REACTION OF 3a,4-DIHYDROPHTHALIDES WITH ACETYLENIC DIENOPHILES

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Abstract —— The tricyclo[2.2.2]octa-2,5-diene-4,7-carbolactones, the initially-formed Diels-Alder adducts from 3a,4-dihydrophthalides and acetylenic dienophiles, were so strained that they underwent the retro-Diels-Alder reaction to afford the benzene derivatives in good vields.

The Diels-Alder reactions utilizing a variety of novel diene systems have provided a significant advance on the methodologies for the ring construction of the stereochemically interesting poly-Previously, we also reported that the 3a,4-dihydrophthalides 1-3, which were prepared by the intramolecular "diene-regenerable" Diels-Alder reaction of 2-pyrones, behaved as a novel type of the fused 1,3-cyclohexadiene system and underwent the intermolecular Diels-Alder reaction with olefinic dienophiles to yield tricyclo[2.2.2]oct-2-ene-4,5-carbolactones stereoselectively.3



<u>2</u>: R= Ph <u>3</u>: R= CO<sub>2</sub>Me

In the course of our study on the fused 1,3-cyclohexadiene systems, we have investigated the cycloaddition reaction of 1-3 with acetylenic dienophiles expecting the formation of the much highly strained cycloadducts, tricyclo[2.2.2]octa-2,5-diene-4,7-carbolactones. We wish to communicate here that the reaction of 1-3 with acetylenes gives the benzene derivatives via the cycloreversion of the primarily-formed tricyclo[2.2.2]octa-2,5-diene system.

When I was allowed to react with dimethyl acetylenedicarboxylate (DMAD)(1.2 equiv.) in refluxing xylene under nitrogen atmosphere for 40 h, a 1:1 adduct 4a and phthalide (5) were obtained in 45 and 3% yields, respectively, together with polymeric products, The structure of 4a was deduced to be an unsymmetrical allyl dimethyl benzene-1,2,3-tricarboxylate from the spectroscopic

Table 1. Reaction of 3a,4-Dihydrophthalides 1 and 2 with Acetylenic Dienophiles

					Phthalides
Compds	R	$R^1$	R <sup>2</sup>	Yield/%	(Yield/%)
<u>4a</u>	Н	CO <sub>2</sub> Me	CO <sub>2</sub> Me	45	<u>5</u> (3)
<u>4b</u>	Н	COPh	COPh	46	<u>5</u> (trace)
<u>4c</u>	Ph	CO <sub>2</sub> Me	CO <sub>2</sub> Me	62	<u>6</u> (23)
$\frac{4d}{2}$ $\left\{ \frac{1}{2} \right\}$	Н	CO <sub>2</sub> Me	Н	10	F (*****)
		н	CO <sub>2</sub> Me		<u>5</u> (trace)

properties and elemental analysis. The reaction of  $\underline{1}$  with dibenzoylacetylene (DBZA) gave similarly 3-allyloxycarbonyl-2-benzoylbenzophenone ( $\underline{4b}$ ) and  $\underline{6}$ . An unsymmetrical  $\underline{trans}$ -cinnamyl dimethyl benzene-1,2,3-tricarboxylate ( $\underline{4c}$ ) and 4-phenylphthalide ( $\underline{6}$ ) were obtained from 2 and DMAD.

These findings indicated that the tricyclo[2.2.2]octa-2,5-diene-4,7-carbolactones  $\underline{A}$ , which are expected to form initially in the reaction, are too strained to isolate under the conditions and undergo the retro-Diels-Alder reaction to give the benzene derivatives  $\underline{A}$ .

$$\frac{1}{2} \text{ and } \frac{2}{2} \qquad \frac{R^1}{R^2} \qquad \frac{R^2}{R^2} \qquad \frac{R}{R} \qquad \frac{4}{R}$$

In order to investigate the regionselectivity of the addition, the reaction with methyl propiolate (MP) was carried out. The reaction of  $\underline{1}$  with an excess of MP under reflux in xylene and the usual working-up gave ca. 1:1 mixture of allyl methyl isophthalate ( $\underline{4d-1}$ ) and phthalate ( $\underline{4d-2}$ ) in total yield of 10%.

On the other hand, the reaction of 4-methoxycarbonyl-3a,4-dihydrophthalide (3) with acetylenes

Table 2. Reaction of 4-Methoxycarbonyl-3a,4-dihydrophthalide (3) with Acetylenic Dienophiles

Compds	R <sup>1</sup>	R <sup>2</sup>	Yield/%	<u>8</u> Yield/%
<u>7a</u>	CO <sub>2</sub> Me	CO <sub>2</sub> Me	61	28
<u>7b</u>	COPh	COPh	60	31
- ( <u>1</u>	CO <sub>2</sub> Me	Н	41	37
$\frac{7c}{2}$	Н	CO <sub>2</sub> Me	10	37

proceeded in a slightly different manner from that of  $\underline{1}$  or  $\underline{2}$ ;  $\underline{e} \cdot \underline{q} \cdot$ , firstly the formation of polymeric products was scarcely observed.

The reaction of  $\underline{3}$  with DMAD and DBZA gave trimethyl benzene-1,2,3-tricarboxylate  $(\underline{7a})$  and 3-methoxycarbonyl-2-benzoylbenzophenone  $(\underline{7b})$ , respectively, together with 4-methoxycarbonylphthalide  $(\underline{8})$ . A 1:1 mixture of dimethyl isophthalate  $(\underline{7c-1})$  and phthalate  $(\underline{7c-2})$  was also obtained from 3 and MP.

Therein, the 3a,4-dihydrophthalide  $\underline{3}$  was converted into the 3a,7a-dihydrophthalide ( $\underline{3}$ ) by the thermally-allowed 1,5-hydrogen shift, which underwent Diels-Alder reaction with acetylenes to afford tricyclo[2.2.2]octa-2,5-diene-7,8-carbolactones  $\underline{B}$ . The tetracyclic adducts  $\underline{B}$  yielded the benzene derivatives  $\underline{7}$  via the retro-Diels-Alder reaction accompanied with the extrusion of 2(5H)-furanone.

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## REFERENCES AND NOTES

- Cycloaddition Reactions of 2-Pyrones and Related Compounds. Part III. Part II of this series: M. Noguchi, S. Kakimoto, H. Kawakami, and S. Kajigaeshi, <u>Heterocycles</u>, 1985, 23, 1085.
- For recent reviews: S. Danishefsky, <u>Acc. Chem. Res.</u>, 1981, <u>14</u>, 400.
  S. M. Weinred and R. R. Staib, <u>Tetrahedron</u>, 1982, <u>38</u>, 3087.
  D. L. Boger, <u>Tetrahedron</u>, 1983, <u>39</u>, 2869.
  - Y. Kita and Y. tamura, Yuki Gosei Kagaku Kyokai Shi, 1984, 42, 860. P. Magnus, T Gallagher, P. Brown, and P. Pappalardo, Acc. Chem. Res., 1984, 17, 35.
- 3. M. Noguchi, S. Kakimoto, and S. Kajigaeshi, Chem. Lett., 1985, 151.
- 4. All new compounds in this communication gave satisfactory analytical values and their structures were determined on the basis of the spectral data shown below.
  - <u>4a</u>: Colorless needles; mp 55-56 °C; ir 1740, 1720 cm<sup>-1</sup>(CO); nmr & 3.92, 4.00(2s, 3H each, -CH<sub>3</sub>), 4.82(m, 2H, -CH<sub>2</sub>-), 5.4(m, 2H, =CH<sub>2</sub>), 6.0(m, 1H, -CH=), 7.52(t, 1H, H-5, J=7 Hz), 8.2 (m, 2H, H-4 and H-6); mass m/z 278(M<sup>+</sup>).
  - <u>4b</u>: Yellow oil; ir 1750, 1690 cm<sup>-1</sup>(CO); nmr  $\delta$  4.48(dd, 2H, -CH<sub>2</sub>-, J=6 and 1.5 Hz), 5.18(m, 2H, =CH<sub>2</sub>), 5.6(m, 1H, -CH=), 7.3-7.8(m, 11H, H-3 and phenyl protons), 8.2(m, 2H, H-4 and H-6); mass m/z  $370(M^{+})$ .
  - 4c: Colorless needles; mp 96-97 °C; ir 1730 cm<sup>-1</sup>(CO); nmr  $\delta$  3.92, 3.96(2s, 3H each, -CH<sub>3</sub>), 4.98(d, 2H, -CH<sub>2</sub>-, J=7 Hz), 6.4(m, 1H, H-5, J=7 Hz), 6.7(d, 1H, =CH-Ph, J=15 Hz), 7.3-7.5(m, 5H, phenyl protons), 7.56(t, 1H, H-5, J=7 Hz), 8.2(m, 2H, H-4 and H-5); mass m/z  $354(\text{M}^+)$ .
  - 4d-1: nmr  $\delta$  3.95(s, 3H, -CH<sub>3</sub>), 4.8(-CH<sub>2</sub>-), 5.3(=CH<sub>2</sub>), 5.8-6.1(-CH=), 7.72(m, 1H, H-5), 8.2(m, 2H, H-4 and H-5), 8.68(br t, 1H, H-2, J=1.5 Hz).
  - 4d-2: nmr 6 3.89(s, 3H, -CH<sub>3</sub>), 4.8(-CH<sub>2</sub>-), 5.3(=CH<sub>2</sub>), 5.8-6.2(-CH=), 7.4-7.6(m, 4H, H-3, H-4, H-5, and H-6).
  - <u>7b</u>: Colorless prisms; mp 122-124 °C; ir 1720, 1655 cm<sup>-1</sup>(CO); nmr  $\delta$  3.60(s, 3H, -CH<sub>3</sub>), 7.2(m, 2H, H-4 and H-5), 7.3-7.8(m, 11H, H-6 and phenyl protons); mass m/z 344(M<sup>+</sup>).

The structural confirmations of phthalides  $\underline{5}$ ,  $\underline{6}$ , and  $\underline{8}$  and  $\underline{7a}$  and  $\underline{7c}$  were accomplished by comparing the physical or spectral data with those of the authentic samples or the reported ones.

- $\underline{6}$ ,  $\underline{6}$ , and  $\underline{8}$  and  $\underline{7c}$ : Identified with the authentic samples.
- 7a: Colorless needles; mp 103-104 °C(lit. 5 mp 102 °C).
- 5. C. Graede and M. Leonhardt, Ann. Chem., 1896, 290, 217.

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