(16) For similar observations see S. H. Grover, J. P. Guthrie, J. B. Stothers, and C. T. Tan, *J. Magn. Reson.*, **10**, 227 (1973); S. H. Grover and J. B. Stothers, *Can. J. Chem.*, **52**, 870 (1974).
(17) H. N. Colli, V. Gold, and J. E. Pearson, *J. Chem. Soc., Chem. Commun.*, 408 (1973).
(18) W. Kitching, M. Bullpitt, D. Doddrell, and W. Adcock, *Org. Magn. Reson.*, **6**, 289 (1974).
(19) Shifts in ^{13}C resonances in acyclic amines have recently been discussed by J. E. Sarneski, H. L. Suprenant, F. K. Molen, and C. N. Reilley, *Anal. Chem.*, **47**, 2116 (1975).
(20) Comparison with amine data in $CDCl_3$ is appropriate for the hydrochlorides in $CDCl_3$, but may not be so for trifluoroacetates in trifluoroacetic acid, since differential solvent effects on the substance investigated and on the reference compound cannot be excluded. Such effects may be quite sizable.[1b] In view of this difficulty, the significance of results reported[21] for the protonation of neat piperidines with increasing amounts of trifluoroacetic acid is somewhat questionable.
(21) I. Morishima, K. Yoshikawa, K. Okada, T. Yonezawa, and K. Goto, *J. Am. Chem. Soc.*, **95**, 165 (1973).
(22) M. W. Duch, Ph.D. Thesis, University of Utah, Salt Lake City, Utah, 1970.
(23) A. J. Jones and M. M. A. Hassan, *J. Org. Chem.*, **37**, 2332 (1972).
(24) It may be noted that, although in compound **8m** the *N*-methyl group is entirely axial and hence the lone pair equatorial, this compound, upon protonation, undergoes a normal upfield shift for C-3, and C-10 is actually shifted downfield (cf. Table IX, entry 19).
(25) J. A. Pople and M. S. Gordon, *J. Am. Chem. Soc.*, **89**, 4253 (1967).
(26) H. P. Hamlow, S. Okuda, and N. Nakagawa, *Tetrahedron Lett.*, 2553 (1964); J. B. Lambert, D. S. Bailey, and B. F. Michel, *J. Am. Chem. Soc.*, **94**, 3812 (1972).
(27) Shift values (parts per million) reported earlier[2-6] were calculated using 25.2 MHz and are corrected in this paper. Standard deviations of the chemical shifts of two samples of **1** prepared and recorded 6 months apart was ± 0.03 ppm; the maximum deviation was 0.05 ppm.

Reaction of Geminal Diesters with the Amine Bases 1,5-Diazabicyclo[4.3.0]non-5-ene, 1,4-Diazabicyclo[2.2.2]octane, and 3-Quinuclidinol

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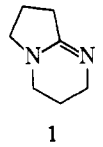
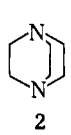
Received August 19, 1975

The bicyclic amidine base 1,5-diazabicyclo[4.3.0]non-5-ene (DBN, 1) transforms relatively hindered geminal diesters to either their corresponding monoesters or monoacids. The composition of the products (monoesters, or monoacids, or a mixture of monoesters and monoacids) can be determined by the reaction time. The bicyclic amine base 1,4-diazabicyclo[2.2.2]octane is useful for the selective decarbalkoxylation of a variety of geminal diesters. The failure to obtain acids as by-products is consistent with previous studies showing that Dabco (2) fails to cleave saturated esters under the same conditions. The bicyclic amine base 3-quinuclidinol (3) is useful for the decarbalkoxylation of a variety of geminal diesters to their corresponding monoesters. Decarbalkoxylation using DBN (1), Dabco (2), and 3-quinuclidinol in *o*-xylene is advantageous in cases where the usual hydrolytic conditions are precluded because of the presence of sensitive moieties, as well as for compounds not soluble in aqueous solvents.

We have reported[1] studies which indicate that the base 1,5-diazabicyclo[4.3.0]non-5-ene (DBN, 1) is useful for the



1



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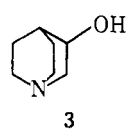
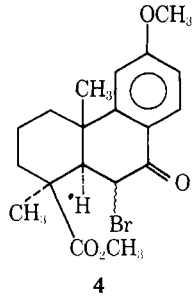


3

O-alkyl cleavage of hindered methyl esters and for the one-step conversion of bromo ketone **4** to the α,β-unsaturated ketone **5**. Similar results were obtained with 1,5-diazabicyclo[5.4.0]undecene-5.[2] Subsequent studies[3] with the base *N*-phenylbenzamidine indicated that treatment of bromo ketone **4** resulted in only dehydrobromination. Thus *N*-phenylbenzamidine was suggested as a relatively mild and selective dehydrobrominating agent. The base diazabicyclo[2.2.2]octane (Dabco, **2**) has been shown[4,5] to be effective for the decarbalkoxylation of β-keto and vinylogous β-keto esters. Similar results were obtained[6] with 3-quinuclidinol. Although a variety of reagents have been utilized[1,2,4,5,7] for cleaving β-keto and vinylogous β-keto esters, this represented the first report involving the use of a base which contains the bicyclic moiety found in quinine and related Cinchona alkaloids.[8] The suggestion was offered that since the cleavage reactions reported[6] are similar to those found in biological systems,[9] the possibility exists that reactions of this type could be catalyzed by amine bases (alkaloids) in plants.



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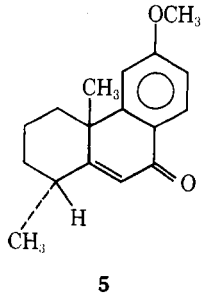


5

This paper describes an investigation into the reactivity and the relative selectivity of the amine bases DBN (1), Dabco (2), and 3-quinuclidinol (3) toward geminal diesters.

Results and Discussion

DBN (1). Initial studies with the base DBN involved the investigation of its reactivity with the geminal diester diethyl octadecylmalonate (**6**). Treatment of 1 equiv of **6** with 5 equiv of DBN (1) in 7 equiv of *o*-xylene at reflux for 6 hr gave white, crystalline compound **7** (52% yield) which was identical with an authentic sample of ethyl eicosanoate. The acidified aqueous extract of the reaction mixture yielded crystalline compound **8** (10% yield) which was shown to be eicosanoic acid.[10]

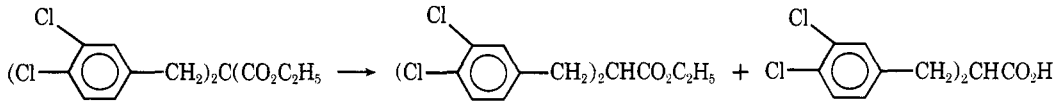
$CH_3(CH_2)_{17}CH(CO_2C_2H_5)_2 \longrightarrow$

6

$CH_3(CH_2)_{18}CO_2C_2H_5 + CH_3(CH_2)_{18}CO_2H$

7 8

Table I
Reaction of DBN (1) with Ethyl Bis(3,4-dichlorobenzyl)malonate (9)



9 10 11

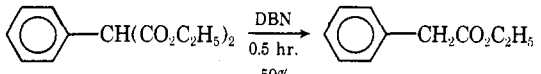
Molar ratio			Reaction	Yield, %		
Diester 9	DNB	o-Xylene	time, hr	Monoester 10	Acid 11	Diester 9
1	6	7	1.5	96[a]	None[b]	4[a]
1	10	15	4	68	29	None[a]
1	15	30	69	Trace[a]	89	None[a]
1	2	28	15	93[a]	None[b]	7[a]

[a] By GLC analyses. [b] By TLC analyses.

The obtainment of both the monoester 7 and monoacid 8 was not expected, since DBN (1) is known[1] to cleave esters to acids. These results led to experiments designed to investigate the possible utilization of DBN (1) as a reagent for the conversion of geminal diesters to either their corresponding monoester or monoacid. Presumably, the process involves decarbalkoxylation of the diester to the monoester and subsequent cleavage of the monoester to the monoacid, since DBN (1) has been shown to be an *O*-alkyl cleavage reagent.

The reaction of DBN (1) with ethyl bis(3,4-dichlorobenzyl)malonate (9) was studied (Table 1) in order to optimize the conditions for obtaining either the monoester or monoacid from geminal diesters. Initially, a mixture of 1 mmol of diester 9 and 10 mmole of DBN (1) in 15 mmol of *o*-xylene was heated at reflux for 4 hr. The usual work-up gave a 68% yield of monoester 10 and a 29% yield of monoacid 11. Compound 10 was identical with an authentic sample of ethyl bis(3,4-dichlorobenzyl)acetate. Compound 11, mp 114.5–116.5°C, was consistent with bis(3,4-dichlorobenzyl)acetic acid. The results shown in Table I indicate that the optimum conditions for the obtainment of the monoester is a reaction time of 1.5 hr with a molar ratio of diester 9:DBN:*o*-xylene of 1:6:7. Under these conditions 10 is obtained in 96% yield with no production of the corresponding acid. The use of the substantially longer reaction time (69 hr) and higher base to substrate molar ratio (15:1) results in the production of acid 11 in 89% isolated yield. Thus, conditions for the synthesis, in high yield, of either monoester 10 or acid 11 from geminal diester 9 were elaborated.

This reaction was extended to other substrates by treatment of 1 equiv of diethyl phenylmalonate (12) with 6 equiv of DBN (1) in 6 equiv of *o*-xylene at reflux for 30 min to yield (59%) ethyl phenylacetate (13).

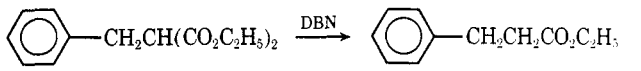


12 13

Treatment of 1 equiv of diester 14 with 5 equiv of DBN (1) in 7 equiv of *o*-xylene at reflux for 6 hr afforded a 21% yield of monoester 15 (Table II). Alternative reaction of 1 equiv of diester 14 with 2 equiv of DBN (1) in 10 equiv of *o*-xylene gave monoester 15 in 34% yield. The resulting monoester 15 was identified as ethyl benzylacetate.

A comparison of the yields obtained with substrates 9, 12, and 14 shows that the yield of monoester decreases as the steric bulk around the α carbon atom decreases. Geminal diesters with less steric bulk around the α carbon form products with a much higher retention time than the monoesters by GLC analysis. Preliminary evidence indicates that these components are a mixture of the Claisen

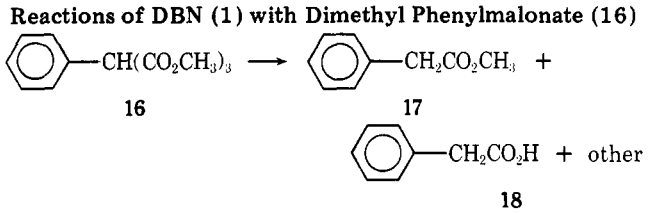
Table II
Reaction of DBN (1) with Diethyl Benzylmalonate (14)



14 15

Diester 14	DBN	o-Xylene	Reaction time, hr	Yield of monoester 15, %
1	5	7	6	21
1	2	10	25	34

Table III
Reactions of DBN (1) with Dimethyl Phenylmalonate (16)



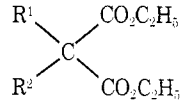
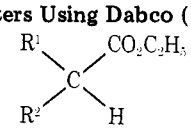
16 17 18

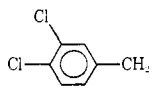
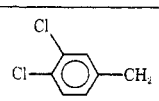
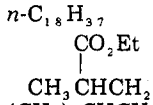
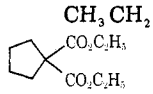
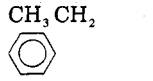
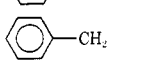
Diester 16	DBN	o-Xylene	Reaction time, hr	Yield, % Monoester 17	Yield, % Acid 18
1	5	6	0.5	34	Trace
1	5	6	2	Trace	29

and acyloin type condensation products which can be envisaged as forming from the monoester. A detailed study involving the characterization of all of these products and the possible utility of the bases DBN (1), Dabco (2), and 3-quinuclidinol (3) in catalyzing the condensation of monoesters is currently in progress.

The final reaction with DBN (1) was performed with dimethyl phenylmalonate (16) and is illustrated in Table III. This substrate was chosen to allow for comparison of the results obtained upon treatment of a dimethyl ester with DBN (1). Treatment of 1 equiv of dimethyl phenylmalonate (16) with 5 equiv of DBN (1) in 6 equiv of *o*-xylene at reflux for 0.5 hr gave a 34% yield of monoester 17 which was identical with methyl phenylacetate.[11] Similarly, treatment of the same molar ratio of reactants at reflux for 2 hr afforded a 29% yield of acid 18, which was identical with phenylacetate acid.[11] In comparison with diethyl phenylmalonate (59% yield) under approximately the same conditions the yield of monoester 17 is lower (34% yield), which is probably a reflection of less steric bulk around the dimethyl ester and hence the formation of a larger quantity of condensations products. The majority of the monoester 17 formed is converted smoothly to acid 18 (29% yield) upon heating for an additional 1.5 hr. This is a reflection of the greater ease with which methyl esters are cleaved with

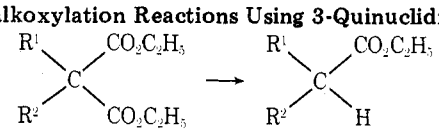
Table IV
Decarbethoxylation Reactions of Geminal Diesters Using Dabco (2)

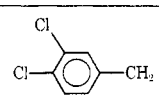
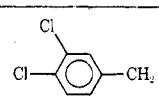



Geminal diester	Reactant R¹	Reactant R²	Refluxing time, hr	Product Monoester	Product Yield, %	Product Unreacted diester, %
9			4	10	79	None
6	n-$C_{18}H_{37}$	H	10.5	7	77	
19		CH_3	29	20	50	
21	$(CH_3)_2CHCH_2CH_2$	CH_3CH_2	48	22	62	13
23			48	24	73[a]	16[a]
25	CH_3CH_2	H	27	26	33[a]	3[a]
27		CH_3CH_2	10	28	31	20
14		H	6	15	42	

[a] Determined by GLC analyses.

Table V
Decarbalkoxylation Reactions Using 3-Quinuclidinol (3)



Geminal diester	R_1	R_2	Refluxing time, hr	Product Monoester	Product Yield, %
9			6	10	93
6	n-$C_{18}H_{37}$	H	7	7	96[b] 21[c]

[a] GLC analysis. [b] Base to substrate ratio 1:1; [c] Base to substrate ratio 10:1.

DBN (1) as compared with ethyl esters. Ethyl ester **9** required 69 hr at a base to subtrate ratio of 15:1 for complete conversion to the acid **11** and complete disappearance of the monoester **10**.

1,4-Diazabicyclo[2.2.2]octane (Dabco, 2). The ditertiary amine base Dabco (2) is useful for the cleavage of geminal diesters to their corresponding monoester as is shown by its initial reaction with diethyl bis(3,4-dichlorobenzyl)malonate (**9**). A mixture of 1 equiv of **9** and 10 equiv of Dabco (**2**) in 14 equiv of *o*-xylene was heated at reflux for 4 hr to yield (79%) white, crystalline monoester **10**.

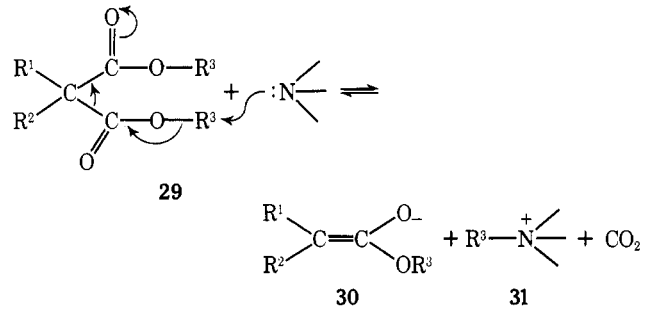
The generality of Dabco (**2**) as a reagent for cleaving geminal diesters is demonstrated by the results illustrated in Table IV. Typically, 1 equiv of the appropriate geminal diester was treated with 10 equiv of Dabco (**2**) in 30 equiv of *o*-xylene for an appropriate period of time to yield 30–80% of the corresponding monoester.

Examination of substrates **9**, **6**, **19**, and **21** in Table IV seems to indicate that as the electron-withdrawing ability of the α-substitution group decreases, the time required to complete the reaction increases. A GLC study of substrates **25**, **27**, **16**, and **14** (which gave low yields of the monoesters) showed peaks with a higher retention time than the monoesters. This result was suggestive (as previously indicated) of condensation of the monoesters formed in the reaction mixture. This is reasonable since Table IV shows that generally the amount of condensation product by GLC analysis increases as the steric bulk of the α-substitution alkyl group decreases. The fact that Dabco (**2**) does not cleave monoesters to their corresponding acids[4,5] eliminates the possibility of acids as by-products. Thus Dabco is a reagent which is useful for decarbalkoxylation of hindered geminal diesters to their corresponding monoesters in good yield.

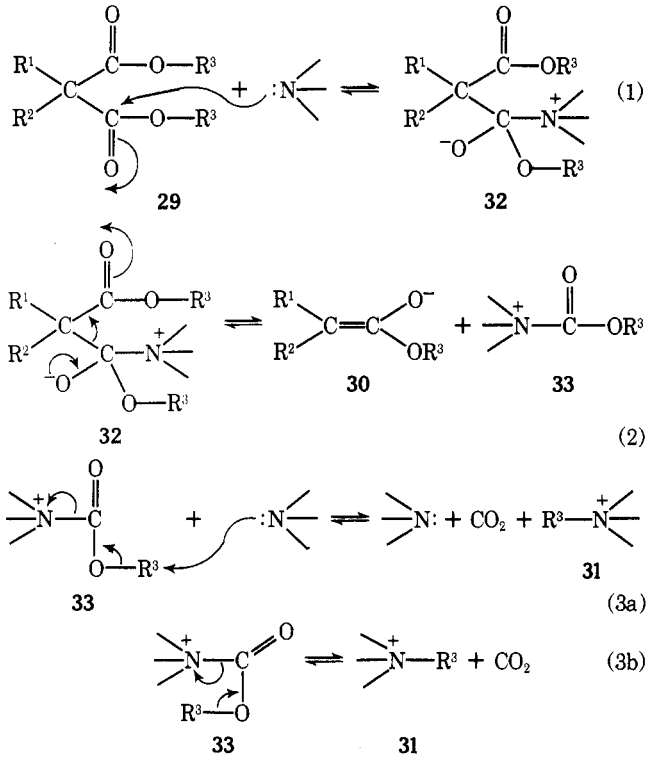
3-Quinuclidinol. The base 3-quinuclidinol (**3**), which contains a bicyclic moiety similar to that found in quinine and related Cinchona alkaloids, is useful for the cleavage of geminal diesters to the monoester as shown in Table V. Geminal diester **9** gave a 93% yield of product upon refluxing with 20 equiv of 3-quinuclidinol in 30 equiv of *o*-xylene. The attainment of a high yield (93%) of product **17** from geminal diester **16** required a much smaller base to substrate molar ratio (1:1). Using a large excess of 3-quinuclidinol results in a low yield of monoester because of the occurrence of condensation under these conditions for relatively unhindered esters as is shown for geminal diester **6** in Table V.

Postulated Mechanisms for Decarbalkoxylation Reactions. Two mechanisms are consistent with the facile cleavage of a variety of geminal diesters with amine bases DBN (**1**), Dabco (**2**), or 3-quinuclidinol (**3**) in *o*-xylene. These possible mechanisms are illustrated in Schemes I

Scheme I

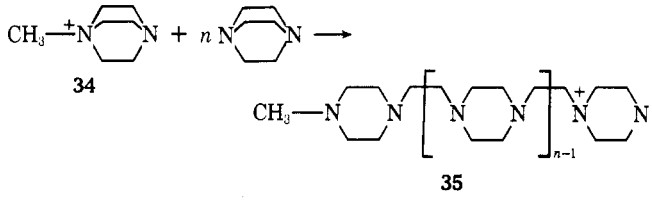


Scheme II



and II. Since DBN (1) is an *O*-alkyl cleavage reagent, it may operate through a mechanism such as that shown in Scheme I, while the bases Dabco (2) and 3-quinuclidinol may operate through another. However, it is possible that all bases (1, 2, and 3) may operate via the same mechanism for decarbalkoxylation.

The following observations are consistent with both mechanisms. First, carbon dioxide was evolved from all reactions and collected quantitatively as barium carbonate. Secondly, the rate of cleavage was enchanced by electron-withdrawing α-substituents (R^1 and R^2). Thirdly, methyl esters were cleaved faster under same reaction conditions than their corresponding ethyl esters.



All attempts to isolate alkylated bases as their salts failed. This could be due to the fact that the quaternary ammonium salt (e.g., 34) reacted with other molecules of the base which was generally present in excess to form a polymer (e.g., 35). This postulation is supported by a similar reaction observed by Viche.[12] Another reasonable explanation for the failure to isolate salt 32 is the ease with which tertiary amine salts have been reported[13,14] to dealkylate in excess base. The literature contains[13,14] references which seem to support the formation of salts such as 34.

Conclusions

Reactions involving base-catalyzed[15] alkylation and acylation of malonic esters have significant roles in organic synthesis. Their products, geminal diesters, act as important intermediates in syntheses and are usually cleaved to the corresponding diacid by conventional methods which include aqueous acid or base hydrolysis. These methods[16] normally include subsequent decarboxylation by heating and then esterification to give the monoester. Alternatively, cleavage and subsequent decarboxylation of β-keto esters has been achieved in one step[7,17,18].

Cleavage of hindered geminal diesters using DBN (1) is advantageous, not only for the nonaqueous reaction conditions, but also for the selectivity of the products. Esters such as 9 provide a good yield of either the monoester or monoacid. The product obtained can be determined by the reaction time in a one-step reaction. The majority of known methods[16] have required two steps to achieve the monoacid and three steps to the monoester.

Decarbalkoxylation of hindered geminal diesters to monoesters with Dabco (3) is also advantageous because of the efficiency of the process (one-step). Furthermore, it is desirable in cases where the usual hydrolytic conditions are precluded because of the presence of acid- or base-sensitive functional groups, as well as for compounds which are not soluble in aqueous solvents.

Decarbalkoxylation reactions involving 3-quinucidinol (3) are efficient and advantageous in many instances for the reasons similar to those elaborated above for Dabco (2).

Since the cleavage reactions reported in this paper are similar to those found in biological systems,[9,19] the possibility exists that reactions of this type could be catalyzed by amine bases (alkaloids) in plants.

Experimental Section

Nuclear magnetic resonance spectra were obtained using a Jeolco Minimar spectrometer equipped with a spin decoupler. Tetramethylsilane was used as the internal standard and chloroform-*d*, 99.8% ($CDCl_3$), and acetone-d_6, 99+% (CD_3COCD_3), were used as solvents. Mass spectral data (MS, GLC–MS) were obtained using a Hewlett-Packard Model 5930, or a Perkin-Elmer Model 270 mass spectrometer. Infrared spectra were obtained using a Perkin-Elmer Model 137B Infracord, a Beckman IR5A spectrophotometer, or a Perkin-Elmer Model 521 grating infrared spectrophotometer. The spectra of liquids were taken on films formed between two sodium chloride plates; potassium bromide was used in preparing pellets of solid samples for infrared spectra. The band 1603 cm^{-1} of a polystyrene film (0.05 mm) was used as a reference peak. Column chromatography was performed in glass columns (wet or dry packed) with sintered glass using Woelm absorption silica gel (activity 1) of M. Woelm, Eschwege, Germany (distributed by ICN Pharmaceuticals) as the solid support. Thin layer chromatography (TLC) was performed using E. Merck (Darmstardt) silica gel G of Applied Science Laboratories, Inc., coated glass plates. Chromatoplates (20 × 20 cm and 5 × 20 cm) were prepared by using a Desaga spreader with thickness of 0.25 mm for qualitative TLC and 0.50 mm for preparative TLC. The plates were activated at 110°C for 1 hr. Potassium dichromate in sulfuric acid was used as the detecting agent. Gas–liquid chromatography (GLC) was performed using a Hewlett-Packard Model 402 gas chromatograph with a hydrogen flame detector. Glass columns (6 ft × 3.0 mm i.d.) and 12 ft × 3.0 mm i.d.) bent in a U shape were used. The column temperature, nitrogen flow rate, types and amount of liquid phase, and the retention time (t_R) are given in the Experimental Section for each sample. The column substrates and solid supports used in the GLC analyses were obtained from Applied Sciences Laboratories

or from Hewlett-Packard Analytical Instruments. Melting points were obtained on a Fisher-Jones apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Reaction of DBN (1) with Geminal Diesters. A. Preparation of Ethyl Eicosanoate (7) and Eicosanoic Acid (8). A mixture of 0.412 g of geminal diester **6** (Aldrich reagent) and 0.635 g (5.1 mmol) of DBN (1) in 0.645 g (6.8 mmol) of *o*-xylene was heated at reflux for 6 hr. To the reaction mixture was added dilute sodium hydroxide which was followed by extraction with ether. The ether extract was washed with dilute acid, washed with water, dried over anhydrous sodium sulfate, and evaporated in vacuo to yield 0.177 g (52%) of monoester **7**. Monoester **7** was identical by ir, NMR, and GLC retention time (t_R 1 min 30 sec using a 6-ft 5% SE-30 on 80/100 mesh Chromosorb W column, nitrogen flow rate 11 ml/min, column temperature 292°C) on comparison with an authentic sample. The aqueous portion was acidified and extracted with ether. The ether extract was washed with water, dried over anhydrous sodium sulfate, and evaporated in vacuo to give 0.030 g (10%) of crystalline compound **8**, mp 73–75°C (lit.[10] 75–76°C). Compound **8** was identical by ir and MS comparison with authentic spectra of eicosanoic acid.[10]

B. Preparation of Ethyl Bis(3,4-dichlorobenzyl)acetate (10) and Bis(3,4-dichlorobenzyl)acetic Acid (11). A mixture of 0.479 g (1.0 mmol) of diester **9** (Alfred Bader Chemicals) and 1.241 g (10.0 mmol) of DBN (1) in 1.616 g (15.2 mmol) of *o*-xylene was heated at reflux (163°C) for 4 hr. The cooled reaction mixture was acidified with dilute acid and extracted with ether. The ether extract was washed first with saturated aqueous sodium chloride and then with water, dried over anhydrous magnesium sulfate, and evaporated in vacuo to give 0.391 g of solid materials.

The crude solid (0.391 g) was dissolved in a small amount of chloroform and transferred onto a glass column (2.54 cm o.d.) which was packed with 27 g of silica gel. The column was eluted with the following solvent ratios of ether in hexane (ml/ml): 0/50, 15/285, 35/315, 30/170, 40/160 60/140 80/120, 100/100, 250/0. A total of 30 fractions were collected, with 50 ml each for the first 27 fractions, 100 ml each for the 28th and 29th fractions, and 250 ml for the 30th fraction. Fractions 2–16 yielded 0.278 g (68%) of white, crystalline material, mp 75–76°C, which was identical by ir, NMR, and GLC retention time on comparison with an authentic sample of compound **10**. Fractions 17–30 were combined and treated with diazomethane to yield 0.109 (29%) of a white, crystalline compound **11**: mp 114.5–116.5°C; ir ν_{max} (KBr) 3571–2326 (broad, hydrogen bonding), 2857 (saturated C–H stretching), 1695 (–C=O), 1471, 1408 cm^{-1}; NMR ($CDCl_3$) δ 2.82 [5 H, broad, Ar**CH**$_2$CH-(CO)**CH**$_2$Ar], 6.75–7.14 (6 H, m, ArH); MS *m/e* (rel abundance) 379 (17), 377 (35), 375 (26), 219 (62), 217 (100), 201 (30), 199 (41), 161 (65), 159 (92).

Anal. Calcd for $C_{16}H_{12}Cl_4O_2$ (378.08): C, 50.83; H, 3.20. Found: C, 51.11; H, 3.23.

C. Preparation of Ethyl Bis(3-4-dichlorobenzyl)acetate (10). Procedure I. A mixture of 0.121 g (0.25 mmol) of diethyl ester **9** (Alfred Bader Chemicals), 0.164 g (1.47 mmol) of DBN (1), and 0.191 g (1.80 mmol) of *o*-xylene was heated at reflux for 1.5 hr. The ether extract of the acidified (0.6 *M* HCl) reaction mixture was washed with water, dried over anhydrous sodium sulfate, and evaporated under reduced pressure to obtain 0.090 g of a crystalline solid, mp 75–78°C, containing 96% of monoester **10** and 4% of starting diester **9** by GLC analysis (6 ft, 5% SE-30 on 80/100 mesh Chromosorb W column, nitrogen flow rate 10 ml/min, column temperature 300°C) on comparison with authentic standards. TLC analysis of the crude product showed the absence of acid **11**.

Procedure II. A mixture of 0.240 g (0.5 mmol) of geminal diester **9** (Aldrich reagent) and 0.132 g (1.1 mmol) of DBN (1) in 1.479 g (1.4 mmol) of *o*-xylene was heated at reflux for 15 hr. The ether extract of the acidified reaction mixture contained 93% monoester **10** and 7% starting diester **9** by GLC comparison with authentic standards. TLC analysis of this ether of the acidified reaction mixture failed to show the presence of acid **11**.

D. Preparation of Bis(3,4-dichlorobenzyl) acetic Acid (11). A mixture of 0.124 g (0.25 mmol) of diethyl ester **9** (Alfred Bader Chemicals) and 0.463 g (3.73 mmol) of DBN (1) in 0.798 g (7.52 mmol) of *o*-xylene was heated at reflux for 69 hr. The ether extract of the acidified (0.6 *M* HCl) reaction mixture was washed with water, dried over anhydrous sodium sulfate, and evaporated under reduced pressure to give 0.074 g (89%) of crude crystalline compound **11**, mp 108°C (pure **11**, mp 114.5–116.5°C), containing mainly bis(3-4-dichlorobenzyl)acetic acid (**11**) by TLC and GLC comparison with authentic standards.

E. Preparation of Ethyl Phenylacetate (13). A mixture of 0.239 g (1.0 mmol) of diethyl phenylmalonate (**12**) and 0.765 g (6.2 mmol) of DBN (**1**) in 0.643 g (6.0 mmol) of *o*-xylene was heated at reflux for 30 min. The ether extract of the acidified (0.6 *M* HCl) reaction mixture was washed with water, dried over anhydrous sodium sulfate, and evaporated in vacuo to yield 59% of monoester **13** (t_R 1 min 45 sec) and 9% of starting diester **12** (t_R 6 min 42 sec) upon comparison with authentic standard by GLC analysis (6 ft, 5% SE-30 on 80/100 mesh Chromosorb W column, nitrogen flow rate 11 ml/min, column temperature 140°C).

F. Preparation of Ethyl Benzylacetate (15). Procedure I. A mixture of 1.005 g (4.0 mmol) of diester **14** (Aldrich reagent) and 0.998 g (28.0 mmol) of DBN (**1**) in 4.239 g (40.0 mmol) of *o*-xylene was heated at reflux for 25 hr. The organic portion of the acidified (0.6 *M* HCl) reaction mixture was poured onto a glass column (2.54 cm o.d.) which was packed with 52.5 g of silica gel. The column was developed and eluted with hexane and 2% ether in hexane to yield 0.241 g (34%) of ester **15** which was identical by ir, NMR, and GLC retention time on comparison with an authentic sample.

Procedure II. A mixture of 0.251 g (1.0 mmol) of diester **14** (Aldrich reagent) and 0.621 g (5.0 mmol) of DBN (**1**) in 0.737 g (7.0 mmol) of *o*-xylene was heated at reflux for 6 hr. The ether extract of the acidified (0.6 *M* HCl) reaction mixture was washed with water, dried over anhydrous sodium sulfate, and evaporated to yield 21% of ester **15** (t_R 3 min 56 sec) on comparison with an authentic sample by GLC analysis (6 ft, 5% SE-30 on Chromosorb W column, nitrogen flow rate 11 ml/min, column temperature 146°C).

G. Preparation of Phenylacetic Acid (18.) A mixture of 0.420 g (2.0 mmol) of dimethyl phenylmalonate (**16**) (Aldrich reagents) and 1.242 g (10.0 mmol) of DBN (**1**) in 1.275 g (12.0 mmol) of *o*-xylene was heated at reflux for 2 hr. To the reaction mixture was added 10 ml of 5% sodium hydroxide. The reaction mixture was then extracted with chloroform. The aqueous portion was acidified with concentrated hydrochloric acid and extracted with ether. The ether extract was washed with water, dried over anhydrous sodium sulfate, and evaporated under reduced pressure to yield 0.078 g (29%) of a white, crystalline compound **18**, mp 77°C (lit.[11] 77°C). Compound **18** was identical by ir and NMR comparison with known spectra[11] of phenylacetic acid.

H. Preparation of Methyl Phenylacetate (17). A mixture of 0.840 g (4.0 mmol) of dimethyl phenylmalonate (**16**) (Aldrich reagent) and 2.496 g (20.1 mmol) of DBN (**1**) in 2.576 g (24.3 mmol) of *o*-xylene was heated at reflux for 30 min. The reaction mixture was acidified with cold dilute acid. The organic layer was separated and poured onto a silica gel column. The column was eluted with 1000 ml of hexane and 500 ml of 5% ether in hexane, respectively. Fractions with t_R 1 min 30 sec (column temperature 139°C, nitrogen flow rate 12 ml/min) were combined to yield 0.204 g (34%) of a colorless liquid compound **17**, which was identical by ir, NMR, and mass spectral comparison with literature value[11] of methyl phenylacetate.

Reaction of Dabco (2) with Geminal Esters. A. Preparation of Ethyl Bis(3,4-dichlorobenzyl)acetate (10). A mixture of 0.920 g (1.9 mmol) of geminal diester **9** (Alfred Bader Chemicals) and 2.212 g (19.2 mmol) of Dabco (**2**) in 3.017 g (28.4 mmol) of *o*-xylene was heated at reflux for 4 hr. A trap containing a solution of barium hydroxide was connected to the apparatus through a drying tube attached to the top of the condenser. A white precipitate of barium carbonate was collected. The ether extract of the acidified (0.6 *M* HCl) reaction mixture was washed with 5% bicarbonate and water, dried over anhydrous sodium sulfate, and evaporated in vacuo to give 0.620 g (79%) of white, crystalline compound **10**, which was purified further with the aid of a silica gel column to a compound with mp 75–75.5°C; ir ν_{max} (KBr) 3390 (w, ArH), 2857 (w, CH), 1724 (s, C=O), 1471 cm^{-1} (s); NMR ($CDCl_3$) δ 1.03 (3 H, t, –OCH$_2$**CH**$_3$), 2.80 (5 H, broad, Ar**CH**$_2$**CH**), 3.90 (2 H, q, –O**CH**$_2$CH$_3$) 6.95 (6 H, m, ArH); MS *m/e* (rel abundance) 407 (5), 405 (3), 402 (2.1), 247 (57), 245 (100), 219 (17), 218 (23), 201 (23), 199 (33), 161 (40), 159 (63).

Anal. Calcd for $C_{18}H_{16}Cl_4O_2$ (406.13): C, 53.23; H, 3.97; Cl, 34.92. Found: C, 53.04; H, 4.07; Cl, 34.75.

B. Preparation of Ethyl Eicosanate (7). A mixture of 0.827 g (2.0 mmol) of geminal diester **6** (Alfred Bader Chemicals), 2.200 g (19.6 mmol) of Dabco (**2**), and 3.181 g (30.0 mmol) of *o*-xylene was heated with constant stirring at reflux in an oil bath for 10.5 hr. The resulting reaction mixture was acidified with 0.6 *M* cold hydrochloric acid and extracted with ether. The ethereal portions were separated, washed with saturated sodium chloride solution, washed with water, and then dried over anhydrous magnesium sulfate. The solvent was removed in vacuo to give 0.525 g (77%) of a

solid which was further purified with a silica gel column to yield white, crystalline ethyl eicosanoate (7).

Anal. Calcd for $C_{22}H_{44}O_2$ (340.60): C, 77.58; H, 13.02. Found: C, 77.46; H, 13.11.

C. Preparation of Diethyl 2,4-Pentanedicarboxylate (20). A mixture of 0.868 g (3.0 mmol) of ester **19** (Alfred Bader Chemicals) and 3.365 g (30.0 mmol) of Dabco (**2**) in 4.774 g (45.0 mmol) of *o*-xylene was heated at reflux for 29 hr. The progress of the reaction was monitored by GLC analysis with a 6-ft glass column packed with 5% SE-30 on 80/100 mesh Chromosorb W (nitrogen flow rate 11 ml/min, column temperature 200°C). The reaction mixture was acidified with cold 0.6 *M* hydrochloric acid and extracted with ether. The ethereal portions were separated, combined, washed with water, and dried over anhydrous magnesium sulfate. The solvent was removed in vacuo to give 0.348 g of crude product which yielded 50% compound **20** and 2% starting diester **19** by GLC analysis. The crude product was distilled (1.5 mm, 57°C) using a Kugelrohr distillation apparatus to give a colorless liquid compound **20:** ir ν_{max} (thin film) 2857 (saturated aliphatic C–H stretching), 1724 (–C=O), 1453 cm^{-1}; NMR ($CDCl_3$) δ 1.25–1.75 (14 H, m, $-CH_2CH_3$, $-CHCH_2CH$, $-CHCH_3$), 2.45 [2 H, quintet, $CH_3CH(CO)CH_2CH(CO)CH_3$], 4.05 (4 H, q, $-OCH_2CH_3$); MS *m/e* (rel abundance) 216 (1), 172 (100), 143 (75), 116 (85), 102 (55), 69 (55).

Anal. Calcd for $C_{11}H_{20}O_4$ (216.28): C, 61.09; H, 9.32. Found: C, 60.91; H, 9.37.

D. Preparation of Ethyl Ethylisoamylacetate (22) A mixture of 1.304 g (5.1 mmol) of geminal diester **21** (Alfred Bader Chemicals) and 5.780 g (51.6 mmol) of Dabco (**2**) in 8.309 g (78.4 mmol) of *o*-xylene was heated at reflux for 48 hr. The reaction mixture was acidified with cold dilute acid. The organic portion was separated and poured onto a dried column (2 cm i.d.) which was packed with 33 g of silica gel. The column was developed and eluted with pentane. All fractions were monitored by GLC analysis. A glass column (12 ft × 3 mm) packed with 10% silicon rubber OV-17 on 80/100 mesh Chromosorb W was used. The nitrogen flow rate was 11 ml/min. The column temperature was maintained at 245°C. Fractions containing more than one component were combined and rechromatographed (same column packed with 42.4 g of silica gel). All fractions containing the same compound were combined to give 0.170 g (13%) of diester **21** (identified by GLC analysis on comparison with starting material having t_R 7 min 30 sec) and 0.572 g (62%) of compound **22.** Compound **22** showed the following spectral properties: MS *m/e* (rel abundance) 186 (3), 116 (100), 101 (53), 73 (27), 71 (27), 57 (37); ir ν_{max} (thin film) 2857 (saturated aliphatic C–H stretching), 1724 (–C=O), 1471 cm^{-1}; NMR ($CDCl_3$) δ 0.90–1.32 [19 H, m, $CH_3CH_2CHCH_2CH(CH_3)_2$, $-OCH_2CH_3$], 2.16 [1 H, sextet, $-CH_2CH(CH_2)CO$], 4.10 (2 H, q, $-OCH_2CH_3$).

Anal. Calcd for $C_{11}H_{22}O_2$ (186.30): C, 70.92; H, 11.90. Found: C, 70.96; H, 11.74.

E. Preparation of Ethyl Cyclopentanecarboxylate (24). A mixture of 1.347 g (6.3 mmol) of diester **23** (Alfred Bader Chemicals) and 7.225 g (62.6 mmol) of Dabco (**2**) in 10.108 g (95.3 mmol) of *o*-xylene was heated at reflux for 48 hr. The reaction mixture was cooled and acidified with dilute hydrochloric acid.

The organic constituents of the acidified reaction mixture was separated through a glass column packed with 48 g of dry silica gel. The column was developed and eluted with 1500 ml of pentane and 600 ml of 5% ether in pentane, respectively, to give 0.370 g (liquid) of a mixture. Fractions containing mainly compound **24** were combined and rechromatographed twice to give 0.054 g of a colorless liquid compound **24:** ir ν_{max} (thin film) 2857 (aliphatic C–H stretching), 1724 cm^{-1} (–C=O); NMR ($CDCl_3$) δ 1.25 (3 H, t, $-OCH_2CH_3$), 1.70–1.80 (8 H, m, protons of cyclopentane ring except the one attached to the carbon next to carbonyl carbon), 2.65 (1 H, m, –CHCO), 4.05 (2 H, q, $-OCH_2CH_3$); MS *m/e* (rel abundance) 142 (9), 101 (53), 88 (53), 84 (82), 69 (76), 43 (100), 41 (51).

Anal. Calcd for $C_8H_{14}O_2$ (142.20): C, 67.57; H, 9.93. Found: C, 67.54; H. 9.77.

F. Preparation of Ethyl *n*-Butanoate (26). A mixture of 1.894 g (10.0 mmol) of diester **25** (Aldrich reagent) and 11.278 g (97.7 mmol) of Dabco (**2**) in 17.020 g (160.5 mmol) of *o*-xylene was heated at reflux for 27 hr. The organic constituents of the reaction mixture were separated through a glass column (2.54 cm o.d.) packed with 100 g of silica gel (Woelm, activity 1). The column was developed and eluted with 1500 ml of hexane and 300 ml of 5% ether in hexane to give 0.064 g (6%) of a colorless liquid compound **26.** The spectra (ir, NMR, and MS) of compound **26** were identical with those reported[21] for ethyl *n*-butanoate.

G. Preparation of Ethyl 2-Phenylbutanoate (28). A mixture of 2.007 g (7.6 mmol) of geminal diester **27** (Alfred Bader Chemicals) and 9.215 g (82.6 mmol) of Dabco (**2**) in 12.845 g (121.1 mmol) of *o*-xylene was heated at reflux for 10 hr. The cold reaction mixture was acidified with dilute hydrochloric acid. The organic portion was separated and poured onto a glass column (2 cm i.d.) packed with 38.2 silica gel (Woelm, activity 1). The column was eluted with 1200 ml of hexane, 600 ml of 5% ether in hexane, and 200 ml of 16.7% ether in hexane, respectively. The fractions were monitored by GLC analysis using a glass column (12 ft × 3 mm) packed with 10% OV-17 on 80/100 mesh Chromosorb W with a nitrogen flow rate of 11 ml/min. The column temperature was maintained at 260°C. Fractions with retention time of 5 min 12 sec were combined and the solvent was removed to give 0.421 g (31%) of liquid compound **28** which was distilled at 72°C and 3.6 mmHg pressure to give a colorless liquid compound **28:** ir ν_{max} (thin film) 3030 (aromatic C–H stretching), 2941 (saturated aliphatic C–H stretching), 1724 (–C=O), 1471 cm^{-1}; NMR ($CDCl_3$) δ 0.88 (3 H, t, $-CHCH_2CH_3$), 1.17 (3 H, t, $-OCH_2CH_3$), 1.94 (2 H, quintet, $-CHCH_2CH_3$), 3.42 [1 H, t, $-CH_2CH(C_6H_5)C=O$], 4.06 (2 H, q, $-OCH_2CH_3$), and 7.27 (5 H, s, ArH); MS *m/e* (rel abundance) 192 (21), 118 (16), 119 (79), 91 (100), 41 (13), 29 (18).

Anal. Calcd for $C_{12}H_{16}O_2$ (192.26): C, 74.97; H, 8.39. Found: C, 74.77; H, 8.30.

H. Preparation of Ethyl Phenylacetate (17). A mixture of 1.934 g (8.0 mmol) of diester **16** (Aldrich reagent) and 8.972 g (78.0 mmol) of Dabco (**2**) in 12.713 g (120.0 mmol) of *o*-xylene was heated at reflux for 10 hr. The acidified reaction mixture was separated through a glass column (2.54 cm o.d.) packed with 51.5 g of silica gel. The column was eluted with 1800 ml of hexane and 700 ml of 5% ether in hexane to give 0.557 g (43%) of methyl phenylacetate (**17**).

I. Preparation of Ethyl 3-Phenylpropionate (15). A mixture of 2.012 g (8.0 mmol) of diester **14** (Aldrich reagent) and 9.055 g (78.4 mmol) of Dabco (**2**) in 12.667 g (119.5 mmol) of *o*-xylene was heated at reflux for 6 hr. The usual organic portion of the work-up yielded 0.595 (42%) of 3-phenylpropionate (**15**).

Reaction of 3-Quinuclidinol with Geminal Diesters. A. Preparation of Ethyl Bis(3,4-dichlorobenzyl)acetate (10). A mixture of 0.121 g (0.25 mmol) of diethyl ester **9** and 0.630 g (5.0 mmol) of 3-quinuclidinol (**3**) in 0.794 g (7.5 mmol) of *o*-xylene was heated at reflux for 6 hr. The ether extract of the acidified (0.6 *M* HCl) reaction mixture was washed with water, dried over anhydrous sodium sulfate, and evaporated in vacuo to give compound **10** in 93% yield (0.087 g).

B. Preparation of Methyl Phenylacetate (17). A mixture of 1.663 g (8.0 mmol) of dimethyl phenylmalonate (**16**) (Aldrich reagent) and 1.016 g (8.0 mmol) of 3-quinuclidinol (**3**) in 8.486 g (80.0 mmol) of *o*-xylene was heated at reflux for 1 and 1.5 hr. The ether extract of the acidified (0.6 *M* HCl) reaction mixture was washed with water, dried over anhydrous sodium sulfate, and evaporated to yield 92% (GLC) of methyl phenylacetate (**17**).

C. Preparation of Ethyl Eicosonate (7). Procedure I. A mixture of 0.204 g (0.5 mmol) of diester **6** (Alfred Bader Chemicals) and 0.661 g (5.0 mmol) of 3-quinuclidinol (**3**) in 1.600 g (15.0 mmol) of *o*-xylene was heated at reflux for 7 hr. The cooled reaction mixture was diluted with 80 ml of ether and extracted with 5% sodium hydroxide. The ethereal portion was separated, washed with dilute acid, washed with water, dried over anhydrous sodium sulfate, and evaporated under reduced pressure to give 0.054 g of crude product. The crude product gave a 21% yield of monoester **7** which was identified as ethyl eicosonate. The ether extract was washed with water, dried over anhydrous sodium sulfate, and evaporated under reduced pressure to give 0.004 g of crystal containing equal amounts of two compounds with higher retention time (t_R 3 min 24 sec and 8 min 24 sec) than the starting diester **19** (t_R 3 min 6 sec) by GLC analysis (conditions were the same as above).

Procedure II. A mixture of 0.204 g (0.5 mmol) of diester **6** and 0.066 g (0.50 mmol) of 3-quinuclidinol (**3**) in 1.600 g (15.0 mmol) of *o*-xylene was heated at reflux for 7 hr. The cooled reaction mixture was diluted with 80 ml of ether and extracted with 5% sodium hydroxide. The ethereal portion was separated, washed with dilute acid, washed with water, dried over anhydrous sodium sulfate, and evaporated under reduced pressure to give 0.246 g of monoester **7.**

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Registry No.—**1,** 3001-72-7; **2,** 280-57-9; **3,** 1619-34-7; **6,** 7154-71-4; **7,** 18281-05-5; **9,** 57197-27-0; **10,** 57197-28-1; **11,** 1610-66-8;

12, 83-13-6; 14, 607-81-8; 16, 37434-59-6; 19, 57197-29-2; 20, 21239-22-5; 21, 77-24-7; 22, 57197-30-5; 23, 4167-77-5; 24, 5453-85-0; 25, 133-13-1; 27, 75-67-5; 28, 119-43-7.

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Preparation and Reactions of 2,6-Di-*tert*-butyl-4-(9-fluorenylidene)-1,4-benzoquinone

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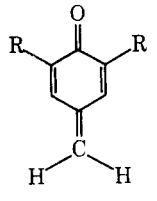
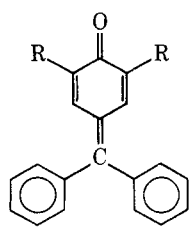
2,6-Di-*tert*-butyl-4-(9-fluorenylidene)-1,4-benzoquinone (**3**) was prepared from 2,6-di-*tert*-butyl-1,4-benzoquinone and fluorenylidenetriphenylphosphorane at 200°. In contrast to its α,α-diphenylmethylene analogue (**2b**), the 9-fluorenylidenequinone **3** smoothly undergoes electrophilic substitution reactions with phenols to give bisphenols. With anions as well as with amines, **3** reacts by 1,6 addition, yielding the correspondingly substituted phenols. Fluorenylidenequinone **3** was found to undergo a unique one-electron reduction with both hydrogen in the presence of platinum and with phenylmagnesium bromide. The acetyl derivative of the resulting 9-substituted fluorenyl radical was characterized by its ESR spectrum.

p-Methylenequinones of structure **1** play an important role as reactive intermediates in phenol oxidation.[1] Generally, they are easily reduced to the corresponding *p*-alkylphenols, they can dimerize by disproportionation, and they can undergo nucleophilic 1,6 addition resulting in aromatization.[1c] In the case of α,α-diphenylmethylene-substituted *p*-quinones (**2**, henceforth called fuchsones), disproportionation is structurally impossible, and reductive dimerization has not been encountered yet, probably because of the instability of the resulting hexaphenylethanes. Aromatization of fuchsones by acid-catalyzed 1,6 addition, however, occurs quite readily. For example, fuchsone itself (**2a**) rapidly adds water to give 4-hydroxytriphenylcarbinol.[2]



1

e.g., R = CH_3



2a, R = H

b, R = *tert*-butyl

c, R = CH_3

The chemistry of 3,5-di-*tert*-butylfuchsone (**2b**) has been the subject of detailed investigations.[3] This compound is easily reduced to give 3,5-di-*tert*-butyl-4-hydroxytriphenylmethane, and it readily aromatizes by addition of carbanions[4] as well as by photoinduced free-radical addition.[5] In contrast to **2a**, however, 3,5-di-*tert*-butylfuchsone does not add any nucleophiles in acid-catalyzed reactions and it does not undergo any electrophilic reactions with aromatic compounds such as phenols.[5b] Presumably, impaired protonation of the sterically hindered carbonyl group in conjunction with the steric hindrance of the methylene carbon caused by the out-of-plane position of the phenyl substituents may be responsible for the observed lack of reactivity. To test the validity of this assumption, it appeared interesting to replace the diphenylmethylene moiety in **2b** by the 9-fluorenylidene group and compare the chemistry of **2b** with that of its 9-fluorenylidene analogue. We have, therefore, prepared 2,6-di-*tert*-butyl-4-(9-fluorenylidene)-1,4-benzoquinone (**3**) and studied the effect of the rigidity of the fluorenylidene moiety and inherent planarity of **3** on its chemical properties.

Results and Discussion

A. Preparation of 2,6-Di-*tert*-butyl-4-(9-fluorenylidene)-1,4-benzoquinone. In contrast to the large number of known fuchsones, the synthesis of 9-fluorenylidenebenzoquinones has not been described before. The only 9-fluorenylidenequinones known are those derived from 1,4-naphthoquinone,[6] 9,10-anthraquinone,[7] and 9,10-phenanthrenequinone,[6] though little has been reported about their chemistry. The desired 2,6-di-*tert*-butyl-4-(9-fluorenylidene)-1,4-benzoquinone was most conveniently prepared in