

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Diels-Alder Reactions of *trans*-4,4,4-Trifluorocrotonic Acid. II

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trans-4,4,4-Trifluorocrotonic acid undergoes the Diels-Alder reaction smoothly with various dienes. The determination of the structures of the isoprene, 1-phenyl-1,3-butadiene, 1,3-butadiene and anthracene adducts is discussed.

Discussion

The initial study of *trans*-4,4,4-trifluorocrotonic acid as a dienophile¹ has now been extended to the reaction with isoprene, 1-phenyl-1,3-butadiene, 1,3-butadiene and anthracene. In the case of isoprene and 1-phenyl-1,3-butadiene, two isomeric products are possible. Usually only one structural isomer is isolated from this type of Diels-Alder reaction. For example, the product from isoprene would be expected to have the electron-withdrawing substituent *para* to the methyl group; whereas, from 1-phenyl-1,3-butadiene, the electron-withdrawing substituent would be *ortho* to the diene substituent. In *trans*-4,4,4-trifluorocrotonic acid two electron-withdrawing groups are present, and it was of interest to determine what directive influence the trifluoromethyl group had in competition with the carboxyl group.

trans-4,4,4-Trifluorocrotonic acid and isoprene gave a 90% yield of the adduct I, 4-methyl-6-trifluoromethylcyclohex-3-enecarboxylic acid. The structure of I was shown by dehydrogenation and decarboxylation to the known aromatic hydrocarbon II, *m*-trifluoromethyltoluene. During the dehydrogenation a saturated product, III, 2-trifluoromethyl-4-methylcyclohexanecarboxylic acid, was also obtained. This type of disproportionation has been shown to be common in the noble metal-catalyzed dehydrogenation.²

The reaction of *trans*-4,4,4-trifluorocrotonic acid and 1-phenyl-1,3-butadiene gave two adducts, IVA and IVB, which upon heating with palladium-on-charcoal both gave the same aromatic compound V, *m*-trifluoromethylbiphenyl. The *meta* structure of V was proved by hydrolysis with concentrated sulfuric acid by the method of Pettit and Tatlow³ to the *m*-biphenylcarboxylic acid (VI).

trans-4,4,4-Trifluorocrotonic acid also reacted with butadiene and anthracene to yield 1:1 adducts. The structure of the butadiene adduct VII was identified by dehydrogenation to the known acid VIII, *o*-trifluoromethylbenzoic acid. The structure of the anthracene adduct IX, as a 9,10-adduct, was established by its ultraviolet absorption spectrum.⁴ Analogous to the typical benzenoid absorption, XII exhibits maxima at 265 μ ($\log \epsilon$ 2.83) and 272 μ ($\log \epsilon$ 2.93) and also two "shoulders" at 252 μ ($\log \epsilon$ 2.54) and 258 μ ($\log \epsilon$ 2.66).

The data cited indicate that *trans*-4,4,4-trifluoro-

crotonic acid is a good dienophile in the Diels-Alder reaction. They also show that the acid group is the active orienting factor in the reaction and that the trifluoromethyl group does not affect the isomeric distribution of products.

Experimental⁵

Starting Materials.—*trans*-4,4,4-Trifluorocrotonic acid was prepared from trifluoroacetic acid according to the described method.⁶ 1-Phenylbutadiene was prepared by the addition of methylmagnesium iodide to cinnamaldehyde, and subsequent dehydration of the carbinol with iodine.⁷

Diels-Alder Reaction of Isoprene and *trans*-4,4,4-Trifluorocrotonic Acid.—Isoprene (7.5 g., 0.11 mole) and *trans*-4,4,4-trifluorocrotonic acid (14 g., 0.1 mole) were heated in a Carius tube for 3 hr. at 140–150°. A light yellow solid resulted; this was dissolved in ether and transferred to a distilling flask. Upon distillation under a reduced pressure, 18.6 g. (90%) of adduct I was obtained, b.p. 108–109° (2 mm.). The adduct solidified on standing and was recrystallized from aqueous acetic acid to give pure product, m.p. 104–106°.

Anal. Calcd. for C₉H₁₁F₃O₂: C, 51.92; H, 5.28; F, 27.40. Found: C, 51.90; H, 5.46; F, 27.15.

Dehydrogenation and Decarboxylation of Adduct I.—Five grams (0.024 mole) of adduct I was mixed with 2.5 g. of a 10% palladium-on-charcoal catalyst and heated at 300–310° for 3 hr. The resulting mixture was refluxed with 25 ml. of benzene for 1 hr. The catalyst was removed by filtration, and the benzene solution was refluxed with 25 ml. of a 10% solution of sodium hydroxide for 1 hr. The benzene solution was separated, dried and distilled to give 0.4 g. (10%) of *m*-trifluoromethyltoluene (II), b.p. 127–129°, n_D^{20} 1.4290 (lit.⁸ b.p. 127°, n_D^{20} 1.4254). The infrared spectrum of V showed *m*-disubstituted bands at 12.65 and 14.3 μ .^{9,10}

The sodium hydroxide solution was acidified with 10% sulfuric acid and extracted with ether. The ether extract was dried over anhydrous magnesium sulfate and distilled. Two grams (40%) of liquid VI was obtained, b.p. 107° (2 mm.), n_D^{20} 1.4242. It did not decolorize potassium permanganate solution.

Anal. Calcd. for C₉H₁₁F₃O₂: C, 51.43; H, 6.19; F, 27.14. Found: C, 51.46; H, 6.16; F, 27.34.

Diels-Alder Reaction of 1-Phenyl-1,3-butadiene and *trans*-4,4,4-Trifluorocrotonic Acid.—A mixture of 13.2 g. (0.102 mole) of 1-phenyl-1,3-butadiene, 14 g. (0.1 mole) of *trans*-4,4,4-trifluorocrotonic acid and 80 ml. of petroleum ether (90–100°) was refluxed for 18 hr. After cooling to the room temperature, the mixture was filtered and chilled. A white solid IVA separated out. It was filtered and recrystallized from aqueous acetic acid to give 9.8 g. (36%) of product, m.p. 143–144.5°.

Anal. Calcd. for C₁₄H₁₈F₃O₂: C, 62.22; H, 4.82; F, 21.11. Found: C, 62.30; H, 4.99; F, 21.28.

The petroleum ether mother liquor was evaporated suc-

(5) All temperatures are uncorrected, the melting points were determined with a Fisher-Johns melting points apparatus. Carbon and hydrogen analyses by Mrs. C. S. Yeh of this department. Fluorine analyses by Clark Microanalytical Laboratory, Urbana, Illinois.

(6) E. T. McBee, O. R. Pierce and D. D. Smith, *THIS JOURNAL*, **76**, 3722 (1954).

(7) M. G. Voronkov, *et al.*, *J. Gen. Chem. (U.S.S.R.)*, **19**, 1357 (1949).

(8) I. Wender, *et al.*, *THIS JOURNAL*, **74**, 4079 (1952).

(9) H. W. Thompson and R. B. Temple, *J. Chem. Soc.*, 1432 (1948).

(10) C. G. Cannon and G. B. B. M. Sutherland, *Spectrochim. Acta*, **4**, 373 (1951).

(1) E. T. McBee, C. W. Roberts and C. G. Hsu, *THIS JOURNAL*, **78**, 3389 (1956).

(2) N. D. Zelinsky, *Ber.*, **57B**, 2055 (1924); **66B**, 1420 (1933).

(3) M. R. Pettit and J. C. Tatlow, *J. Chem. Soc.*, 3459 (1951).

(4) (a) E. Clar, *Ber.*, **65**, 503 (1932); (b) D. D. Phillips and J. Cason, *THIS JOURNAL*, **74**, 2934 (1952); (c) E. T. McBee, C. G. Hsu, O. R. Pierce and C. W. Roberts, *ibid.*, **77**, 915 (1955).

cessively and a second solid IVB was obtained, m.p. 90–110°. This, on recrystallization from hexane, gave 10 g. (37%) of product, m.p. 122.5–124.5°.

Anal. Calcd. for $C_{14}H_{13}F_3O_2$: C, 62.22; H, 4.82; F, 21.11. Found: C, 62.33; H, 4.99; F, 20.59.

Dehydrogenation and Decarboxylation of Adducts IVA and IVB. A.—A mixture of adduct IVA (5 g., 0.019 mole) and 10% palladium-on-charcoal (2.5 g.) was heated at 290–300° until the gas ceased (about 2.5 hr.). The resulting mixture was boiled with 30 ml. of benzene for 1 hr. and filtered. The benzene solution was refluxed with 20 ml. of 10% sodium hydroxide for an additional hour. The benzene solution was separated and dried over calcium chloride. Upon distillation, 2.7 g. (55%) of *m*-trifluoromethylbiphenyl (V) was obtained, b.p. 77° (1.5 mm.), n_D^{25} 1.5342 (lit. b.p. 118–119° (13 mm.), n_D^{30} 1.5304¹¹; b.p. 117–120° (13 mm.), n_D^{30} 1.5302³). The infrared spectrum of V showed three bands for *m*-substituted biphenyl at 12.45, 13.25 and 14.3 μ .¹⁰ The ultraviolet spectrum of V showed a maximum at 249 $m\mu$ ($\log \epsilon$ 4.17), which was comparable with that of biphenyl¹² (λ_{max} 248 $m\mu$, $\log \epsilon$ 4.22) and 3,3'-bis-(trifluoromethyl)-biphenyl,¹³ (λ_{max} 245 $m\mu$, $\log \epsilon$ 4.25, in isoöctane).

Anal. Calcd. for $C_{18}H_9F_3$: C, 70.27; H, 4.05; F, 25.68. Found: C, 70.08; H, 4.04; F, 25.38.

The sodium hydroxide solution was acidified with 10% sulfuric acid and extracted with ether. The ether extract was dried over anhydrous magnesium sulfate and distilled. About 0.1–0.2 g. of white solid was left in the flask; this was recrystallized from aqueous acetic acid to give pure 2-trifluoromethyl-6-phenylcyclohexanecarboxylic acid, m.p. 191.5–193.5°.

Anal. Calcd. for $C_{14}H_9F_3O_2$: C, 61.76; H, 5.52; F, 20.96. Found: C, 61.71; H, 5.54; F, 20.32.

B.—Adduct IVB was dehydrogenated in the same manner. The products in these two experiments were proved to be identical. They had the same physical properties and infrared spectra.

Hydrolysis of *m*-Trifluoromethylbiphenyl (V).—*m*-Trifluoromethylbiphenyl was hydrolyzed in concentrated sulfuric acid to the *m*-biphenylcarboxylic acid (VI) by the procedure of Pettit and Tatlow.³ The melting point, 166°, of compound VI was higher than the value reported, m.p. 164°, but checked with the value reported by Jacobson and Lischke, m.p. 166°.¹⁴

The ultraviolet spectrum of VI showed a maximum at 231

(11) C. K. Bradsher and J. B. Bond, *THIS JOURNAL*, **71**, 2659 (1949).

(12) R. A. Friedel, M. Orchin and L. Reggel, *ibid.*, **70**, 199 (1948).

(13) S. D. Ross, M. Markarian and M. Schwarz, *ibid.*, **75**, 4967 (1953).

(14) P. Jacobson and W. Lischke, *Ber.*, **28**, 2541 (1895).

$m\mu$ ($\log \epsilon$ 4.32) and a shoulder at 250 $m\mu$ ($\log \epsilon$ 4.10) which were comparable with those of 3,3'-biphenyldicarboxylic acid (shoulder λ_{max} 252 $m\mu$, $\log \epsilon$ 4.19).¹⁵

Diels-Alder Reaction of 1,3-Butadiene and *trans*-4,4,4-Trifluorocrotonic Acid.—Butadiene (6 g., 0.11 mole) was heated in a Carius tube with *trans*-4,4,4-trifluorocrotonic acid (14 g., 0.1 mole) for 3 hr. at 150°. A yellow solid resulted; this was dissolved in ether, transferred and distilled. Eighteen grams (93%) of adduct VII was obtained, b.p. 112° (5 mm.), m.p. 89–91° (from *n*-heptane).

Anal. Calcd. for $C_8H_9F_3O_2$: C, 49.48; H, 4.64; F, 29.38. Found: C, 49.60; H, 5.01; F, 29.06.

Dehydrogenation of Adduct VII.—Adduct VII (5 g., 0.026 mole) was dehydrogenated with a 10% palladium-on-charcoal catalyst (2.5 g.) at 300–310°. One gram (20%) of *o*-trifluoromethylbenzoic acid (VIII) was obtained, m.p. 107–108° (recrystallized from *n*-hexane, lit. m.p. 107–107.5°,¹⁶ 108–109°¹⁷). In addition, 1 g. of high boiling acidic product was also obtained which probably was the disproportionation product, 2-trifluoromethylhexahydrobenzoic acid. The infrared spectrum of VIII showed an acid carbonyl band at 5.9 μ and a shifted *ortho* disubstituted band at 13.1 μ .⁹

Diels-Alder Reaction of Anthracene and *trans*-4,4,4-Trifluorocrotonic Acid.—A mixture of 3.5 g. (0.025 mole) of *trans*-4,4,4-trifluorocrotonic acid and 2.3 g. (0.013 mole) of anthracene in 15 ml. of benzene was heated in a Carius tube at 190° for 14 hr. The resulting dark brown solution was evaporated under reduced pressure to remove all the solvent. The residue was washed with 50 ml. of water, dissolved in absolute ethanol, decolorized and precipitated by addition of water. After recrystallization from aqueous ethanol 3.8 g. (92%) of adduct IX was obtained, m.p. 182–183°.

Anal. Calcd. for $C_{18}H_{13}F_3O_2$: C, 67.93; H, 4.09; F, 19.92. Found: C, 67.94; H, 4.27; F, 18.27.

Absorption Spectra.—Ultraviolet absorption spectra were determined with a Cary recording spectrophotometer in 95% ethanol at a concentration of 3.4×10^{-4} mole per liter. The infrared spectra were obtained either using the pure liquids or using Nujol mulls of the solids with a Perkin-Elmer, model 21 recording spectrometer.

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(15) B. Williamson and W. H. Rodebush, *THIS JOURNAL*, **63**, 3018 (1941).

(16) (a) S. DeBrouwer, *Bull. soc. chim. Belg.*, **39**, 298 (1930); (b) R. G. Jones, *THIS JOURNAL*, **69**, 2346 (1947).

(17) J. D. Roberts and D. Y. Curtin, *ibid.*, **68**, 1658 (1946).