to air dry to yield 200 g (83%), mp 173–175 °C (lit.[15] mp 177 °C).

Preparation of Aldehydes Using 2. (1) Liquid Product. A solution of 3.52 g of furfuryl chloride (27 mmol) in 40 mL of acetone was added to a suspension of 20 g (33 mmol) of **2** and 15.2 g (60 mmol) of triphenylphosphine in 100 mL of acetone. After 1 h, the solution was filtered, and the filter cake was washed with three 50-mL portions of ether. The combined filtrates were evaporated to dryness at reduced pressure. The residue was dissolved in ether, and the solution was filtered and then evaporated to give an oil. Evaporation distillation at reduced pressure gave 2.06 g (78%) of furfural.

(2) Solid Product. To a stirred solution of 4.6 g (25 mmol) of *p*-nitrobenzoyl chloride and 13.0 g (50 mmol) of triphenylphosphine in 50 mL of acetone was added 15.5 g (26 mmol) of **2** in one portion. After 1 h, the solution was filtered, and the filter cake was washed with three 50-mL portions of ether. The combined filtrates were evaporated to dryness, and the residue was dissolved in 40 mL of chloroform. The resulting solution was treated with 6 g of commercial cuprous chloride, allowed to stir for 1 h, and filtered. The solvent was evaporated at reduced pressure, and the residue was crystallized from aqueous ethanol to give 2.14 g (57%) of *p*-nitrobenzaldehyde.

Bis(trimethyl phosphite)tetrahydroboratocopper(I) (4a). To a stirred solution of 25 mL of trimethyl phosphite and 5 g (50 mmol) of CuCl in 250 mL of chloroform was added dropwise a solution of 2.47 g (65 mmol) of $NaBH_4$ in 175 mL of absolute ethanol. The resulting solution was stirred for 15 min, filtered, and evaporated at reduced pressure to give a colorless oil. The oil was dissolved in a mixture of 25 mL of methylene chloride and 175 mL of pentane, and the resulting solution was filtered and cooled to −78 °C. The supernatant was decanted from the oil and the procedure repeated. The oil was placed under high vacuum until it just began to darken, and then it was dissolved in acetone and stored at −20 °C or used immediately. The solution is stable for 1–2 weeks.

Bis(triisopropyl phosphite)tetrahydroboratocopper(I) (4b). The same procedure described for the trimethyl phosphite complex was followed except that the product did not oil from solution at −78 °C. Thus, the solvent was evaporated and the oil placed under high vacuum until it just began to darken.

Preparation of Aldehydes Using 4a and 4b. A solution of 0.33 g (2.35 mmol) of benzoyl chloride and 0.6 g (2.3 mmol) of triphenylphosphine in 15 mL of acetone was treated with 12.5 mL of 0.2 M **4a** in acetone. The solution was stirred for 15 min and evaporated to dryness. The residue was dissolved in methanol and the resulting solution filtered, concentrated, and treated with 2,4-dinitrophenylhydrazine reagent.[16] The 2,4-DNP derivative was filtered and then crystallized from aqueous ethanol to yield 0.547 g (83%) of benzaldehyde 2,4-dinitrophenylhydrazone, mp 235–237 °C (lit.[17] mp 237 °C).

Polymeric Bis(phosphine)tetrahydroboratocopper(I) (5). Polystyryldiphenylphosphine was prepared by the method of Regen.[18] Anal. Found: P, 7.27 (43% ring substitution).

Polystyryldiphenylphosphine (10 g) was added to 75 mL of dry tetrahydrofuran under a nitrogen atmosphere and allowed to swell. To this slurry was added 0.635 g (6.35 mmol) of CuCl in 20 mL of dry, degassed acetonitrile. After being stirred under N_2 for 48 h, the suspension was filtered under a nitrogen atmosphere, and the resin was washed with degassed THF, 1:1 THF–CH_3CN, and ether and then dried under vacuum. Anal. Found: P, 6.94; Cu, 3.68.

The above polymer (10.5 g) was suspended in 50 mL of chloroform and allowed to swell. A solution of 0.46 g of sodium borohydride in 50 mL of absolute ethanol was added dropwise and the slurry allowed to stir for 36 h. The resin was filtered, washed with $CHCl_3$, 2:1 $CHCl_3$–ethanol, 1:1 $CHCl_3$–ethanol, and ether. Anal. Found: B, 0.36.

Reduction of Benzoyl Chloride by 5. A solution of 141 mg (1.07 mmol) of benzoyl chloride in 7 mL of acetone was added to 2.4 g of polymeric reagent **5** in 15 mL of THF. After 90 min, GC analysis using an internal standard indicated a 73% yield of benzaldehyde.

Registry No. Nonanoyl chloride, 764-85-2; cinnamoyl chloride, 102-92-1; benzoyl chloride, 98-88-4; 4-chlorobenzoyl chloride, 122-01-0; 4-nitrobenzoyl chloride, 122-04-3; furfuryl chloride, 527-69-5; nonanal, 124-19-6; cinnamaldehyde, 104-55-2; benzaldehyde, 100-52-7; 4-chlorobenzaldehyde, 104-88-1; 4-nitrobenzaldehyde, 555-16-8; furfural, 98-01-1; $(Ph_3P)_2CuBH_4$, 16903-61-0; $[(CH_3O)_3P]_2CuBH_4$, 67784-66-1; $[(i\text{-}C_3H_7O)_3P]_2CuBH_4$, 74113-18-1.

(15) J. M. Davidson, *Chem. Ind. (London)*, 2021 (1964).

(16) D. J. Pasto and C. R. Johnson, "Organic Structure Determination", Prentice-Hall, Englewood Cliffs, NJ, 1969, p 383.

(17) A. Vogel, "A Textbook of Practical Organic Chemistry", Longman, London, 1978, p 1192.

(18) S. L. Regen and D. P. Lee, *J. Org. Chem.*, **40**, 1669 (1975).

Indenone Chemistry. 4.[1] Synthesis of Substituted 1-Naphthalenols and 8-Oxoindeno[1,2-*c*]pyrroles: Mechanism of an Indenone–Naphthalenol Rearrangement

Hugo Lahousse,[2a,b] Henri J. Martens,[2c] and Georges J. Hoornaert*[2b]

Department of Chemistry, Katholieke Universiteit Leuven, Celestijnenlaan 200 F, 3030 Leuven, and Limburgs Universitair Centrum, Universitaire Campus, 3610 Diepenbeek, Belgium

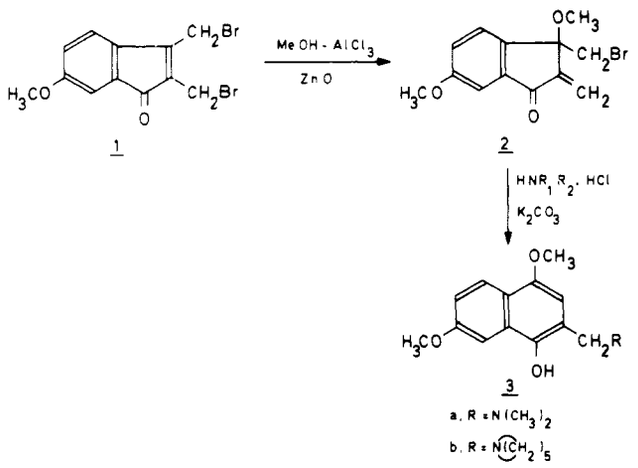
Received November 27, 1979

Treatment of 2,3-bis(bromomethyl)-6-methoxy-1-indenone (**1**) with various nucleophiles constitutes a one-step synthesis of 2,4-disubstituted 1-naphthalenols **3**. The mechanism of this reaction has been explored. This study reveals the intermediacy of 3-(bromomethyl)-6-methoxy-2-methylene-1-indanones of type **7**, which are thought to be formed by a S_N2' substitution on the allylic bromide system of **1**. A second nucleophilic attack on **7** leads to cycloprop[*a*]inden-6-ones **9** via a homo S_N2' substitution. The latter rearrange spontaneously into the 1-naphthalenols **3**. With carefully controlled reaction conditions an intermediate of type **7** could be isolated; it has been used in separate experiments with other nucleophiles. Depending on the nucleophile, this leads either to naphthalenols **3** or to 8-oxoindeno[1,2-*c*]pyrrolidines **5**.

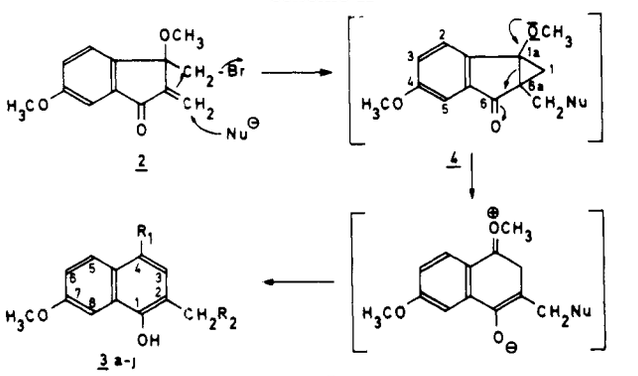
In order to synthesize heterocyclic compounds incorporating the indenone system, we tried to condense secondary amines with the indanone **2**, which had been prepared from the indenone **1** according to an earlier de-

0022-3263/80/1945-3451$01.00/0

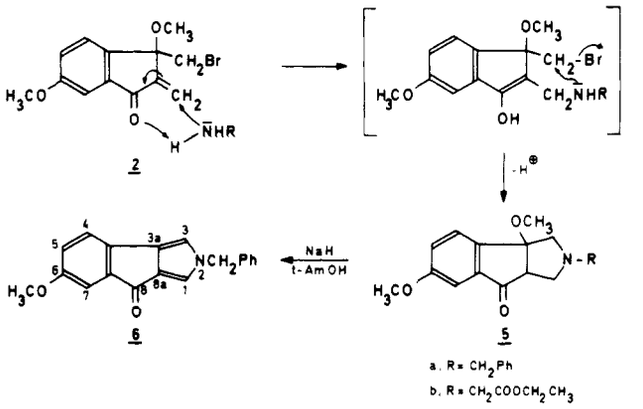
Scheme I



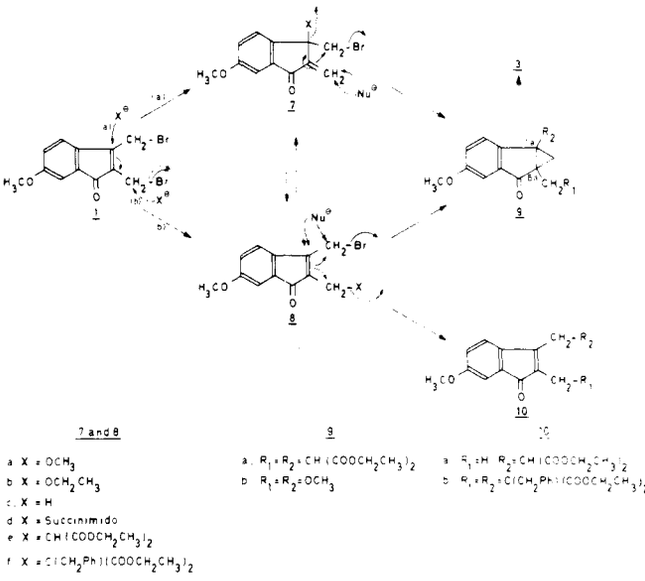
Scheme II



Scheme III



Scheme IV



scribed method.[3] Instead of the anticipated addition product of the amine to the α,β-unsaturated ketone, substituted 1-naphthalenols **3** were obtained in high yield (Scheme I). These naphthalenols could be useful synthons for vitamin K analogues.[4]

The formation of the 1-naphthalenol derivatives is thought to proceed via the intermediate cycloprop[*a*]-inden-6-ones **4** (Scheme II). The heterolytic C(1a)–C(6a) cleavage in the intermediate **4** is facilitated because the developing positive charge on C(1a) is stabilized by the 1a- and 4-methoxyl functions, whereas the negative charge on C(6a) is stabilized by the carbonyl. When the diethyl malonate anion is used as nucleophile, the intermediate cycloprop[*a*]inden-6-one **4** (Nu = $CH(COOEt)_2$) could be detected by characteristic NMR absorptions for the cyclopropane protons at δ 1.78 and 1.84 (AB system, J = 5 Hz) and for the methylene protons in $CH_2CH(COOEt)_2$ (ABX pattern at δ 2.36 and 2.69 with J_{AB} = 15 Hz, J_{AX} = 6 Hz, and J_{BX} = 9 Hz). These absorptions appeared right after mixing the reagents and decreased slowly in intensity at room temperature. The absorptions of the naphthalenol **3c**, which were not visible at first, increased in intensity. Bubbling HCl gas through the reaction mixture increased the rate of rearrangement substantially. This can be explained by protonation of the carbonyl oxygen in **4**, which increases its electron-withdrawing properties with respect to the C(1a)–C(6a) bond. When methoxide, ethoxide, or hydroxide is used as nucleophile, the reaction is very fast. The naphthalenols **3d**, **3e**, and **3f** formed in these reactions are readily air oxidized[5] and could only be purified after acylation of the naphthalenol with acetic anhydride.

Cycloprop[*a*]inden-6-one derivatives have been obtained earlier by a number of routes.[6] The rearrangement of some of these compounds to naphthalenol derivatives has also been observed.[7]

Treatment of **2** with primary amines instead of secondary amines resulted in the formation of indeno[1,2-*c*]pyrrolidines **5** and only minor amounts of naphthalenol derivatives (Scheme III). This reaction is thought to proceed via the addition product of the amine to the α,-

(1) Part 3: G. Jammaer, H. Martens, and G. Hoornaert, *Tetrahedron*, 31, 2293 (1975).

(2) (a) Predoctoral Fellow of the Instituut tot aanmoediging van Wetenschappelijk Onderzoek in Nijverheid en Landbouw (IWONL); (b) Leuven; (c) Diepenbeek.

(3) H. Martens and G. Hoornaert, *Tetrahedron*, **30**, 3641 (1974).

(4) (a) M. Bockmühl, O. Schaumann, E. Bartholomäus, and H. Leditschke, U.S. Patent 2372655 (1945); *Chem. Abstr.*, **39**, P4723 (1945); (b) E. A. Doisy, S. B. Binkley, and S. A. Thayer, *Chem. Rev.*, **28**, 477 (1941); (c) M. B. Moore and W. H. Washburn, *J. Am. Chem. Soc.*, **77**, 6384 (1955); (d) C. D. Snyder and H. Rapoport, *ibid.*, **96**, 8046 (1974), and references therein.

(5) F. M. Dean and D. A. Matkin, *J. Chem. Soc., Perkin Trans. 1*, 2289 (1977).

(6) (a) R. Fraisse-Jullien, C. Frejaville, and V. Toure, *Bull. Soc. Chim. Fr.*, 4444 (1968); (b) G. R. Elling, R. C. Hahn, and G. Schwab, *J. Am. Chem. Soc.*, **95**, 5659 (1973); (c) H. E. Zimmerman and T. P. Cutler, *J. Org. Chem.*, **43**, 3283 (1978).

(7) (a) C. F. Koelsch, *J. Org. Chem.*, **26**, 1003 (1961); (b) K. Buggle and D. O'Sullivan, *J. Chem. Soc., Perkin Trans. 1*, 572 (1975); (c) E. C. Friedrich, D. B. Taggart, and M. A. Saleh, *J. Org. Chem.*, **42**, 1437 (1977).

β-unsaturated ketone system. The next step is an intramolecular nucleophilic attack of the amine, instead of the enol, on the bromomethyl group, leading to the formation of a pyrrolidine ring instead of a cyclopropane ring. This can be explained by the more pronounced nucleophilic properties of the amine function of the addition product. Treatment of **5a** with sodium *tert*-amylate affords the 8-oxoindeno[1,2-*c*]pyrrole **6**, probably after air oxidation.[8] These reactions represent synthetic routes for 8-oxoindeno[1,2-*c*]pyrrolidines and 8-oxoindeno[1,2-*c*]pyrroles, which so far have not been synthesized.[9]

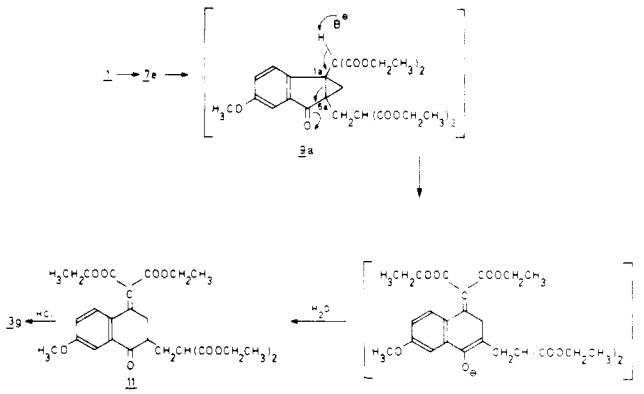
As the indanone **2** was thought to be formed from the indenone **1** through a nucleophilic attack of methanol on the polarized α,β-unsaturated ketone system,[3] we also investigated the reactivity of the indenone **1** toward stronger nucleophiles such as alkoxides. Treatment of the indenone **1** with 3 equiv of sodium methoxide instantaneously produced the naphthalenol **3d**.

The mechanism for the formation of naphthalenols from the indenone **1** is discussed below. Conversion of **1** into **7** or **8** is possible along pathways a or b of Scheme IV. These intermediates can lead then to the cycloprop[*a*]inden-6-one derivative **9** via different paths.

The formation and isolation of **7a** when **1** is treated with $ZnO-AlCl_3$ in methanol[3] show that path a indeed can occur. Without $AlCl_3$ no reaction takes place. Although strongly deactivated in a methanolic medium, $AlCl_3$ probably exerts a Lewis acid activity and complexes the carbonyl oxygen, thereby increasing the polarization of the double bond of the α,β-unsaturated ketone system. This makes the β-carbon a better substrate for a S_N2'-type substitution.[10] Intermediate **7a** can be transformed into the cycloprop[*a*]indenone **9b** by a one-step process. This implies a second attack of the nucleophile on the polarized exocyclic double bond of **7a** and expulsion of the bromide by the shifting electron pair of the double bond. This reaction can be considered as a homo S_N2' substitution. Another alternative would be the transformation **7a** → **8a** → **9b**. Equilibration between **7** and **8** can be explained by a second nucleophilic attack on the β-carbon atom of the conjugated enone system in **7** or **8** and expulsion (S_N2' substitution) of the nucleophile X introduced first along path a or b in Scheme IV. These two alternatives can be distinguished by treatment of **7a** (X = OMe) with sodium ethoxide in ethanol. Expulsion of the methoxyl group in **7a** would lead to **8b**, which results in the ultimate formation of **3h**, a naphthalenol with two ethoxyl substituents.

On the other hand, when the attack of the ethoxide results in expulsion of the bromide, the naphthalenol **3e** would be formed (retaining its 4-methoxyl group). Reaction of **7a** with sodium ethoxide only yields the naphthalenol **3e**, showing that **7a** was converted directly to **9**

Scheme V



and not via **8b** (Scheme IV). As we also had indenones of type **8** at our disposal, we could study the feasibility of the conversion of **8** into **9**. On treatment of **8c** (X = H) the naphthalenol **3j** was indeed obtained. With the indenone **8a** (X = OMe) we could verify in the same way as for **7a** whether the transformation of **8a** to **9b** proceeded directly or via a **8a** → **7a** → **9b** sequence. Treatment of **8a** (X = OMe) with sodium ethoxide in ethanol yielded only the 4-ethoxy-2-(methoxymethyl)-1-naphthalenol (**3i**) and no 4-ethoxy-2-(ethoxymethyl)-1-naphthalenol (**3h**), proving that the transformation of **8** to **9** is possible and that this transformation proceeds directly from **8a** to the intermediate **9** and not via **7b**.

So far we have only shown that there is no interconversion of compounds of type **7** and **8** in the nucleophilic reaction conditions used in the transformation of the dibromoindenone **1** to naphthalenols. However, both intermediates (**7** and **8**) can be obtained from **1** and can be converted to naphthalenols by treatment with strong nucleophiles. To settle the question concerning the pathways a and b in the reaction of the dibromoindenone **1** with strong nucleophiles, we performed the following experiment. Equal amounts of the indenone **1** and the indenone **8c** were treated with 2 equiv of sodium methoxide in methanol at room temperature. Analysis of the reaction products showed that only the 1-naphthalenol **3d** and some indanone **7a** were formed. No 1-naphthalenol **3j** (the expected reaction product of **8c**) could be detected. This proves that the conversion of **8** to **9** cannot be part of the total conversion of **1** to **3** as it proceeds much slower. As there is no interconversion of **7** to **8** with alkoxides, this leaves the path **1** → **7** → **9** → **3** as the most probable for this kind of nucleophiles.

The higher reactivity of **7** toward nucleophiles, compared to that of **8**, can probably be attributed partly to electronic effects—the conjugation of the double bond with a *p*-methoxyphenyl group in **8**, making it less reactive—and partly to steric effects—the exocyclic double bond in **7** being less hindered for nucleophilic attack.

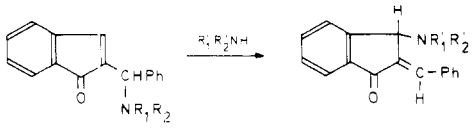
The fact that no naphthalenol derivative, but, instead, the monosubstitution product **8a**, is formed when **7a** is heated in methanol points to the occurrence of competitive ways, depending on the nucleophile, for conversion of **7** to **8** or **9**. Therefore, we studied the behavior of other nucleophiles toward indenone **1** and products of type **7**.

Treatment of **1** with 3 equiv of diethyl sodiomalonate in benzene yielded the tetralone **11** (Scheme V), which is transformed into the naphthalenol **3g** on treatment with HCl. The formation of the tetralone **11** can also be explained by the intermediate formation of the cycloprop[*a*]inden-6-one derivative **9a**. Even with lower quantities of diethyl sodiomalonate no cycloprop[*a*]indenone could be detected (the only products were the tetralone **11** and

(8) (a) H. W. Heine and R. Peavy, *Tetrahedron Lett.*, 3123 (1965); (b) A. Padwa and L. Hamilton, *ibid.*, 4363 (1965).

(9) Some indeno[1,2-*c*]pyrrolidines without the 8-oxo function have been synthesized: (a) S. C. Lahiri and B. Pathak, *J. Pharm. Sci.*, **57**(6), 1013 (1968); (b) A. U. Dey and B. Pathak, *Indian J. Chem.*, **3**(2), 93 (1965); (c) S. C. Lahiri and B. Pathak, *J. Med. Chem.*, **8**(1), 131 (1965).

(10) (a) A similar reaction of amines with indenones has been observed and explained by an S_N2' type mechanism:



G. Maury, E. M. Wu, and N. H. Cromwell, *J. Org. Chem.*, **33**, 1900, 1907 (1968). (b) F. G. Bordwell, *Acc. Chem. Res.*, **3**, 281 (1970); (c) N. H. Cromwell and Hiu-Kwong Leung, *J. Org. Chem.*, **41**, 3241 (1976), and references therein.

some starting product). The question of whether **9a** is formed via **1** → **7e** → **9a** or via **1** → **8e** → **9a** has been settled by the following experiment. Treatment of the indenone **8c** with diethyl sodiomalonate does not lead to a naphthalenol derivative via **9**, as was the case with sodium methoxide as nucleophile, but to a substitution product, **10a**. In our opinion, this rules out the intervention of **8e** as an intermediate in the formation of **9a**. The fact that **8c** reacts in a different way with sodium methoxide compared to diethyl sodiomalonate remains a puzzling feature. The cycloprop[*a*]inden-6-one derivative **9a** can be transformed to the tetralone **11** as is depicted in Scheme V. In the intermediate **9a** the α-H of the CH(COOEt)$_2$ in position C(1a) is abstracted in the basic medium. This creates a carbanion which destabilizes the C(1a)–C(6a) cyclopropane bond even more than the methoxyl group (Scheme II), and ring opening occurs. In order to prevent this deprotonation, we repeated the reaction with the sodium salt of diethyl benzylmalonate. The result was a disubstituted product, the indenone **10b**, and no cycloprop[*a*]indenone, tetralone, or naphthalenol. With the anion of succinimide, the monosubstitution product **8d** was obtained. Whether these last two substitution products are formed from **1** via route b to **8** and then to **10** or via **1** → **7** → **8** → **10** is not clear.

The products of type **7** can be regarded as kinetically controlled products, whereas the products of type **8** are thermodynamically controlled products. Such behavior has been observed with other comparable mobile keto–allyl systems.[10a] So when the indenone **1** was treated with ZnO/AlCl$_3$ in refluxing methanol, the monosubstitution product **8a** was formed. At room temperature **7a** was obtained predominantly, but at higher temperatures **7a** was transformed to **8a**. Whether this **7a** → **8a** transformation is a S_N1 or a S_N2' reaction is not clear, and no effort has been made to settle this difficult question.[10b,c,11] The presence of AlCl$_3$, even if it is strongly deactivated in a methanolic medium, promotes the S_N1 type reaction by complexing the 3-OMe and in this way improves its leaving-group capacity. The 6-OMe also does this by stabilizing a developing positive charge on C(3). The substantial rate enhancement for the **7a** → **8a** transformation, when HCl gas is bubbled through a methanolic solution of **7a**, is also in agreement with a possible S_N1 reaction.

Summarizing the results obtained from the attack of the various nucleophiles on compounds of type **7**, we observe a different behavior which depends on the leaving group X. When X is a good leaving group (OMe, complexed with AlCl$_3$, or succinimide anion), the S_N1 or S_N2' transformation of **7** → **8** leading to a thermodynamically more stable compound is preferred to a homo-S_N2'-type substitution of the bromide, which would lead to highly energetic compounds as the cycloprop[*a*]indenones **9**. On the contrary, when X is a poor leaving group (OMe, CH(COOEt)$_2$), the homo-S_N2'-type substitution of a bromide is preferred, leading to 1-naphthalenol derivatives via **9**. An increased steric hindrance in the nucleophile, which would favor path b instead of path a, constitutes a possible explanation for the unexpected behavior of the diethyl benzylmalonate anion compared to the diethyl malonate anion.

Conclusion

The formation of either substituted indenones **10** or naphthalenols **3** on treatment of the brominated indenone **1** with nucleophiles can be satisfactory explained on the basis of Scheme IV, taking nucleophilic properties and leaving group properties into account. With brominated indenones of types **1** and **8** readily accessible, the reactions presented here constitute valuable synthetic routes to a number of 2,4-substituted 1-naphthalenols and to 8-oxoindeno[1,2-*c*]pyrrolidines and 8-oxoindeno[1,2-*c*]pyrroles.

Experimental Section

The IR spectra have been recorded with a Perkin-Elmer 257 grating spectrophotometer. The ^{1}H NMR spectra have been taken on a Varian XL-100 spectrometer and the ^{13}C NMR on a Bruker WP-80 spectrometer. For the mass spectra an AEI-MS-12 was used; the ionization energy was 70 eV, and samples were injected directly at a temperature between 100 and 200 °C. All melting points are uncorrected. 2,3-Bis(bromomethyl)-6-methoxy-1-indenone (**1**), 3-(bromomethyl)-3,6-dimethoxy-2-methylene-1-indanone (**2**), and 3-(bromomethyl)-2-methyl-1-indenone (**8c**) were synthesized according to earlier described methods.[3]

4,7-Dimethoxy-2-[(dimethylamino)methyl]-1-naphthalenol (3a). To a suspension of 4 mmol of dimethylamine hydrochloride and 8 mmol of potassium carbonate in 20 mL of glyme is added a solution of 4 mmol indanone **2**. The mixture is stirred for 3 h at 60 °C. The mixture is filtered, and the filtrate is chromatographed on silica gel with 90% benzene–10% ethyl acetate, which affords 3.6 mmol of **3a** (yield 90%): IR (CHCl$_3$) 3200–2500 (ν_{OH}), 1610 cm^{-1} ($\nu_{C=C}$); NMR (CDCl$_3$) δ 2.36 (6, s, N(CH$_3$)$_2$), 3.70 (2, s, 2-CH$_2$–N), 3.88 and 3.92 (2 s, 3 H each, 4- and 7-OCH$_3$), 6.24 (1, s, 3-H), 7.08 (1, dd, J_o = 8 Hz, J_m = 2 Hz, 6-H), 7.48 (1, d, J_m = 2 Hz, 8-H), 8.04 (1, d, J_o = 8 Hz, 5-H), 10.8 (1, br s, 1-OH); mass spectrum, *m/e* (relative intensity) 261 (11), 246 (3), 216 (100), 173 (32), 58 (16). Anal. Calcd for M$^+$: *m/e* 261.1364. Found: *m/e* 261.1367.

4,7-Dimethoxy-2-(1-piperidinylmethyl)-1-naphthalenol (3b). The same procedure as for **3a** was used: yield 87%; IR (CHCl$_3$) 3200–2500 (ν_{OH}), 1605 cm^{-1} ($\nu_{C=C}$); NMR (CDCl$_3$) δ 1.4–1.8 (6, br m, 3 (CH$_2$)), 2.5 (4, br s, 2 N–CH$_2$), 3.66 (2, s, 2-CH$_2$–N), 3.84 and 3.92 (2 s, 3 H each, 4 and 7-OCH$_3$), 6.22 (1, s, 3-H), 7.06 (1, dd, J_o = 8 Hz, J_m = 2 Hz, 6-H), 7.48 (1, d, J_m = 2 Hz, 8-H), 8.04 (1, d, J_o = 8 Hz, 5-H), 11.05 (1, br s, 1-OH); mass spectrum, *m/e* (relative intensity) 301 (10), 286 (2), 216 (100), 173 (34), 84 (14). Anal. Calcd for M$^+$: *m/e* 301.1677. Found: *m/e* 301.1679.

Acetate of 2-(2,2-Dicarbethoxyethyl)-4,7-dimethoxy-1-naphthalenol (3c). To a solution of 8 mmol of diethyl sodiomalonate in 10 mL of glyme, prepared from diethyl malonate and 1 equiv of NaH, is added 4 mmol of indanone **2** dissolved in 40 mL of glyme in one portion. After 5 min at 60 °C the reaction is completed, and a TLC analysis shows only one product. Due to its facile air oxidation, which is found for many 4-methoxy-1-naphthalenols,[5] this naphthalenol is immediately converted to its acetate by treatment with 10 mL of acetic anhydride and 2.5 mL of triethylamine during 3 h at room temperature under a nitrogen atmosphere. The mixture is poured into ice water–K_2CO_3 and extracted three times with 20 mL of CH_2Cl_2. Purification by preparative TLC on silica gel with benzene–ethyl acetate (90/10) affords 3.68 mmol of the acetate of **3c** as a colorless oil: yield 92%; IR (CHCl$_3$) 1750 cm^{-1} ($\nu_{C=O}$); NMR (CDCl$_3$) δ 1.20 (6, t, 2 OCH$_2$CH$_3$), 2.46 (3, s, CH$_3$CO), 3.28 (2, d, J = 7 Hz, CH$_2$–CH), 3.78 (1, t, J = 7 Hz, CH$_2$–CH), 3.82 and 3.88 (2 s, 3 H each, 4-and 7-OCH$_3$), 4.16 (4, q, OCH$_2$CH$_3$), 6.56 (1, s, 3-H), 6.90 (1, d, J_m = 2 Hz, 8-H), 7.06 (1, dd, J_o = 9 Hz, J_m = 2 Hz, 6-H), 8.05 (1, d, J_o = 9 Hz, 5-H); mass spectrum, *m/e* (relative intensity) 418 (26), 376 (100), 373 (10), 330 (50), 302 (5). Anal. Calcd for M$^+$: *m/e* 418.1627. Found: *m/e* 418.1624.

Acetate of 4,7-Dimethoxy-2-(methoxymethyl)-1-naphthalenol (3d). To a solution of 8 mmol of NaOCH$_3$ in 10 mL of absolute methanol, cooled in an ice bath, is added in one portion 4 mmol of indanone **2** dissolved in 50 mL of absolute methanol precooled to 0 °C. After 1 min the reaction is completed, and the methanol is evaporated in vacuo without warming. The residue is treated as in the previous procedure with acetic anhydride and triethylamine to yield 3.76 mmol of the acetate of **3d** (yield 94%). Recrystallization from hexane–benzene gives white crystals: mp 114 °C; IR (CHCl$_3$) 1755 cm^{-1} ($\nu_{C=O}$); NMR (CDCl$_3$) δ 2.42 (3, s, CH$_3$CO), 3.38 (3, s, CH$_2$OCH$_3$), 3.86 and 3.96

(11) (a) R. A. Sneen, *Acc. Chem. Res.*, **6**, 46 (1973); (b) F. G. Bordwell, P. F. Wiley, and T. G. Mecca, *J. Am. Chem. Soc.*, **97**, 132 (1975). (c) M. C. Eagen and N. H. Cromwell, *J. Org. Chem.*, **39**, 3863 (1974).

(2 s, 3 H each, 4- and 7-OCH_3), 4.50 (2, s, 2-CH_2), 6.73 (1, s, 3-H), 6.94 (1, d, J_m = 2 Hz, 8-H), 7.08 (1, dd, J_o = 9 Hz, J_m = 2 Hz, 6-H), 8.10 (1, d, J_o = 9 Hz, 5-H); mass spectrum, *m/e* (relative intensity) 290 (14), 248 (10), 217 (28), 216 (100), 189 (7). Anal. Calcd for M^+: *m/e* 290.1154. Found: *m/e* 290.1151. Anal. Calcd for $C_{16}H_{18}O_5$: C, 66.20; H, 6.25. Found: C, 65.95; H, 6.28.

Acetate of 4,7-Dimethoxy-2-(ethoxymethyl)-1-naphthalenol (3e). The same procedure as for **3d** was used: yield 89%; mp 54 °C; IR ($CHCl_3$) 1755 cm^{-1} ($\nu_{C=O}$); NMR ($CDCl_3$) δ 1.20 (3, t, OCH_2CH_3), 2.38 (3, s, $OCOCH_3$), 3.51 (2, q, CH_2CH_3), 3.82 and 3.92 (2 s, 3 H each, 4- and 7-OCH_3), 6.74 (1, s, 3-H), 6.93 (1, d, J_m = 2 Hz, 8-H), 7.07 (1, dd, J_o = 9 Hz, J_m = 2 Hz, 6-H), 8.10 (1, d, J_o = 9 Hz, 5-H); mass spectrum, *m/e* (relative intensity) 304 (15), 262 (11), 217 (27), 216 (100), 189 (6). Anal. Calcd for M^+: *m/e* 304.1310. Found: *m/e* 304.1312. Anal. Calcd for $C_{17}H_{20}O_5$: C, 67.09; H, 6.62. Found: C, 66.71; H, 6.78.

Diacetate of 4,7-Dimethoxy-2-(hydroxymethyl)-1-naphthalenol (3f). Four millimoles of indanone **2** is dissolved in 20 mL of dioxane (freshly distilled from $LiAlH_4$). To this solution is added slowly 8 mmol of NaOH in 10 mL of water, under a N_2 atmosphere. After 10 min of additional stirring at room temperature, the mixture is concentrated in vacuo. The residue is treated with acetic anhydride and triethylamine as for **3c**. The diacetate is purified by preparative TLC on silica gel with benzene–ethyl acetate, yielding 3.28 mmol of the diacetate as a colorless oil: yield 82%; IR ($CHCl_3$) 1715 cm^{-1} ($\nu_{C=O}$); NMR ($CDCl_3$) δ 2.09 (3, s, 2-CH_2OCOCH_3), 2.45 (3, s, 1-$OCOCH_3$), 3.87 and 3.96 (2 s, 3 H each, 4- and 7-OCH_3), 5.16 (2, s, 2-CH_2O), 6.72 (1, s, 3-H), 6.92 (1, d, J_m = 2 Hz, 8-H), 7.10 (1, dd, J_o = 9 Hz, J_m = 2 Hz, 6-H), 8.11 (1, d, J_o = 9 Hz, 5-H); mass spectrum, *m/e* (relative intensity) 318 (33), 276 (8), 217 (62), 216 (100). Anal. Calcd for M^+: *m/e* 318.1098. Found: *m/e* 318.1057.

2-(2,2-Dicarbethoxyethyl)-4-(dicarbethoxymethyl)-7-methoxy-1-naphthalenol (3g). A solution of 4 mmol of tetralone **11** in 30 mL of dry ether is treated with a stream of dry HCl gas at room temperature. The solvent is evaporated in vacuo, and the residue is purified by preparative TLC on silica gel with benzene–ethyl acetate (90/10). A 3.85-mmol sample of **3g** is obtained as a colorless oil: yield 96%; IR ($CHCl_3$) 1725 cm^{-1} ($\nu_{C=O}$); NMR ($CDCl_3$) δ 1.21 and 1.24 (12, 2 t, 4 OCH_2CH_3), 3.28 (2, d, J = 7 Hz, CH_2–CH), 3.76 (1, t, J = 7 Hz, CH_2–CH), 3.88 (3, s, 7-OCH_3), 4.19 and 4.22 (9, 2q, 4 OCH_2CH_3 and 4-CH($COOEt)_2$, hidden absorption), 5.21 (1, s, 3-H), 7.13 (1, dd, J_o = 8 Hz, J_m = 2 Hz, 6-H), 7.63 (1, d, J_m = 2 Hz, 8-H), 7.73 (1, d, J_o = 8 Hz, 5-H), 8.08 (1, br s, 1-OH); mass spectrum, *m/e* (relative intensity) 504 (5), 459 (35), 458 (15), 431 (4), 412 (31), 367 (9), 344 (100), 298 (7). Anal. Calcd for M^+: *m/e* 504,1995. Found: *m/e* 504,1999.

Acetate of 4,7-Dimethoxy-2-methyl-1-naphthalenol (3j). To an ice-cooled solution of 8 mmol of $NaOCH_3$ in 10 mL of methanol is added a solution of 4 mmol of indenone **8c** in 30 mL of dry methanol over a period of 30 min. After an additional 10 min, the starting product has disappeared, and the reaction mixture is concentrated in vacuo. The residue is treated with acetic anhydride and triethylamine as for **3c**. After preparative TLC on silica gel with benzene–ethyl acetate (90/10), the product is recrystallized from hexane–benzene. This gives white crystals: mp 124 °C; yield 67%; IR ($CHCl_3$) 1750 cm^{-1} ($\nu_{C=O}$); NMR ($CDCl_3$) δ 2.26 (3, s, 2-CH_3), 2.41 (3, s, 1-$OCOCH_3$), 3.85 and 3.89 (2 s, 3 H each, 4- and 7-OCH_3), 6.44 (1, s, 3-H), 6.89 (1, d, J_m = 2 Hz, 8-H), 7.03 (1, dd, J_o = 9 Hz, J_m = 2 Hz, 6-H), 8.04 (1, d, J_o = 9 Hz, 5-H); mass spectrum, *m/e* (relative intensity) 260 (27), 218 (100), 203 (38), 189 (4), 174 (7); Anal. Calcd for M+: *m/e* 260.1048. Found: *m/e* 260.1041. Anal. Calcd for $C_{15}H_{16}O_4$: C, 69.22; H, 6.20. Found: C, 68.83; H, 6.31.

2-Benzyl-3a,6-dimethoxy-2,3,3a,8a-tetrahydroindeno[1,2-*c*]pyrrol-8(1*H*)-one (5a). A mixture of 4 mmol of indanone **2**, 4.5 mmol of benzylamine, and 4.5 mmol potassium carbonate in 50 mL of dry glyme is stirred for 3 h at 60 °C. After cooling, the mixture is filtered, and the filtrate is concentrated in vacuo. Preparative TLC on silica gel with benzene–ethyl acetate (90/10) yields 3.04 mmol of **5a** as a colorless oil: yield 76%; IR ($CHCl_3$) 1720 cm^{-1} ($\nu_{C=O}$); NMR ($CDCl_3$) δ 2.54–3.28 (5, m, 1-H, 3-H, and 8a-H), 3.04 (3, s, 3a-OCH_3), 3.52 (2, s, $PhCH_2N$), 3.82 (3, s, 6-OCH_3), 7.00–7.12 (6, m, (7-H and Ph), 7.18 (1, dd, J_o = 8 Hz, J_m = 2 Hz, 5-H), 7.38 (1, d, J_o = 8 Hz, 4-H); mass spectrum, *m/e* (relative intensity) 323 (18), 308 (21), 293 (5), 133 (74), 91 (100). Anal. Calcd for M^+: *m/e* 323.1521. Found: *m/e* 323.1516.

2-(Carbethoxymethyl)-3a,6-dimethoxy-2,3,3a,8a-tetrahydroindeno[1,2-*c*]pyrrol-8(1*H*)-one (5b). The same procedure as for **5a** was used: yield 75%; IR ($CHCl_3$) 1740–1720 cm^{-1} ($\nu_{C=O}$); NMR ($CDCl_3$) δ 1.22 (3, t, OCH_2CH_3), 2.84–3.24 (5, m, 1-H, 3-H, and 8a-H), 3.10 (3, s, 3a-OCH_3), 3.26 (2, s, NCH_2COOEt), 3.86 (3, s, 6-OCH_3), 4.10 (2, q, OCH_2CH_3), 7.14 (1, d, J_m = 2 Hz, 7-H), 7.24 (1, dd, J_o = 9 Hz, J_m = 2 Hz, 5-H), 7.48 (1, d, J_o = 9 Hz, 4-H); mass spectrum, *m/e* (relative intensity) 319 (37), 304 (7), 247 (43), 246 (100), 232 (7), 214 (9), 129 (64). Anal. Calcd for M^+: *m/e* 319.1418. Found: *m/e* 319.1400.

2-Benzyl-6-methoxyindeno[1,2-*c*]pyrrol-8(1*H*)-one (6). Three millimoles of **5a** is treated with 3 mmol of sodium *tert*-amylate in 30 mL of dry *tert*-amyl alcohol. The mixture is refluxed for 3 h. After being concentrated in vacuo, the mixture is purified by preparative TLC on silica gel with benzene–ethyl acetate (95/5), which affords 2.55 mmol of **6** (yield 85%). Recrystallization from hexane gives orange yellow crystals: mp 114 °C; IR ($CHCl_3$) 1695 cm^{-1} ($\nu_{C=O}$); NMR ($CDCl_3$) δ 3.69 (3, s, 6-OCH_3), 4.80 (2, s, NCH_2Ph), 6.33 (1, d, J = 1 Hz, 3-H), 6.70 (1, dd, J_o = 9 Hz, J_m = 2 Hz, 5-H), 6.80 (1, d, J = 1 Hz, 1-H), 6.93 (1, d, J_o = 9 Hz, 4-H), 7.00 (1, d, J_m = 2 Hz, 7-H), 7.00–7.28 (5, m, Ph); mass spectrum, *m/e* (relative intensity) 289 (71), 274 (5), 198 (11), 91 (100). Anal. Calcd for M^+: *m/e* 289.1103. Found: *m/e* 289.1094. Anal. Calcd for $C_{19}H_{15}NO_2$: C, 78.87; H, 5.23; N, 4.84. Found: C, 78.94; H, 5.33; N, 4.79.

3-(Bromomethyl)-6-methoxy-2-(methoxymethyl)-1-indenone (8a). A solution of 4 mmol of indanone **2** in 30 mL of dry methanol is refluxed with 4 mmol of $AlCl_3$ and 4 mmol of ZnO for 2 h under a N_2 atmosphere. After cooling, the mixture is poured into ice and acidified with HCl (10%). Most of the methanol is removed by evaporation in vacuo, and the remaining aqueous phase is extracted with CH_2Cl_2 (3 × 20 mL). These extracts are evaporated, and the residue is chromatographed on silica gel with benzene. Recrystallization from hexane affords 3.72 mmol of **8a** as orange-red crystals: mp 110 °C; yield 93%; IR ($CHCl_3$) 1710 cm^{-1} ($\nu_{C=O}$); ^1H NMR ($CDCl_3$) δ 3.40 (3, s, CH_2OCH_3), 3.83 (3, s, 6-OMe), 4.22 (2, s, 2-CH_2), 4.50 (2, s, 3-CH_2), 6.80 (1, dd, J_o = 8 Hz, J_m = 2 Hz, 5-H), 7.02 (1, d, J_m = 2 Hz, 7-H), 7.16 (1, d, J_o = 8 Hz, 4-H); ^{13}C NMR ($CDCl_3$) δ 21.54 (CH_2Br), 55.77 (6-OCH_3), 58.72 (2-CH_2OCH_3), 63.42 (2-CH_2O), 110.82 (C-7), 116.67 (C-5), 121.59 (C-4), 130.56 (C-3a), 132.74 (C-7a), 134.88 (C-2), 155.71 (C-3), 161.39 (C-6), 196.00 (CO); mass spectrum, *m/e* (relative intensity) 298 (1), 296 (1), 218 (16), 217 (100), 186 (18), 174 (8), 115 (10). Anal. Calcd for M^+: *m/e* 298.0026 and 296.0047. Found: *m/e* 298.0017 and 296.0050. Anal. Calcd for $C_{13}H_{13}O_3Br$: C, 52.55; H, 4.41. Found: C, 53.08; H, 4.54.

The positions of the 3-CH_2Br and 2-CH_2OCH_3 groups have been secured by the following experiments. A selective decoupling at δ 4.5 results in a triplet to singlet transformation of the ^{13}C absorption at 21.37 ppm, which was assigned to the CH_2Br carbon. Hence the absorption at 4.5 ppm must be assigned to the CH_2Br and that at 4.22 ppm to the CH_2OCH_3. A ^1H NMR in C_6D_6 afforded the the following ASIS values for these two absorptions ($\Delta = \delta_{CDCl3} - \delta_{C6D6}$): for the CH_2Br, Δ = +0.38 ppm; for the CH_2OCH_3, Δ = +0.18 ppm. This indicates that the CH_2 is located at the 3-position and the CH_2OCH_3 at the 2-position.

3-(Bromomethyl)-6-methoxy-2-(succinimidomethyl)-1-indenone (8d). Four millimoles of succinimide and 4 mmol of NaH are stirred for 3 h at room temperature in 20 mL of dry glyme. To this suspension is added 4 mmol of indenone **1** dissolved in 50 mL of dry glyme in one portion. The mixture is stirred for 5 h at 50 °C. After evaporation of the solvent, 10 mL of water is added, and the mixture is extracted three times with 20 mL of CH_2Cl_2. Preparative TLC on silica gel with benzene–ethyl acetate (90/10), followed by a recrystallization from hexane, affords 2.52 mmol of **8d** as red crystals, mp 161 °C (yield 63%) **8d** is also obtained when 2 equiv of the anion are used: IR ($CHCl_3$) 1720 cm^{-1} ($\nu_{C=O}$); ^1H NMR ($CDCl_3$) δ 2.77 (4, s, 2 CH_2CON), 3.85 (3, s, 6-OCH_3), 4.43 (4, s, 2- and 3-CH_2), 6.80 (1, dd, J_o = 10 Hz, J_m = 3 Hz, 5-H), 7.03 (1, d, J_m = 3 Hz, 7-H), 7.20 (1, d, J_o = 10 Hz, 4-H); ^{13}C NMR ($CDCl_3$) 21.37 (CH_2Br), 28.35 (CH_2CO), 30.69 (CH_2N), 56.01 (OCH_3), 111.31 (C-7), 117.06 (C-5), 121.59 (C-4), 128.20 (C-3a), 132.63 (C-7a), 135.10 (C-2), 155.72 (C-3), 161.89

(C-6), 177.10 (OCN), 195.10 (C=O); mass spectrum, *m/e* (relative intensity) 365 (3), 363 (3), 285 (21), 284 (100), 266 (3), 264 (3), 202 (36), 201 (10), 186 (10). Anal. Calcd for M^+: *m/e* 365.0085 and 363.0106. Found: *m/e* 365.0082 and 363.0081. Anal. Calcd for $C_{16}H_{14}NO_4Br$: C, 52.77; H, 3.87. Found: C, 53.19; H, 4.11. The ^1H and ^{13}C absorptions for the CH_2Br group of 4.43 and 21.37 ppm, compared to 4.50 and 21.54 ppm for the indenone **8a**, indicate that also in this case the CH_2Br must be located on C-3.

3-(2,2-Dicarbethoxyethyl)-6-methoxy-2-methyl-1-indenone (10a). A solution of 4 mmol of diethyl sodiomalonate in 10 mL of dry glyme is prepared from equivalent amounts of NaH and diethyl malonate. To this solution is added 4 mmol of indenone **8c** dissolved in 40 mL of dry glyme in one portion. The mixture is heated for 5 min at 40 °C. After filtration, the reaction mixture is concentrated, and the residue is purified by preparative TLC on silica gel with benzene–ethyl acetate (90/10). Recrystallization from hexane affords 3.86 mmol of indenone **10a** as red crystals: mp 71 °C; yield 96%; IR ($CHCl_3$) 1730, 1710 cm^{-1} ($\nu_{C=O}$); NMR ($CDCl_3$) δ 1.24 (6, t, 2 $OCHCH_3$), 1.81 (3, s, 2-CH_3), 3.13 (2, d, J = 7 Hz, 3-CH_2-CH), 3.69 (1, t, J = 7 Hz, CH_2CH), 3.83 (3, s, 6-OCH_3), 4.22 (4, q, 2 OCH_2CH_3), 6.74 (1, dd, J_o = 8 Hz, J_m = 2 Hz, 5-H), 6.96 (1, d, J_o = 8 Hz, 4-H), 7.01 (1, d, J_m = 2 Hz, 7-H); mass spectrum, *m/e* (relative intensity) 346 (35), 301 (5), 272 (4), 254 (4), 227 (6), 187 (55), 186 (100). Anal. Calcd for M^+: *m/e* 346.1416. Found: *m/e* 346.1410.

2,3-Bis(2-benzyl-2,2-dicarbethoxyethyl)-6-methoxy-1-indenone (10b). Eight millimoles of diethyl benzylmalonate is stirred with 8 mmol of NaH in 10 mL of dry glyme until all the NaH has disappeared. A 4-mmol sample of indenone 1 dissolved in 50 mL of dry glyme is added in one portion. The mixture is stirred for 3 h at room temperature and then filtered, and the filtrate is evaporated. The residue is purified by a chromatography on silica gel with benzene–ethyl acetate (90/10), affording 2.7 mmol of **10b** as a red oil which could not be crystallized: yield 67%; IR ($CHCl_3$) 1760 and 1730 cm^{-1} ($\nu_{C=O}$); NMR δ 0.98–1.36 (12, m, 4 OCH_2CH_3), 3.12 (2, s, 3-CH_2), 3.22 (2, s, 2-CH_2), 3.48 and 3.50 (2 s, 2 H each, 2 CH_2Ph), 4.14–4.56 (8, m, 4 OCH_2CH_3), 7.16 (1, dd, J_o = 8 Hz, J_m = 2 Hz, 5-H), 7.44 (1, d, J_m = 2 Hz, 7-H), 7.56 (1, d, J_o = 8 Hz, 4-H), 7.56–7.72 (10, m, 2 Ph); mass spectrum, *m/e* (relative intensity) 684 (17), 593 (15), 91 (100). Anal. Calcd for M^+: *m/e* 684.2934. Found: *m/e* 684.2929.

2-(2,2-Dicarbethoxyethyl)-4-(dicarbethoxymethylene)-7-methoxy-1-tetralone (11). A solution of 12 mmol of diethyl sodiomalonate in 10 mL of dry glyme is prepared by reacting equivalent amounts of sodium hydride and diethyl malonate for 1 h. To this mixture is added 4 mmol of indenone 1 dissolved in 50 mL of dry glyme in one portion, and the mixture is stirred for an additional hour at room temperature, after which it is filtrated. The filtrate is concentrated in vacuo, and the residue is purified by a preparative TLC on silica gel with benzene–ethyl acetate (85/15), yielding 3.55 mmol of **11** as a slightly yellow oil: yield 89%; IR ($CHCl_3$) 1730 cm^{-1} ($\nu_{C=O}$); ^1H NMR ($CDCl_3$) δ 1.12–1.41 (12, m, 4 OCH_2CH_3), 1.90–3.02 (4, m, 2 CH-CH_2), 3.42–3.80 (2, m, 2 CH-CH_2), 3.86 (3, s, 7-OCH_3), 4.09–4.22 (8, m, 4 OCH_2CH_3), 7.05 (1, dd, J_o = 9 Hz, J_m = 3 Hz, 6-H), 7.42 (1, d, J_o = 9 Hz, 5-H), 7.52 (1, d, J_m = 3 Hz, 8-H); ^{13}C NMR ($CDCl_3$) 13.5 and 13.7 (4 OCH_2CH_3), 29.3 (2-CH_2-CH), 35.5 (C-3), 45.7 (C-2), 49.5 (-CH), 55.4 (OCH_3), 61.3 and 61.5 (4 OCH_2CH_3), 110.4 (C-8), 120.7 (C-6), 124.8 (C-5), 128.9 (4 =C), 131.1 (C-4a), 133.6 (C-8a), 149.2 (C-4), 161.8 (C-7), 164.8 and 166.9 (2 =$C(COOEt)_2$), 169.1 and 169.3 (2 $CH(COOEt)_2$), 197.8 (C-1); mass spectrum, *m/e* (relative intensity) 504 (4), 459 (35), 458 (100), 413 (16), 412 (42), 385 (5), 367 (10), 366 (20), 298 (33). Anal. Calcd for M^+: *m/e* 504.1995. Found: *m/e* 504.1999.

Acknowledgment. The authors are indebted to the Instituut tot aanmoediging van Wetenschappelijk Onderzoek in Nijverheid en Landbouw for a predoctoral fellowship (to H. L.) and to the FKFO for financial support. They are also grateful to Dr. S. Toppet and P. G. Verschave for NMR analysis and synthetic work.

Registry No. 1, 55288-51-2; 2, 73636-05-2; 3a, 73636-06-3; 3b, 73651-38-4; 3c, 73636-07-4; 3c acetate, 73636-08-5; 3d, 73636-09-6; 3d acetate, 73636-10-9; 3e, 73636-11-0; 3e acetate, 73636-12-1; 3f, 73636-13-2; 3f acetate, 73636-14-3; 3g, 73651-39-5; 3j, 73636-15-4; 3j acetate, 73636-16-5; 5a, 73636-17-6; 5b, 73636-18-7; 6, 73636-19-8; 8a, 73636-20-1; 8c, 55288-50-1; 8d, 73636-21-2; 10a, 73636-22-3; 10b, 73636-23-4; 11, 73636-24-5; diethyl malonate, 105-53-3; succinimide, 123-56-8; diethyl benzylmalonate, 607-81-8.

Cycloaddition Reactions of Indenes. 1. Adducts of 1*H*-Indene-3-carboxylic Acid with Ethylenic Dienophiles

Wayland E. Noland,* Lawrence L. Landucci,[1a] and Venkataraman Kameswaran[1b]

School of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

Received February 26, 1980

1*H*-Indene-3-carboxylic acid (**1b**) and its methyl ester (**1c**) react when heated via intermediate 2*H*-indenes (isoindenes) with the more reactive ethylenic dienophiles, giving the corresponding 1:1 Diels–Alder adducts as 1,2,3,4-tetrahydro-1,4-methanonaphthalene-1-carboxylic acid 2,3-derivatives **3**. Thus, 1:1 adducts were obtained with **1b** in refluxing xylene with maleic anhydride (**3b**, 71%) and *N*-phenylmaleimide (**3g**, 46%) and in refluxing 1,2-dichlorobenzene (but not in xylene) with dimethyl fumarate (**5c**, 19%). The less reactive **1c** gave a 1:1 adduct (**3c**, 43%) in refluxing xylene with maleic anhydride but not with *N*-phenylmaleimide. That the reaction is quite sensitive to steric hindrance is shown by the facts that **1b** failed to give 1:1 adducts in refluxing xylene with citraconic (methylmaleic) anhydride, dichloromaleic anhydride, β-nitrostyrene, tetracyanoethylene, and diethyldiazenedicarboxylate, neat at 130 °C with phenylmaleic anhydride, or in refluxing 1,2-dichlorobenzene with cinnamic acid. The transformations which were carried out include hydrolysis of adduct **3b** to the 2-endo,3-endo triacid **4b** (64%), Fischer esterification to the trimethyl ester **4d** (69% from **3b**, 66% from **4b**), thermal dehydration of **4b** back to **3b**, and methanolysis of **3b** to a monomethyl 3-ester (**4e**, 83%) which underwent simple hydrolysis in 5% NaOH to **4b** (22%) but epimerized during hydrolysis in methanolic 5% KOH to the 2-endo,3-exo triacid **5a** (83%; similarly from **4d**, 60%), which at 300 °C was reepimerized and dehydrated to **3b** (22%). Hydrolysis of the 2,3-diester adduct **5c** with both 5% NaOH (68%) and methanolic 5% KOH (60%) also gave **5a**, showing that **5c** has the same stereochemistry as **5a**. With diazomethane, **5a** gave its trimethyl ester (**5b**, 59%). Hydrolysis of adduct **3c** with 5% NaOH gave **4b** (68%), while neutral hydrolysis gave the 1-methyl ester **4c** (78% as a hydrate), which at 150–160 °C was reconverted to **3c** (99%). Epimerization also occurred during the acidic hydrolysis of adduct **3g**, giving **5a** (11%). With diazomethane, **3g** gave the 1-methyl ester **3h** (72%), which was not obtained directly by reaction of **1c** with *N*-phenylmaleimide.

The thermal addition (at 250 °C in benzene) of 1*H*-indene (**1a**) to maleic anhydride to give a 1:1 adduct (**3a**, 30%) was first reported by Alder, Pascher, and Vagt,[2] who postulated a mechanism involving prior isomerization to

0022-3263/80/1945-3456$01.00/0