tem. At *p*H 6.85, K_m values have been determined by plotting *s versus s/v* and determining the negative *y* intercept. For both substrates a value of 7×10^{-4} mole/l. has been found.

These results indicate that under these conditions at equimolar concentrations the enzyme hydrolyzes isomaltotriose more readily than isomaltose. The chain length specificity of the enzyme is therefore raised to include the trisaccharide. With the availability of suitable substrates it would be of interest further to delineate the chain length specificity of the enzyme.

The ability of digestive enzyme to hydrolyze isomaltotriose brings to mind the interesting possibility of the occurrence of two adjacent α-1,6-linkages of starch. Such "double" branch points could conceivably arise from the action of a branching enzyme in which an α-1,6-linked disaccharide or oligosaccharide such as isomaltose or "panose" served as cosubstrate or acceptor of the linear segment transferred in the branching reaction. Such a reaction in which maltose acts as a cosubstrate has been described in the case of *Polytomella coeca* branching enzyme.[9]

Experiments testing the specificities of branching enzymes from potato, liver, broad bean and wrinkled pea with maltose, isomaltose and "panose" as cosubstrates are in progress and thus far have shown no stimulation of the branching reaction by these saccharides. Because of their relation to the mechanism of action of branching enzymes, these experiments will be reported separately.

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The Diels–Alder Reaction of Cyclopentadiene with Nitroölefins. Tertiary Nitro Adducts

BY WAYLAND E. NOLAND AND RONALD E. BAMBURY[1]

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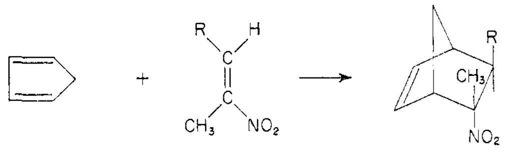
Cyclopentadiene is known to undergo Diels–Alder reactions with several unsubstituted and 2-substituted nitroölefins: nitroethylene[2] in 61[3] to 66%[4] yield, 1-nitropropene in 55[2] to 59%[5] yield, 1-nitropentene in 72% yield[2] and β-nitrostyrene in 88[6] to 95%[7,8] yield, giving adducts containing secondary nitro groups. Nightingale and Janes[9] report, however, that all efforts to condense the longer chain 2-substituted nitroölefin, 1-nitroheptene, with cyclopentadiene were unsuccessful. Also, they report that 3-nitro-3-hexene, 2-nitro-4-methyl-2-pentene and 2-nitro-4-ethyl-2-hexene, which would yield tertiary nitro adducts, did not add to cyclopentadiene. Similarly, it has been found[10] that β-methyl-β-nitrostyrene and β-ethyl-β-nitrostyrene do not react with cyclopentadiene in refluxing toluene solution, the only product being dicyclopentadiene.

The Diels–Alder reaction of cyclopentadiene with a nitroölefin may be regarded as involving a competition between two dienophiles, the nitroölefin and cyclopentadiene itself. Whether or not a nitroölefin adduct is formed will depend upon the relative reactivity of the nitroölefin and cyclopentadiene, acting as a dienophile, except at temperatures sufficiently high so that the formation of dicyclopentadiene is reversible. The great tendency of the simplest non-aromatic nitroölefins to polymerize is a complicating factor. Refluxing the simplest 2,2-disubstituted nitroölefin, 2-methyl-1-nitropropene, which shows very little tendency to polymerize, with dicyclopentadiene at 150–180° gave the nitro adduct in 10–15% yield (not isolated in pure form),[11] but in our hands under the mild conditions of refluxing with cyclopentadiene on the steambath, dicyclopentadiene was the only product isolated.

In an attempt to obtain tertiary nitro adducts, we have carried out reactions between cyclopentadiene and the simplest 1- and 1,2-disubstituted nitroölefins. 2-Nitropropene reacted vigorously with cyclopentadiene and, after considerable purification, a waxy solid adduct, m.p. 104°, was obtained in 27% yield. 2-Nitro-2-butene also reacted, but without vigor, and another waxy solid adduct, m.p. 84.5–86.5°, was obtained in 41% yield.



R = H or CH_3

To our knowledge, these are the first examples of the formation of tertiary nitro compounds by the Diels–Alder reaction. The tertiary nitro adducts have considerably higher melting points than those of the secondary nitro adducts previously reported.

Experimental

Melting points were determined on a calibrated thermometer.

5-Nitro-5-methylbicyclo[2,2,1]-2-heptene (With Paul E. Swartzentruber).—The procedure[2,5] for the preparation of 5-*endo*-nitro-6-*exo*-methylbicyclo[2,2,1]-2-heptene was adapted for use here.

Previously cooled freshly cracked cyclopentadiene (87.8 g., 1.33 moles), glacial acetic acid (65 cc.), 2-nitropropene[12] (90.6 g., 1.04 moles) and hydroquinone (0.1 g.) were mixed at about 10°, where no apparent reaction took place. The solution was warmed gently to 30° and heating was discon-

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[1] Taken in part from the senior research of Ronald E. Bambury, University of Minnesota, 1954–1955.

[2] K. Alder, H. F. Rickert and E. Windemuth, *Ber.*, **71B**, 2451 (1938).

[3] J. D. Roberts, C. C. Lee and W. H. Saunders, Jr., THIS JOURNAL, **76**, 4501 (1954).

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[5] E. E. Van Tamelen and R. J. Thiede, THIS JOURNAL, **74**, 2615 (1952).

[6] W. E. Parham, W. T. Hunter and R. Hanson, *ibid.*, **73**, 5068 (1951).

[7] C. F. H. Allen and A. Bell, *ibid.*, **61**, 521 (1939).

[8] C. F. H. Allen, A. Bell and J. W. Gates, Jr., *J. Org. Chem.*, **8**, 373 (1943).

[9] D. Nightingale and J. R. Janes, THIS JOURNAL, **66**, 352 (1944).

[10] With Paul Melnychyn and Gerald R. Modig in these laboratories.

[11] D. S. Noyce, THIS JOURNAL, **73**, 20 (1951).

[12] (a) B. M. Vanderbilt and H. B. Hass, *Ind. Eng. Chem.*, **32**, 34 (1940); (b) G. D. Buckley and C. W. Scaife, *J. Chem. Soc.*, 1471 (1947).

tinued. The temperature rose slowly at first, and then more rapidly, to 45°, at which point the solution was cooled in an alcohol–Dry Ice-bath. In spite of shaking in the Dry Ice-bath, the temperature rose rapidly to 98°, white fumes were evolved and the solution refluxed vigorously. During this time the color changed from yellow to green, brown and almost black. After a few minutes the temperature began to drop slowly. When the reaction appeared to have subsided completely, the solution was warmed at 80–85° for 3.5 hours. Distillation under reduced pressure removed a forerun containing largely acetic acid, followed by a yellowish-orange solid, b.p. 90–105° (18 mm.), having a strong odor of dicyclopentadiene. Redistillation removed another forerun and gave a waxy white solid (42.4 g., 0.276 mole, 27%), b.p. 105–110° (18 mm.). Recrystallization from ethanol–water gave a sample, m.p. 88–93°. Two sublimations at 1 mm. yielded white crystals of 5-nitro-5-methylbicyclo[2,2,1]-2-heptene, m.p. 104°, having an odor resembling dicyclopentadiene; ν_{NO_2} (cm.$^{-1}$) 1537, 1387 or 1357 in Nujol, 1530, 1388 or 1357 in $CHCl_3$.

Anal. Calcd. for $C_8H_{11}NO_2$ (153.18): C, 62.72; H, 7.24; N, 9.14. Found: C, 62.57, 62.76; H, 7.34, 7.15; N, 9.02.

5-Nitro-5,6-dimethylbicyclo[2,2,1]-2-heptene (With Peter Pappas).—Freshly cracked cyclopentadiene (68.0 g., 1.03 moles) and 2-nitro-2-butene[13] (32.7 g., 0.323 mole) were warmed for 5 hours on a steam-bath. During this time the temperature of the refluxing liquid rose slowly from 54 to 95° as the cyclopentadiene reacted or dimerized. Two vacuum distillations yielded crude product (22.2 g., 0.133 mole, 41%), b.p. 65° (2 mm.), which solidified in the receiver. Several sublimations yielded waxy white crystals of 5-nitro-5,6-dimethylbicyclo[2,2,1]-2-heptene, m.p. 84.5–86.5°, having an odor resembling dicyclopentadiene; ν_{NO_2} (cm.$^{-1}$) 1531, 1388 or 1354 in Nujol, 1390 or 1355 in CS_2.

Anal. Calcd. for $C_9H_{13}NO_2$ (167.20): C, 64.65; H, 7.84; N, 8.38. Found: C, 64.75, 64.37, 64.38; H, 8.18, 8.03, 7.65; N, 8.41, 8.32, 8.42.

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[13] H. B. Hass, A. G. Susie and R. L. Heider, *J. Org. Chem.*, **15**, 8 (1950).

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The Reduction of Fluorine-containing Carbonyl Compounds with Heptafluoropropyllithium[1]

BY E. T. MCBEE, C. W. ROBERTS AND SADIE G. CURTIS[2]

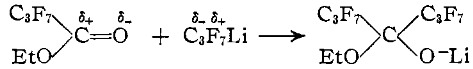
RECEIVED JUNE 24, 1955

The preparation and some reactions of perfluoropropyllithium recently were reported.[3] The preparation of perfluoro-4-propyl-4-heptanol (I) from heptafluoropropyllithium and ethyl heptafluorobutyrate was claimed. An attempt to apply this reaction to the preparation of perfluoro-4-methyl-4-heptanol from the organolithium reagent and ethyl trifluoroacetate was unsuccessful; this led to a repetition of the earlier work. The exchange reaction between methyllithium and heptafluoro-1-iodopropane went smoothly, and addition of ethyl heptafluorobutyrate to the perfluoroalkyllithium resulted in the isolation of a product having physical properties, derivatives, and an infrared spectrum identical with those reported for I.[3,4] However, a comparison of the physical properties of the alcohol, and those of its 3,5-dinitrobenzoate, with those reported for 1,1,1,2,2,3,3,5,5,6,6,7,7,7-tetradecafluoro-4-heptanol[5] (II) indicated that the product actually obtained was the secondary alcohol II. Lithium aluminum hydride reduction of tetradecafluoro-4-heptanone (III) gave an authentic sample of the secondary alcohol. The analytical data for three derivatives of the alcohol (see experimental) provide further evidence that this product is the secondary alcohol II. The infrared spectrum of this alcohol is in agreement with data previously reported for II.[5,6]

Further attempts to prepare I from the reaction of heptafluoropropyllithium with the ester produced only II and III in varying yields depending on the conditions (Table I). By-products of the reaction were hexafluoropropene (from decomposition of the organolithium reagent), small amounts of perfluorohexane and tetradecafluoro-4-methyl-4-heptanol (IV), and large amounts of polymeric material. Attempts to prepare I by treating III with heptafluoropropyllithium were unsuccessful, resulting in the formation of hexafluoropropene and, in one instance, a 20% yield of IV. A large part of the ketone was recovered from the reactions.[7]

There are numerous examples in the literature of reduction of a carbonyl compound to the corresponding alcohol by a Grignard reagent.[9] In the present work the reaction of heptafluoropropylmagnesium iodide with ethyl heptafluorobutyrate gave a small amount of the secondary alcohol II. Since there is no β-hydrogen on this Grignard reagent, the Whitmore mechanism does not apply, and it was concluded[7] that the mechanism probably involves a hydride shift from the ether of solvation. No previous instance of reduction by an organolithium reagent of this type has been reported.

Table I indicates that the time of reaction has a marked effect on the products formed in the reaction of heptafluoropropyllithium with ethyl heptafluorobutyrate. A shorter time favors the formation of the ketone III, and a longer time results in reduction to the secondary alcohol II. The initial reaction is undoubtedly the addition of one molecule of the organolithium to the carbonyl group of the ester.[10]



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[1] From a thesis submitted by S. G. Curtis to the Graduate School, Purdue University, in partial fulfillment of the requirements for the degree of Master of Science in Chemistry, January, 1955.

[2] National Science Foundation Fellow, 1952–1953.

[3] O. R. Pierce, E. T. McBee and G. F. Judd, THIS JOURNAL, **76**, 474 (1954).

[4] G. F. Judd, Doctorate Thesis, Purdue University, 1953.

[5] A. L. Henne and W. C. Francis, THIS JOURNAL, **75**, 991 (1953).

[6] R. N. Haszeldine, *J. Chem. Soc.*, 1757 (1953).

[7] R. N. Haszeldine, *ibid.*, 748 (1953), has reported the formation of I from the reaction of heptafluoropropylmagnesium iodide with ethyl heptafluorobutyrate. No properties were reported, however, and other workers[8] have not been able to duplicate these results.

[8] A. L. Henne and W. C. Francis, THIS JOURNAL, **75**, 992 (1953).

[9] This is particularly common in reactions of Grignard reagents with fluorine-containing carbonyl compounds; see also E. T. McBee, O. R. Pierce and D. D. Meyer, *ibid.*, **77**, 83 (1955), for lead references.

[10] C. G. Swain and L. Kent, *ibid.*, **72**, 518 (1950), have proposed a mechanism for the reaction of alkyllithium reagents with ketones, involving the slow, reversible formation of a complex between the lithium atom and the carbonyl oxygen followed by a rapid intramolecular rearrangement. However, it has been demonstrated that there is little, if any, complexing between fluorine-containing carbonyl compounds and magnesium bromide.[9] Since magnesium bromide is undoubtedly a stronger complexing agent than an organolithium reagent, it is not likely that such a complex is formed in the present case. It is not necessary to assume the formation of a complex to explain addition to a fluorine-containing carbonyl compound. The inductive effect of the perfluoroalkyl group is sufficient to render the carbonyl carbon quite positive.