

Diels-Alder Reaction of 2,3-Dimethylbutadiene-1,3 with *cis*- and *trans*-Ethylatropic Acids

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Cis- and *trans*-ethylatropic acids have been used as dienophiles in the reaction with 2,3-dimethyl-butadiene-1,3. The products were identified as conventional Diels-Alder adducts, *i.e.*, 1-phenyl-*cis*-3,4-dimethyl-6-ethyl-3-cyclohexene-1-carboxylic acid and the corresponding *trans*-compound. The structures were ascertained with the aid of nuclear magnetic resonance and ultraviolet spectra. A tentative assignment of configuration is made, based on the "*cis*-addition-principle" of Diels-Alder reactions.

In order to prepare 1-phenyl-3,4-dimethyl-6-ethyl-3-cyclohexene-1-carboxylic acids 2,3-dimethylbutadiene-1,3 was reacted with *cis*- and *trans*-ethylatropic acid, respectively. The reaction was found to be best performed in sealed tubes at 150°C. Different products were isolated in the two cases. The empirical formulas were the expected for addition products.

That the products obtained were the ones desired, *i.e.*, conventional Diels-Alder adducts, was proved in the following way. All possible open-chain products resulting from a simple addition of one of the reactants to a double bond (including 1,4-addition) in the other or from double bond migration in these products, will have either ethylenic hydrogens or a double bond conjugated with the phenyl and the carboxylic groups. The former can be ruled out on the basis of nuclear magnetic resonance spectra. Ethylenic hydrogen has absorption in the neighbourhood of $\delta = 5$ ppm ($\delta = 0$ for tetramethylsilane) but the spectra show no absorption at all between 3 and 7 ppm. Conjugation with the phenyl and carboxylic groups can be excluded on the basis of the ultraviolet spectra. The substances have their main absorption bands below 2200 Å. Above this wavelength there are only weak bands showing the vibration structure characteristic of benzene and unconjugated benzene derivatives (Fig. 1). Compounds of the type mentioned ought to have an absorption of the same type as *cis*- or *trans*-ethylatropic acids.¹ A Diels-Alder reaction would produce compounds with a structure having an ultraviolet spectrum similar to that of phenylacetic acid.² In fact there is good agreement, which is shown in Table 1.

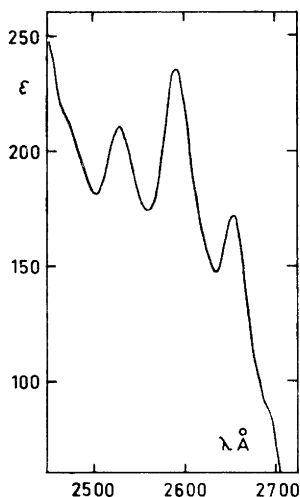


Fig. 1. Ultraviolet spectrum of 1-phenyl-*cis*-3,4-dimethyl-6-ethyl-3-cyclohexene-1-carboxylic acid in ethanol. The spectrum of the corresponding *trans*-form is similar.

Other rather improbable structures of the reaction products are those resulting from a cycloaddition with the formation of a cyclobutane ring. Such compounds would also have ethylenic hydrogens and thus can be ruled out as inconsistent with the NMR-spectra.

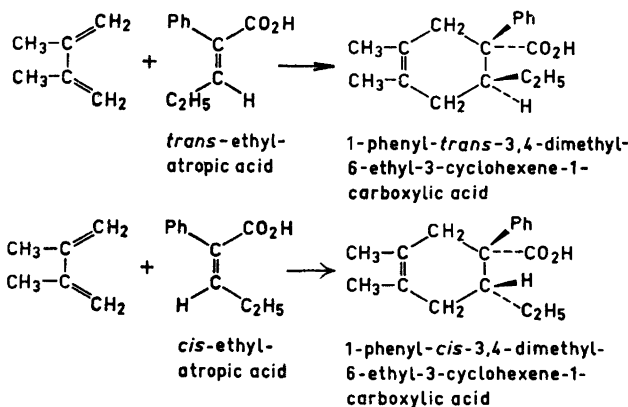
The only possibility left is an ordinary Diels-Alder reaction. Double bond migration after the addition can be excluded as all other structures than the conventional would have ethylenic hydrogens.

With the structures ascertained two configurations are possible. As the Diels-Alder reaction is known to give stereospecific *cis*-addition^{3,4} the following configurations of the products are proposed.

Only in the case of *cis*- and *trans*- β -sulfoacrylic acids⁵ have results been reported which may indicate that the stereospecificity is not absolute. In the

Table 1. Ultraviolet spectra of 1-phenyl-*trans*-3,4-dimethyl-6-ethyl-3-cyclohexene-1-carboxylic acid ("*trans*-acid"), 1-phenyl-*cis*-3,4-dimethyl-6-ethyl-3-cyclohexene-1-carboxylic acid ("*cis*-acid") and phenylacetic acid² in ethanol solution. Inflection points are indicated with an s.

<i>trans</i> -acid		<i>cis</i> -acid		Ph.CH ₂ .COOH	
λ Å	log ϵ	λ Å	log ϵ	λ Å	log ϵ
2200 s	3.73			2410 s	2.03
		2470 s	2.33	2475	2.05
2530	2.33	2530	2.32	2525	2.17
2590	2.36	2590	2.37	2585	2.26
2655	2.22	2655	2.24	2645	2.15
2690 s	1.85	2690 s	1.96	2675 s	1.85



reaction of both these acids with cyclopentadiene and furan only one and the same product was isolated. The experiments also showed, however, that the isomeric product might well be present in the reaction mixture, though it could not be isolated. This is the only contradiction of the “*cis*-principle”, but as the yields were rather low the reason may well be another than an exception to this principle. In the case of *cis*- and *trans*-ethylatropic acids different products are isolated, and it seems therefore reasonable to assume that the reaction has followed the “*cis*-principle”. Another factor, which may influence the reaction, so that the configuration of the products is not the expected, is isomerization of the reactants before the reaction or of the products formed in the reaction.⁴ Jönsson⁶ has shown that the *cis*-methylatropic acid can be completely rearranged to the *trans*-configuration by heating to 170°C. Experiments have shown that also in the case of the ethylatropic acids the *trans*-form is the more stable and is formed when the *cis*-acid is heated. If isomerization of the acids had influenced the course of the reaction, however, it seems plausible that the same products would have been formed in both cases, because of the stability of the *trans*-form. Depending on the reversibility of the Diels-Alder reaction, it has sometimes been found that, especially when heating and long reaction times are used, the first-formed kinetically favoured product has been rearranged to the thermodynamically more stable,⁴ thus producing an “exception” to the *cis*-principle. This possibility can be excluded in this case on the basis of the same argument as above. If it were so, only one product would be expected from both acids.

EXPERIMENTAL

All melting points were determined on a Kofler micro hot stage. The infrared spectra given below were recorded with the KBr disc technique (ca. 1 mg of the sample in 300 mg of KBr). Percentage absorption is indicated in brackets after the wave number in cm⁻¹. The abbreviations used are: b broad, vb very broad and sh shoulder. Nuclear magnetic resonance spectra were measured in trifluoroacetic acid solution.

1-Phenyl-trans-3,4-dimethyl-6-ethyl-3-cyclohexene-1-carboxylic acid. 3.5 g (0.02 mole) of *trans*-ethylatropic acid¹ dissolved in 4.9 g (0.06 mole) of freshly distilled 2,3-dimethyl-

butadiene-1,3' in a sealed tube were heated to 150°C for 84 h. On cooling the addition product crystallized, was filtered and recrystallized from petroleum (b.p. 80–110°C). The yield was 2.7 g (53 %) melting at 190–191°C. After further recrystallizations and sublimation pure acid melting at 191.5–192.5°C was obtained. (Found: C 79.2; H 8.68; O 12.4. Required for $C_{17}H_{22}O_2$: C 79.0; H 8.58; O 12.4.) Infrared spectrum: 3040 sh (55), 2945 sh (73), 2920 (76), 2900 (76), 2870 sh b (75), 2840 sh (73), 2800 sh (63), 2610 b (52), 2540 sh (49), 1780 vb (21), 1675 (83), 1646 sh (49), 1588 (25), 1485 (37), 1450 sh (43), 1430 (51), 1399 (41), 1369 (28), 1289 (70), 1260 (69), 1209 (44), 1177 (27), 1151 (36), 1066 (17), 1024 (23), 938 (53), 860 (17), 801 (18), 763 (20), 713 (66), 684 (62), 640 (30), 583 (13), 500 (7), 484 (19), 429 (32), 352 (9).

1-Phenyl-cis-3,4-dimethyl-6-ethyl-3-cyclohexene-1-carboxylic acid. 7.0 g (0.04 mole) of *cis*-ethylatropic acid¹ dissolved in 9.8 g (0.12 mole) of freshly distilled 2,3-dimethylbutadiene-1,3' in a sealed tube were heated to 150°C for 84 h. As the product did not crystallize (not even on seeding), the reaction mixture was dissolved in 2.5 N sodium hydroxide, washed with ether and acidified. The addition product precipitated as a slowly solidifying oil. The precipitate was collected, washed with water, dried and recrystallized from petroleum (b.p. 80–110°C). The yield was 4.4 g (43 %) melting at 134–137°C. Further recrystallizations raised the melting point to 139.0–139.5°C. (Found: C 79.1; H 8.57; O 12.2. Required for $C_{17}H_{22}O_2$: C 79.0; H 8.58; O 12.4.) Infrared spectrum: 3070 sh (47), 3045 (52), 3005 sh (52), 2940 (57), 2895 b (56), 2855 (66), 2795 sh (52), 2600 b (41), 2510 sh b (36), 2340 sh vb (23), 1679 (76), 1645 sh (38), 1585 (24), 1570 sh (22), 1488 (31), 1445 (41), 1437 (41), 1427 sh (40), 1393 (38), 1369 (30), 1265 (65), 1225 sh (33), 1215 sh (31), 1177 (30), 1124 (28), 1066 (22), 1027 (22), 920 b (40), 746 (17), 716 (55), 683 (42), 605 (19), 571 (21), 510 (15), 490 (22), 480 (15), 460 (11), 422 (28).

The ultraviolet spectra were measured with a Beckman DU spectrophotometer. The infrared spectra were recorded with a Perkin-Elmer Model 221 prism-grating instrument at the Infrared Laboratory, Chemical Institute, Lund. The nuclear magnetic resonance spectra were recorded with a Varian A-60 spectrometer at the Instrument Station of the University of Lund and the analyses were carried out at the Department of Analytical Chemistry, Chemical Institute, Lund.

REFERENCES

1. Nilsson, K. *Acta Chem. Scand.* **19** (1965) 612.
2. Buckles, R.E. and Bremer, K.G. *J. Am. Chem. Soc.* **77** (1955) 805.
3. Huisgen, R., Grashey, R. and Sauer, J. In Patai, S. (Ed.) *The Chemistry of Alkenes*. Interscience Publishers, London — New York — Sydney 1964.
4. Martin, J.G. and Hill, R.K. *Chem. Rev.* **61** (1961) 537.
5. Hendrickson, J.B. *J. Am. Chem. Soc.* **84** (1962) 653.
6. Jönsson, G.W. *Svensk Kem. Tidskr.* **34** (1922) 89.
7. Horning, E.C. (Ed.) *Org. Syn. Coll. Vol.* **3** (1955) 312.

Received June 25, 1965.