TABLE I

Eu(II)–Eu(III) EXCHANGE RATES AT 39.4°, $\mu = 2.0$

Total Eu(II) + Eu(III) concn., *f*	Eu(II) concn., *f*	Eu(III) concn., *f*	H^+ concn., *f*	Cl^- concn., *f*	Half-time, minutes	*k* moles^{-2}-l^{2}-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 Eu^{152} activity.

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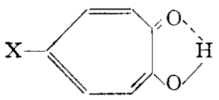
ON *p*-AMINOTROPOLONE

Sir:

Very recently, Dewar[1] not only reported a molecular orbital calculation[2] of tropolone (I, X = H) but also predicted that *p*-aminotropolone (II, X = NH_2), 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 I[3] (independent of other three laboratories[4]), α-aminohinokitiol,[5] *i.e.*, *p*-amino-*m*-isopropyltropolone (III), *o*-bromo-*p*-aminotropolone[6] (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 phenylazotropolone[3] (m.p. 161–161.5°; *anal.* Calcd. for $C_{13}H_{10}N_2O_2$: N, 12.39. Found: N, 12.58) or *p*-tolylazotropolone[3] (m.p. 202.5–203°; *anal.* Calcd. for $C_{14}H_{12}N_2O_2$: 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 $C_7H_7O_2N$: 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*-nitrosotropolone[7] (X = NO), charring at 180° ·(*Anal.* Calcd. for $C_7H_5O_3N$: N, 9.27. Found: N, 9.10) in better yield (70–80%). II is 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 $C_{13}H_{10}O_9N_4$: N, 15.30. Found: N, 15.42. Diacetate: colorless scaly crystals, m.p. 180.5–181°; *anal.* Calcd. for $C_{11}H_{11}O_4N$: 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,[3] 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 unfailing encouragement and to the Ministry of Education of Japan for the financial support.

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(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.

(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 alkalies, undergo benzylic rearrangement to carboxylic acids of benzenoid series. According to Raistrick[1] and Dewar,[2] tropolones can be taken as precursors, *in vivo*, of natural benzenoid carboxylic acids, and recently Robinson[3] 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*-cumic acid or its respective esters quantitatively.[4]

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(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.*, I, **34**, in press (1951)].