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Chlorodecarboxylation of 3-Methyl-3-(1,4-dimethyl-9-triptycyl)butanoic Acid Rotamers with Lead(IV) Acetate in the Presence of Lithium Chloride. Facile Hydrogen Transfer from the 1-Methyl Group in the sc-Isomer[1)]

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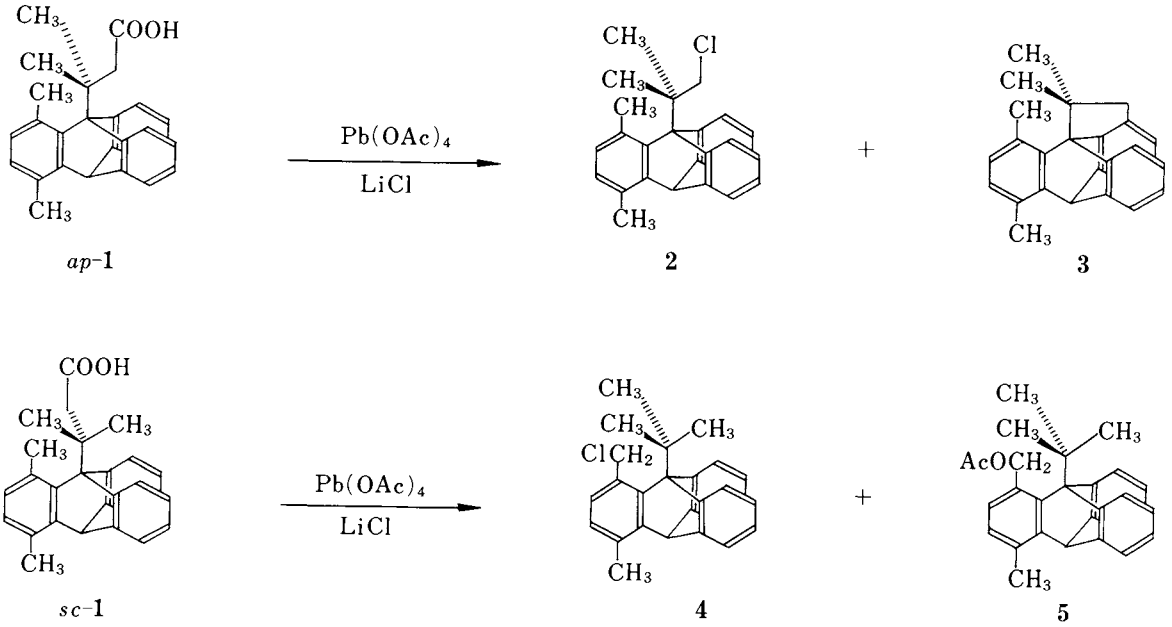
Oxidation of ap-3-methyl-3-(1,4-dimethyl-9-triptycyl)butanoic acid with lead(IV) acetate in the presence of lithium chloride afforded expected ap-9-(2-chloro-1,1-dimethylethyl)-1,4-dimethyltriptycene and 1,1,7,10-tetramethyl-1,2,6,10b-tetrahydro-6,10b-o-benzenoaceanthrylene, whereas the sc-isomer did 9-t-butyl-1-chloromethyl-4-methyltriptycene as a main product. The formation of the last compound is the implication of the facile hydrogen transfer from the 1-methyl group to the radical center formed in the 9-substituent of the triptycene.

As a part of studies on the reactivities of stable rotamers,[2)] we have carried out the Hunsdiecker reaction of the title compound to find a striking difference in the reactivities of the rotamers, one isomer giving "normal" products and the other those after rearrangement. This paper is to report such a finding and to discuss the possible origin of the difference.

The carboxylic acid rotamers (ap-1 and sc-1) were prepared as reported previously.[3)] The carboxylic acid was treated under the standard conditions of chlorodecarboxylation with the use of lead(IV) acetate and lithium chloride.[4)] The products were separated by preparative TLC on silica gel (hexane-dichloromethane eluent) and/or HPLC (Hitachi L-6250, 50:1 hexane-ether for those from the ap-isomer). There were two major products, which were identified as ap-9-(2-chloro-1,1-dimethylethyl)-1,4-dimethyltriptycene (2) (yield 15%) and 1,1,7,10-tetramethyl-1,2,6,10b-tetrahydro-6,10b-o-benzenoaceanthrylene (3) (yield 70%) on the spectroscopic grounds,[5)] from ap-1 in addition to other minor products. There were also obtained two major products from sc-1 but the structures of them were not those expected from the simple considerations: they were 9-t-butyl-1-chloromethyl-4-methyltriptycene (4) (yield 35%) and 1-acetoxymethyl-9-t-butyl-4-methyltriptycene (5) (yield 50%), the structures of which were also determined on the spectroscopic grounds.[5)] These product distributions reveal two points of interest. One is the facile formation of the cyclized compound (3) from ap-1 and the other is the unusual products from sc-1.

The chlorodecarboxylation is believed to proceed generally via radical-chain

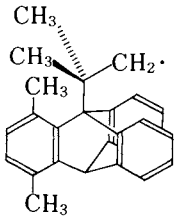


ap-1 2 3

sc-1 4 5

mechanisms, the organic radical undergoing a radical transfer in the propagation steps.[6] Although it is true that radical substitution of benzene takes place when a carboxylic acid is oxidized with lead(IV) acetate in benzene[7] and the aromatic substitution is more facile if the reaction occurs intramolecularly than intermolecularly,[8] no such instances are reported in the case of chlorodecarboxylation.[4] Therefore, it is interesting that the cyclized product is formed more than the chloride (2). It might be argued that the formation of 3 is secondary, namely 3 is formed by intramolecular Friedel-Crafts alkylation of 2, in which the corresponding cation (7) is formed from 2 in the presence of the lead salts. However, product ratios, 2/3, examined at various intervals during the reaction are practically constant. In addition, the formation of 2 is enhanced in the presence of a large excess of lithium chloride but that of 3 is major if the molar ratio of lithium chloride to ap-1 is 4 or less than that. Furthermore, the oxidation of the radical (6) to produce the cation 7 under the conditions is known to be rather slow. This means that the rates of cyclization of the radical (6) to produce 3 are comparable at least with the rates of the ligand transfer that are known to be very large. This easy cyclization is reasonable, if one considers the fact that the distance between the radical center and the aromatic carbon that is to be attacked is very short[9-11] in addition to the fact that the addition of radicals to the benzene ring is known fast for the phenyl.[12]

If a radical center is formed at one of the carbon atoms which are ±sc to the 1-methyl group, the radical center is expected to be within 300 pm from the methyl carbon.[9-11] One of the hydrogens of the 1-methyl group is thus in very close proximity of the radical center and prone to easy abstraction. Absence of any products derived from sc-2-(1,4-dimethyl-9-triptycyl)-2-methylpropyl radical (8) and overwhelming formation of products derived from (9-t-butyl-4-methyl-1-triptycyl)methyl radical (10) are the consequence of this proximity of the two



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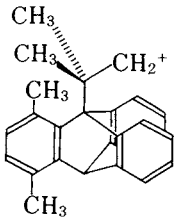

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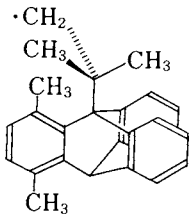

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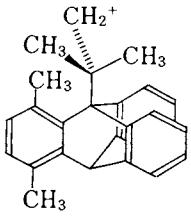

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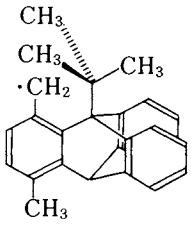

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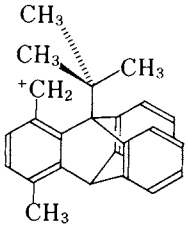

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groups concerned. The product distribution also suggests that the hydrogen transfer from the 1-methyl group to the radical center in 8 to produce 10 is faster than the cyclization to produce 3, because no 3 was detected among the products. Whether the facile hydrogen transfer is due to tunneling or not awaits further study.

It may be argued again that it is not the hydrogen transfer in 8 to form 10 but the hydride shift in the cation (9) which is formed by oxidation of the radical (8). However, since oxidation of the radicals formed during the Hunsdiecker reaction by lead(IV) salt is rather slow, this mechanism would not explain the facile formation of the 1-substituted compounds. The slow oxidation would have resulted in the formation of derivatives which carry substituents in the 9-substituent. Furthermore, since it is known that methide shift in the neopentyl-type cation is very fast,[13] we should expect products which are derived from the rearranged cations. The fact that none of the acetate expected from the ap-cation (7) was detected among the products is additional supporting evidence that the oxidation of radicals (6 and 8) is slow under the conditions. Although it may require to produce 7 or the corresponding sc-cation directly to disprove the hydride transfer, evidence presently available strongly supports the hydrogen transfer mechanism from 8 to 10.

The formation of 5 from sc-1 is also unusual, because in ordinary chloro-decarboxylation reactions, no ester is formed. Esters are known to be formed easily in the presence of copper(II) acetate due to the oxidation of radicals formed by the copper(II) ion. However, the oxidation of radicals with lead(IV) ion is believed to be slow.[4] The formation of 5 will mean that the radical 10 can survive until it is oxidized to (9-t-butyl-4-methyl-1-triptycyl)methyl cation (11). It is conceivable that the steric effect given by the t-butyl group in the 9-position lengthens the life-time of the radical 10 to make it possible to survive until it is oxidized by lead(IV) acetate to produce the corresponding

cation (**11**) and then the attack of the acetate ion present in the system takes palce to produce **5**.

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References

1) Part 28 of the series, Reactivities of Stable Rotamers. For Part 27, see Y. Tanaka, G. Yamamoto, and M. Ōki, Chem. Lett., 1989, 2019.
2) M. Ōki, Acc. Chem. Res., 17, 154 (1984).
3) T. Tanaka, K. Yonemoto, Y. Nakai, G. Yamamoto, and M. Ōki, Bull. Chem. Soc. Jpn., 61, 3239 (1988).
4) R. A. Sheldon and J. K. Kochi, Org. React., 19, 279 (1972).
5) The new compounds exhibited the following spectroscopic data.
Compound **2**: ^{1}H NMR ($CDCl_3$, δ) 2.34 (6H, s), 2.49 (3H, s), 2.65 (3H, s), 4.67 (2H, s), 5.59 (1H, s), 6.76 (2H, s), 7.00-7.04 (4H, m), 7.37-7.40 (2H, m), 7.81-7.83 (2H, m); MS M^+ = 372 and 374.
Compound **3**: ^{1}H NMR ($CDCl_3$, δ) 1.50 (3H, s), 2.27 (3H, s), 2.52 (3H, s), 2.56 (3H, s), 3.04 and 3.10 (2H, ABq, J = 15.1 Hz), 5.45 (1H, s), 6.70-6.78 (3H, m), 6.83-6.87 (2H, m), 6.97 (1H, app t, J = 7.3 Hz), 7.13 (1H, dd, J = 1.4 and 7.2 Hz), 7.19 (1H, d, J = 7.2 Hz), 7.73 (1H, d, J = 7.2 Hz); MS M^+ = 336.
Compound **4**: ^{1}H NMR ($CDCl_3$, δ) 2.10 (3H, s), 2.27 (6H, s), 2.52 (3H, s), 5.09 (2H, s), 5.59 (1H, s), 6.90 and 7.12 (2H, ABq, J = 8.0 Hz), 6.99-7.01 (4H, m), 7.36-7.38 (2H, m), 7.88-7.90 (2H, m); MS M^+ = 372 and 374.
Compound **5**: ^{1}H NMR ($CDCl_3$, δ) 2.02 (3H, s), 2.09 (3H, s), 2.21 (6H, s), 2.53 (3H, s), 5.47 (2H, s), 5.60 (1H, s), 6.90 and 6.97 (2H, ABq, J = 8.0 Hz), 6.97-7.02 (4H, m), 7.36-7.39 (2H, m), 7.88-7.90 (2H, m). This compound was also prepared by treating **4** with silver tetrafluoroborate in acetic acid.
6) J. K. Kochi, J. Org. Chem., 30, 3265 (1965).
7) J. K. Kochi, J. Am. Chem. Soc., 87, 3609 (1965).
8) D. I. Davies and C. Waring, J. Chem. Soc., Chem. Commun., 1965, 263; idem, J. Chem. Soc., C, 1968, 1865; W. H. Starnes, Jr., J. Org. Chem., 33, 2767 (1968).
9) M. Mikami, K. Toriumi, M. Konno, and Y. Saito, Acta Crystallogr., Sect. B, 28, 3441 (1972).
10) N. Nogami, M. Ōki, S. Sato, and Y. Saito, Bull. Chem. Soc. Jpn., 55, 3580 (1982).
11) M. Ōki, N. Takiguchi, S. Toyota, G. Yamamoto, and S. Murata, Bull. Chem. Soc. Jpn., 61, 4295 (1988).
12) E. G. Janzen and C. A. Evans, J. Am. Chem. Soc., 97, 205 (1975).
13) T. Ando, H. Yamataka, H. Morisaki, J. Yamawaki, J. Kuramochi, and Y. Yukawa, J. Am. Chem. Soc., 103, 430 (1981); V. J. Shiner, Jr., and J. J. Tai, ibid., 103, 436 (1981).

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