The 1.40 g. of white solid was recrystallized successively from acetone–water, acetone–benzene and ethanol–water to yield 0.24 g. of 2,3′-dicarboxydiphenyl ether, m.p. 220–221°. The melting points reported for this acid are 202°[7] and 215°.[8] A mixture of the product and an authentic specimen[21] of 2,3′-dicarboxydiphenyl ether (m.p. found 205–210°) melted over the range 208–215°. The infrared spectra of the two samples were superimposable.

Hydrogenolysis of 4,6-Phenoxathiindicarboxylic Acid.— A mixture of 2.00 g. (0.007 mole) of 4,6-phenoxathiindicarboxylic acid, 600 ml. of 0.5% sodium carbonate solution and 25–30 g. of Raney nickel was stirred at 75° for 1.25 hr., filtered and worked up as in the preceding experiment. There was collected 1.5 g. of white solid melting over the range 109–230°.

When a solution of ferric chloride was added to a sample of the crude acid, there resulted a purple color which was of the same hue as that given by a salicylic acid blank. Authentic samples of benzoic acid[22] and 2,2′-dicarboxydiphenyl ether gave negative ferric chloride tests. It was believed that the reaction mixture contained benzoic acid, salicylic acid and 2,2′-dicarboxydiphenyl ether, the first two acids having been produced by cleavage of the diphenyl ether linkage.

The mixture was subjected to vacuum sublimation at 100–120°, yielding 1.12 g. of sublimate, melting range 112–129°. The residue was successively recrystallized from water and a mixture of benzene and methyl ethyl ketone to yield 0.20 g. (11.2%) of 2,2′-dicarboxydiphenyl ether, m.p. and mixed m.p. with an authentic specimen 227–229°. The infrared spectra of the product and the authentic specimen were identical.

Hydrogenolysis of 1,9-Phenoxathiindicarboxylic Acid 10-Dioxide.—A mixture of 3.20 g. (0.01 mole) of 1,9-phenoxa-

(21) Kindly provided by Dr. M. Tomita.

(22) Benzoic acid was isolated and identified as one of products from one run of the hydrogenolysis of 1,9-phenoxathiindicarboxylic acid 10-dioxide.

thiindicarboxylic acid 10-dioxide, 750 ml. of 0.5% sodium carbonate solution and ca. 40 g. of Raney nickel was stirred at 75° for 30 minutes, filtered and worked up according to the procedure used for the 1,6-diacid. There was collected 2.03 g. of white product, melting range 103–237°, and, upon further concentration of the aqueous filtrate, 0.34 g., melting range 108–289°. The larger fraction was digested with hot water and the hot suspension was filtered. Collected from the filter paper was 0.72 g. of crude product, m.p. 244–247°, which was recrystallized twice from acetone–water to yield 0.43 g. (16.7%) of 3,3′-dicarboxydiphenyl ether, m.p. 249–250°. A mixture of this product and an authentic specimen[20] of 3,3′-dicarboxydiphenyl ether (m.p. reported[8] 243–245°, found 247–251°) melted at 247–250°. The infrared spectra of the two samples were superimposable.

Dimetalation of Dibenzothiophene by n-Butyllithium (Attempted).[23]—An ethereal solution of dibenzothiophene and 2.2 molar equivalents of n-butyllithium was stirred at the reflux temperature for 36 hr. and then carbonated. Color Test II was negative at the time of carbonation. Following hydrolysis and acidification there was obtained a 90.9% yield of crude acid melting over the range 237–245°. The following fractions were separated after extraction with methanol: 35.4% of exceptionally pure 4-dibenzothiophenecarboxylic acid, m.p. 255–255.5° (identified by a mixed m.p. determination); 22.2%, m.p. 250–252°; and 16.7%, melting range 244–250°.

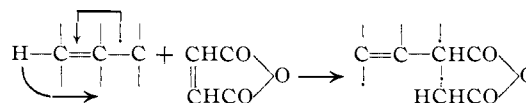
Thermal Addition of Monoölefins to Dienophiles

BY C. J. ALBISETTI, N. G. FISHER, M. J. HOGSED AND R. M. JOYCE

Olefins containing at least 3 carbons have been shown to add to α,β-unsaturated nitriles, esters and ketones at elevated temperatures to form δ,ε-unsaturated nitriles, esters and ketones, respectively. When the double bond of the initial product is terminal, a second molecule of the α,β-unsaturated compound can add, producing an unsaturated bifunctional product. Structures of the products indicate that the addition proceeds through the formation of a quasi-6-membered ring.

Several workers[1] have reported that nonconjugated olefinic compounds add to maleic anhydride at elevated temperatures. The uncatalyzed thermal addition of such monoölefins as butenes to maleic anhydride was first reported by Alder[2] to proceed by addition of allylic hydrogen across the double bond of maleic anhydride with the olefinic double bond remaining intact. More recent studies on the addition to maleic anhydride of methyl undecylenate,[3] methylenecyclohexane[4] and other olefins[5] demonstrate that the addition proceeds by direct attachment of the maleic anhydride to an olefinic carbon atom followed by double bond migration and transfer of a hydrogen to saturate the anhydride.

(1) E. A. Bevan, Oil and Colour Chem. Assoc., **34**, 1939 (1940); F. T. Clocker, U. S. Patent 2,188,882, 1940; W. G. Bickford, P. Krauczunas and D. H. Wheeler, Oil and Soap, **19**, 23 (1942).

(2) K. Alder, F. Pascher and A. Schmitz, Ber., **76B**, 27 (1943).

(3) J. Ross, A. I. Gebhart and J. F. Gerecht, THIS JOURNAL, **68**, 1373 (1946).

(4) R. T. Arnold and J. F. Dowdall, ibid., **70**, 2590 (1948).

(5) K. Alder and H. A. Dortmann, Ber., **85**, 556 (1952).

Addition of allylbenzene to aryl maleic anhydrides has been described,[6] but the utility of other dienophiles in this thermal addition reaction has not been reported.

We have investigated the scope of the reaction with regard to α,β-unsaturated compounds known to be dienophiles in the Diels–Alder diene addition and have also studied the influence of various olefinic structures. Thermal adducts with propylene and higher olefins have been obtained from a variety of known dienophiles including acrylonitrile, methacrylonitrile, methyl acrylate, methyl methacrylate, methyl vinyl ketone, ethyl vinyl sulfone, acrylic acid and diethyl vinylphosphonate. Olefins examined include propylene, the butenes,

(6) C. S. Rondestvedt and A. H. Filbey, J. Org. Chem., **19**, 548 (1954).

diisobutylene, β-pinene and several higher olefins. In each case, the product was a δ,ε-unsaturated compound of the type

$$C=C-C-\ \boxed{C-\ C-X}$$

H
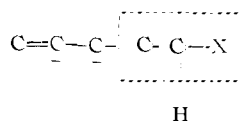
in which C–C represents the original position of the double bond in the olefinic component, H is the hydrogen atom which has migrated from an allylic position in the olefin, and C–C–X is the dienophile with activating group X (CN, CO₂R, etc.). For example, the adduct of 1-butene and methyl acrylate gave methyl heptanoate on hydrogenation and glutaric acid on oxidation after hydrolysis, indicating that compound I was the structure of the primary adduct.

$$CH_3CH_2CH{=}CH_2 + CH_2{=}CHCO_2CH_3 \longrightarrow$$
$$CH_3CH{=}CH(CH_2)_3CO_2CH_3$$
I
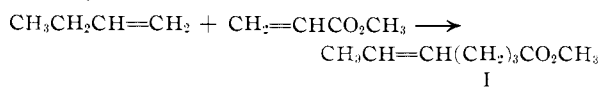
Addition of propylene to methyl acrylate gave methyl 5-hexenoate (CH₂=CHCH₂CH₂CH₂CO₂-CH₃). This compound was identified by conversion after hydrolysis to the known p-toluidide of 5-hexenoic acid. Hydrogenation of the unsaturated ester gave methyl caproate which was identified by conversion to caproamide. Isobutylene and methyl acrylate gave methyl 5-methyl-5-hexenoate (CH₂=C(CH₃)CH₂CH₂CH₂-CO₂CH₃) which exhibited terminal olefinic unsaturation in the infrared and which was converted by hydrogenation to the known methyl 5-methyl-hexanoate. The saturated ester was identified by conversion to the amide.

The structures of the products obtained by thermal addition of olefins to methyl acrylate are in accord with those predicted if the reaction follows the course outlined by Arnold.[4] Formation of the δ,ε-unsaturated products can be depicted by
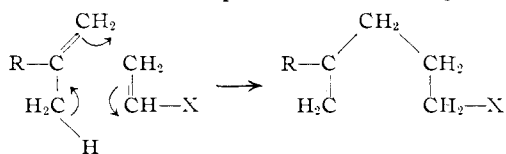
where X = CO₂R, CN, COR, SO₂R, etc.

Structures for the other thermal addition products described have been assigned by analogy with the products obtained from additions with methyl acrylate. In such cases as diisobutylene, where the double bond can shift into two different δ,ε-positions, the location of the double bond was not determined and the products are simply described as 1:1 adducts.
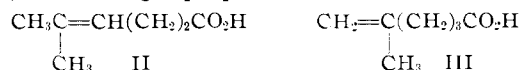
Thermal reaction of acrylonitrile with isobutylene gave 5-methyl-5-hexenenitrile in 49% yield.[7] The methylhexenenitrile gave formaldehyde and the expected 5-oxohexanenitrile on ozonization. Under approximately comparable conditions, diisobutylene, β-pinene, propylene, tetramethylethylene and 2-butene gave the corresponding δ,ε-unsaturated nitriles in 42, 41, 18, 9 and 4% yields. 1,1-Disubstituted ethylenes, i.e., olefins of the type RR'C=

(7) C. J. Albisetti and N. G. Fisher. U. S. Patent 2,641,607 (1953).

CH₂, were found to give higher yields than linear or non-terminal olefins in all the thermal addition reactions examined.

α-Methyl-δ,ε-unsaturated nitriles were obtained by thermal addition of olefins to methacrylonitrile but yields were low and isolation was difficult because of the concurrent thermal dimerization of the methacrylic component.[8] Similar difficulties owing to dimerization were encountered with olefin/methyl methacrylate additions. 3-Methylcrotononitrile did not add isobutylene under the conditions examined.

Ethyl vinyl sulfone, diethyl vinylphosphonate[9] and acrylic acid were also found to react with olefins in the thermal addition reaction with the formation of 1:1 adducts. Vinyl butyl ether was unreactive. The acrylic acid/isobutylene adduct was found by Raman spectroscopy and by ozonization to be approximately an 80:20 mixture of 5-methyl-4-hexenoic acid (II) and 5-methyl-5-hexenoic acid (III). The high proportion of II over the ex-

$$CH_3C{=}CH(CH_2)_2CO_2H \qquad CH_2{=}C(CH_2)_3CO_2H$$
$$\ \ |\qquad\qquad\qquad\qquad\qquad\qquad |$$
$$\ CH_3 \quad II \qquad\qquad\qquad\qquad CH_3 \quad III$$

pected δ,ε-unsaturated acid III is probably best explained on the basis that the initial adduct III is isomerized to II by the organic acids at the temperatures employed.

Several products were isolated from the thermal addition of isobutylene to acrolein. In initial experiments, there was obtained the known Diels–Alder type of product,[10] dimethyldihydropyran (IV) together with a liquid, b.p. 172–173°, which was thought to be the δ,ε-unsaturated aldehyde V. The infrared spectrum of the substance indicated absence of C=O and presence of CH₂= and –OH. These data suggested that it might be 3-methylenecyclohexanol (VI), formed by cyclization of the expected 5-methyl-5-hexenal (V).
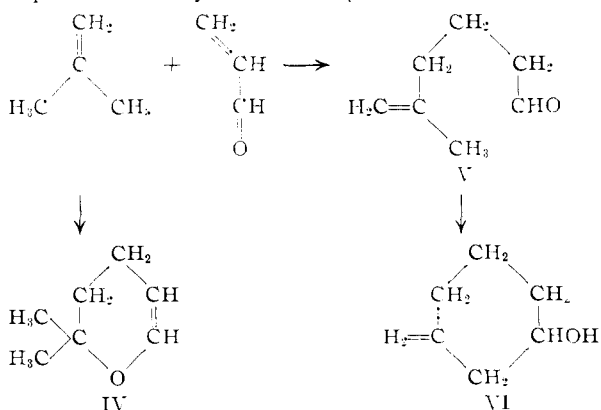
The cyclohexanol VI was identified by hydrogenation followed by oxidation to form the known 3-methylcyclohexanone. At lower temperatures the 5-hexenal (V) was obtained, usually contaminated with the known dimer of acrolein.[11] It was shown that V could be converted to VI by heating. The

(8) C. J. Albisetti, D. C. England. M. J. Hogsed and R. M. Joyce. THIS JOURNAL, 78, 472 (1956).

(9) C. J. Albisetti and M. J. Hogsed. U. S. Patent 2,671,106 (1954).

(10) C. W. Smith, D. G. Norton and S. A. Ballard, THIS JOURNAL, 73, 5273 (1951).

(11) K. Alder, H. Offermanns and E. Rüden. Ber., 74, 905 (1941).

dihydropyran IV was stable to heat when anhydrous but resinified when heated with water.

The addition of isobutylene to methyl vinyl ketone[12] resulted in a convenient synthesis of methylheptenone $(CH_2=C(CH_3)-CH_2-CH_2-CH_2-CO-CH_3)$. At lower temperatures a portion of the product was the Diels–Alder type of adduct, i.e., compound IV with a 6-methyl substituent.

The 1:1 addition products having branched terminal olefinic structures, obtained in the addition of isobutylene to acrylonitrile or methyl acrylate, were found to undergo addition of a second mole of α,β-unsaturated compound to form 10-carbon unsaturated dinitriles or diesters.[7,13]

$$XCCCC{=}C + C{=}CX \longrightarrow XCCCCCCCX$$
$$X = -CN \text{ or } -CO_2CH_3$$
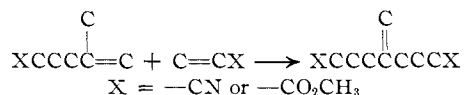
Small amounts of such products were isolated from higher-boiling residues obtained in the 1:1 addition reactions. They could also be obtained as the major products. For example, treatment of acrylonitrile with a 100% excess of 5-methyl-5-hexenenitrile at 300° for 15 minutes in the presence of water gave a 61% yield of 5-methylenenonanedinitrile. The position of the double bond in the dinitrile was established by ozonizing to form formaldehyde. The infrared spectrum showed a strong band at 11.09 μ, somewhat displaced from the usual band for $RR'C{=}CH_1$ at 11.25. Hydrogenation eliminated the 11.09$_2$ band and resulted in the introduction of a band for the methyl group at 7.29 μ. With methyl acrylate and methyl 5-methyl-5-hexenoate, the isobutylene/methyl acrylate adduct, the yield of dimethyl 5-methylenenonanedioate was 26%. In contrast, only small amounts of dimethyl 4-nonenedioate were obtained in the corresponding synthesis using propylene. The product was identified by hydrogenation followed by hydrolysis to form azelaic acid.

Diadducts derived from 1 molecule of isobutylene or diisobutylene and 2 molecules of methacrylonitrile, methyl methacrylate or diethyl fumarate were also prepared. No structural studies were carried out but the diadducts are presumed, on the basis of the above work, to be derivatives of nonenedioic acid with the double bond attached to the δ-carbon atom.

Experimental

General.—All thermal addition reactions described were carried out in stainless steel-lined 400-ml. or 1-l. tubes agitated by rocking or shaking and heated at 200–300°. A 2–4 molar excess of olefin was generally employed. Low-boiling olefins were introduced by distillation into cooled, evacuated tubes previously charged with the α,β-unsaturate. In the case of propylene and the butenes, initial pressures up to 1000 atm. resulted. Lower yields resulted when lower pressures and smaller proportions of olefin were used.

Those α,β-unsaturates considered to be vinyl-type monomers were purified by distillation. Common inhibitors, 0.25–1.0%, were added. Care was taken to remove peroxides from the liquid olefins. In many experiments an inert solvent such as benzene was employed. Surprisingly, in the case of the polymerizable nitriles, use of water as the medium prevented formation of the tars usually associated with high-temperature treatment of acrylonitrile or methacrylonitrile.

The 1:1 adducts not described below are listed in Table I'

Methyl 5-Alkenoates from Methyl Acrylate.—The preparation and properties of the methyl 5-alkenoates from methyl acrylate and olefins are listed in Table I.

A. Methyl 5-Hexenoate.—The adduct from propylene and methyl acrylate was saponified with aqueous alkali and the unsaturated acid treated with thionyl chloride followed by p-toluidine. A solid, m.p. 58°, was obtained. The p-toluidide of 5-hexenoic acid has been reported[14] to melt at 58°. A portion of the unsaturated ester was treated with hydrogen at room temperature in the presence of a palladium catalyst; 82% of the theoretical amount of hydrogen was absorbed. Treatment of the saturated ester with ammonia in methanol gave caproamide, m.p. 97–98°.

B. Methyl 5-Heptenoate.—The ester from 1-butene and methyl acrylate was catalytically hydrogenated to give methyl heptanoate which was characterized by conversion to its amide, m.p. 95–97°. The p-bromophenacyl ester prepared from the free acid melted at 72°; reported[15] m.p. is 72°. A portion of the unsaturated ester was saponified and the free acid oxidized in aqueous sodium bicarbonate with potassium permanganate. The solid acid product, purified from benzene, melted at 93.5–94°. A mixture of it and glutaric acid melted at 93.5–95.5°.

C. Methyl 5-Methyl-5-hexenoate.—The 1:1 addition product of isobutylene and methyl acrylate was catalytically hydrogenated to methyl 5-methylhexanoate and converted to the amide, m.p. 102°, reported[16] m.p. 103°. Infrared spectrum of the unsaturated ester confirmed the presence of terminal $H_2C{=}$. Hydrolysis of the unsaturated ester with alcoholic alkali gave 5-methyl-5-hexenoic acid, p-bromophenacyl derivative, m.p. 49–51°.

5-Methyl-5-hexenenitrile.—A mixture of 200 g. (3.6 moles) of isobutylene and 80 g. (1.5 moles) of acrylonitrile (stabilized) was heated 4 hours at 235° in a 400-ml. stainless steel-lined agitated pressure tube. The initial pressure was 990 atm. and the pressure drop was 530 atm. There was obtained 135 g. of liquid products containing 80 g. (49%) of 5-methyl-5-hexenenitrile, b.p. 181–184°. Residues amounted to 38 g.

Alkaline hydrolysis of the unsaturated nitrile gave 5-methyl-5-hexenoic acid identical to that obtained from methyl 5-methyl-5-hexenoate described previously. A sample of the nitrile was ozonized in methanol and the reaction mixture hydrogenated. Water was added and the mixture distilled. Methanol was removed and the residues distilled in vacuum. The highest boiling fraction, b.p. 64° (0.1 mm.), $n^{25}D$ 1.4285, gave a 2,4-dinitrophenylhydrazone, m.p. 155–157°. The melting point was not depressed on admixture with an authentic sample of the 2,4-dinitrophenylhydrazone of 5-oxohexanenitrile.

Isobutylene and Acrylic Acid.—On the basis of previous work, the isobutylene/acrylic acid addition product was presumed to be 5-methyl-5-hexenoic acid. Further studies suggested that another isomer was present. In order to check the position of the double bond, a sample was ozonized in methanol until no test for unsaturation was given by bromine. The methanol solution was hydrogenated using a Pd/charcoal catalyst. Water was added and the mixture distilled. The methanolic distillate was treated with 2,4-dinitrophenylhydrazine and H_2SO_4. The acetone 2,4-dinitrophenylhydrazone, m.p. 124–126°, precipitated. Raman spectroscopy indicated a 4:1 ratio of 5-methyl-4-hexenoic acid (II) to 5-methyl-5-hexenoic acid (III). Aqueous as well as anhydrous acrylic acid could be used in these syntheses.

Acrolein and Isobutylene. A. Conditions for Dimethyldihydropyran (IV) and 3-Methylenecyclohexanol (VI).—A mixture of 84 g. (1.5 moles) of acrolein (hydroquinone) and 196 g. (3.5 moles) of isobutylene was heated at 300° for 15 minutes in a pressure vessel. Distillation of the liquid products gave 35 g. of crude dimethyldihydropyran (IV), b.p. 110–115°, 16 g. of crude 3-methylenecyclohexanol (VI), b.p. 170–185°, and 60 g. of residues. A redistilled sample of 3-methylenecyclohexanol, b.p. 172–174°, $n^{25}D$ 1.4797, was hydrogenated to the saturated alcohol, b.p. 170–174°, $n^{25}D$ 1.4558.[17] Three grams of the saturated

(12) C. J. Albisetti, U. S. Patent 2,628,252 (1953).

(13) C. J. Albisetti and N. G. Fisher, U. S. Patent 2,584,527 (1952).

(14) R. P. Linstead and H. N. Rydon, J. Chem. Soc., 1995 (1934).

(15) C. G. Moses and E. E. Reid, THIS JOURNAL, **54**, 2101 (1932).

(16) O. Wallach, Ann., **408**, 190 (1915).

(17) A. Skita and W. Faust, Ber., **64**, 2878 (1931), report b.p. 173–174°, $n^{25}D$ 1.4540 and 1.4550 for the cis and trans forms.

TABLE I

δ,ε-Unsaturated Compounds from Olefins and α,β-Unsaturates

α,β-Unsaturate, g.		Olefin, g.		Time, hours	Temp., °C.	Yield,[a] %	B.p. °C.	B.p. Mm.	Adduct formula	Analysis type	Calcd.	Found
$CH_2=CH—CO_2CH_3$	52	Propylene	42	9	250	13	150	Atm.	$C_7H_{12}O_2$	Sapn. equiv.	128.2	125.8
$CH_2=CH—CO_2CH_3$	86	1-Butene	84	6	250	8.5	172	Atm.	$C_8H_{14}O_2$	Sapn. equiv.	142.2	141.0
$CH_2=CH—CO_2CH_3$	65	Isobutylene	200	1/4	300	46	169	Atm.	$C_8H_{14}O_2$	Sapn. equiv.	142	151
$CH_2=CH—CO_2CH_3$	75	2-Methyl-1-butene	175	4	210	20	190	Atm.	$C_9H_{16}O_2$	Sapn. equiv.	156.2	157.7
$CH_2=C(CH_3)—CO_2CH_3$	320	Isobutylene	620	6	245	35	177	Atm.	$C_9H_{16}O_2$	Sapn. equiv.	156.2	156.5, 155.6
$CH_2=C(CH_3)—CO_2CH_3$	80	Propylene	120	6	245	9	164	Atm.	$C_8H_{14}O_2$	Sapn. equiv.	142	142.8
$CH_2=CHCN$	80	Isobutylene	200	4	235	49	180–182	Atm.	$C_7H_{11}N$	N	12.8	12.6
$CH_2=CHCN$	53	Diisobutylene	224	4	245	42	124	21	$C_{11}H_{19}N$	N	8.5	9.0
$CH_2=CHCN$	50	β-Pinene	200	6	230	41	133–142	5	$C_{13}H_{19}N$	N	7.4	7.4, 7.6
$CH_2=CHCN$	50	Tetramethylethylene	200	8	235	9	205–209	Atm.	$C_9H_{15}N$	N	10.2	10.2, 10.3
$CH_2=CHCN$	70	2-Butene	200	5	245	4	174	Atm.	$C_7H_{11}N$	N	12.8	12.5, 12.3
$CH_2=CHCN$	50	Propylene	200	4	240	18	162	Atm.	C_6H_9N	N	14.7	14.5, 14.3
$CH_2=CHCN$	40	Bimethylallyl	165	3	245	16	108	7	$C_{11}H_{17}N$	N	8.6	9.3, 9.9
$CH_2=CHCN$	53	Cyclohexene	246	5	250	5	230	Atm.	$C_9H_{13}N$	N	10.4	10.1, 9.9
$CH_2=CHCN$	53	Vinylcyclohexene	216	4	240	3	117	7	$C_{11}H_{15}N$	N	8.7	9.0
$CH_2=CHCN$	53	Triisobutylene	252	4	245	3.5	125–128	6	$C_{15}H_{27}N$	N	6.3	7.3
$CH_2=CHCN$	53	Tetrapropylene[b]	168	1/4	300	5	121–130	5	$C_{15}H_{27}N$	N	6.3	6.7
$CH_2=CHCN$	40	Methallylbenzene[c]	155	6	240	23	142	4	$C_{13}H_{15}N$	N	7.6	7.8
							151	4	$C_{13}H_{15}N$	N	7.6	7.7
$CH_2=C(CH_3)CN$	268	Isobutylene	672	6	245	25	186	Atm.	$C_8H_{13}N$[d]	N	11.4	11.8
$CH_2=CH—SO_2—C_2H_5$	40	Isobutylene	200	2	280	17	135	3	$C_8H_{16}O_2S$	C,H,S	54.6, 9.1, 18.2	54.7, 9.1, 18.4
$CH_2=CH—PO(OEt)_2$	80	Isobutylene	200	1	280	45	124	8.5	$C_{10}H_{21}O_3P$	C,H,P	54.6, 9.5, 13.9	55.0, 10.1, 14.1
$CH_2=CH—CO_2H$[e]	60	Isobutylene	200	4	245	51[f]	132–138	45	$C_7H_{12}O$	Neut. equiv.	128.2	128.7
$CH_2=CH—CO_2H$[e]	45	Triisobutylene	168	5	240	5	145–150	5	$C_{15}H_{28}O$	Neut. equiv.	240.4	240

[a] Based on α,β-unsaturate. [b] H₂O added. [c] Methallylbenzene gave 2 products, presumably 5-benzyl-5-hexenenitrile and 6-phenyl-5-methyl-5-hexenenitrile. [d] Saponification and hydrogenation gave an acid which gave methylisoamylacetamide, m.p. 100–102°. [e] As 60% aqueous acrylic acid. [f] Mixture of γ,δ- and δ,ε-unsaturate.

alcohol was oxidized at 50° for 20 minutes with 5.3 g. of sodium dichromate, 2.5 ml. of H_2SO_4 and 25 ml. of water. The mixture was extracted with ether and the washed extract was concentrated to an oil. The dinitrophenylhydrazone, m.p. 162–165°, and the semicarbazone, m.p. 178–180°, showed no depression when melted with known samples prepared from 3-methylcyclohexanone. Infrared analysis indicated terminal CH_2= which led to the assignment VI.

B. Conditions for 5-Methyl-5-hexenal (V).—A mixture of 42 g. of acrolein, 225 g. of isobutylene and 25 ml. of methanol was heated at 200° under autogenous pressure (985 atm.) for 1 hour. Distillation gave 14 g. of dimethyldihydropyran, b.p. 112–114°; 20 g. of crude 5-methyl-5-hexenal, b.p. 65–70° (50 mm.), $n^{25}D$ 1.4370, containing 70.5% carbon; 3 g. of 3-methylenecyclohexanol, b.p. 90° (35 mm.), $n^{25}D$ 1.4768, and 8 g. of tar. [Acrolein dimer b.p. 146° (760 mm.), 70° (50 mm.), $n^{25}D$ 1.4620, contains 63.4% carbon. 5-Methyl-5-hexenal, b.p. 150° (760 mm.), 70° (50 mm.), $n^{25}D$ 1.4350, contains 75.0% carbon.] In the absence of methanol, the hexenal fraction, 13 g., b.p. 70–71° (50 mm.), $n^{25}D$ 1.4430, contained 70.7% carbon. Treatment of a mixture containing more acrolein at 170° for 8 hours gave a dimer/hexenal fraction, b.p. 143–148°, $n^{25}D$ 1.4500, containing only 37% hexenal by carbon analysis.

5-Methyl-5-hexenal, washed with water to remove dimer and redistilled, gave a semicarbazone, m.p. 92–93°; a methone derivative, m.p. 110–111°; a 2,4-dinitrophenylhydrazone, m.p. 97–98°. The purified hexenal had $n^{25}D$ 1.4350.

Anal. Calcd. for $C_7H_{12}O$: C, 75.0; H, 10.7. Found: C, 73.1; H, 10.3.

C. Stability of IV and V.—A 15-g. sample of 5-methyl-5-hexenal, $n^{25}D$ 1.4368, was heated at 250° for 1 hour in 100 ml. of benzene. There was obtained 5 g. of recovered hexenal, b.p. 65–71° (50 mm.), $n^{25}D$ 1.4385, and 2 g. of 3-methylenecyclohexanol (VI), b.p. 90–95° (50 mm.). From the latter there was obtained an α-naphthylurethan, m.p. 129–130°, which was identical with that from a previously characterized sample of the cyclohexanol.

A 50-g. sample of the dimethyldihydropyran (IV), b.p. 112–114°, $n^{25}D$ 1.4340, was heated for 2 hours at 270° in the presence of 90 ml. of dried benzene. Forty-three grams of the pyran, $n^{25}D$ 1.4350, was recovered by distillation. However, treatment of a similar sample at 220° in the presence of water gave 5 g. of pyran; 2.5 g., b.p. 149–152°, $n^{25}D$ 1.4368 (corresponds to V); 1.3 g. b.p. 170–175°, $n^{25}D$ 1.4773 (corresponds to VI); and 20 g. of residues.

6-Methyl-6-hepten-2-one.—A mixture of 200 g. of isobutylene and 100 g. of the technical 85/15 methyl vinyl ketone/water azeotrope was heated in a stainless pressure vessel at 300° for 15 minutes. There was obtained 42 g. (27.5%) of 6-methyl-6-hepten-2-one, b.p. 170–172°, $n^{25}D$ 1.4358. Residues amounted to 23 g. Treatment of 70 g. of methyl vinyl ketone and 200 g. of isobutylene at 245° for 4 hours gave 17.5 g. (14%) of 2,2,5-trimethyl-3,4-dihydro-1,2-pyran,[10] b.p. 130°, and 17 g. (13%) of methylheptenone.

Anal. Calcd. for $C_8H_{14}O$: C, 76.2; H, 11.2. Found: C, 76.1; H, 11.3.

The structure of 6-methyl-6-hepten-2-one was established by comparison with the infrared spectrum of 4-methyl-4-penten-2-one (A.P.I. Serial No. 634). The ketone gave a semicarbazone, m.p. 122–124°. The m.p. was not depressed on admixture with the semicarbazone from the ketone obtained from 5-methyl-5-hexenenitrile by addition of methylmagnesium iodide followed by acid hydrolysis.

Dimethyl 4-Nonenedioate.—From the 1:1 propylene/methyl acrylate adduct, methyl 5-hexenoate, only sufficient 1:2 adduct was obtained to demonstrate the course of the addition. A mixture of 18 g. of methyl 5-hexenoate, 34 g. of methyl acrylate, 25 g. of benzene and 1 g. of hydroquinone was heated at 260° for 4 hours. Distillation gave 5 g. of crude dimethyl 4-nonenedioate, b.p. 265–280°. Hydrogenation with platinum–carbon catalyst followed by hydrolysis with refluxing ethanolic NaOH gave a red oil which solidified on cooling. The product, crystallized from hot water, melted at 105–106.5°. A mixture of it and azelaic acid melted at 104–106°.

5-Methylenenonanedinitrile.—A mixture of 218 g. (2 moles) of 5-methyl-5-hexenenitrile, 53 g. (1 mole) of acrylo-

nitrile and 36 g. of water was heated 15 minutes at 300°. Distillation gave 32 g. of unreacted 5-methyl-5-hexenenitrile and 100 g. (61%) of 5-methylenenonanedinitrile, b.p 152–154° (2.5 mm.), $n^{25}D$ 1.4668.

Anal. Calcd. for $C_{10}H_{14}N_2$: N, 17.25. Found: N, 16.96, 17.04.

Ozonization of the dinitrile gave formaldehyde, identified as the dimethone derivative, m.p. 187–189°. The methylene structure was also confirmed by infrared analysis. The spectrum showed a strong band at 11.09 μ somewhat displaced from the band at 11.25 usually associated with RR_1-C=CH_2. A hydrogenated sample showed elimination of the 11.09 band and introduction of the band for methyl groups at 7.29 μ.

Hydrogenation at 1000 lb. hydrogen pressure in methanol with a palladium catalyst at 50° converted the methylenedinitrile to 5-methylnonanedinitrile. Hydrolysis of the saturated dinitrile gave 5-methylnonanedioc acid, m.p. 69–71°, from nitromethane. Reduction of 5-methylnonanedinitrile with hydrogen at 2000 lb. in the presence of ammonia and a cobalt–alumina catalyst at 125° gave 5-methyl-1,9-nonanediamine, b.p. 114–116° (4.5 mm.), $n^{25}D$ 1.4658, neutral equivalent 86.33 (calcd. 86.16).

Dimethyl 5-Methylenenonanedioate.—A mixture of 213 g. (1.5 moles) of methyl 5-methyl-5-hexenoate and 86 g. (1.0 mole) of methyl acrylate was heated at 230° for 4 hours. Distillation gave 142 g. of recovered monoester and 45 g. (26% yield) of dimethyl 5-methylenenonanedioate, b.p. 121–123° (2.5 mm.), $n^{25}D$ 1.4500, sapn. equiv. 114.2 (calcd. 114.1). Hydrogenation with a palladium catalyst in methanol gave dimethyl 5-methylnonanedioate, b.p. 127.5–128.5° (3.0 mm.), $n^{25}D$ 1.4370, sapn. equiv. 115.1 (calcd. 115.2). Saponification with alcoholic KOH gave 5-methylnonanedioc acid, m.p. 69–71°, identical with that described above.

Anal. Calcd. for $C_{10}H_{18}O_4$: C, 59.38; H, 8.97; neut. equiv., 101.5. Found: C, 59.39, 59.01; H, 9.16, 9.14; neut. equiv., 101.2.

Other Difunctional Adducts. A. Dimethylmethylenenonanedinitrile.—Conversions of about 10% were realized in the addition of methacrylonitrile to excess 2,5-dimethyl-5-hexenenitrile (the 1:1 isobutylene/methacrylonitrile product) at 245°. The unsaturated dinitrile boiled at 124–128° (0.7 mm.), $n^{25}D$ 1.4603.

Anal. Calcd. for $C_{12}H_{18}N_2$: N, 14.73. Found: N, 14.92, 14.91.

Complete reduction gave 2,5,8-trimethyl-1,9-nonanediamine, b.p. 142–143° (12 mm.).

Anal. Calcd. for $C_{12}H_{28}N_2$: neut. equiv., 100.18. Found: neut. equiv., 100.4.

B. Dimethyl Dimethylmethylenenonanedioate.—A 17% conversion was obtained at 255° in the thermal addition of methyl methacrylate to excess methyl 2,5-dimethyl-5-hexenoate (the 1:1 isobutylene/methyl methacrylate adduct). The dimethyl ester boiled at 119–121° (2 mm.), $n^{25}D$ 1.4481, saponification equivalent 128.8 (calcd. 128.2). Hydrogenation gave dimethyl 2,5,8-trimethylnonanedioate, b.p. 116–118° (1.5 mm.), $n^{25}D$ 1.4368, sapn. equiv. 131.1 (calcd. 129.2). Refluxing the saturated ester with alcoholic NaOH followed by acidification gave liquid 2,5,8-trimethylnonanedioic acid, b.p. 180° (0.5 mm.), neutral equiv. 115.4 (calcd. 115.15).

C. Tetraester from Diisobutylene and Ethyl Fumarate.—Treatment of 344 g. (2 moles) of ethyl fumarate and 244 g. (2 moles) of diisobutylene for 2 hours at 280° gave 80 g. of diisobutylene, 44 g. of ethyl fumarate, 225 g. of the monoadduct, b.p. 126–131 (2 mm.), and 105 g. of an addition product of 2 moles of fumarate and 1 mole of diisobutylene, a viscous yellow liquid, b.p. 173° (0.3 mm.), $n^{25}D$ 1.4588.

Anal. Calcd. for $C_{24}H_{40}O_8$: C, 63.2; H, 8.84; sapn. equiv., 114.1. Found: C, 63.4; H, 8.93; sapn. equiv., 113.9.

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