

tigators<sup>2,3c,7,15</sup> to predict the preferred regioisomers in the Diels-Alder reaction. A simple second-order perturbation treatment<sup>16</sup> predicts a decrease in the rate of reaction as the terminal frontier electron density decreases (assuming that frontier orbital energies are constant). The calculations, however, show a decrease in the terminal frontier electron density of the dienes as the logarithm of the relative rate of reaction increases (Table I).<sup>17</sup> This lack of correlation between the terminal frontier electron densities of the dienes and the logarithm of the relative rates is not unexpected when one considers the large change ( $\sim 30$  kcal) in the energy of the diene HOMO. Consequently, the terminal electron densities of the dienes are not useful in predicting diene reactivity in such cases.

In conclusion, the linear relationships between the energy of HOMO of the diene and the logarithm of the relative rates of reaction and between the total  $p_z$  density of the butadiene moiety and the logarithm of the relative rates of reaction indicate that these molecular properties do have a significant effect on the stability of the transition state of this normal electron demand Diels-Alder reaction. Subsequently, the relative reactivities of the dienes can be predicted from either the HOMO energy or the total  $p_z$  density of the butadiene moiety. Though the terminal frontier electron densities of the dienes are useful for determining regioselectivity, they were not found to be useful for predicting relative diene reactivity in cases where the energy of the diene HOMO varied significantly.

**Acknowledgments.** P. V. Alston thanks Texaco Inc. for their fellowship support. Also, we thank the Virginia Commonwealth University Computer Center for a grant of computer time and D. D. Shillady for helpful discussions.

**Registry No.**—Maleic anhydride, 108-31-6.

### References and Notes

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- (9) The maleic anhydride molecule was assumed to be planar with a plane of symmetry bisecting the COC angle of the ring. No significant change in the energies of HOMO and LUMO was found by varying this angle between 104 and 109°.
- (10) We have found that the relationship between the CNINDO energy of the highest occupied molecular orbital and the experimental ionization potential for dienes and dienophiles with electron-donating substituents ( $\text{OCH}_3$ ,  $\text{CH}_3$ ) and conjugating substituents ( $\text{C}_6\text{H}_5$ ) is satisfactory. The general qualitative trend of the experimental ionization potential is correctly represented by the CNINDO methods in these systems. However, for electron-withdrawing substituents such as CHO and CN, the theory predicts  $\pi$  HOMO values which are higher than that of ethylene, while the experimental values<sup>2a</sup> are lower. These observations are in agreement with Bloor and Breen's CNDO study of monosubstituted benzenes.<sup>11</sup> Thus, we expect that the qualitative trend observed in the CNINDO HOMO energies of the 1-( $p$ -substituted phenyl)-1,3-butadienes will be real. Also, the CNINDO HOMO energies of the transoid and cisoid conformations of the dienes studied varied by less than 0.1 eV. This gives some justification to the widely accepted use of experimental ionization potentials to determine the energies of the HOMO of the cisoid conformations of open-chain dienes.
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### Polyphenylated Cyclobuten-4-ones from Squaryl Dichloride

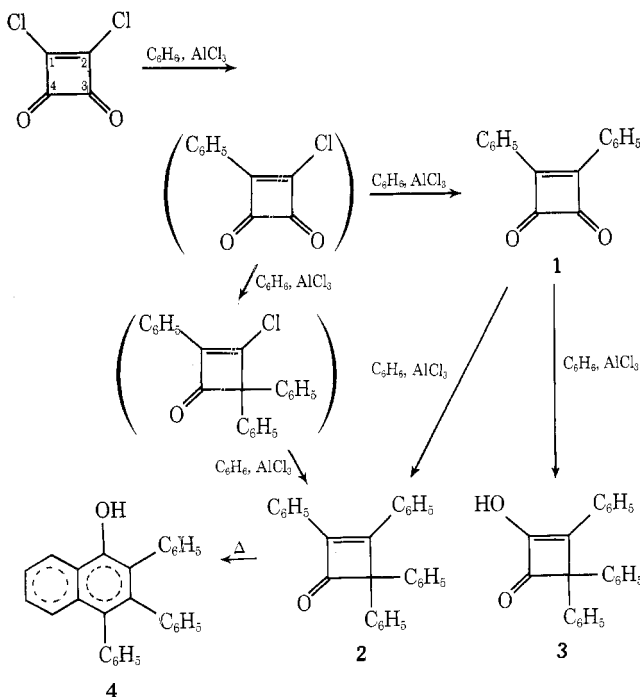
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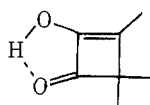
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The high-yield synthesis of 1,2-diphenylcyclobutene-3,4-dione (1) from squaryl dichloride in benzene solution under Friedel-Crafts conditions was reported in a recent communication.<sup>1</sup> At the low temperatures ( $\sim 10^\circ$ ) employed in that work, the reaction did not proceed substantially beyond the stage of 1 despite a benzene/squaryl dichloride molar ratio of nearly 43 and a moderate excess of Lewis acid ( $\text{AlCl}_3$ , freshly sublimed, 2.26 mol per mol of dichloride).

We now report that, at higher temperatures, the dichloride reacts with more than 2 mol of benzene. As a result, one observes drastically lowered yields, or even complete disappearance, of 1 in favor of the successor species 2, 1,2,3,3-tetraphenylcyclobuten-4-one, whose yield in the previous work<sup>1</sup> had amounted to a mere 1%. In addition, the enolone 3, 1-hydroxy-2,3,3-triphenylcyclobuten-4-one, arises in appreciable yields, and small quantities of the naphthol 4, resulting from thermal electrocyclic ring opening<sup>2</sup> of 2 and intramolecular cyclization of the intermediary vinyl ketene species, are also formed. For example, at the reflux temperature of the benzene medium (24 hr), with catalyst ( $\text{AlCl}_3$ , freshly sublimed) and reactant concentrations the same as in the preceding investigation,<sup>1</sup> squaryl dichloride was found to convert to 2 and 3 in 53 and 27% yields, respectively; furthermore, 4 was separated in 1.5% yield.



Under conditions similar to those delineated, yet with  $\text{AlCl}_3$  "as received" (*i.e.*, no resublimation done prior to use), at a Lewis acid/squaryl dichloride molar ratio of 2.3, the intermediary 1 is not entirely consumed but remains in the reaction mixture in 10–20% yield. The less efficacious catalyst system in this case, moreover, produces slightly diminished yields of 3 and grossly reduced yields of 2. Increased quantities (up to 10%) of 4 can be collected instead. For example, after a reflux period of 20 hr we obtained 10% 1, 16% 2, 21% 3, and 7% 4. The products in all reactions were separated by column chromatography. The known compounds 1, 2, and 4 were identified by comparison (melting point, ir) with products described in the literature. The structure of 3 derives from elemental analysis and spectral data. The parent ion peak in the mass spectrum appears at  $m/e$  312. The ir spectrum displays the broad OH stretching absorption with maxima at 3183 and  $3445\text{ cm}^{-1}$  characteristic of the 1-hydroxycyclobuten-4-one system capable of strong intramolecular hydrogen

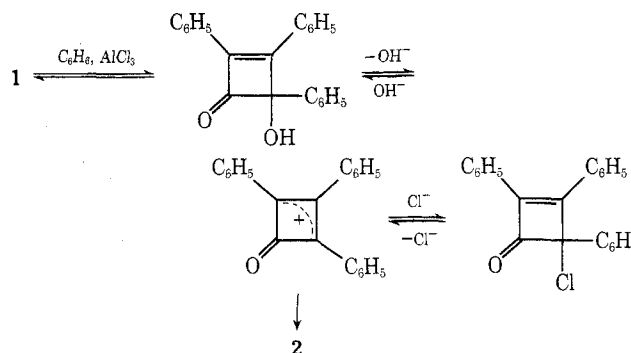


bonding,<sup>3</sup> and  $\nu_{\text{C=O}}$  is shown at the low-frequency position ( $1730\text{ cm}^{-1}$ ) expected<sup>3,4</sup> for the hydrogen-bonded carbonyl group in this system.<sup>5–7</sup> The  $^1\text{H}$  nmr spectrum reveals the anticipated low-field multiplet at  $\delta$  7.5–7.8 ppm (2 H) due to the two deshielded ortho protons of the phenyl substituent at C-2, whereas the remaining phenyl protons (13 H) resonate at 7.1–7.5 ppm.<sup>8,9</sup>

In order to demonstrate the anticipated intermediacy of 1 in the reaction course leading to the compounds discussed, we conducted a run in which 1 was employed in place of squaryl dichloride under conditions otherwise identical with those of the first-mentioned experiment (24 hr in refluxing benzene; freshly sublimed  $\text{AlCl}_3$ , 2.26 mol per mol of 1). The same products 2, 3, and 4 were collected, as expected, and both the combined yield of 2 plus 3 (81%) and the yield of 4 (1.6%) were nearly identical with the corresponding yield data of the squaryl dichloride experiment. In outstanding contrast, however, the yield of 2 (40%) was found to be decreased and that of 3 (41%) increased, relative to the original experiment. This shows that the sequence  $1 \rightarrow 2$  is not the sole path leading to the tetraphenyl ketone. A second reaction sequence involving the two monochlorides, 2-chloro-1-phenylcyclobuten-3,4-dione and 2-chloro-1,3,3-triphenylcyclobuten-4-one (not isolated here and, hence, placed in parentheses in the scheme above), is likely to contribute to the formation of 2. As the latter sequence is not operative in the reaction starting out from 1, 2 will arise in lower yield in that case; on the other hand, formation of 3 from 1 must be correspondingly favored because of the high initial concentration of the latter compound.

Our results, as seen against the background of the preceding work,<sup>1</sup> indicate that step  $1 \rightarrow 2$  proceeds with a slightly lower activation energy than is required for path  $1 \rightarrow 3$ . The most probable mechanism leading to 3 involves 1,3-addition of benzene across the enone system (*e.g.*, at C-1 and C-3) of 1, a process resisted by the requirement of two rehybridization steps, to a minor extent also by the steric demand of the phenyl group at C-1.<sup>10</sup> At low temperatures, therefore, addition at one of the carbonyl C atoms (and further rapid reaction with benzene of the allylic-type cyclobutenyl cation<sup>11–13</sup> resulting from Lewis acid-induced ionization of the primary adduct carbinol) is probably the preferred path. This may account for both

the formation of 2 and the absence of 3 in the low-temperature reactions of the previous study. At the boiling temperature of benzene, on the other hand, the competitive-



ness of the 1,3-addition becomes appreciable, as the yield data for 3 attest.

The enhanced conversion of 2 to the naphthol 4 in reactions catalyzed with low-activity Lewis acid confirms the expectation that the process of ring opening (and subsequent cycloaddition) is retarded by complexation, *i.e.*, enolate formation, of 2 with active  $\text{AlCl}_3$ . This question is under further investigation.

### Experimental Section

**Friedel-Crafts Reaction of Squaryl Dichloride with Benzene. A. With Freshly Sublimed  $\text{AlCl}_3$ .** In oven-dried and nitrogen-purged equipment, 0.80 g (6.0 mmol) of freshly sublimed  $\text{AlCl}_3$  was added to the stirred solution of 0.40 g (2.65 mmol) of resublimed squaryl dichloride<sup>14</sup> in 10 ml (8.79 g) of dry benzene at  $18^\circ$ . Under a blanket of predried nitrogen, the mixture was stirred for 1 hr at the same temperature, followed by 24 hr at reflux. After the addition of 100 ml of benzene, the reaction mixture was shaken with 100 ml of ice-cold 0.1 M hydrochloric acid. The benzene layer, combined with the benzene washings of the aqueous phase, was washed with water and dried over  $\text{Na}_2\text{SO}_4$ . The residue remaining after solvent removal *in vacuo* was chromatographed on silica gel, Merck 7734, with band separation monitored by tlc on silica gel. Elution with the solvents indicated (redistilled prior to use), followed by evaporation of the eluates to dryness under reduced pressure, furnished the following compounds.

**Band I** (40/60 benzene-hexane): 0.015 g (1.5%) of crude 2,3,4-triphenyl-1-naphthol (4). Repeated recrystallizations from benzene-hexane produced the compound as fine white needles: mp  $163^\circ$  (lit.<sup>15</sup>  $163^\circ$ ); mass spectrum,  $m/e$  372 ( $\text{P}^+$ ); ir spectrum (KBr)  $\nu_{\text{O-H}}$   $3535\text{ cm}^{-1}$  (sh  $3521\text{ cm}^{-1}$ ).

**Anal.** Calcd for  $\text{C}_{28}\text{H}_{20}\text{O}$  (372.4): C, 90.29; H, 5.41. Found: C, 90.78, 88.99; H, 4.99, 5.40.

**Band II** (40/60 benzene-hexane): 0.52 g (52.7%) of crude 1,2,3,3-tetraphenylcyclobuten-4-one (2). Recrystallization from benzene-hexane to constant melting point gave light yellow needles, mp  $129\text{--}130^\circ$  (lit.<sup>16</sup>  $139^\circ$ ), undepressed on admixture of authentic product prepared by Ried's procedure<sup>16</sup> (mp  $129\text{--}130^\circ$ ): mass spectrum,  $m/e$  372 ( $\text{P}^+$ ).

**Band III** (50/50 benzene-hexane): 0.010 g of fine-crystalline, white solid decomposing over range  $130\text{--}230^\circ$ ; not further investigated.

**Band IV** (50/50 benzene-acetone): 0.22 g (26.6%) of crude 1-hydroxy-2,3,3-triphenylcyclobuten-4-one (3). Recrystallization from benzene-hexane furnished fine, colorless needles: mp  $206\text{--}208^\circ$  dec; mass spectrum,  $m/e$  312 ( $\text{P}^+$ ); ir spectrum (KBr)  $3445$  (m-s) and  $3183$  (s)  $\text{cm}^{-1}$  ( $\nu_{\text{O-H}}$ , H-bonded),  $1730$  ( $\nu_{\text{C=O}}$ ),  $1640$  ( $\nu_{\text{C=C}}$ );  $^1\text{H}$  nmr spectrum (60 MHz in  $\text{CDCl}_3$ ,  $\delta$  relative to TMS) 7.5–7.8 ppm (2 H), 7.1–7.5 (13 H).

**Anal.** Calcd for  $\text{C}_{22}\text{H}_{16}\text{O}_2$  (312.4): C, 84.58; H, 5.17. Found: C, 83.81; H, 5.12.

An experiment conducted as above, yet with 2.65 mmol of 1 in place of squaryl dichloride, gave 4 (1.6%), 2 (40.2%), 1 (3.1% recovery), and 3 (40.9%), in that order, on chromatographic work-up.

**B. With  $\text{AlCl}_3$  "as Received."** Following the addition of 1.54 g (11.5 mmol) of commercial-grade  $\text{AlCl}_3$  "as received" (Merck

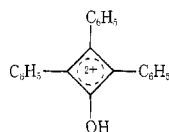
sublimed, code 1082) to the solution of 0.755 g (5.0 mmol) of squaryl dichloride, the mixture was stirred for 1 hr at 20° and another 20 hr at reflux under the conditions of the experiment described in (A). Work-up as before furnished four chromatographic bands, from which the following compounds were isolated: band I, 0.126 g (6.8%) of crude 4, mp 163° (from benzene-hexane); band II, 0.291 g (15.6%) of crude 2, mp 130–131° (from benzene-hexane); band III, 0.119 g (10.2%) of crude 1, mp 95° (from benzene-chloroform) (lit. 97–97.2°, 17 98°, 3a 94–95° 1), undepressed on admixture of authentic<sup>1</sup> compound; band IV, 0.328 g (21.0%) of crude 3, mp 204–208° dec (from benzene-hexane).

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**Registry No.**—2, 28480-68-4; 3, 51065-83-9; 4, 2892-40-2; squaryl dichloride, 2892-63-9; benzene, 71-43-2.

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- (8) This nmr pattern, for which there is precedence in the spectra of 1-phenylcyclobutene-3,4-dione<sup>9a</sup> and some 1-chloro-2-phenylcyclobutene derivatives,<sup>9b</sup> rules out the alternative structure of the 3-hydroxy-1,2,3-triphenylcyclobuten-4-one isomer expected to give a 4:11 intensity ratio of the low-field to high-field phenyl proton signals.
- (9) (a) W. Ried and A. H. Schmidt, *Angew. Chem.*, **84**, 1048 (1972); *Angew. Chem., Int. Ed. Engl.*, **11**, 997 (1972). Much of the pioneering work done by Roberts' and Ried's schools on unsaturated four-membered ring ketones is covered in this review on phenylcyclobutenediones. (b) Y. Kitahara, M. C. Caserio, F. Scardiglia, and J. D. Roberts, *J. Amer. Chem. Soc.*, **82**, 3106 (1960).
- (10) In the sterically more favorable case of 1-phenylcyclobutene-3,4-dione as the substrate, Ried and Schäfer<sup>3a</sup> observed the  $\text{AlCl}_3$ -catalyzed 1,3-addition of aromatics (involving positions 2 and 4 of the four-membered ring system) to proceed without restriction.
- (11) The existence of suitably substituted cyclobutenyl and oxocyclobutenyl cations in acidic solution,<sup>12a</sup> and even in the solid state,<sup>12b-d</sup> has been demonstrated. On the other hand, protonation (at oxygen) of the oxocyclobutenyl cation, which would give the formally dicationic species



is most unlikely to occur in the environment of our experiments, as highly acidic conditions are required even for the generation of the tetraphenyl-substituted dication,<sup>13</sup> in which a higher extent of stabilization through charge delocalization is expected than in the hydroxytriphenyl species drawn above.

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### Birch Reduction of *N*-Methylindoline

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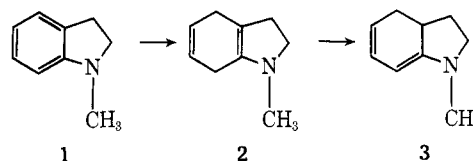
Pursuant to a need for some intermediate compounds in our development of certain synthetic routes, we investigated the Birch reduction of *N*-methylindoline<sup>2</sup> (1). It has been suggested<sup>3</sup> that 3 is the probable product of this reaction and that in the case of *N,N*-dimethyl-*p*-toluidine<sup>4</sup> a mixture of 2,3-dihydro-*N,N*-dimethyl-*p*-toluidine and 2,5-dihydro-*N,N*-dimethyl-*p*-toluidine are the products.

Our conditions for the reduction require lithium in liquid ammonia-tetrahydrofuran-isopropyl alcohol, and, upon subjection of 1 to this reaction, *N*-methyl-4,7-dihydroindoline (2) is the sole product. Our experience with the reduction of 1 and its product 2 indicates that no 3 is formed during the reduction. However, 2 is a very labile substance with respect to rearrangement to 3 and extreme care is required to prevent this rearrangement from occurring. As one might expect, exposure of 2 to acidic substances accelerates the conversion to 3. For example, using commercial  $\text{CCl}_4$  or  $\text{CDCl}_3$ , which may contain even trace amounts of HCl, will cause 3 to develop. We also found that the following drying agents also cause the 2 to 3 reaction:  $\text{CaCl}_2$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{MgSO}_4$ , and  $\text{CaSO}_4$ . However, 2 appears stable, neat or in ether solutions, when stored in the cold (0°) over solid KOH. Product 2 can be distilled without rearrangement but rigorous treatment of the glassware with ammonium hydroxide is necessary to prevent rearrangement from happening.

One can, of course, produce 3 directly from the reduction by purposely exposing the reduction product to acid during work-up. One such method is distillation from a small amount of acidic ion-exchange resin.

The structures for 2 and 3 follow directly from their spectral and analytical data. For 2 in its nmr spectrum the broad singlet of 2 H at  $\tau$  4.4 and the 4 H in the  $\tau$  7.2 region are fully characteristic of the 1,4-diene in a cyclohexene ring. In the case of 3, it has three separate single proton vinyl resonances at  $\tau$  4.1, 4.9, and 5.6. The first two are multiplets and the third is a broad doublet in a chemical shift region typical of a  $\beta$ -vinylamine type. In addition 3 gives a uv spectrum with  $\lambda_{\text{max}}$  3306 ( $\epsilon$  5200) indicative of the conjugated enamine.

It appears from these results that 1 indeed gives the normal product (2) from the Birch reduction and that 2 can be used in some synthetic operations with due cau-



tion. Also one can easily prepare 3 from 1 and it too may be of use in synthetic sequences.

It would seem to be a logical extension of our results that *N,N*-dialkyl aromatic amines will in general give the usual unconjugated diene as the sole primary product. However, due caution must be taken to see that the very facile rearrangement of the unconjugated to the conjugated diene does not take place.