

(1) H. Raistrick, *Proc. Roy. Soc. (London)*, **A199**, 141 (1949).

(2) M. J. S. Dewar, *Nature*, **166**, 790 (1950).

(3) R. Robinson, *ibid.*, **166**, 930 (1950).

(4) T. Nozoe, *Science of Drugs*, **3**, 171 (1949) [English translation, *Sci. Rep. Tohoku Univ.*, **1**, 84, in press (1951)].