# Diels–Alder Adducts from Reactive Aryl Acetoxy Dienes and the Effect of Stereochemistry on Their Cycloacylations[1,2]

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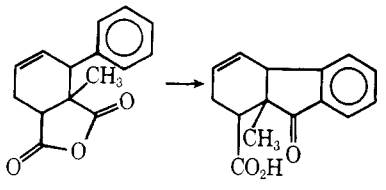
*Received March 7, 1977*

The interaction of aryl butenones with maleic and citraconic anhydride in the presence of isopropenyl acetate under acid conditions yielded Diels–Alder normal adducts (**4a, 4b, 6**) in 41–70% yields. When mesaconic acid was used, a 25% yield of trans 1,2-anhydride (**8b**) was realized. Friedel–Crafts cycloacylation of the cis anhydrides yielded bicyclo[3.3.1]nonanone ring systems (**18, 19**), whereas the trans anhydride produced substituted hydrofluorenones (**20, 21**). These observations are interpreted in terms of stereochemistry of cis and trans anhydrides.

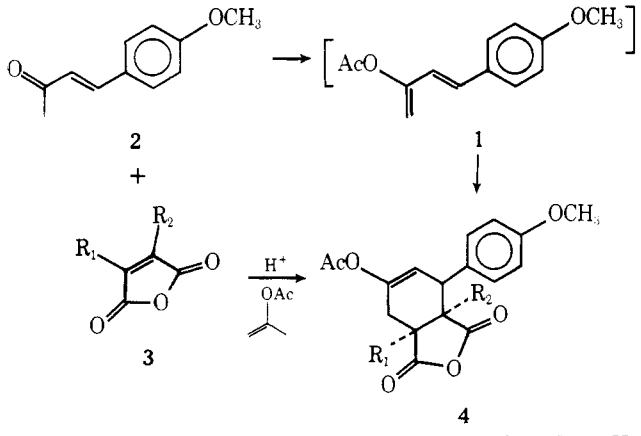
The cycloacylation of 2-phenylcyclohexanecarboxylic acids and its derivatives provides a convenient and reliable entry into the hydrofluorenone ring system.[3] A similar treatment of citraconic anhydride–arylbutadiene adducts was previously considered to form analogous products (eq 1).[4,5]



(1)

We anticipated using this method for the construction of a hydrofluorenone nucleus, with sufficient functionality as to be a convenient intermediate to some diterpenes.[6]

This paper deals with the formation of 2-arylcyclohexene-*cis*- and -*trans*-1,2-dicarboxylic anhydrides and the effect of stereochemistry on their cycloacylations. Initial studies were directed toward the synthesis of 3-acetoxy-1-anisyl-1,3-butadiene (**1**) and its subsequent Diels–Alder reactions with appropriately substituted dienophiles. However, the high reactivity of this diene under the usual conditions[7] for enol ester formation rendered this approach unattractive. Utilization of Wolinsky's procedure[8] for in situ formation and Diels–Alder trapping of reactive dienes, such as **1**, offered a relatively simple procedure for making the desired adducts.



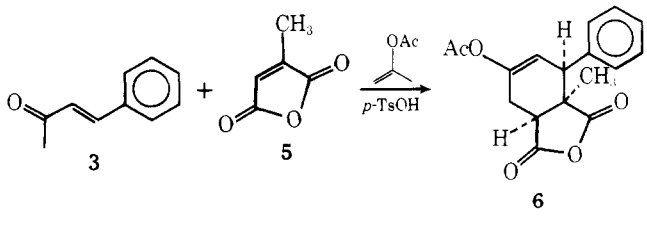
a, $R_1 = R_2 = H$; b, $R_1 = H$, $R_2 = CH_3$; c, $R_1 = CH_3$, $R_1 = H$

## Results and Discussion

The reaction of 4-(*p*-methoxyphenyl)-3-buten-2-one (**2**) with citraconic anhydride (**3b**) in the presence of *p*-toluenesulfonic acid in a solution of isopropenyl acetate proceeded in a "normal" Diels–Alder fashion to give **4b** in a 54.5% yield. The structure of **4b** was assigned first by analogy with other Diels–Alder type reactions[9] involving cyclic dienophiles and acyclic dienes and second with the following spectral evidence. The IR spectrum of **4b** displayed expected anhydride peaks at 1785 and 1845 $cm^{-1}$, with the former band at higher intensity, characteristic of cyclic anhydrides; the enol acetate carbonyl absorbed at 1755 $cm^{-1}$, attesting to the intermediacy of an aryl acetoxy butadiene, such as **1**. In the NMR spectrum, the vinyl proton appeared as a pair of triplets, with a major splitting ($J_{3,4}$) of 6.5 Hz and a long range splitting ($J_{4,6}$) of 1.5 Hz. Had there been a proton at $C_3$ (e.g., **4c**), additional coupling ($^4J_{2,4}$, where $\theta = 170°$ and $\theta' = 50°$, calculated value of ~0.40 Hz[10]) would have been expected. The position of the angular methyl group was verified by decoupling experiments.[11a] When the vinyl proton was irradiated, the benzyl proton ($C_3$), which had been split into a broad pair of peaks, collapsed to a broad singlet.[12] Irradiation of the $C_3$ proton, on the other hand, caused a collapse of the vinyl proton, with no apparent change of the rest of the spectrum. We concluded, therefore, that the angular methyl group was on $C_2$, and not on $C_1$ as would be expected on steric grounds. These results and those of its cyclization (see **18** and **19**) established the stereochemistry of **4b**.

Interaction of **2** with maleic anhydride (**3a**) produced adduct **4a** in 70% yield. Anhydride **4a** exhibited cyclic anhydride absorptions at 1784 and 1856 $cm^{-1}$, and an enol acetate absorption at 1755 $cm^{-1}$. The NMR spectrum, consistent with the proposed structure, shows a one-proton vinyl doublet of triplets with a major splitting of 5.7 Hz and a minor splitting of 1.2 Hz, similar to **4b**. A molecular ion at *m/e* 316 established its molecular weight.

We turned next to *trans*-4-phenylbut-3-en-2-one (**5**) as a diene source. Interaction of **5** with citraconic anhydride (**3b**) under identical conditions gave a single adduct **6** whose structure was assigned on the basis of its spectral similarity to **4a** and **4b**, in addition to results of its cycloacylation (see below).



In an effort to examine the effect, if any, of dienophile geometry on the regioselectivity of the reaction, a trans diacid was used in place of a cyclic anhydride. To this end, **2** was allowed to react with mesaconic acid (**7**) under identical conditions. This reaction yielded a cyclic anhydride (**8**) instead of a diacid (vida infra), and from the results of spin decoupling experiments[11b] the angular methyl group was placed at $C_2$ rather than at $C_1$.

Since the reaction was run under acid conditions, it was

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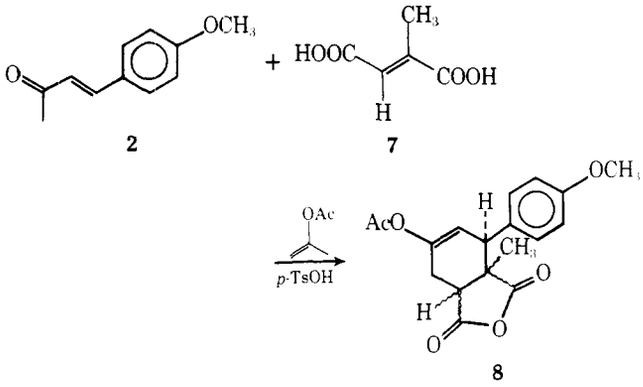
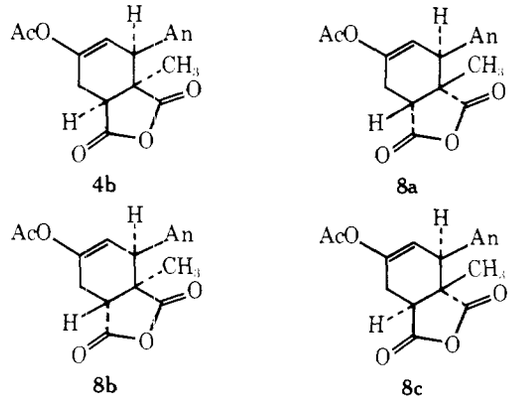


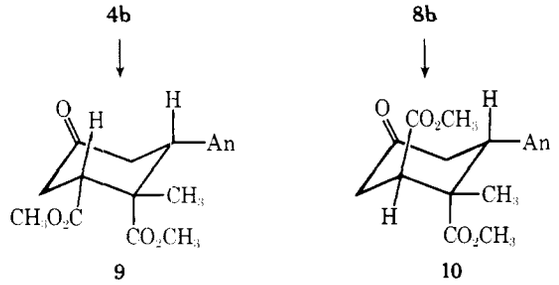
2 7 8

conceivable that an isomerization of starting compounds and/or product had taken place. It behooved us, therefore, to consider all possible isomers resulting from such a reaction before proceeding. Thus, four stereoisomers were theoretically possible for 8, each differing in geometry about the anhydride and aryl groups. These were **4b** (cis/cis), **8a** (cis/trans), **8b** (trans/cis), and **8c** (trans/trans) isomers.



4b 8a 8b 8c

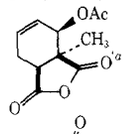
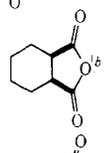
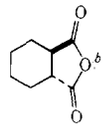
First, anhydride **4b** was quickly eliminated from this list since its IR and NMR spectra were different from those of **8**. Assuming there was coordination of the carbonyl and aromatic functions with bond formation, leading to a "cis" juncture,[9] an acid-catalyzed isomerism of dienophile (**7** → **3b**) or of the "trans" product (acid or anhydride) could not have occurred since either of these transformations would have formed **4b**. Second, anhydrides **4b** and **8** were hydrolyzed (**4b** → **9a**) and then esterified with diazomethane to diesters (**9** and **10**) without a change in their stereochemistry. The carbomethoxyl protons of one ester group from both keto diesters absorbed at almost the same position (**9**, 220 Hz; **10**, 224 Hz), indicating to us that both isomers had one ester group experiencing similar chemical environments. Since **9** and **10** both had a cis carbonyl/aryl relationship (vida supra), this was considered



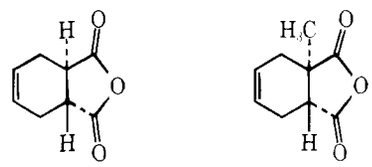
9 10

to be the ester at $C_2$. The other carbomethoxyl group had chemical shifts of 222 Hz for **9** and 213 Hz for **10**, representing ester groups at equatorial and axial positions, respectively. The cyclization of this anhydride offered further evidence that it had the stereochemistry of **8b**. Thus, trans 1,2-anhydride **8b** was formed, and the geometrical integrity of dienophile **7** was thereby retained throughout the acid-catalyzed reaction. The formation of a trans 1,2-anhydride, such as **8b**, is not without precedence. Both **11** and **12**, having a trans 1,2-anhydride moiety fused to a cyclohexene ring, were reported to have been readily synthesized.[15]

**Table I. Anhydride Absorptions for Cis and Trans Compounds**

| compd | registry no. | absorptions, $cm^{-1}$ 1st band (w) | 2nd band (s) |
|---|---|---|---|
| **4a** (cis) | 68036-57-7 | 1856 | 1784 |
| **4b** (cis) | 68036-58-8 | 1845 | 1785 |
| **6** (cis) | 68036-59-9 | 1845 | 1783 |
| **8b** (trans) | 68036-60-2 | 1865 | 1795 |
|  | 68036-61-3 | 1845 | 1775 |
|  | 13149-00-3 | 1845 | 1765 |
|  | 14166-21-3 | 1860 | 1785 |

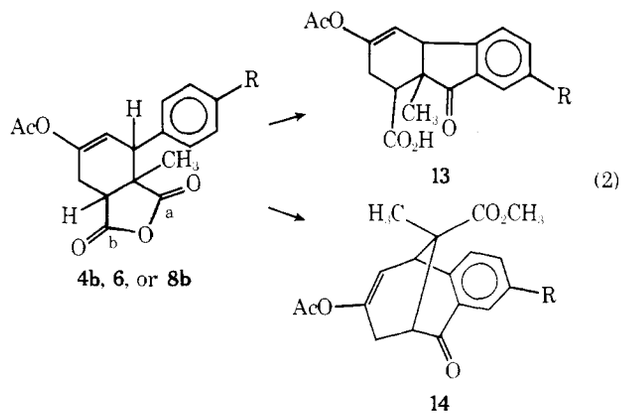
[a] Synthesized in these laboratories. [b] Aldrich Chemical Co., Inc.



11 12

In retrospect, we have examined our cis and trans anhydrides spectroscopically and compared them to simple anhydrides with similar stereochemistry.[16] It can be seen (Table I) that each band of trans anhydrides absorbs some 10–20 $cm^{-1}$ higher than their cis counterparts, suggesting a fair degree of strain in trans structures.[17]

**Cycloacylations.** Two modes of cyclizations are theoretically possible on the basis of proximities of carbonyl and aromatic carbons in molecular models. Bond formation with carbonyl a yields a hydrofluorenone **13**, while a similar reaction with carbonyl b would give a bicyclo[3.3.1]nonane ring system (**14**) (eq 2).



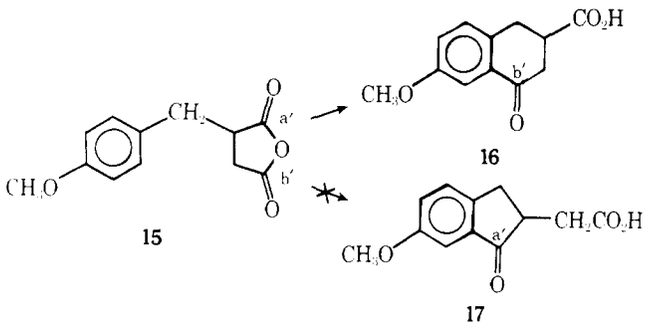
4b, 6, or 8b 13 14 (2)

Campbell[18] found that intramolecular cyclization of anhydride **15**, having carbonyl groups (a′ and b′) in equivalent

**Table II. Chemical Shifts of Methyl Protons (Hz)**

| compd | registry no. | $CH_3$-C(=O)O- | $CH_3C\lessgtr$ | $CH_3O$- | $CH_3O_2C$- |
|---|---|---|---|---|---|
| **18a** | 68036-62-4 | 124 | 94 | 228 | 206 |
| **19a** | 68036-63-5 | | 100 | 228 | 209 |
| **18b** | 68036-64-6 | 123 | 93 | | 206 |
| **19b** | 68036-65-7 | | 99 | | 209 |
| **20** | 68036-66-8 | 124 | 78 | 231 | 223 |
| **21** | 68036-67-9 | | 91 | 236 | 230 |

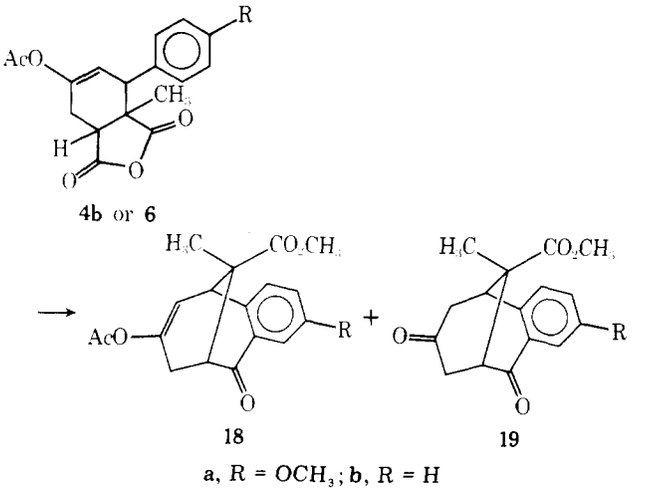
positions, gave only the six-membered ketone **16**, favoring b′.



15 16 17

Similarly, difficulties were encountered in the acid-catalyzed cyclization of arylpropionic acids and their analogues to indanones.[19] Cyclization of the citraconic–phenylbutadiene adduct (eq 1)[3,5] appears to be incongruous in light of this work.

Cyclization of anhydrides **4b, 6,** and **8b** was effected by the slow addition of anhydrous aluminum chloride, under nitrogen, to stirred substrates in either benzene, carbon disulfide, or their mixtures. Anhydrides **4b** and **6,** having identical geometries, were cyclized in benzene and their products isolated as their methyl esters following separation on silica gel chromatography. These gave three compounds: enol acetate **18,** diketo ester **19,** and acetophenone; the latter was identified by its characteristic odor and mobility on TLC.

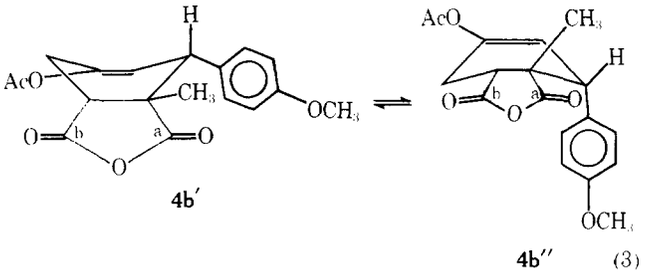


4b or 6 → 18 + 19

a, R = $OCH_3$; b, R = H

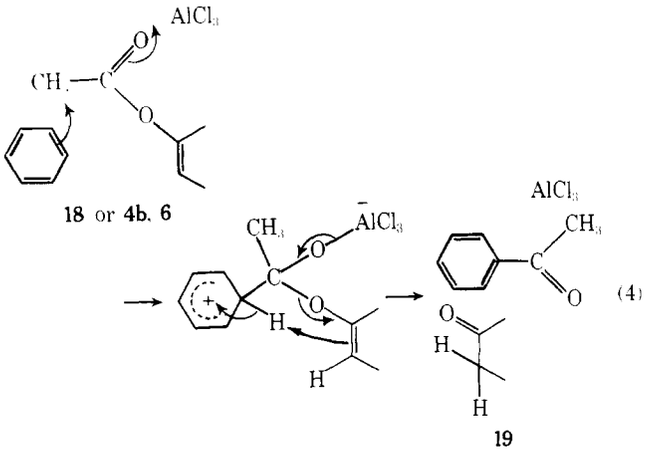
Two features lead us to assign the bicyclo[3.3.1]nonanone ring system for **18** and **19.** First, both compounds absorbed at 1685 $cm^{-1}$, indicative of a six-membered aryl ketone conjugated to an aromatic ring.[20] A hydrofluorenone structure (such as **13**) would have had a carbonyl absorption higher than 1713 $cm^{-1}$.[19a,21] Second, a comparison of chemical shifts (Table II) for methyl protons in **18** and **19** shows an upfield shift of the carbomethoxyl protons, relative to those of other methyl groups. This is readily accountable in the bicyclic structure where the carbomethoxyl groups sit above an aromatic ring, and thus experience pronounced shielding. Such shielding would not be available in hydrofluorenones.

Conformation **4b″** reveals that the ortho carbon is as near b as it is to a (eq 3). Bond formation is thus reduced to the comparative stabilities of six- or five-membered rings.



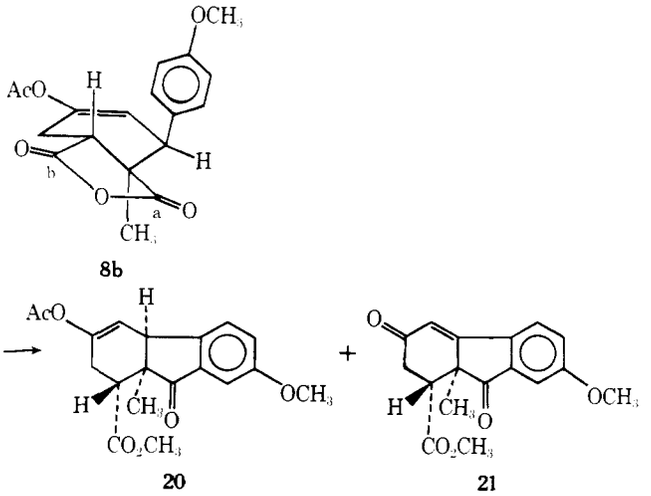
4b′ ⇌ 4b″ (3)

The origin of ketone **19** (**a** and **b**) was rationalized on the basis of a solvent acylation (eq 4). When carbon disulfide was used alone, the above solvent acylation was eliminated, producing **18b** in 30% yield.



18 or 4b, 6 → 19 (4)

"Trans" anhydride **8b** was cyclized in carbon disulfide containing some tetrachloroethane to enhance its solubility. Two cyclic products were obtained: enol acetate **20** and unsaturated diketone **21.** The former product was assigned a hydrofluorenone structure on the basis of its IR spectrum (broad absorption at 1700–1750 $cm^{-1}$)[19a,21] and carbomethoxyl proton chemical shift compared with those of other methyl groups (see Table II). A molecular model of **8b** reveals that carbonyl b was inaccessible for cyclization to give either bicyclic or hydrofluorenone compounds. Thus, only carbonyl a was available for cyclization in the "trans" anhydride and could only yield a hydrofluorenone structure.



8b → 20 + 21

The structure of unsaturated ketone **21** was secured conclusively by its ultraviolet maxima at 314 nm (log$\epsilon$ 4.85) and 250 (4.78) and a broad carbonyl absorption between 1610 and 1660 $cm^{-1}$ ($\alpha,\beta$ unsaturation). The NMR spectrum was consistent with the proposed structure, showing one vinyl proton, and a molecular ion at *m/e* 300, with major fragmentation at *m/e* 241 (loss of $COOCH_3$) and 212 (loss of $COOCH_3$ and HCO), was observed in its mass spectrum. Ketone **21** was rationalized on the basis of a hydride abstraction at $C_3$ followed by hydrolysis. We are currently investigating the mechanism of this oxidation.

## Experimental Section

**General.** Melting points were obtained on a Thomas-Hoover apparatus and are not corrected. Infrared spectra (IR) were determined on Perkin-Elmer 257 and 457 spectrometers using methylene chloride as the solvent unless otherwise indicated, where s = strong, m = medium, and w = weak. Nuclear magnetic resonance spectra (NMR) were recorded on Varian T-60 and A-60 Models using deuterated chloroform as the solvent unless otherwise indicated. Absorption peaks are reported in $\delta$ units downfield from tetramethylsilane as an internal standard, where s = singlet, d = doublet, t = triplet, and m = multiplet. Mass spectra were obtained on an LKB G.C.M.S. type 9000, and data were reported as *m/e*. Solvents used were reagent grade except when noted. The term "in vacuo" refers to the distillation of reaction or crystallization solvents with a Buchi rotating evaporator.

***cis,cis*-2-Methyl-3-(*p*-anisyl)-5-acetoxycyclohex-4-ene-1,2-dicarboxylic Anhydride (4b).** A solution of 8.8 g (50.5 mmol) of 4-(*p*-methoxyphenyl)-3-buten-2-one and 7.0 g (62.5 mmol) of citraconic anhydride in 30 mL of isopropenyl acetate containing 50–60 mg of *p*-toluenesulfonic acid was heated to reflux. After 24 h, the mixture was concentrated "in vacuo" to remove excess isopropenyl acetate and acetone. The solid that formed was filtered and recrystallized with a mixture of ether and ethyl acetate to give 9.0 g (54.5%) of **4b**: mp 195–197 °C; IR 1845 (w) and 1785 (s) (cyclic anhydride), 1758 (m), 1695 (w), 1608 (w), 1500 (m), 1367 (w), 1217 (m), 1191 (m), 1132 (m) $cm^{-1}$; NMR $\delta$ 6.99 ($A_2B_2$ pattern, 4 H, aromatic), 5.50 (d of t, 1 H, vinyl, $J_{AM}$ = 6.5 Hz, $J_{AX}$ = 1.5 Hz), 2.18 (s, 3 H, acetate methyl), 1.60 (s, 3 H, angular methyl).

Anal. Calcd for $C_{18}H_{18}O_6$: C, 65.45; H, 5.45. Found: C, 65.51; H, 5.54.

***cis,cis*-2-Methyl-3-phenyl-5-acetoxycyclohex-4-ene-1,2-dicarboxylic Anhydride (6).** A solution containing 7.3 g (50.0 mmol) of *trans*-4-phenyl-3-buten-2-one and 7.0 g (62.5 mmol) of citraconic anhydride in 30.0 mL of isopropenyl acetate containing 50–60 mg of *p*-toluenesulfonic acid was heated to reflux. After 24 h, TLC analysis (silica gel) indicated that only a small amount of butenone and anhydride remained in solution. The mixture was concentrated "in vacuo" to remove excess isopropenyl acetate and acetone. Crystallization was induced by the addition of ether, and the resulting solution was cooled with ice. Filtration gave 6.1 g (40.5%) of **6**: mp 137–139 °C; IR 1845 (w) and 1783 (s) (cyclic anhydride), 1757 (s), 1696 (w), 1600 (w), 1492 (w), 1368 (m), 1215 (s), 1191 (s), 1133 (s), 962 (m), 957 (m), 915 (m) $cm^{-1}$; NMR $\delta$ 7.28 (m, 5 H, aromatic), 5.65 (d of t, 1 H, vinyl, $J_{AM}$ = 6.0 Hz, $J_{AX}$ = 1.5 Hz), 3.65 (broad d, 1 H, benzylic, $J_{AM}$ = 6.0 Hz), 3.10 (m, 2 H, ring methylene), 2.59 (m, 1 H, $\alpha$ to anhydride), 2.17 (s, 3 H, acetate methyl), 1.61 (s, 3 H, angular methyl).

Anal. Calcd for $C_{17}H_{16}O_5$: C, 68.00; H, 5.33. Found: C, 67.75; H, 5.38.

**3-(*p*-Anisyl)-5-acetoxycyclohex-4-ene-1,2-dicarboxylic Anhydride (4a).** A solution of 8.8 g (50.0 mmol) of 4-(*p*-methoxyphenyl)-3-buten-2-one and 6.2 g (62.5 mmol) of maleic anhydride in 30 mL of isopropenyl acetate containing 50–60 mg *p*-toluenesulfonic acid was refluxed for 24 h and worked up in the usual manner. Crystallization from ethyl acetate gave 11.0 g (69.5%) of **4a**: mp 130–134 °C; IR 1856 (w) and 1784 (s) (cyclic anhydride), 1755 (m), 1607 (w), 1510 (m), 1364 (w), 1210 (m), 1130 (m) $cm^{-1}$, and several peaks in the fingerprint region; NMR $\delta$ 7.02 ($A_2B_2$ pattern, 4 H, aromatic), 5.79 (d of t, 1 H, vinyl, $J_{AM}$ = 5.7 Hz, $J_{AX}$ = 1.2 Hz), 4.01 (m, 1 H, benzylic), 3.78 (s, 3 H, methoxy), 2.19 (s, 3 H, acetate methyl), and four other protons between $\delta$ 2.30 and 3.70 were difficult to distinguish; $M^+$ = *m/e* 316.

Anal. Calcd for $C_{17}H_{16}O_6$: C, 64.55; H, 5.06. Found: C, 64.08; H, 5.20.

***cis,trans*-2-Methyl-3-(*p*-anisyl)-5-acetoxycyclohex-4-ene-1,2-dicarboxylic Anhydride (8b).** A solution of 4.4 g (25.0 mmol) of 4-(*p*-methoxyphenyl)-3-buten-2-one and 4.0 g (31.0 mmol) of mesaconic acid in 20.0 mL of isopropenyl acetate containing 30 mg of *p*-toluenesulfonic acid was refluxed for 24 h. Acetone and excess isopropenyl acetate were removed "in vacuo", and the residue was allowed to stand overnight at 4 °C. The precipitate was triturated with acetone and isopropyl ether, filtered, and washed with isopropyl ether to give 2.1 g (25%) of **8b**: mp 174–177 °C; IR 1865 and 1795 (cyclic anhydride), 1753 (m), 1664 (w), 1610 (w), 1510 (m), 1370 (w), 1215 (s), 1207 (s), 1180 (m), 1130 (s), 905 (m) $cm^{-1}$; NMR $\delta$ 7.13 ($A_2B_2$ pattern, 4 H, aromatic), 5.43 (d of t, 1 H, vinyl, $J_{AM}$ = 5.50 Hz, $J_{AX}$ = 1.4 Hz), 3.85 (broad d, partially obscured by methoxy peak, 1 H, benzyl), 3.75 (s, 3 H, methoxy), 3.36 (m, pseudo quartet, 1 H, $\alpha$ to anhydride, $J$ = 8.0 Hz), 2.63 (d, 2 H, ring methylene, $J$ = 8.0 Hz), 2.15 (s, 3 H, acetate methyl), 1.60 (s, 3 H, angular methyl).

Anal. Calcd for $C_{18}H_{18}O_6$: C, 65.45; H, 5.45. Found: C, 65.23; H, 5.50.

***cis,cis*-2-Methyl-3-anisyl-5-cyclohexanone-1,2-dicarboxylic Acid (9a).** A mixture containing 660 mg (2.0 mmol) of **3b** plus 652 mg (6.2 mmol) of $Na_2CO_3$ in 25 mL of water was refluxed for about 16 h. After cooling to room temperature, the sodium salt of the keto diacid was filtered, treated with 2 N hydrochloric acid, and extracted with methylene chloride. This gave 450 mg (74%) of **9a** from three crops: mp 232–234 °C; IR (KBr) 3480 (sharp s), 3300–2800 (broad), 1730 (s), 1610 (m), 1580 (w), 1515 (s) $cm^{-1}$; NMR ($CDCl_3$ and $Me_2SO$-$d_6$) $\delta$ 8.51 (broad, 2 H, carboxylic), 6.88 ($A_2B_2$ pattern, 4 H, aromatic, $J$ = 9 Hz), 3.73 (s, 3 H, methoxy), 1.03 (broad s, 3 H, angular methyl, $J_{1/2}$ = 10 Hz; absorption became broad and sharp when a sample was heated from room temperature to 140 °C).

**Dimethyl *cis,cis*-2-Methyl-3-anisyl-5-cyclohexanone-1,2-dicarboxylate (9).** The keto diacid (**9a**; 300 mg, 1.02 mmol) from above was dissolved in methylene chloride and esterified with diazomethane. Crystallization from methanol gave 150 mg (44%) of **9**: mp 106–109 °C; IR 1740 (s), 1720 (s), 1618 (w), 1520 (m), 1240 (m), 1210 (m), 1195 (s), 1050 (w) $cm^{-1}$; NMR $\delta$ 6.96 ($A_2B_2$ pattern, 4 H, aromatic, $J$ = 8 Hz), 3.81 (s, 3 H, methoxy), 3.68 (s, 3 H, $C_1$ methyl ester), 3.71 (s, 3 H, $C_2$ methyl ester), 1.16 (s, 3 H, angular methyl).

Anal. Calcd for $C_{18}H_{22}O_6$: C, 64.67; H, 6.59. Found: C, 64.63; H, 6.57.

**Dimethyl *cis,trans*-2-Methyl-3-anisyl-5-cyclohexanone-1,2-dicarboxylate (10).** A mixture containing 1.1 g (3.3 mmol) of **8b** plus 1.3 g (12.2 mmol) of $Na_2CO_3$ in approximately 50 mL of water was refluxed for 16 h. The reaction mixture was cooled and acidified with 2 N hydrochloric acid. The organic material was extracted three times with methylene chloride and filtered through Watman phase separating paper to remove water. The filtrate was concentrated "in vacuo" to give a clear oil. The oil (keto diacid) was esterified with diazomethane in ether. This gave, after recrystallization from ether and petroleum ether, 200 mg (18%) of **10**: mp 78–80 °C; IR 1730 (broad s), 1620 (m), 1618 (w), 1240 (m), 1220 (m), 1195 (m), 1050 (w), 855 (w) $cm^{-1}$; NMR $\delta$ 6.73 ($A_2B_2$ pattern, 4 H, aromatic, $J$ = 8 Hz), 3.80 (s, 3 H, $C_1$ methyl ester), 3.66 (s, 3 H, $C_2$ methyl ester), 1.4 (s, 3 H, angular methyl).

Anal. Calcd for $C_{18}H_{22}O_6$: C, 64.67; H, 6.59. Found: C, 64.60; H, 7.01.

**General Cyclization Procedure.** The following general cyclization procedure, modeled after Hori and Nakanishi[22] and others,[21,23] proved to be successful for these compounds. To a solution or partial solution of anhydride dissolved in a suitable solvent in a flask previously and continuously flushed with nitrogen was added aluminum chloride in three portions at room temperature. The aluminum chloride was added via a system open only to the reaction vessel, which vented through a nitrogen gas bubbler apparatus. Since the aluminum chloride became gummy, presumably due to complex formation, the mixture was mechanically stirred throughout the addition. The mixture was refluxed for 4 h and stirred at room temperature for an additional 20 h. Workup included hydrolysis of the solid complex with 2 N HCl and dissolving the organic material in ether. The ether layer was washed two times with water and one time with saturated NaCl solution and dried over anhydrous sodium sulfate. After filtration, ether was evaporated to yield an oil. In each case, the entire residue was esterified with diazomethane. Silica gel on TLC plates was used to indicate component mixtures. The chromatograms were developed in 100% chloroform and visualized after spraying with $KMnO_4$.

**Cycloacylation of 4b.** To a mixture containing 3.0 g (9.1 mmol) of **4b** in 40.0 mL of spectroquality benzene was added 3.0 g (22.5 mmol) of aluminum chloride in the manner outlined above. This mixture was refluxed for 6 h and stirred at room temperature for 20 h. The workup produced 2.1 g of an oil, containing two components by TLC analysis. The oil was esterified with diazomethane to give 2.0 g of an oil (three components by TLC), and the resulting oil was chromatographed on a dry silica gel (Baker Analyzed Reagent, 60–20 mesh) column (diameter = 3.0 cm, length = 22 cm). The material was

dissolved in a small amount of benzene, dropped via a pipet onto the dry silica gel, and eluted with solvents and solvent mixtures varying in polarity from 100% benzene to 2% methanol plus 98% methylene chloride. The two products expected were separated and isolated, one as an oil and the other as a solid. The less polar compound (more mobile on TLC) was eluted with 1.0 L of 50% benzene and 50% methylene chloride. Solvent evaporation gave 672 mg (21.5%) of **methyl 7-acetoxy-9-methyl-2-oxo-3,4-(2'-methoxybenzo)bicyclo[3.3.1]nona-3,6-diene-9-carboxylate (18a):** IR 1750 (s), 1730 (s), 1685 (s), 1607 (m), 1492 (m), 1461 (w), 1435 (m), 1422 (m), 1365 (m), 1330 (m), 1280 (s), 1262 (s), 1225 (s), 1130 (s) $cm^{-1}$; NMR $\delta$ 7.50 (d, 1 H, aromatic, $J$ = 6 Hz), 3.81 (s, 3 H, methoxy), 3.43 (s, 3 H, methyl ester), 2.06 (s, 3 H, acetate methyl), 1.56 (s, 3 H, angular methyl).

Anal. Calcd for $C_{19}H_{20}O_6$: C, 66.28; H, 5.81. Found: C, 66.60; H, 5.84.

The more polar compound was eluted with 500 mL of 2% methanol–98% methylene chloride. After concentrating the solvent "in vacuo", the residue was crystallized from ether to give 118 mg of a first crop, having mp 149–151 °C, plus a second fraction eluted later with 500 mL of 5% methanol–95% methylene chloride, which gave, on crystallization from ether plus ethyl acetate, 120 mg, mp 142–145 °C. Both crops, found to be identical by TLC, were combined, and the total was recrystallized from ethyl acetate plus ether to give 143 mg of **methyl 9-methyl-2,7-dioxo-3,4-(2'-methoxybenzo)-bicyclo[3.3.1]non-3-ene-9-carboxylate (19a):** mp 149–151 °C; IR (run on the first crop) 1727 (broad s), 1690 (s), 1610 (m), 1495 (m), 1285 (broad m), 1230 (m) $cm^{-1}$; NMR (first crop) $\delta$ 7.49 (m, 1 H, aromatic), 3.80 (s, 3 H, methoxy), 3.49 (s, 3 H, methyl ester), 1.66 (s, 3 H, angular methyl).

Anal. Calcd for $C_{17}H_{18}O_5$: C, 67.61; H, 5.96. Found: C, 67.35; H, 6.02.

**Cycloacylation of 6 (Benzene Used as Solvent).** To a mixture containing 6.0 g (20.0 mmol) of **6** in 80.0 mL of spectroquality benzene was added 6.0 g (45.0 mmol) of aluminum chloride as outlined above. After the reaction period, the reaction was worked up and esterified. Three main spots were visible on TLC (under UV light and after spraying with potassium permanganate). The most polar compound (slowest moving on TLC) was crystallized directly with hexane–ether to give 645 mg (11.8%) of **methyl 9-methyl-2,7-dioxo-3,4-benzobicyclo[3.3.1]non-3-ene-9-carboxylate (19b):** mp 169–174 °C; IR 1725 (broad s), 1690 (s), 1600 (m), 1280 (broad m), 1225 (m), 1106 (m) $cm^{-1}$; NMR $\delta$ 7.97 (d, 1 H, aromatic, $J$ = 8 and 2 Hz), 7.20 (m, 3 H, aromatic), 3.73 (m, 1 H, benzylic), 3.48 (s, 3 H, methyl ester), 1.17 (s, 3 H, angular methyl), and remaining protons between $\delta$ 3.4 and 2.2.

Anal. Calcd for $C_{16}H_{16}O_4$: C, 70.59; H, 5.89. Found: C, 70.59; H, 6.02.

The less polar compound was crystallized from methanol to give 660 mg (10.5%) of **methyl 7-acetoxy-9-methyl-2-oxo-3,4-benzobicyclo[3.3.1]nona-3,6-diene-9-carboxylate (18b):** mp 125–128 °C; IR 1750 (s), 1730 (s), 1686 (s), 1600 (m), 1215 (s), 1135 (s) $cm^{-1}$; NMR $\delta$ 8.03 (m, 1 H, aromatic), 7.38 (m, 3 H, aromatic), 5.70 (m, 1 H, vinyl, $J$ = 7 Hz), 3.73 (broad d, 1 H, benzylic, $J$ = 7 Hz), 3.40 (s, 3 H, methyl ester), 2.05 (s, 3 H, acetoxy methyl), 1.54 (s, 3 H, angular methyl).

Anal. Calcd for $C_{18}H_{18}O_5$: C, 68.79; H, 5.73. Found: C, 68.89, H, 5.89.

The very nonpolar (on TLC) compound was crudely separated from the reaction mixture by Kugelrohr distillation and had the characteristic odor or acetophenone, obviously due to the acylation of the solvent benzene by the enol acetate of the starting material.

**Cyclization of 6 ($CS_2$ Used as Solvent).** To a mixture containing **6** (6.0 g, 20 mmol) in 80.0 mL of carbon disulfide was added 6.0 g (45 mmol) of aluminum chloride. After the addition, the heterogeneous mixture was heated at reflux for 16 h. The reaction mixture was poured into 2 N HCl and extracted with methylene chloride. The methylene chloride extract was washed twice with water and once with saturated NaCl solution, dried over anhydrous sodium sulfate, and filtered. The extract was concentrated "in vacuo", and the residue was crystallized from ether to give 3.5 g, mp 136–139 °C, of starting material plus 3.0 g of an oily liquid. The recovered starting material was rereacted with aluminum chloride in carbon disulfide in the manner described above to obtain, after a similar work up, 1.62 g, mp 137–139 °C, of starting material plus 1.4 g of an oil. The oils from both reactions were combined and esterified with diazomethane, and after the usual workup the residue obtained was crystallized from methanol to give 1.9 g (30.2%) of **18b.**

**Cycloacylation of 8b.** To a mixture containing 2.2 g (6.6 mmol) of **8b** in 50 mL of carbon disulfide plus 10 mL of tetrachloroethane was added 2.2 g (16.5 mmol) of aluminum chloride. This mixture was refluxed for 6 h and stirred at room temperature for 20 h. The workup outlined above gave 1.3 g (mp 175–177 °C) of the starting adduct **8b** (TLC analysis) plus 1.3 g of a yellow oil which was esterified with diazomethane in ether to give 700 mg of an oil. This oil was chromatographed on six silica gel thick layers. The material was dissolved in 6.0 mL of methylene chloride and spotted in a straight line approximately 1.5 in. from the bottom of the plate, allowing approximately 100 mg of material per plate. The plates were placed in a developing tank, previously equilibrated, containing 1500 mL of a 1% methanol–99% chloroform solution. The developed bands were removed with a vacuum apparatus into thimbles. The silica gel from the thimbles was stirred in a solution of ethyl acetate and methanol for 0.5 h and then filtered through a sintered glass funnel. The filtrates were then concentrated "in vacuo" go give oils. The less polar (TLC analysis) fraction gave 440 mg (20%) of a liquid, identified as **methyl 3-acetoxy-1,2,4a,9a-tetrahydro-9a-methyl-7-methoxy-9-oxofluorene-1-carboxylate (20):** IR 1740 (s) and 1715 (s) (both broad and overlapping), 1610 (w), 1495 (m), 1230 (s), 1140 (m), 1040 (m) $cm^{-}$; NMR $\delta$ 7.30 (m, 3 H, aromatic), 5.78 (m, 1 H, vinyl), 3.86 (s, 3 H, methoxy), 3.71 (s, 3 H, methyl ester), 2.06 (s, 3 H, acetoxy methyl), 1.3 (s, 3 H, angular methyl).

Anal. Calcd for $C_{19}H_{20}O_6$: C, 66.28; H, 5.81. Found: C, 66.05; H, 5.75.

The more polar compound was recrystallized from ether to afford 50 mg (6.1%) of **methyl 3-oxo-1,2,9a-trihydro-9a-methyl-7-methoxy-9-oxofluorene-1-carboxylate (21):** mp 185–186 °C; IR 1730 (s), 1660 (s), 1640 (shoulder, w), 1605 (s), 1495 (m), 1310 (s), 1240 (s), 1108 (m), 1040 (m), 1020 (m), 860 (m) $cm^{-1}$; NMR $\delta$ 7.53 (m, 3 H, aromatic), 6.26 (s, 1 H, vinyl), 3.93 (s, 3 H, methoxy), 3.83 (s, 3 H, methyl ester), 1.52 (s, 3 H, angular methyl); $M^+$ = $m/e$ 300, 241, 212.

Anal. Calcd for $C_{17}H_{16}O_5$: C, 68.00; H, 5.33. Found: C, 67.81; H, 5.02.

**Acknowledgments.** Financial support of a Grant-In-Aid (R.A.B.) and from the Honors Program (K.H.T.) of Fairleigh Dickinson University is sincerely appreciated. We are also indebted to Dr. Robert Coombs for helpful discussions.

**Registry No.**—**2,** 3815-30-3; **3a,** 108-31-6; **3b,** 616-02-4; **5,** 1896-62-4; **9,** 68036-68-0; **9a,** 68070-72-4; **10,** 68070-05-3; mesaconic acid, 498-24-8.

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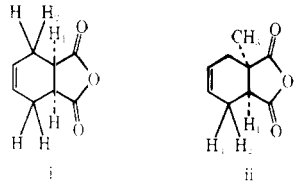

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# Mechanism of Conversion of 1:1 Anion-Radical Salts of Tetracyano-*p*-quinodimethane to Their 1:2 Analogues

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*Received March 14, 1978*

Some anion-radical salts of TCNQ with composition $D^+TCNQ^-\cdot$ can be converted to their complex analogues, $D^+TCNQ^-\cdot TCNQ^0$, by simple recrystallization from pure acetonitrile. This conversion proceeds through disproportionation of $TCNQ^-\cdot$, which produces $TCNQ^0$ and $TCNQ^{2-}$. $TCNQ^0$ is incorporated into $D^+TCNQ^-\cdot$ forming the 1:2 salt. $TCNQ^{2-}$ is irreversibly oxidized to $\alpha,\alpha$-dicyano-*p*-toluoyl ion, $DCTC^-$, a process which comprises the driving force for the overall conversion mechanism. In cases where some formation of a 1:2 analogue occurs in the attempted synthesis of a 1:1 salt, rigorous exclusion of $O_2$ from the preparation causes exclusive production of the simple analogue.

The preparation of 1:2 donor-acceptor salts of the acceptor tetracyano-*p*-quinodimethane, TCNQ, is a process of great interest. This interest derives from the fact that in anion-radical salts of TCNQ, the 1:2 or "complex" species is, with rare exceptions,[1,2] a better conductor than the 1:1 or "simple" species with a common donor.[3,4]

Complex anion-radical salts with 1:2 stoichiometry conform to the formula $D^+TCNQ^-\cdot TCNQ^0$. The usual qualitative reason given for the enhanced conductivity of these compounds relative to their simple $D^+TCNQ^-\cdot$ counterparts is that the presence of $TCNQ^0$ in the crystal lattice creates a greater number of sites than conducting electrons, providing a mechanism of conduction which never necessitates double occupancy of a TCNQ moiety.[5] The net result of this phenomenon is a substantial decrease in unfavorable Coulombic interactions between mobile electrons, creating a reduced energy gap between the valence and conduction bands. In ideal cases of close, uniform, segregated TCNQ stacking, the bands may overlap, resulting in a semimetal.[6]

Generally, three methods for the preparation of 1:2 anion-radical salts of TCNQ are presently in use. They are: direct combination of equimolar amounts of $Li^+TCNQ^-\cdot$, $TCNQ^0$, and donor in near boiling 50% ethanolic acetonitrile; recrystallization of the 1:1 salt from acetonitrile containing an equimolar equivalent of $TCNQ^0$; and recrystallization of the 1:1 salt from pure acetonitrile, i.e., in the absence of any added $TCNQ^0$.

This study is focused upon the last method of synthesis described above. The source of $TCNQ^0$ ultimately incorporated into the $D^+TCNQ^-\cdot$ structure under those experimental conditions is not immediately obvious, nor has it been satisfactorily explained even though the reaction has been known for some time.[1,7]

## Results and Discussion

Recrystallization of 1-benzyl-3-cyanopyridinium tetracyano-*p*-quinodimethane (B-3CN-1) and 1-benzyl-4-cyanopyridinium tetracyano-*p*-quinodimethane (B-4CN-1) from pure acetonitrile affords their 1:2 analogues, 1-benzyl-3-cyanopyridinium bis(tetracyano-*p*-quinodimethane) (B-3CN-2) and 1-benzyl-4-cyanopyridinium bis(tetracyano-*p*-quinodimethane) (B-4CN-2), respectively. During the conversions, the originally dark green solutions develop a reddish cast, producing an absorption maximum at 480 nm, an anomaly in the visible spectra of the 1:1 and 1:2 salts.[7,8,9] This is shown in Figure 1 for the B-3CN-1 to B-3CN-2 conversion. The filtrates which result from complete precipitation of the complex salts are markedly reddish in color and exhibit only the absorption maximum at 480 nm. These results are consistent with the presence of $\alpha,\alpha$-dicyano-*p*-toluoylcyanide ion, $DCTC^-$, first prepared and characterized as its sodium salt by Hertler et al.[10] Recently, Suchanski and VanDuyne showed that in acetonitrile solutions containing ionic species of TCNQ, $DCTC^-$ arises as an oxygen decay product of $TCNQ^{2-}$.[11] Thus, we suggest the mechanism shown in Scheme I for the conversion of simple salts of pyridinium tetracyano-*p*-quinodimethane ($Py^+TCNQ^-\cdot$) to their complex analogues ($Py^+TCNQ^-\cdot TCNQ^0$) during recrystallization from pure acetonitrile.

Disproportionation of $TCNQ^-\cdot$ readily accounts for the $TCNQ^0$ required for complex salt formation, and for $TCNQ^{2-}$, the direct precursor of $DCTC^-$. The mechanism only requires that disproportionation maintain an equilibrium concentration of $TCNQ^{2-}$ sufficient to allow its irreversible oxidation to drive the reaction to completion. This proposal is strongly supported by studies on other organic anion-radicals pub-

0022-3263/79/1944-0209$01.00/0 