[CONTRIBUTION NO. 307 FROM THE CHEMICAL DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY]

Thermal Addition of β-Methylcrotononitrile to Ethylene

BY M. J. HOGSED AND R. V. LINDSEY

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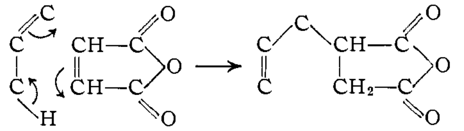
The products obtained by the thermal addition of β-methylcrotononitrile to ethylene at 290° and 3000 atm. have been shown to include a mono- and a diadduct identified as 2-ethyl-3-methyl-2-butenenitrile and 2-ethyl-3-methyl-2-hexenenitrile, respectively, and a triadduct of undetermined structure. A mechanism to account for the formation of these products has been proposed.

The thermal addition of propylene and higher olefins to maleic anhydride has been the subject of a number of investigations.[1] The structures of a number of adducts have been established and a mechanism to account for their formation has been proposed. Essentially the reaction involves the transfer of a hydrogen atom from the olefin (donor) to the α,β-unsaturated compound (acceptor) with migration of the double bond.

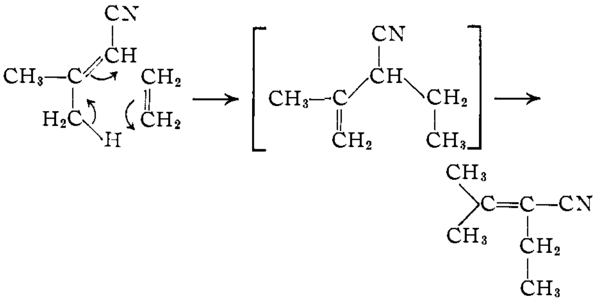


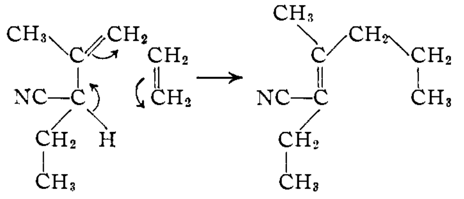
Since ethylene cannot participate as a donor in such a pseudo-6-membered ring intermediate, it was of interest to determine its behavior in typical thermal addition reactions.

Although a 1:1 adduct was not obtained from ethylene and maleic anhydride, uncatalyzed thermal reactions occurred between ethylene and the α,β-unsaturated compounds, β-methylcrotononitrile and mesityl oxide, at 290° and 3000 atm. With β-methylcrotononitrile, the products obtained corresponded to the addition of 1, 2 and 3 moles of ethylene. The 1:1 adduct was shown to be 2-ethyl-3-methyl-2-butenenitrile by ozonolysis and subsequent hydrogenation to give acetone, and propionyl cyanide, identified through its hydrolysis products, hydrogen cyanide and propionic acid.[2] The diadduct was shown to be 2-ethyl-3-methyl-2-hexenenitrile through identification of the ozonization products and the congruency of its infrared spectrum with that of an authentic sample.[3] The structure of the triadduct was not further investigated.

The formation of these products may be accounted for by the mechanism of Arnold and Dowdell[1,d] if the role of the olefin and the α,β-unsaturated compound are reversed; that is, the ethylene becomes the acceptor and β-methylcrotononitrile the donor.

Ethylene also reacted with mesityl oxide at 280° and 3000 atm. to produce two monoadducts and a diadduct in very low yields. Identification of acetone among the ozonolysis products of the monoadduct having the higher boiling point and higher refractive index indicated it to be 3-ethyl-4-methyl-3-pentene-2-one, a structure exactly analogous to the β-methylcrotononitrile monoadduct. The lower boiling monoadduct was not further characterized, but is believed to be 2,4,4-trimethyldihydropyran by analogy with the acrolein/olefin adducts described by Smith, Norton and Ballard.[4] Extension of the proposed mechanism suggests that the 2:1 ethylene/mesityl oxide adduct is 3-ethyl-4-methyl-3-heptene-2-one.





Experimental

Reaction of Ethylene with β-Methylcrotononitrile.—Distillation of the reaction mixture obtained by heating 98 g. of β-methylcrotononitrile and excess ethylene at 3000 atm. and 290° for 3 hr. gave 26.5 g. of recovered β-methylcrotononitrile, $n^{25}\mathrm{D}$ 1.4346, and 83.5 g. of higher boiling material. By fractional distillation of the latter, there were obtained 17 g. (18%) of monoadduct, b.p. 105–109° (100 mm.), $n^{25}\mathrm{D}$ 1.4454 (*Anal.* Calcd. for $C_7H_{11}N$: C, 77.0; H, 10.2; N, 12.8. Found: C, 77.3; H, 10.2; N, 13.1); 19 g. (16%) of diadduct, b.p. 133–134° (100 mm.), $n^{25}\mathrm{D}$ 1.4513 (*Anal.* Calcd. for $C_9H_{15}N$: C, 78.8; H, 11.0; N, 10.2. Found: C, 78.5; H, 11.2; N, 10.1); and 5 g. (3%) of triadduct, b.p. 153–157° (100 mm.), $n^{25}\mathrm{D}$ 1.4561 (*Anal.* Calcd. for $C_{11}H_{19}N$: C, 79.9; H, 11.6; N, 8.5. Found: C, 80.3; H, 11.8; N, 8.4).

Structure of Monoadduct.—Nine grams of the monoadduct was ozonized in absolute ethanol for 2 hr. and hydrogenated at 2 atm. using 5% palladium-on-charcoal as catalyst. The odor of hydrogen cyanide was evident in the alcohol solution. The reaction mixture was flash distilled to obtain a residue from which 4.9 g. of unchanged monoadduct was recovered. The distillate was fractionated and the material boiling at 37–70° was treated with excess 2,4-dinitrophenylhydrazine and sulfuric acid to yield a derivative melting at 120–125° which, after recrystallization, melted at 125–127° alone or when mixed with a known sample of acetone 2,4-dinitrophenylhydrazone.

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[1] (a) K. Alder, F. Pascher and A. Schmitz, *Ber.*, **76**, 27 (1943); (b) J. Ross, A. J. Gebhart and J. F. Gerecht, THIS JOURNAL, **68**, 1373 (1946); (c) K. Alder, H. Söll and H. Söll, *Ann.*, **565**, 73 (1949); (d) R. T. Arnold and J. F. Dowdell, THIS JOURNAL, **70**, 2590 (1948).

[2] E. H. Rodd, "Chemistry of Carbon Compounds," Vol. I, Elsevier Publishing Co., Amsterdam, 1952, p. 863.

[3] E. M. Osman and A. C. Cope, THIS JOURNAL, **66**, 881 (1944). A sample was kindly supplied by Professor A. C. Cope.

[4] C. W. Smith, D. G. Norton and S. A. Ballard, *ibid.*, **73**, 5273 (1951).

The entire ethanol solution boiling higher than 70° was saponified with 10 g. of potassium hydroxide by refluxing overnight. After distillation of the ethanol and acidification of the residues with excess sulfuric acid, the solution was extracted with ether five times. The ether solution was dried and concentrated by distillation. The residue, approximately 3 ml., was treated with excess phosphorus trichloride and the acid chloride distilled. The *p*-toluidide, prepared in the usual manner, melted at 122–124° alone or when mixed with the *p*-toluidide of propionic acid. Identification of hydrogen cyanide, acetone and propionic acid from the ozonization of the monoadduct proved that the structure was 2-ethyl-3-methyl-2-butenenitrile.

Structure of the Diadduct.—In the same manner described above for the monoadduct, the diadduct was ozonized and the products identified as propionyl cyanide and methyl propyl ketone, showing that the diadduct was 2-ethyl-3-methyl-2-hexenenitrile. This structure was confirmed by the congruency of its infrared spectrum with that of a sample of 2-ethyl-3-methyl-2-hexenenitrile, previously reported by Osman and Cope.[3]

Reaction of Ethylene with Mesityl Oxide.—The crude *product obtained by heating 100 g. of mesityl oxide with an* excess of ethylene at 3000 atm. and 280° for 3 hr. was distilled to obtain 20 g. of recovered mesityl oxide and 33 g. of higher boiling material. Fractional distillation of the latter gave 5 g. of monoadduct I, b.p. 144–148°, $n^{25}\text{D}$ 1.4294 (*Anal.* Calcd. for $C_8H_{14}O$: C, 76.1; H, 11.2. Found: C, 76.3; H, 11.3); 8 g. of monoadduct II, b.p. 163–165°, $n^{25}\text{D}$ 1.4456 (*Anal.* Calcd. for $C_8H_{14}O$: C, 76.1; H, 11.2. Found: C, 76.1; H, 11.2); and 5 g. of diadduct, b.p. 118–121° (100 mm.), $n^{25}\text{D}$ 1.4412 (*Anal.* Calcd. for $C_{10}H_{18}O$: C, 77.9; H, 11.8. Found: C, 78.2; H, 11.8).

The monoadduct boiling at 164° was dissolved in ethanol and ozonized for 3 hr. Excess ozone was removed with a stream of nitrogen and the ozonization mixture was hydrogenated at 2 atm. pressure using 10% palladium-on-charcoal catalyst. The reaction mixture was filtered, the ethanol was removed by distillation, and the distillate was treated with 2,4-dinitrophenylhydrazine and sulfuric acid to obtain a derivative which melted at 124–126° alone or when mixed with acetone 2,4-dinitrophenylhydrazone. This indicated that the higher boiling monoadduct was 3-ethyl-4-methyl-3-pentene-2-one.

Attempts to isolate a recognizable ozonization fragment from the lower boiling monoadduct were unsuccessful. This suggests that it may be dihydropyran derivative. The low refractive index also suggests a very different structure.

No effort was made to establish the structure of the product corresponding to the addition of two moles of ethylene to one mole of mesityl oxide.

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A Reformatsky Type Condensation of Aroyl Chlorides with Ethyl α-Bromoisobutyrate by Means of Zinc to Form β-Keto Esters[1,2]

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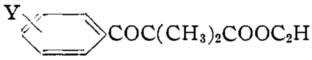
A Reformatsky type condensation between aroyl chlorides and ethyl α-bromoisobutyrate by means of zinc has been realized. The reaction furnishes a convenient method for preparing certain β-keto esters and, through ketonic cleavage, certain ketones. Ethyl mesitoyldimethylacetate was cleaved by acid to form mesitylene instead of the ketone.

It has previously been shown in this Laboratory[3] that a Reformatsky type condensation may be effected between phenyl benzoate and ethyl α-bromoisobutyrate by means of zinc to form ethyl benzoyldimethylacetate (I) in 52% yield. This condensation involves, presumably, the intermediate formation of the zinc bromoester which is benzoylated, the over-all reaction being represented by equation 1 ($X = OC_6H_5$)

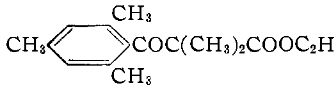
$$C_6H_5COX + BrC(CH_3)_2COOC_2H_5 \xrightarrow{Zn} \underset{\text{I}}{C_6H_5COC(CH_3)_2COOC_2H_5} + ZnBrX \quad (1)$$

We have now realized this type of acylation with benzoyl chloride to form β-keto ester I in 57% yield (equation 1, X = Cl), and with four appropriately substituted benzoyl chlorides to give β-keto esters IIA–C and III in yields of 65–72% (Table I). Also, corresponding acylations were carried out with phenyl *p*-methoxybenzoate and phenyl *p*-chlorobenzoate, but the yields were lower than those obtained with the acid chlorides (see note *c*, Table I). Phenyl mesitoate failed to react under similar conditions.

The reactions with the substituted benzoyl chlorides were effected in refluxing ether, whereas those with benzoyl chloride and the phenyl esters were carried out in a refluxing mixture of benzene and toluene. At least with the acid chloride, ether would presumably also be suitable.[4]

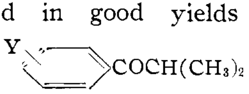


IIA, Y = *p*-OCH$_3$
IIB, Y = *p*-Cl
IIC, Y = *o*-Cl



III

β-Keto esters I and IIA–C underwent the expected ketonic cleavage on refluxing with mixtures of sulfuric and acetic acids,[5] ketones of type IV being obtained in good yields (Table II).



IV

However, under the same conditions, ethyl mesitoyldimethylacetate (III) gave mesitylene (87%). Apparently this hydrocarbon resulted

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[1] Supported by the Office of Ordnance Research, U. S. Army.

[2] Paper LIII on condensations.

[3] M. S. Bloom and C. R. Hauser, THIS JOURNAL, **66**, 152 (1944).

[4] In the reactions with acid chlorides, the zinc became coated with a dark oil which appeared to be kept at a minimum in ether. Although benzoyl chloride reacted in the refluxing benzene–toluene mixture, *p*-methoxy- and *p*-chlorobenzoyl chlorides failed to react appreciably under the same conditions, and the starting materials or their hydrolysis products were largely recovered.

[5] B. E. Hudson, Jr., and C. R. Hauser, THIS JOURNAL, **63**, 3163 (1941).