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REACTION OF *SYN* HEAD-TO-HEAD COUMARIN DIMER WITH AMINES AND THERMAL BEHAVIOR OF THE ADDUCTS

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The lactone-opening reaction of *syn* head-to-head coumarin dimer with amines gave *c*-3,*c*-4-bis(2-hydroxyphenyl)-*r*-1,*c*-2-cyclobutanedicarboxamides and/or -dicarboximides. The product ratio of the amide to the imide varied with the reaction temperature and the amount of amine used. Thermal reaction of these lactone-opened derivatives proceeded in two ways depending on the nature of amine moiety to give either the original coumarin dimer or 2,2'-dihydroxystilbene and the maleimide derivative.

Both cyclobutane and lactone rings in *anti* head-to-head coumarin dimer are so strained that the lactone rings readily open by nucleophilic attack and release their strain energy.[1-3] Since the four substituents of *syn* head-to-head coumarin dimer (1), in contrast with those of *anti* head-to-head dimer, are situated in the same side of the cyclobutane ring,[4-6] the enhanced steric effect may be anticipated in the reactions. Based on this consideration, we examined reactivity of 1 with amines and thermal behavior of the adducts.[7]

The reaction of 1 with a large excess of butylamine at -25°C gave N,N'-dibutyl-*c*-3,*c*-4-bis(2-hydroxyphenyl)-*r*-1,*c*-2-cyclobutanedicarboxamide (2) in 48% yield[8] as a sole product. At higher temperature the formation of N-butyl-*c*-3,*c*-4-bis(2-hydroxyphenyl)-*r*-1,*c*-2-cyclobutanedicarboximide (3) was accompanied with the formation of diamide 2. The product ratio of 3/2 was 41/59 when the reaction was carried out at 40°C.[9] No conversion of 2 to 3 was observed under the same conditions. The results indicate that intra- and intermolecular lactone-opening reac-

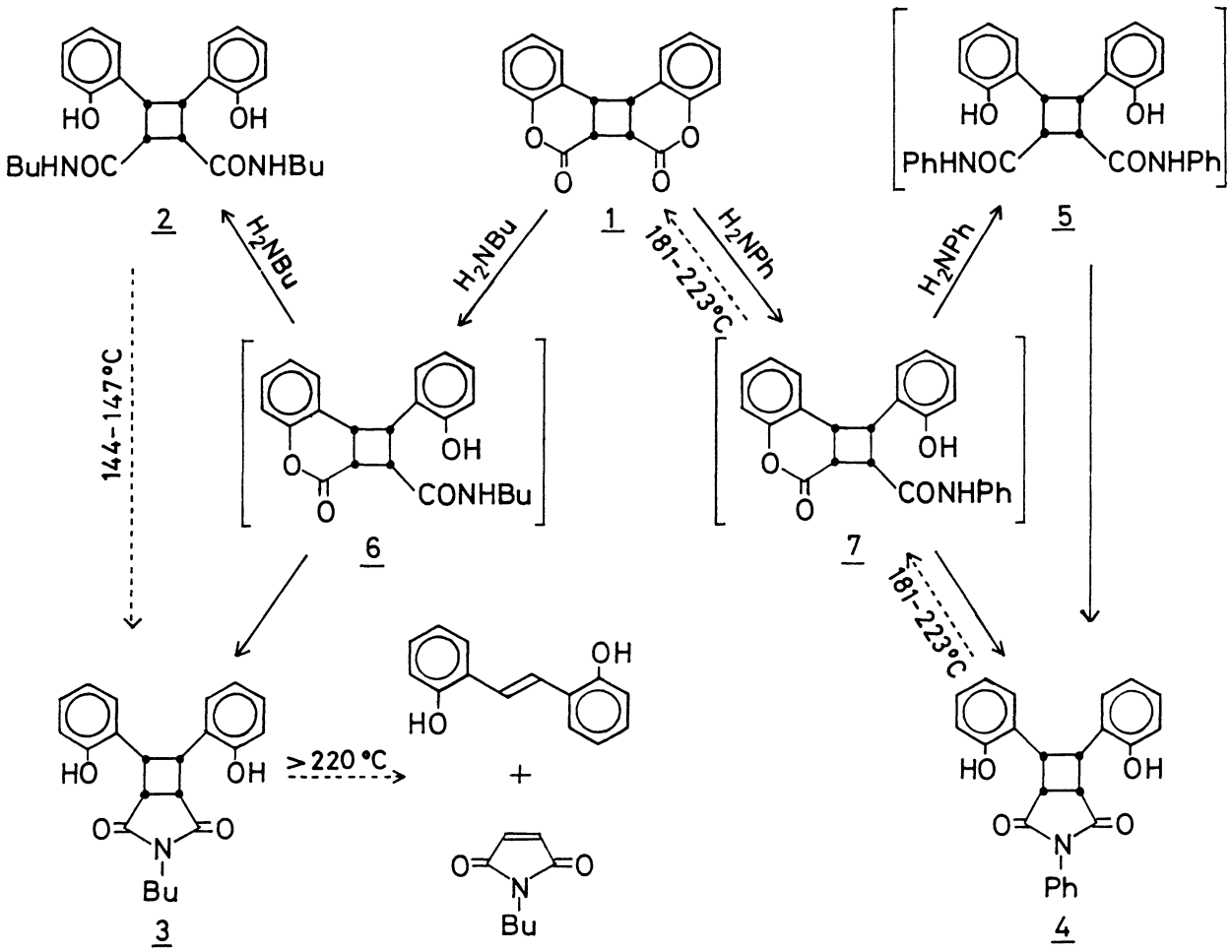
tions of the monoamide/monolactone intermediate (6) proceed simultaneously. The ratio of 3/2 increased with rising the temperature and with decreasing the amount of butylamine. The reaction of 1 with 7 molar amounts of butylamine in methanol at refluxing temperature gave only 3 in 47% yield.[8)]

No reaction occurred between 1 and aniline at 2°C, but at room temperature N-phenyl-*c*-3,*c*-4-bis(2-hydroxyphenyl)-*r*-1,*c*-2-cyclobutanedicarboximide (4) was obtained in 70% yield.[8)] The formation of *c*-3,*c*-4-bis(2-hydroxyphenyl)-*r*-1,*c*-2-cyclobutanedicarboxanilide (5) was not observed under any reaction conditions examined. Considering bulkier molecular size and less nucleophilic character of aniline compared to butylamine, the reaction behavior of 1 with aniline may be explained as follows: At the temperature required for the formation of the monoanilide/monolactone intermediate (7), the intramolecular attack to give 4 overcomes the intermolecular attack to give 5; and/or dianilide (5), if formed by the intermolecular attack of aniline, is too reactive to be isolated and converted immediately to 4.

Thermal behaviors of 1-4 were investigated by DSC-TG, ^{1}H-NMR, IR, TLC and HPLC. The DSC-TG curves of 2 (fig.1) show sharp endo- and exothermic peaks about 144 and 147°C, accompanying the 16.4% weight loss. These two peaks and weihgt loss are attributed to the melting of 2 and crystallization of 3 formed with the elimination of one mole of butylamine (the calculated weight loss is 16.7%). The imide formation was confirmed by ^{1}H-NMR and IR spectra of the product obtained by heating 2 at 200°C. Further heating of 3 (above 220°C) caused the thermal cleavage of the cyclobutane ring to give 2,2'-dihydroxystilbene and N-butylmaleimide.

On heating 4, the unexpected conversion into 1 occurred with the elimination of aniline, prior to the cleavage of the cyclobutane ring. In the DSC-TG curves of 4 (Fig.2) a broad endothermic peak and a sharp exothermic peak are observed in the temperature range of 181-223°C and at 190°C, respectively. These two peaks correspond to the vaporization of the eliminated aniline during the decomposition of 4 and the crystallization of 1. The weight loss of 21.4% at the same temperature range supports the above explanation on DSC-TG curves (the calculated weight loss of aniline is 24.2%). Furthermore, the decomposition mode of 4 above 223°C is essentially the same as that of 1. The product obtained by heating 4 at 240°C was identified as 1 by spectrmetrical methods.

The reaction of 1 with amines and the thermal reaction of 1-4 described above are summarized in the follwing scheme.



The coumarin dimer (1) is highly reactive to nucleophilic reagents, but still thermally so stable that the imide (4) is converted to the coumarin dimer (1) at fairly high temperature (above 181°C). On the other hand, thermal cleavage of the cyclobutane ring of 3 is predominant, showing that the electron-deficient character of the carbonyl carbon in 4 is stronger than that in 3. It is surprising that anilino group is removed by the neighboring phenoxy group in the conversion of 4 tc 1, in view of the fact that phenoxy group is one of the most effective leaving groups in substitution reactions.

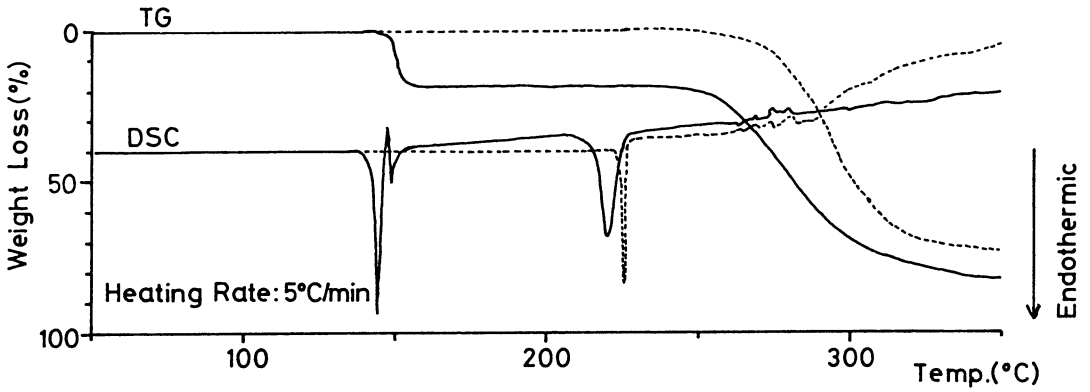


Fig. 1 DSC-TG Curves of 2(—, 6.8mg) and 3(----, 6.0mg).

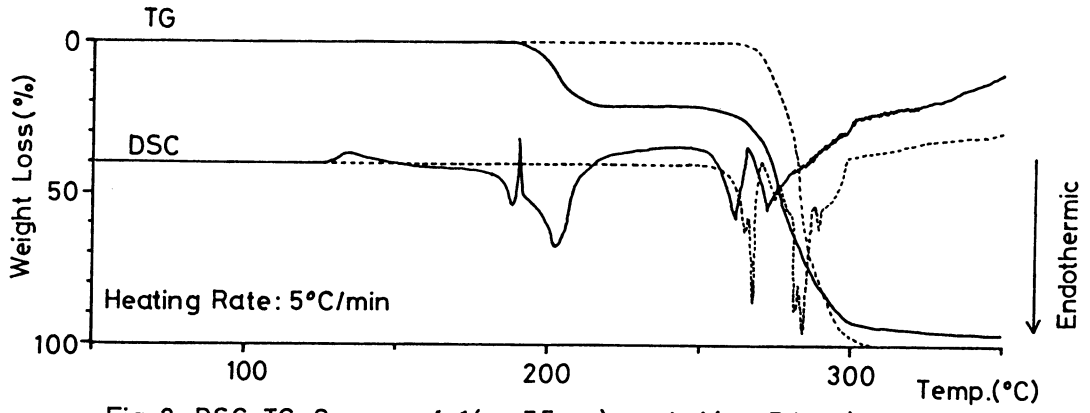


Fig. 2 DSC-TG Curves of 1(----, 7.5mg) and 4(—, 7.4mg).

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7) The structures of these compounds were confirmed by ^{1}H-NMR, IR and elemental analyses.

8) Nearly quantitative yield is presumed, because the ^{1}H-NMR and IR spectra of crude product are identical with those of recrystallized one.

9) The ratio of 3/2 was determined by ^{1}H-NMR spectra.

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