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SYNTHESIS AND VALENCE ISOMERIZATION OF 7-ALKYL-7-METHOXYCARBONYLCYCLOHEPTATRIENES[1]

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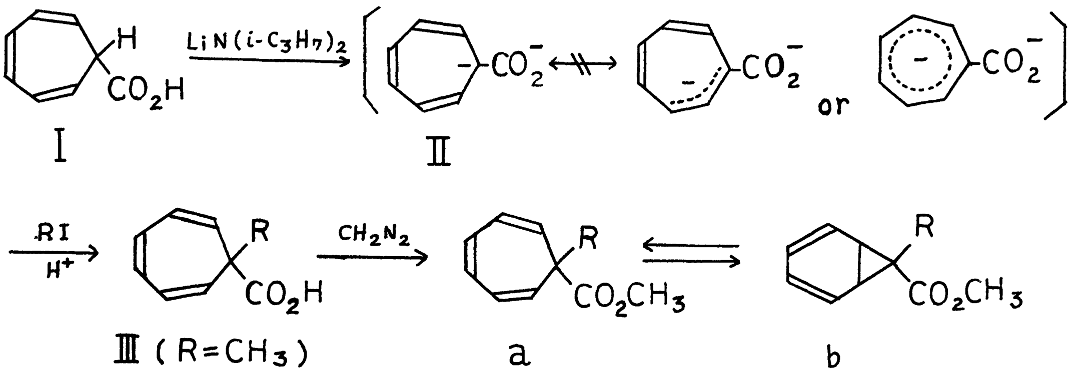
7-Methyl- (IV), 7-ethyl- (V) and 7-isopropyl-7-methoxycarbonylcycloheptatrienes (VI) could be easily synthesized by alkylation of cycloheptatriene-7-carboxylic acid (I), followed by methylation with diazomethane. Valence isomerization between cycloheptatriene (a-form) and norcaradiene (b-form) is observed and steric factors controlling the equilibrium are discussed.

7,7-Disubstituted cycloheptatrienes and the corresponding norcaradienes have mostly been synthesized by the addition of carbene species to benzene and dihydrobenzene.[2,3] Differing from this, we found a convenient method for introducing an alkyl group only into the C_7-position of cycloheptatriene-7-carboxylic acid (I) by application of the process originally developed by Creger.[4] In addition, we disclosed the existence of norcaradiene isomers in a series of 7-alkyl-7-methoxycarbonylcycloheptatrienes, such as IV, V and VI, independently from Klärner's recent finding concerning the substituent effect on the norcaradiene-cycloheptatriene (NCD-CHT) equilibrium.[5] His report prompts us to publish our study,[6] in which steric factors of the C_7-alkyl substituent are especially considered to explain problems on the NCD-CHT valence isomerization.

At -40° C, treatment of I with 2 equiv. of lithium diisopropylamide followed by addition of hexamethylphosphortriamide afforded dianion (II),[7] which, on treating with methyl iodide, provided 7-methylcycloheptatriene-7-carboxylic acid (III). Methylation of III with diazomethane gave 7-methyl-7-methoxycarbonylcycloheptatriene (IV)(bp. 80°C /6mmHg; M^+, 164) in 40% yield, in which case the other isomeric ester could not be detected. The structural assignment of IV was based on its nmr spectrum (100 MHz, CCl_4), δ 0.97 (singlet, CH_3), 3.36 (singlet, $COOCH_3$), 4.03 (C_1-, C_6-H) and 5.90-6.30 (other olefinic proton). As Klärner has pointed out,[5] the NCD-CHT



IV (R=CH_3)
V (R=C_2H_5)
VI (R=i-C_3H_7)

equilibrium exists in IV (v.i.). Its ir spectrum showing two carbonyl bands (see Table) should also support the existence of IVa and IVb.2) The compound IV is fairly stable to heat and was recovered unchanged after heating at 175° C for 20 hrs.3) The isolation of only IV indicates that the alkylation took place selectively at the C_7-position, thus eliminating the possibility of delocalization of the negative charge over not only the seven-membered ring but also the allylic part. This is a good contrast to the cycloheptatrienide anion, in which the anion charge is distributed in the allylic part.8)

Under the same condition, the alkylation of II with ethyl or isopropyl iodide, followed by methylation produced 7-ethyl- (V)(bp. 72°C /4mmHg; M^+, 178) or 7-isopropyl-7-methoxycarbonylcycloheptatriene (VI)(bp. 94°C /5mmHg; M^+, 192) in 42 and 47% yields, respectively.9) Some spectral properties of IV, V, and VI are shown in the Table along with those of 7-methoxycarbonylcycloheptatriene itself (VII).

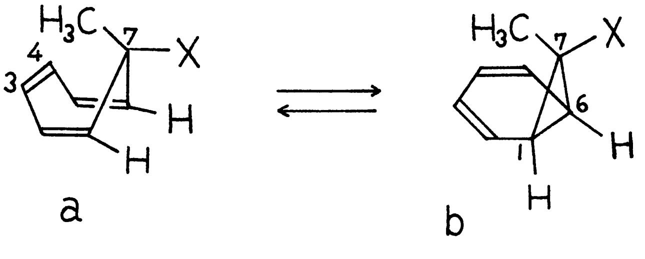
As shown in the Table, chemical shifts of the C_1- and C_6-protons and coupling constants between the $C_1(C_6)$- and $C_2(C_5)$-protons suggest that V and VI are also in the NCD-CHT equilibrium.10) The ratio of CHT : NCD could be calculated from the values of the chemical shifts of the C_1- and C_6-protons at room temperature and -100° C.5) It should be noted that this ratio increases in the order of methyl, ethyl and isopropyl compounds. Furthermore, the shift in the uv spectra of IV, V and VI is likely in this order. There exist many factors of the C_7-substituent which control the NCD-CHT equilibrium.11) For example, it was reported that the π-system12,13,14) or electron-withdrawing group15,16) located at the C_7-position

TABLE. Spectral properties of 7-methoxycarbonylcycloheptatriene and its 7-alkyl derivatives.

prod.	uv max in MeOH nm (ε)	ir max in CCl_4 cm^{-1}	δ (C_1-,C_6-H) in CCl_4 room temp.	$J_{1,2}$ (Hz)	δ(C_1-,C_6-H) in CS_2-$CDCl_3$ at -100° C	ratio of CHT : NCD (at t° C)
IV	265(2680)	1742, 1720	4.03	6.0	2.49^a, 5.26^b	1.25 (22.0)
V	263(2700)	1741, 1724	4.35	6.5	2.52^a, 5.35^b	2.11 (21.5)
VI	261(2400)	1740, ---	4.87^{**}	8.5	2.30^a, 5.33^b	6.05 (21.5)
VII		1754^* ---	5.32	9.0	--- ---	---

* neat, ** at 60 MHz and, other at 100 MHz.
a .... cycloheptatriene, b .... norcaradiene

stabilizes the norcaradiene form. From this view-point, it should be noted that IV possessing a saturated electron-releasing group is in equilibrium between IVa and IVb. A plausible explanation for this seems to be the relief from the non-bonding interaction between an axial C_7-alkyl substituent and the C_3-C_4 π-bond in the boat form of the cycloheptatriene.[14,17)] Furthermore, Klärner's finding that 7-cyano-7-methylcycloheptatriene (VIII) contains no norcaradiene isomer (VIIIb)[5)] seems interest compared with the case of IV. This fact would be explained by additional non-bonding interactions between an equatorial C_7-substituent and the C_1-hydrogen in the cycloheptatriene (a-form), and in the norcaradiene (b-form). These interactions, although being very small, should act competitively in the CHT-NCD system, and relief from such repulsions seems to affect the direction of the equiliblium. Thus, occurrence of IVb in IV, if compared with VIII, would be attributed to the repulsion between the C_1-hydrogen and C_7-methoxycarbonyl group in a-form.



IV ($X=CO_2CH_3$)
VIII (X=CN)

However, our finding, that as the C_7-alkyl group becomes more bulky the proportion of the norcaradiene (b-form) decrease, requires other explanations. Our study is continuing in order to clarify this ambiguity.

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