[Contribution from the Northern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture]

Reactions of Conjugated Fatty Acids. IV. Diels-Alder Adducts of 9,11-Octadecadienoic Acid[1]

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Adducts of *trans,trans*-9,11-octadecadienoic acid and dienophiles including nitroethylene, β-nitrostyrene, acrylic acid, acrylonitrile, acrolein, methacrolein, methyl vinyl ketone, methyl vinyl sulfone, and acetylene carboxylic acid have been prepared. The presence of a six-membered ring in the adducts of acrolein, acrylic acid, and acetylene carboxylic acid was demonstrated by dehydrogenation of the latter adduct and oxidation of the product to trimellitic acid. Hydrogenation of the acrylic acid and the acetylene carboxylic acid adduct gave the same product. Oxidation of the acrolein adduct gave the acrylic acid adduct. The nitroethylene adduct has been shown to exist in two isomeric forms.

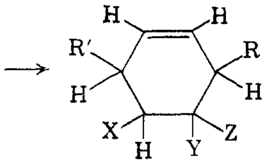
Only a few examples of Diels-Alder-type adducts of dienophiles and pure homogeneous isomers of long-chain conjugated fatty acids have been reported. Among these are the adducts of maleic anhydride with α-, and β-eleostearic acids,[2] α-, and β-licanic acids,[3] and 9,11-,[4] 8,10-,[5] and 10,12-[5] octadecadienoic acid and adducts of acrylonitrile[6] and acrylic esters[7] with β-eleostearic acid, β-licanic acid, and their methyl esters.

Adducts of dienophiles other than maleic anhydride with conjugated octadecadienoic acid do not appear to have been prepared previously. The purpose of this paper is to report the preparation of adducts of *trans, trans*-9,11-octadecadienoic acid with several dienophiles (other than maleic anhydride) of widely differing structures that illustrated the scope of diene synthesis with long-chain conjugated fatty acids. A proof of structure for the acrolein, acrylic acid, and acetylene carboxylic acid adducts is also given.

The adduct of β-eleostearic acid and maleic anhydride has been shown by chemical methods[8] to have the expected six-membered ring structure. Since the maleic anhydride adduct of *trans, trans*-9,11-octadecadienoic acid is obtained under very mild conditions (70°),[4] there is little reason to doubt that it, too, is a cyclohexene derivative. Because temperatures up to 200° were required to form certain of the adducts reported in this paper, evidence was desired that the expected six-membered ring did, in fact, form at these higher temperatures. The adducts obtained in pure condition are shown in Table I. These adducts have the generalized structure (III).

$CH_3(CH_2)_5CH{=}CH{-}CH{=}CH{-}(CH_2)_7COOH$ + $XCH{=}CYZ$

I II



III

$R' = CH_3(CH_2)_5{-}$
$R = {-}(CH_2)_7CO_2H$

If the dienophile adds in the opposite direction to that shown, an isomeric product would be obtained having a structure represented by interchanging the substituents at positions 4 and 5 of the cyclohexene ring. The adducts isolated consist of a mixture of these two isomers. The isomeric nitroethylene adducts were separated. The structure of one of the isomeric adducts of acetylene carboxylic acid is shown by IV.

Crotonaldehyde, crotonic acid, *cis*- and *trans*-cinnamic acid, allyl chloride, allyl acetate, benzalacetone, β-chlorostyrene, and divinyl sulfone were also tried as dienophiles. These compounds were heated with I in chloroform benzene solution in sealed tubes for 24 hr. at temperatures from 150°–200° C. Reaction appeared to occur to a greater or less degree as determined by estimation of unreacted I recovered chromatographically. No adduct or other product of definite constitution could, however, be isolated. When acrylamide was used as a dienophile, only polymers of acrylamide were obtained. Attempts to inhibit this polymerization were unsuccessful.

In general, our results are those expected on the basis that the dienophile should be capable of electron shifts that are required by the anionoid-cat-

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[1] Presented at the Atlantic City meeting of the American Chemical Society, September 1956. Previous paper in series *J. Am. Oil Chemists' Soc.*, **33**, 278 (1956).

[2] R. S. Morrell and H. Samuels, *J. Chem. Soc.*, 2251 (1932).

[3] R. S. Morrell and W. R. Davis, *J. Chem. Soc.*, 1481 (1936).

[4] J. Boeseken and R. Hoevers, *Rec. trav. chim.*, **49**, 1165 (1930).

[5] J. D. Von Mikusch, *J. Am. Oil Chemists' Soc.*, **29**, 114 (1952).

[6] H. A. Bruson and W. D. Niederhauser, U. S. Patent **2,440,140**; *Chem. Abstr.*, **42**, 6376 (1948).

[7] H. A. Bruson and W. D. Niederhauser, U. S. Patent 2,452,029; *Chem. Abstr.*, **43**, 2034 (1949).

[8] I. J. Rinkes, *Rec. trav. chim.*, **62**, 557 (1943).

TABLE I

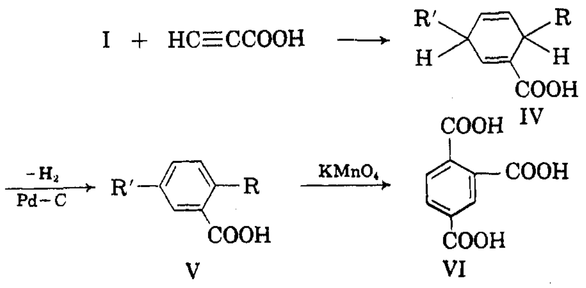
DIELS-ALDER ADDUCTS OF *trans*, *trans*-9,11-OCTADECADIENOIC ACID (I) AND DIENOPHILES XCH = CYZ (II)

Dienophile			Molar Ratio	Temp.,	Time,	Isola-	Yield,	Con-	Analyses			
									Calcd.		Found	
X	Y	Z	II/I	° C.	Hr.	tion[a]	%	stants	C	H	C	H
H	H	NO_2	1.6	Reflux	48[b]	A	16.2[d]	m.p. 85–90°	67.89	9.98	68.09	9.88[d]
							25.2[e]	n_D^{30} 1.4870			67.92	9.82[e]
C_6H_5	H	NO_2	1.0	110	90[b]	A	27.0	liquid	72.69	9.15	72.73	9.24
H	H	COOH	1.5	200	24[b]	B	96.0	n_D^{28} 1.4858	71.55	10.29	71.46	10.17
H	H	CN	1.5	200	24[b]	A	27.0	m.p. 67–77°	75.62	10.58	75.92	10.56
H	H	CHO	2.5	100	22[c]	A	97.0	liquid	74.95	10.78	74.98	10.78
H	CH_3	CHO	2.5	100	20[c]	A	87.0	liquid	75.40	10.92	75.42	10.92
H	H	$COCH_3$	2.5	150	24[c]	A	67.0	liquid	75.40	10.92	75.20	10.74
H	H	SO_2CH_3	0.7	200	24[b]	B	79.5	n_D^{30} 1.4955	65.25	9.91	65.22	9.68
Acetylene carboxylic acid			1.5	130	24[b]	B	Quant.	liquid	71.96	9.78	71.54	9.56

[a] By chromatography. Refer to experimental for details of procedures A and B. [b] Benzene used as solvent. [c] Chloroform used as solvent. [d] Solid isomer. [e] Liquid isomer.

ionoid[9,10] and the ion-pair[11] theories of the Diels-Alder reaction.

To establish the 6-member cyclic structure for the adducts, acetylene carboxylic acid was added to I yielding IV plus its isomer. This adduct was readily dehydrogenated with palladium on charcoal to give V in which the presence of the benzene ring was demonstrated by ultraviolet spectroscopy. V was then oxidized to trimellitic acid (VI), identified by comparison with an authentic specimen prepared by oxidation of pseudocumene.



Further relationships among certain of the adducts were obtained by oxidation of the acrolein adduct to an acid having an infrared spectrum identical with that of the acrylic acid adduct. Hydrogenation of IV and of the acrylic acid adduct likewise gave products having identical infrared spectra.

EXPERIMENTAL

Starting materials. Nitroethylene[12] was prepared by dehydration of 2-nitroethanol.[13] β-Nitrostyrene was prepared according to instructions in *Organic Syntheses*.[14] Methyl vinyl sulfone was synthesized by the method of Buckley *et al.*[15] Acetylene carboxylic acid was prepared by the method of Ingold.[16] *Trans,trans*-9,11-octadecadienoic acid was obtained by dehydration of ricinelaidic acid.[17] Other materials used were prepared by purification of chemicals from commercial sources.

Preparation of adducts. The diene, dienophile, solvent, and a trace of hydroquinone were heated together in a flask or sealed tube under a nitrogen atmosphere. Molar ratio of dienophile to diene, solvent used, and time and temperature of heating are specified in Table I. Approximately 5 ml. of solvent per gram of solute was used. All of the reactions except that with nitroethylene were carried out in sealed tubes. At the completion of the reaction, solvent was removed first at atmospheric pressure and finally *in vacuo*. Purification was effected by chromatography.

Chromatography of products. Two chromatographic techniques were employed as indicated in Table I. Method A employed silicic acid columns prepared according to Nijcamp.[18] Method B was the procedure described by Begemann, *et al.*[19] With either procedure two bands were obtained. The lower, fast-moving band was unreacted *trans,-trans*-9,11-octadecadienoic acid. The upper, slow-moving band was the adduct. Elution of the slow-moving band yielded the adduct in analytical purity. Yields were estimated by weighing the recovered purified adduct or by titration of the recovered fatty acid eluted initially from the column. Products were characterized by elementary and infrared spectra analyses.

The nitroethylene adduct eluted from the column (2.83 g.) was triturated with pentane-hexane. A white insoluble solid (0.88 g.) and a viscous soluble oil (1.6 g.) were obtained. Elemental and spectral analyses showed that these products were isomeric.

Dehydrogenation of IV. A solution of 0.81 g. of VI, 0.30 g. of 10% palladium on charcoal, and 25 ml. of xylene was maintained at reflux in a conventional dehydrogenation apparatus with carbon dioxide as sweep gas and 50% aqueous potassium hydroxide in the gas buret. The theoretical amount of hydrogen was evolved. There was obtained 0.70 g. (85%) of V, m.p. 64–70° after removal of catalyst and solvent. Ultraviolet spectroscopy showed that V had a benzenoid structure: λ_{max} 285.0 mμ; ε, 1119; shoulder at 222.5 mμ; ε, 6091.

Oxidation of V. A solution of 0.52 g. of V, 4.5 g. of potas-

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(9) B. J. F. Hudson and R. Robinson, *J. Chem. Soc.*, 715 (1941).

(10) J. S. Meek and J. W. Ragsdale, *J. Am. Chem. Soc.*, **70**, 2502 (1948).

(11) R. B. Woodward, *J. Am. Chem. Soc.*, **64**, 3058 (1942).

(12) G. D. Buckley and C. W. Seaife, *J. Chem. Soc.*, 1471 (1947).

(13) W. E. Noland and P. J. Hartman, *J. Am. Chem. Soc.*, **76**, 3227 (1954).

(14) *Org. Syntheses*, Coll. Vol. I, 405 (1932).

(15) G. D. Buckley, J. L. Charlish, and J. D. Rose, *J. Chem. Soc.*, 1514 (1947).

(16) E. H. Ingold, *J. Chem. Soc.*, 1199 (1925).

(17) C. Mangold, *Monatsh.* **15**, 309 (1894).

(18) H. J. Nijcamp, *Anal. Chem. Acta*, **10**, 448 (1954).

(19) P. H. Begemann, Kepplor, and H. A. Boelkenoogen, *Rec. trav. chim.*, **69**, 439 (1950).

sium permanganate, 4.0 ml. of 10% aqueous sodium hydroxide, and 90 ml. of water was refluxed for 4 hr. with constant stirring. The product (0.23 g., 67%), isolated by usual means, melted at 210–225° (most at 220–225°). Trituration with hot benzene sharpened the melting point to 224–225.5°.

A sample of trimellitic acid (VI) was prepared by a similar oxidation of pseudocumene. It melted at 214–225° (most at 220–225°). There was no depression of the melting point of a mixture of this product with that obtained from V. Infrared spectra of the two samples of trimellitic acid were identical.

Hydrogenation of IV and of the acrylic acid adduct. These products were hydrogenated at 38 p.s.i. in acetic acid solution with Adam's catalyst. About 2 hr. was required for each hydrogenation. The product from IV was isolated in 90% yield; n_D^{30} 1.4750. The product from the acrylic acid adduct also was isolated in 90% yield; n_D^{30} 1.4780. Infrared spectra of the two products were identical.

Oxidation of the acrolein adduct. The acrolein adduct was oxidized with silver oxide.[20] The product was isolated by chromatographic method B.

Anal. Calcd. for $C_{21}H_{36}O_4$: C, 71.55; H, 10.29. Found: C, 71.38; H, 10.09.

The infrared spectrum of this product was identical with that of the acrylic acid adduct.

Peoria, Ill.

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(20) R. R. Burtner and J. W. Cusic, *J. Am. Chem. Soc.*, **65**, 265 (1943).

[Contribution from the Department of Chemistry, Florida A. and M. University]

Bimolecular Compounds from Dissolving-Metal Reductions of *N*-Heterocyclics[1]

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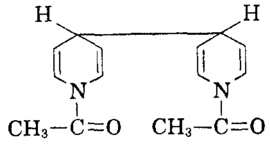
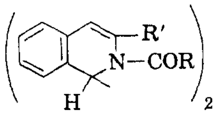
Isoquinoline and its 3-methyl homolog yield the corresponding diacyltetrahydrobiisoquinolines by reduction with zinc dust in either acetic anhydride or benzoyl chloride. Evidence is presented to establish that these dimeric compounds are derivatives of 1,1′-biisoquinoline. From a similar reduction of acridine, biacridanyl is obtained.

Pyridine was reported by Dimroth and Heene[2] to be reduced by zinc in acetic anhydride to 1,1′-diacetyl-1,4,1′,4′-tetrahydro-4,4′-bipyridine (I). When quinoline was reduced under the same conditions the product was assumed to be a bimolecular derivative analogous to I, but no analytical data were given for the product. We originally reinvestigated the zinc–acetic anhydride reduction of quinoline to determine whether the theoretical biquinoline compound was coupled at the 2- or 4- positions, but we were unable to isolate a product identifiable as a diacetyltetrahydrobiquinoline. The main reaction product was in amorphous organozinc complex or mixture.[3]

Quinoline, however, proved to be the anomalous case, for isoquinoline was reduced, like pyridine, to the expected 2,2′-diacetyl-1,2,1′,2′-tetrahydro-1,1′-biisoquinoline (IIa) in 18% yield. A similar compound (IIb) was obtained from 3-methylisoquinoline (1.4% yield), and by substituting benzoyl chloride for acetic anhydride a corresponding dibenzoyltetrahydrobiisoquinoline (IIc) was prepared from isoquinoline in 6% yield.





IIa $R = CH_3, R' = H$
IIb $R = CH_3, R' = CH_3$
IIc $R = C_6H_5, R' = H$

It was postulated that the dimeric isoquinoline compounds should be 2,2′-diacyl-1,2,1′,2′-tetrahydro-1,1′-biisoquinolines (*cf.* II) on the basis that a proposed intermediate 2-acylisoquinolinium ion would bear the highest positive charge at the 1- position,[4] and nucleophilic attack by zinc would occur here.[5] Most of the work of structure determination was done with diacetyltetrahydrobiisoquinoline (IIa) and involved attempts to convert it to an aromatic species since a number of biisoquinolines are known. Air oxidation of the ethanolic solution was successful for degrading the pyridine dimer (I) to 4,4′-bipyridine, but when this method was applied to the isoquinoline analog the only product identifiable was isoquinoline. In other attempts iodine

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(1) We wish to acknowledge a Frederick Cottrell grant from the Research Corp.

(2) Dimroth and Heene, *Ber.*, **54**, 2934 (1921).

(3) Unpublished results, this laboratory.

(4) M. J. S. Dewar, in *Progress in Organic Chemistry* (J. W. Cook, Editor) Academic Press, Inc., New York, N. Y., 1953, Vol. II, p. 13.

(5) The question whether the actual coupling reaction involves ionic or free radical intermediates appears complicated in these heterogeneous systems and probably should be approached through the concept of the chemisorption of the organic cation on the metal surface, which, according to Brewster, *J. Am. Chem. Soc.*, **76**, 6361 (1954), may exist as a resonance hybrid of several ionic or radical forms with participation of the electrons of the metal undergoing oxidation. [*Cf.* also Fouad and Herringshaw, *J. Chem. Soc.*, 1207 (1954) and Morton and Lanpher, *J. Org. Chem.*, **21**, 93 (1956).] One observation that follows from this hypothesis is that proposals of one- or two-electron changes need not be a problem for metals for which extraordinary oxidation states would otherwise have to be postulated.