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DIELS-ALDER REACTION ON SOME TROPONOIDS WITH ACRYLONITRILE

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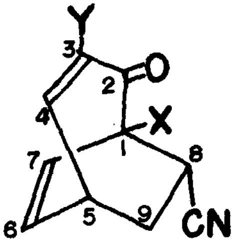
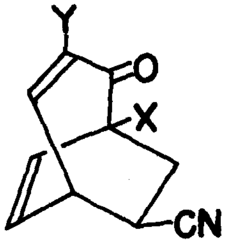
Diels-Alder reaction of troponoids has already been studied by several authors (1), using dienophiles with symmetric structures. Although endo-cis configuration was found in the products in most cases, both endo and exo isomers were obtained in 1:1 ratio in the reaction of tropolone and maleic anhydride (1). We have studied the reaction of the asymmetric dienophile, acrylonitrile, with four troponoids; tropone, 2-chloro-, 2-methoxy- and 2-hydroxytropone (tropolone). The result presented herein clearly indicates that the reaction proceeds through a concerted one-step mechanism and that the nature of the substituents at 2-position controls the orientation of two reactants.

Heating of tropone (I) with acrylonitrile (II) at 130-140° for 20 hours yielded, after repeated silica gel chromatography, four isomeric 1:1 adducts (2): III (m.p. 91-92°, ν 1665, 1630 cm^{-1}), IV (oil, ν 1670, 1633 cm^{-1}), V (m.p. 118-120°, ν 1667, 1633 cm^{-1}) and VI (oil, ν 1667, 1632 cm^{-1}). For all adducts, the presence of $\alpha\beta$-unsaturated carbonyl group was exhibited by UV (2) and IR spectra and that of saturated cyano group by IR band at 2260-2300 cm^{-1}. Their NMR spectra clearly showed the presence of four vinyl protons in each adduct. The position and configuration of cyano group in these adducts were established by the NMR analyses with the aid of NMDR. The analysed NMR parameters are listed in TABLE I and II. Irradiation of H_4 signal easily distinguished H_5 from H_1 and the same procedure on either H_1 or H_5 caused changes in multiplicities of the proton (H_X) at α-position to the cyano group. Position of cyano group was thus established unequivocally. Orientation of cyano group was deduced from the magnitude of coupling constant between H_X and one (H_Y) of the bridge head protons. H_X showed coupling with H_Y in addition to those with adjacent methylene protons. Consideration of the dihedral angles between H_X and H_Y clearly indicated that J_{XY} should be smaller for the adducts with exo-H_X (endo-CN) than for those with endo-H_X (exo-CN).

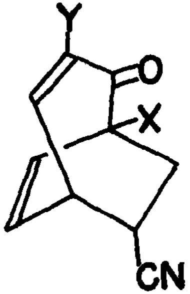
2-Chlorotropone (VII) and II were heated at 140-150° for 14 hours and subsequent silica gel chromatography afforded again four 1:1 adducts: VIII (m.p. 149-152°, ν 1675, 1633 cm^{-1}), IX (m.p. 130-131.5°, ν 1682, 1636 cm^{-1}), X (m.p. 126-128°, ν 1691, 1634 cm^{-1}) and XI (m.p. 127-128°, ν 1681, 1640 cm^{-1}). The position of chlorine atom was deduced from the number of vinyl protons in their NMR spectra; VIII, IX and XI showed only three, revealing chlorine to be situated at the position 3, while X showed four, indicating the



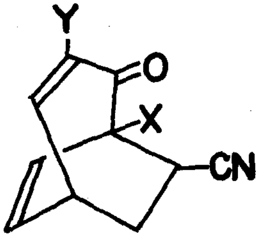
III X=Y=H
VIII X=H, Y=Cl
XIV X=OMe, Y=H
XVIII X=OAc, Y=H



IV X=Y=H
XIII X=H, Y=OMe



V X=Y=H
IX X=H, Y=Cl
XV X=H, Y=OMe



VI X=Y=H
X X=Cl, Y=H
XI X=H, Y=Cl
XVI X=OMe, Y=H
XIX X=OAc, Y=H

TABLE I. Coupling Constant (J) of Troponoid-Acrylonitrile Adducts

	1-3'	1-7	1-8α	1-8β	3-4	3-5	4-5	5-6	5-7	5-9α	5-9β	6-7	6-1	7-8β	8α-8β	8α-9α	8α-9β	8β-9α	8β-9β	9α-9β
III	1.9	7.2	-	1.0	11.0	0.7	8.5	7.4	0.9	4.5	2.2	8.2	1.0	?	-	-	-	6.5	9.8	13.2
IV	2.2	7.2	6.1	1.9	11.1	0.7	8.5	7.2	1.2	3.7	-	8.3	1.2	?	14.1	9.6	-	7.3	-	-
V	2.1	7.2	4.6	2.4	11.1	0.4	8.3	6.7	1.6	-	2.0	8.6	1.5	?	14.5	-	5.3	-	8.0	-
VI	2.1	7.3	6.0	-	11.4	1.0	8.8	7.5	1.1	?	?	8.3	1.1	-	-	8.0	6.6	-	-	?
VIII	-	7.5	-	1.7	-	-	9.6	7.1	1.0	4.5	2.4	8.4	1.3	1.0	-	-	-	7.0	9.6	13.1
IX	-	7.4	3.7	2.5	-	-	9.5	7.0	1.5	-	2.0	8.6	1.5	?	13.9	-	5.6	-	8.3	-
X	-	-	-	-	11.0	1.0	8.3	7.4	1.2	?	?	9.2	-	-	-	7.9	6.7	-	-	?
XI	-	7.5	6.0	-	-	-	9.3	7.3	1.2	?	?	8.4	1.2	-	-	8.6	6.6	-	-	?
XIII	-	7.1	6.2	1.5	-	-	9.3	7.4	1.0	4.0	-	8.2	1.1	1.0	14.0	9.4	-	7.5	-	-
XIV	-	-	-	-	11.2	1.1	8.8	7.5	1.3	5.1	2.3	9.5	-	1.0	-	-	-	6.3	9.4	13.7
XV	-	8.0	?	?	-	-	9.7	7.3	1.3	?	?	8.4	1.4	1.3	?	-	5.3	-	7.7	-
XVI	-	-	-	-	10.9	1.0	8.6	7.3	1.2	?	?	9.0	-	-	-	8.0	6.5	-	-	?
XVIII	-	-	-	-	11.2	1.0	8.8	7.4	1.5	2.9	2.7	9.0	-	1.5	-	-	-	7.3	9.6	13.0
XIX	-	-	-	-	11.2	0.9	8.7	6.9	1.8	?	?	9.4	-	-	-	9.9	6.2	-	-	?

TABLE II. Chemical Shift (δ) of Troponoid-Acrylonitrile Adducts (ppm in $CDCl_3$)

	H_4	H_6	H_7	H_3	H_5	H_1	$H_{8\alpha}$	$H_{8\beta}$	$H_{9\alpha}$	$H_{9\beta}$
III	7.05	6.75	6.18	5.77	3.47	3.77	CN	3.22	2.00	2.48
IV	7.07	6.57	6.15	5.97	3.68	3.52	2.50	2.12	3.00	CN
V	6.98	6.65	6.32	5.80	3.65	3.60	2.22	2.38	CN	3.27
VI	7.20	6.65	6.10	5.88	3.55	3.77	3.23	CN	2.35	2.23
VIII	7.35	6.80	6.23	Cl	3.53	4.03	CN	3.23	1.93	2.53
IX	7.23	6.68	6.35	Cl	3.72	3.83	2.25	2.38	CN	3.27
X	7.22	6.67	6.07	6.05	3.52	Cl	3.58	CN	2.43	2.27
XI	7.47	6.70	6.13	Cl	3.57	4.02	3.23	CN	2.35	2.23
XIII	6.00	6.62	6.13	3.62(OMe)	3.70	3.67	2.43	2.10	2.93	CN
XIV	7.15	6.70	6.23	5.87	3.45	3.67(OMe)	CN	3.40	2.22	2.45
XV	5.95	6.72	6.32	3.55(OMe)	3.75	3.75	2.25	2.38	CN	3.22
XVI	7.18	6.70	6.15	5.99	3.52	3.63(OMe)	3.28	CN	2.33	2.22
XVIII	7.02	6.68	6.07	5.88	3.48	2.27(OAc)	CN	4.05	2.03	2.45
XIX	7.28	6.55	6.33	6.03	3.45	2.23(OAc)	3.37	CN	2.40	2.12

chlorine to be at the position 1 (TABLE I). The position and orientations of cyano groups in VIII, IX and XI were deduced by the same method as in the case of the tropone adducts. For the fourth isomer X, the position of the cyano group was determined from the fact that the methylene protons showed a coupling with H_5. The close similarity of δ_{H_4}, δ_{H_6} and δ_{H_7} in X with those in VI but not in III suggests *exo*-orientation for the cyano group.

2-Methoxytropone (XII) and II were heated at 140-150° for 21 hours and products were separated in the way described above to afford again four 1:1 adducts: XIII (m.p. 130-2°, ν 1676, 1615 cm^{-1}), XIV (m.p. 112-113.5°, ν 1673, 1634 cm^{-1}), XV (m.p. 169-170°, ν 1679, 1621 cm^{-1}) and XVI (oil, ν 1678, 1636 cm^{-1}). In their NMR spectra, XIII and XV showed three olefinic proton signals, while XIV and XVI exhibited four, revealing the positions of the methoxy group. Position and configuration of cyano group in each adduct were deduced by similar method as in VIII-XI. The H_8 signal shows a long-range coupling with H_7 in XIV but not in XVI.

Heating of tropolone (XVII) with II at 120-130° for 25 hours, followed by the acetylation and silica gel chromatography, afforded two isomeric adducts XVIII (m.p. 126-7°, ν 1744, 1680, 1640 cm^{-1}) and XIX (m.p. 117-7.5°, ν 1754, 1677, 1635 cm^{-1}). Their UV, IR and NMR spectra clearly show that the acetoxy group is at bridge head position (4). Multiplicity of H_8 established the structure (TABLE I).

The structures thus deduced from chemical shifts and coupling constants are supported by the regular solvent shift of the hydrogen signals (H_1 to H_7) on going from chloroform to benzene (5).

V, VIII, X and XIV have no tendency to isomerize to the other adducts under the condition in which they were formed, disclosing that none of them was the secondary products. That each adduct was resulted from the different orientation of the reactants (one-step mechanism) and not from a common intermediate (two-step mechanism) was verified by the reaction of acrylonitrile-β-*cis*-*d* and 2-methoxytropone-3,5,7-*d*$_3$. The products, XIII-d, XIV-d and XVI-d isolated showed a large J_{89} (9-11 Hz) revealing that *cis* relation of H_8 and H_9 was maintained for all products.

The yield of the adducts, shown in TABLE III, disclosed a few point in the general pattern of the Diels-Alder reaction of troponoids.

TABLE III. Yield of the Acrylonitrile Adducts (%)

		Structure of Adducts					
Troponoids	Total Yield	[7,4]		[5,2]		[4,7]	
		endo	*exo*	*endo*	*exo*	*endo*	*exo*
Tropone (I)	91	64	8	11	8	*	*
2-Chlorotropone (VII)	81	33	0	0	32	9	7
2-Methoxytropone (XII)	85	19	10	30	26	0	0
Tropolone (XVII)	40	0	0	12	28	0	0

* Impossible to differenciate from [5,2] adducts.

First, a correlation was observed between the reacting site in tropone ring and the electron releasing ability of the substituents at 2-position: β-Carbon of acrylonitrile reacted either at 5 or 7-positions and α-carbon at 2 or 4-positions. The former type of reaction, [5,2], is more prominent for XVII and XII, and the latter type, [7,4], was found more predominantly for I, while both types and another type, [4,7], were observed equally in VII (6). The ratio [5,2]/[7,4] thus has a decreasing order from OH through OMe and Cl to H.

Secondly, the adducts with the *endo* cyano group always predominate in [7,4] reaction. However, the *endo*/*exo* ratio is close to 1 in [5,2] and [4,7] reactions and, in the extreme case of VII, *endo* [5,2] product was not obtained.

Further study is in progress in order to establish the factor controlling the geometry of the products in the Diels-Alder reaction of troponoids.

References and Footnotes

1) For the list of the reference, see S. Itô, H. Takeshita, Y. Shoji, Y. Toyooka and T. Nozoe, *Tetrahedron Letters*, 3215 (1968).
2) Adducts are listed in the order of elution from chromatograph in all cases. NMR spectra were measured at 60 and/or 100 MHz in $CDCl_3$. Chemical shifts (δ) are expressed in ppm from internal TMS. Correct analytical figures were obtained for all compounds described. IR spectra were measured for KBr disc or CCl_4 solution. All UV data are summerized in the previous paper (3).
3) S. Itô, H. Takeshita, Y. Shoji, Y. Toyooka and T. Nozoe, *Tetrahedron Letters*, 443 (1969).
4) The absence of an enolic acetate was acertained by IR spectra of every chromatographic fraction of crude mixture, the formation of an α-diketone was thus excluded.
5) This solvent shift will be discussed elsewhere.
6) Occurence of the [4,7] reaction in VII implies that, at least, a part of [5,2] adduct from tropone have to be classified at [4,7] adduct, although the differenciation is impossible.