Research upon the Retrogression of Diels-Alder's Reaction

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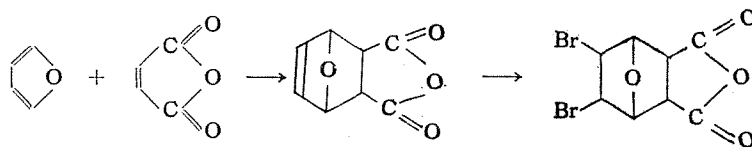
(Oda Laboratory)

In order to convert only the nitrilo- and carboxyl-group of acrylonitrile and methyl acrylate, leaving the double bond unchanged, these compounds were first reacted with anthracene and the adducts, after converted chemically in other forms, were pyrolyzed. From the adduct of acrylonitrile and anthracene the authors could isolate one form of the optical isomers only by recrystallization of the adduct.

The α,β-unsaturated carbonyl-compounds react with various passive components[1] generally in the manner of 1,4-addition. Therefore, it is difficult or rather impossible to convert chemically only the carbonyl-group into another atomic group, leaving the double bond unchanged. To convert the α,β-unsaturated carbonyl- compounds into another α,β-unsaturated compounds, a conventional method is usually taken, i. e. the double bond is at first covered by Diels-Alder's reaction and after the conversion of the carbonyl-group, the double bond is regenerated by pyrolysis. Some examples of this kind, which appeared in the recent publications, are as follows:
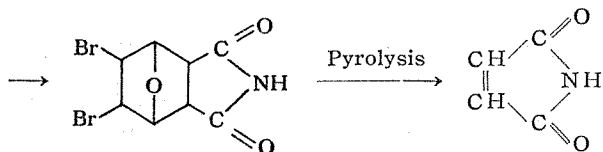
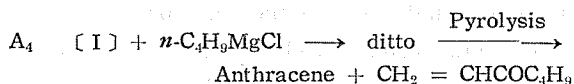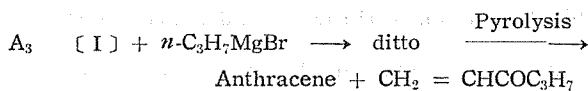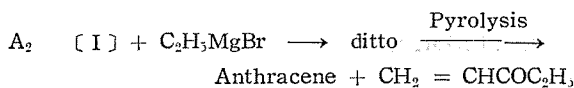(1) The synthesis of polyvinylamine.[2]
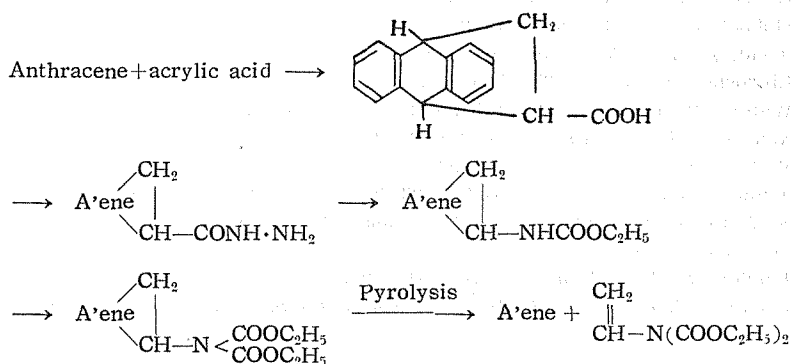
(2) Synthesis of maleimide.[3]

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The authors have also performed some experiments of this kind. The experiments undertaken are as follows:

A. Adduct between anthracene and acrylonitrile

A₁   [I] + CH₃MgI ⟶

$$\xrightarrow{\text{Pyrolysis}} \text{Anthracene} + CH_2 = CHCOCH_3$$

A₂   [I] + C₂H₅MgBr ⟶ ditto $\xrightarrow{\text{Pyrolysis}}$

$$\text{Anthracene} + CH_2 = CHCOC_2H_5$$

A₃   [I] + n-C₃H₇MgBr ⟶ ditto $\xrightarrow{\text{Pyrolysis}}$

$$\text{Anthracene} + CH_2 = CHCOC_3H_7$$

A₄   [I] + n-C₄H₉MgCl ⟶ ditto $\xrightarrow{\text{Pyrolysis}}$

$$\text{Anthracene} + CH_2 = CHCOC_4H_9$$
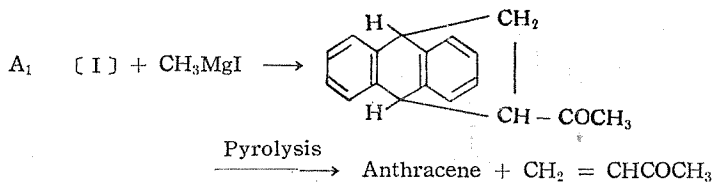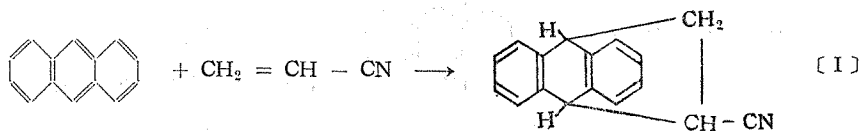
B. Adduct between anthracene and methyl acrylate

B₁   (II) $\xrightarrow{\text{hydrolysis}}$ free carboxylic acid ⟶ acid chloride   (III)

B₂   (III) + NaCH$<^{COCH_3}_{COOC_2H_5}$ ⟶

B₃   (IV) $\xrightarrow[\text{degradation}]{\text{ketonic}}$

$\downarrow$ pyrolysis

$$\text{Anthracene} + CH_2 = CHCOCH_3$$

B_4 (IV) $\xrightarrow[\text{degradation}]{\text{acidic}}$

(VII)   (by-product)

$\downarrow$ pyrolysis

Anthracene$+CH_2=CH-COCH_3+CH_2=CH_2+CO_2$

B_5 (II) $+ C_6H_5MgBr \longrightarrow$

(VIII)

pyrolysis $\xrightarrow{\hspace{2cm}}$

(IX)
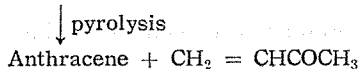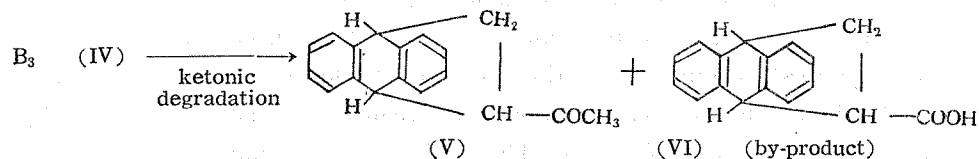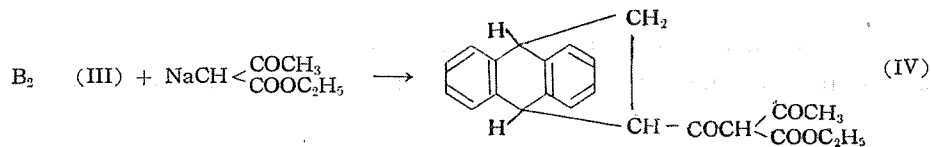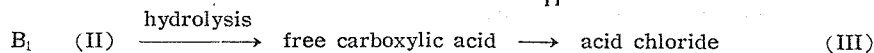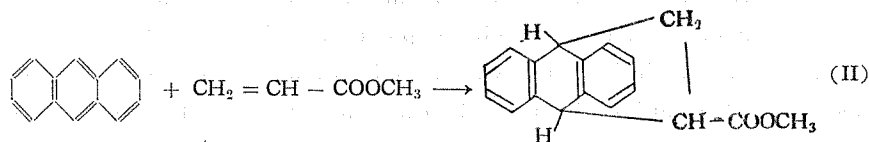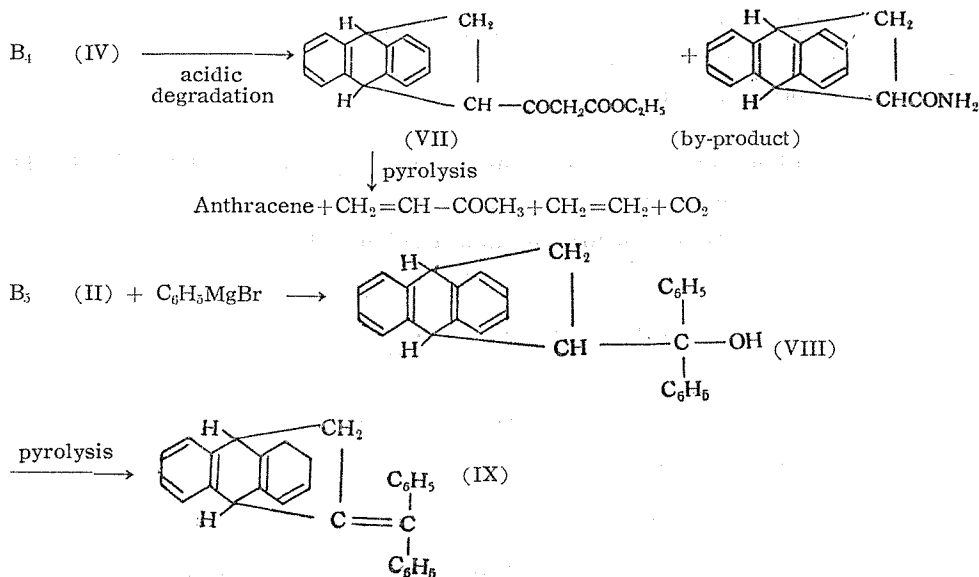
EXPERIMENTAL

A. Preparation of the adduct between anthracene and acrylonitrile

A mixture of anthracene and excess acrylonitrile was heated in an autoclave at 165~175°C for 10 hrs. After cooling and filtering the solid product, the crude adduct was obtained in 46 % yield. This crude product was recrystallized from ether and the nitrogen content was determined. N: found 6.03 %, (calc. 6.06 %). The authors have measured its melting point and found a remarkable fact. The product was pulverized and the melting point was found as 90-110°C. On the other hand one polyhedral crystal was picked up and its melting point was found as 146~149°C. The authors have tried to measure the optical rotation of this one crystal and found the following value:

$$[\alpha]_D^{27} = + 82.27°$$

Therefore it is clear that the racemic adduct was separated in optical isomers only by the recrystallization. Such a fact as this seems to be very rare and notable.

A_1: The reaction between the adduct (I) and methylmagnesiumiodide.

The ether solution of the adduct (1) was added drop-wise to the CH_3MgI solution at 15~20°C (the mole ratio of CH_3MgI : adduct = 4 : 1) and then refluxed for 2.5 hrs. The reaction solution was treated as usual and the crude product was obtained in yield of 81 % of Th. This was recrystallized from alcohol. m.p. = 145~148°C. The product was converted into 2,4-dinitro-phenylhydrazone, its m.p. was 188~189°C.

N found: 13.26; Calc. as $C_{24}H_{20}N_4O_4$: 13.08 %

Next the product was cracked (dry distilled) at 240~300° and a distillate (distilling temp = 80~85°C) was obtained in 59 % yield. This product was converted into semicarbazone. m. p. = 138 ~ 140°C. This product was identified as the semicarbazone of methylvinylketone, by comparing with an authentic sample.

A_2-A_4: The reactions between the adduct (I) and other Grignard's reagents were performed quite similarly as above. The results are as follows:

RMgX	yield (%)	m.p. after recrystallization	2,4-Dinitrophenylhydrazone			
			m.p.	C.	H.	N.
C_2H_5MgBr	76	101.5~103°C	188°	—	—	16.68% (16.67)
n-C_3H_7MgBr	72.5	85.5~86°	161.5~163°	63.79% (68.41)	5.22% (5.30)	—
n-C_4H_9MgCl	74.5	87~88.7°	177~178°	68.80% (68.92)	5.33% (5.57)	—

The values in parentheses are the calculated ones.

The product of the ethylmagnesiumbromide was pyrolyzed at 240~300°C and the ethylvinylketone was obtained in 52 % yield. The ethylvinylketone was converted into its 2,4-dinitrophenylhydrazone (m.p. 125~127°C) and the nitrogen content was measured. N(found): 20.90 %, calculated 20.74 %.

The product of the n-propylmagnesiumbromide was pyrolyzed at 260~310° and the vinylpropylketone was obtained in 63 % yield. This vinylpropylketone was reacted with aniline by mixing the both components at room temperature and the β-anilinoethyl-propylketone was obtained in 86 % yield.

Found :   C, 75.19 % ;   H, 8.87 %

Calculated :   C. 75.35 ;   H, 8.96

The product of the n-butylmagnesium chloride was pyrolyzed at 270 ~ 300°C and the vinylbutylketone was reacted with aniline as above and the β-anilinoethyl-butylketone was obtainedin 80 % yield.

Found :   C, 76.32 % ;   H, 9.40 %

Calculated :   C, 76.05 ;   H, 9.33

B. Reaction of the adduct of anthracene with methyl acrylate

A Mixture of anthracene and excess of methyl acrylate was heated in an autoclave at 190~200°C for 10 hrs. and the adduct was obtained in 98 % yield. The melting point of the adduct was 116.5~119.5°C. This adduct was hydrolyzed by heating with threefold quantity of 10 % aq. NaOH solution for 2.5 hrs. The free acid was obtained in 72~78 % yield, m.p. : 186~189°C. Then this acid was

converted into its acid chloride by treating with fourfold quantity of thionyl chloride under reflux. The yield was quantitative.

Four equivalent quantity of natra-acetoacetic ester was prepared and under cooling externally to -2~0°C one equivalent quantity of the above acid chloride, in ether dissolved, was added in 20 minutes and heated for 2.5 hrs. on water bath.

The crude condensation product (IV) was obtained in 87 % yield. This product was submitted to ketonic cleavage by treating with fivefold quantity of 10 % aq. KOH solution.

The products (V) and (VI) were obtained in 69.5 % and 20.7 % yield respectively. Each product was identified by co-melting with each authentic sample. The product (V) was pyrolyzed to methylvinylketone as before.

The compound (IV) was then submitted to acid cleavage by treating with dry ammonia in ether. The yield of the product (VII) was 69.6 %. This product (VII) was pyrolyzed at 270~300° and methyl-vinylketone was found and identified from the distillate. The expected acryloylacetic ester ($CH_2=CHCOCH_2COOC_2H_5$) could not be detected.

Next the adduct (II) was reacted with excess phenylmagnesiumbromide by the usual manner and the aimed reaction product (VIII) was obtained in 75.8 % yield. The m.p. was 187~188.5° and the analysis coinsides well with the calculated values.

Found :   C, 89.81 % ;   H, 6.05 %
Calculated :   C, 89.69 ;   H, 6.19

This product was pyrolyzed together with 30 % quantity of $KHSO_4$ as dehydrating agent at 290~300°C under 5.5~6 mmHg pressure. As the product only the dehydrated product (IX) was obtained in 73.4 % yield. The melting point was 178~180°C and the analysis coinsides well with the calculated values.

Found :   C, 93.99 % ;   H, 6.19 %
Calculated :   C, 94.05 ;   H, 5.95

REFERENCES

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(3) J. A. Berson, *J. Am. Chem. Soc.,* 76, 2835 (1954).