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REACTION OF SOME TROPONES WITH ETHYL AZODICARBOXYLATE

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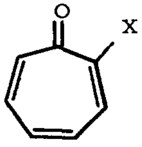
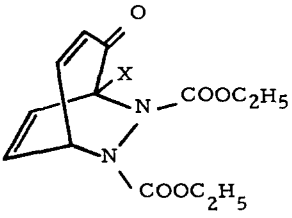
THERE has been a lot of interest in the Diels-Alder reaction of tropone and its derivatives because of the unsaturated nature of tropones(1) and the experimental verification of the concerted 4 + 6 cycloaddition reaction(2) which was proposed by the theoretical point of view.(3)

We wish now to describe the reaction of some tropones with ethyl azodicarboxylate as a mighty dienophile.

Refluxing of tropone (I) and ethyl azodicarboxylate (II) in toluene for 48 hr. under nitrogen atmosphere yielded the 1 : 1 adduct (III), m.p. 102-103°C in 65% yield [Found: C, 55.67; H, 5.49; N, 10.22%. Calcd. for $C_{13}H_{16}O_5N_2$: C, 55.71; H, 5.75; N, 10.00%. UV, λ_{max}^{MeOH} 354 mμ (log ε = 2.32), IR, $\nu_{max}^{CCl_4}$ 1618, 1705, 1725, 1748, 2950 cm^{-1}]. The NMR spectrum of (III) at 60 Mcps in deuterio chloroform as shown in Fig I, exhibited signals at 1.23 (t), 1.26 (t), 4.13 (q), 4.16 (q) due to the two kinds of ethyl groups (J= 7 cps), 4.88 (d.d, 1H), 5.31 (d.d, 1H), 5.70 (d.d, 1H), 6.20 (d.d.d, 1H), 6.79 (d.d, 1H) and 6.92 ppm (d.d, 1H). These evidences support the following structure resulting from a normal 1,4-addition reaction.



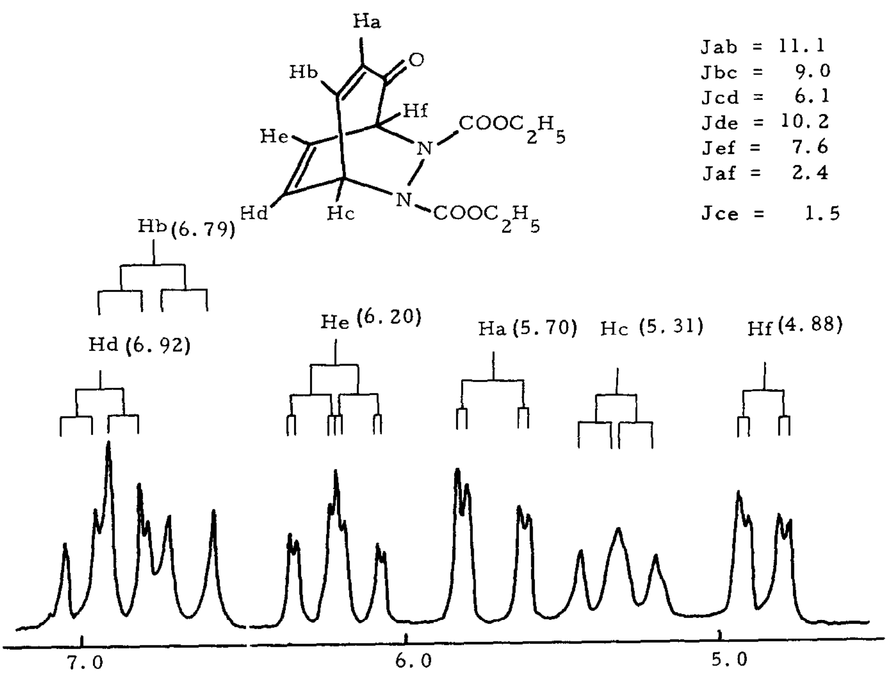
I : X = H
IV : X = OCH_3
VI : X = OH



III : X = H
V : X = OCH_3

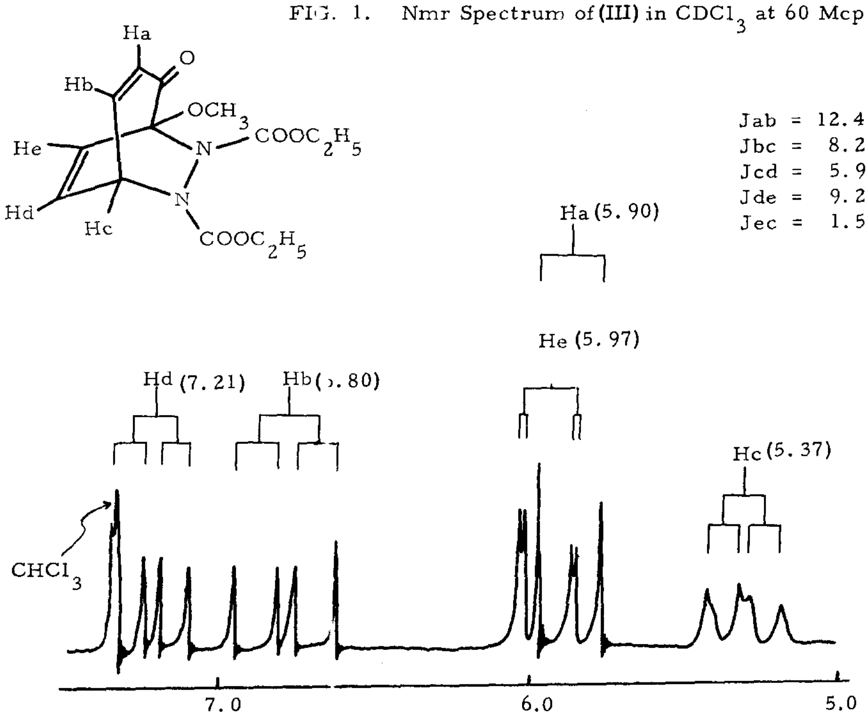
Final assignment of the above mentioned signals and the coupling constants revealed by the NMR spectrum at 100 Mcps and the NMDR technique were presented in Fig. 1.

The reaction of 2-methoxytropone (IV) with (II) afforded same type of adduct (V), m.p. 139-140.5°C, in 45% yield [Found ; C, 54.08; H, 6.08; N, 9.08%. Calcd. for $C_{14}H_{18}O_6N_2$: C, 54.19; H, 5.85; N, 9.03%. UV, λ_{max}^{MeOH} 346 mμ (log ε = 2.31), IR, $\nu_{max}^{CCl_4}$ 1628, 1715, 1742, 2851, 2000 cm^{-1}. NMR, δ^{CDCl_3} 1.23 (t), 1.28 (t), 4.21 (q), 4.26 (q) due to the two kinds of ethyl groups (J = 7 cps), 3.48 (s, 3H, methoxyl group), 5.37 (d.d, 1H), 5.90 (d, 1H), 5.97



Jab = 11.1
Jbc = 9.0
Jcd = 6.1
Jde = 10.2
Jef = 7.6
Jaf = 2.4
Jce = 1.5

FIG. 1. Nmr Spectrum of (III) in $CDCl_3$ at 60 Mcps.



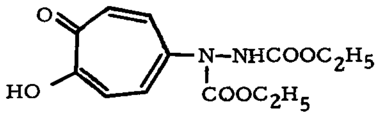
Jab = 12.4
Jbc = 8.2
Jcd = 5.9
Jde = 9.2
Jec = 1.5

FIG. 2. Nmr Spectrum of (V) in $CDCl_3$ at 60 Mcps.

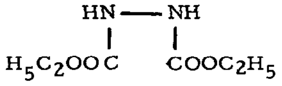
(d.d, 1H), 6.80 (d.d, 1H) and 7.21 ppm (d.d, 1H) [see Fig. 2].

On the other hand, when tropolone (VI) is allowed to react with an equimolar amount of (II) in refluxing toluene, 17% yield of two products, m.p. 129 - 131°C (VII) and m.p. 158.5 - 159.5°C (VIII) in the ratio of 2 : 1 are obtained. The product, m.p. 129 -131°C, was identified as ethyl hydrazodicarboxylate (VII) in all respects.

The structure of (VIII) [Found : C, 52.81; H, 5.60; N, 9.11%. Calcd. for $C_{13}H_{16}O_6N_2$: C, 52.70; H, 5.44; N, 9.46%] was proved to be 5-(diethoxycarbonylhydrazo)tropolone by the following evidences : UV absorption maxima of 333 (log ε = 4.14), 227 mμ (4.44) indicated presence of tropolone nucleus and this is further confirmed by the positive ferric chloride test in chloroform. IR spectrum showed a maxima of 1548, 1620 cm^{-1} for tropolone nucleus, 3360 cm^{-1} for hydroxyl group, 3180 cm^{-1} for imino group, 1720 cm^{-1} for ester group and 860 cm^{-1} band characteristic for CH out-of-plane vibration of the two adjacent hydrogens in tropolone ring.$^{(4)}$ NMR spectrum of (VIII) exhibited signals at 1.25 (t), 1.26 (t), 4.23 (q), 4.24 (q) assigned for two non-equivalent ethyl groups and A_2B_2 - type signals (δ_A = 7.28, δ_B = 7.53 ppm, J_{AB} = 12 cps) for the ring protons. The signals at 7.51 (s, 1H) and 8.60 ppm (broad s, 1H) appeared to be due to hydroxyl and imine protons respectively which disappeared by deuterium exchange [see Fig. 3].



(VIII)



$$\begin{array}{cc} HN & \!\!-\!\!-\; NH \\ | & | \\ H_5C_2OOC & COOC_2H_5 \end{array}$$

(VII)

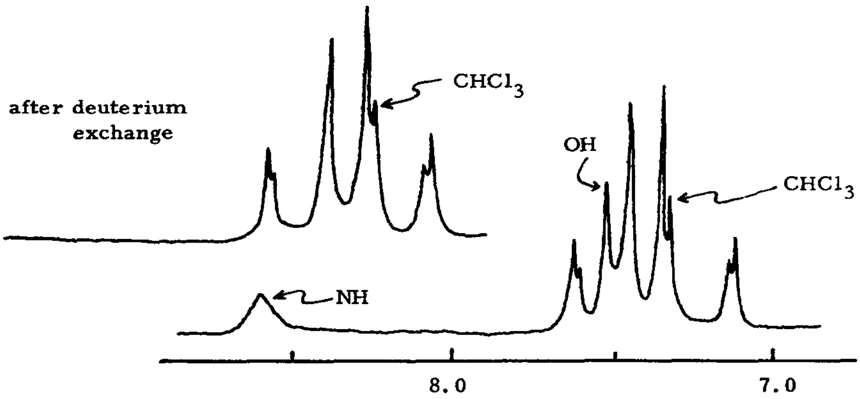


FIG. 3. Nmr Spectrum of (VIII) in $CDCl_3$ at 60 Mcps

It seems fairly certain that the reaction of tropolone with ethyl azodicarboxylate would proceed via hydrogen abstraction(5) at hydroxyl in a chain process.(6)

Although the MO theory(7) predicts that the radical reaction of (VI) occurs at C-3 and C-7 positions rather than C-5 position, it is now evident from the present investigation that the 5-position in tropolone nucleus is more reactive than 3- and 7. The attack at 5-position in the radical reaction was also found in the formation of 3, 5'-bitropolonyl by the reaction of benzoyl peroxide with (VI).(8)

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