internal standard method. All melting points and boiling points are uncorrected.

All reagents were distilled or recrystallized before use. Ethyl crotonate, ethyl β,β-dimethylacrylate, diethyl maleate, diethyl fumarate, and ethyl cinnamate were prepared by esterification of the corresponding acids. β,β-Dimethylacrylic acid was prepared by the procedure reported by Smith, *et al.*[12] 2-Propanol was dried over calcium oxide and acetone was distilled in the presence of magnesium. Mercury was purified with dilute nitric acid.

General Procedure for Radiation-Induced Reaction.—The general procedure was carried out by the method previously reported.[1] For glpc analyses, a 15% FFAP (Free Fatty Acid Polyester) column coated on Diasolid M (Nihon Chromato Work, Ltd.) and a 15% Apieson Grease L column coated on Diasolid L were used at 150–240° with 4-*tert*-butyltoluene and diethyl phthalate as the internal standard.

General Procedure for Electrochemical Reaction.—The electrochemical cell used was a cylindrical vessel, 3 cm in diameter and 15 cm in height, with no partition between the cathode and the anode chamber. The reaction vessel was cooled with running water throughout the electrolysis. The mercury pool (55 g) at the bottom of the cell was used as the cathode. The anode was a platinum plate (1 × 1 cm^2), which was held 1 cm apart from the mercury electrode.

A typical procedure is as follows: a mixture of α,β-unsaturated ester (1 g), acetone (20 ml), 20% sulfuric acid (0.8–3.3 ml), and water (0–5 ml) was electrolyzed for 1 hr with a terminal voltage of 75–95 V at a current of 0.35–1.6 A, and then the resultant mixture was neutralized with a 5% NaOH solution and extracted with ether. The ether solution was analyzed by glpc.

Analysis of Products.—A product was separated by a distillation and a preparative glpc (silicone gum rubber SE-30 or Apieson Grease L), and identified from ir, nmr and mass spectral data. Physical properties are summarized in Table III.

TABLE III

PROPERTIES OF γ-BUTYROLACTONES

Compd	Bp, °C (mm)	n_D (°C)	Found, % C	Found, % H	Calcd, % C	Calcd, % H
5a	110.5–111.5 (45)[a]	1.4352 (15)[b]	62.95	8.79	63.13	8.83
5b	97 (15)[c]	1.4373 (20)[d]	65.32	9.48	65.59	9.44
5c	100–103 (17) mp 100–101.5[e]		67.30	9.85	67.57	9.93
5d	138–140 (8)	1.4445 (25)	58.26	7.71	58.05	7.58
f	mp 174–175[g]		53.05	6.35	53.16	6.37

[a] Lit. bp 201–206° (760 mm): R. T. Arnold, J. S. Buckley, Jr., and J. Richter, *J. Amer. Chem. Soc.*, **69**, 2322 (1947). Lit. bp 89–91° (17 mm): R. L. Frank, R. Armstrong, J. Kwiatek, and H. A. Price, *ibid.*, **70**, 1379 (1948). [b] Lit. n_D 1.4352 (20°): *ibid.*, **70**, 1379 (1948). [c] Lit. bp 216–217° (744 mm): J. W. Huffman and J. W. Bethea, *J. Org. Chem.*, **30**, 2956 (1965). [d] Lit. n_D 1.4402 (17°): M. Pfau, R. Dulou, and M. Vilkas, *C. R. Acad. Sci.*, **251**, 2188 (1960). [e] Lit. mp 99–100°: A. W. Burgstahler and D. E. Wetmore, *J. Org. Chem.*, **26**, 3516 (1961). [f] 2,2-Dimethylparaconic acid. [g] Lit. mp 176°: G. O. Schenck, G. Koltzenburg, and H. Grossmann, *Angew. Chem.*, **69**, 177 (1957). Lit. mp 174°: J. F. Laporte and R. Rambaud, *C. R Acad. Sci., Ser. C*, **262**, 1095 (1966).

Registry No.—**1a**, 140-88-5; **1b**, 623-70-1; **1c**, 638-10-8; **1d**, 141-05-9; **1e**, 623-91-6; **1f**, 4192-77-2; **5a**, 3123-97-5; **5b**, 2981-96-6; **5c**, 16466-24-3; **5d**, 34566-25-1; 2-propanol, 67-63-0; 2,2-dimethylparaconic acid, 79-91-4.

(12) L. I. Smith, W. W. Prichard, and L. J. Spillance, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 302.

The Synthesis of 2,2,5-Trimethyl-6-hydroxy-2*H*-naphtho[1,2-*b*]pyran and 2-(γ,γ-Dimethylallyl)-3-methylnaphthoquinone. A New Route to Naphthopyrans and the Vitamin K_1 Series

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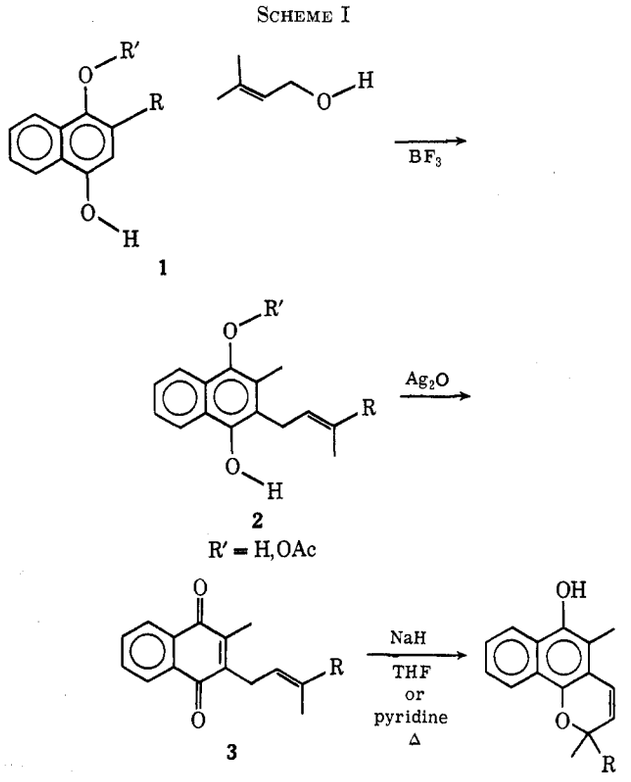
Received May 10, 1971

In connection with an investigation of possible intermediates in oxidative phosphorylation, a moderately large quantity of the naphthopyranol **11** and its acetate ester **8** and methyl ether **10** derivatives were desired. A literature search divulged no specific preparations of these compounds but did suggest several possible general approaches. Alkylation of menadiol or of menadiol-1-acetate (**1**) by allylic alcohols, catalyzed by boron trifluoride,[1] affords intermediates **2** which can be oxidized to quinones **3** and then cyclized to the desired naphthopyranol system by sodium hydride–THF[2] or pyridine[3] (Scheme I). These alkylations suffer, however, from the necessity of using large excesses of **1** to achieve good yields. Yields in the alkylation step are typically 20–40%[4] and conversions range from minute to about 20%. Although the oxidation step is quite efficient, yields in the subsequent cyclization are not

SCHEME I



(1) R. Hirschmann, R. Miller, and N. L. Wendler, *J. Amer. Chem. Soc.*, **76**, 4592 (1954).

(2) A. Wagner, D. Wittreich, B. Arison, N. Trenner, and K. Folkers, *ibid.*, **85**, 1178 (1963).

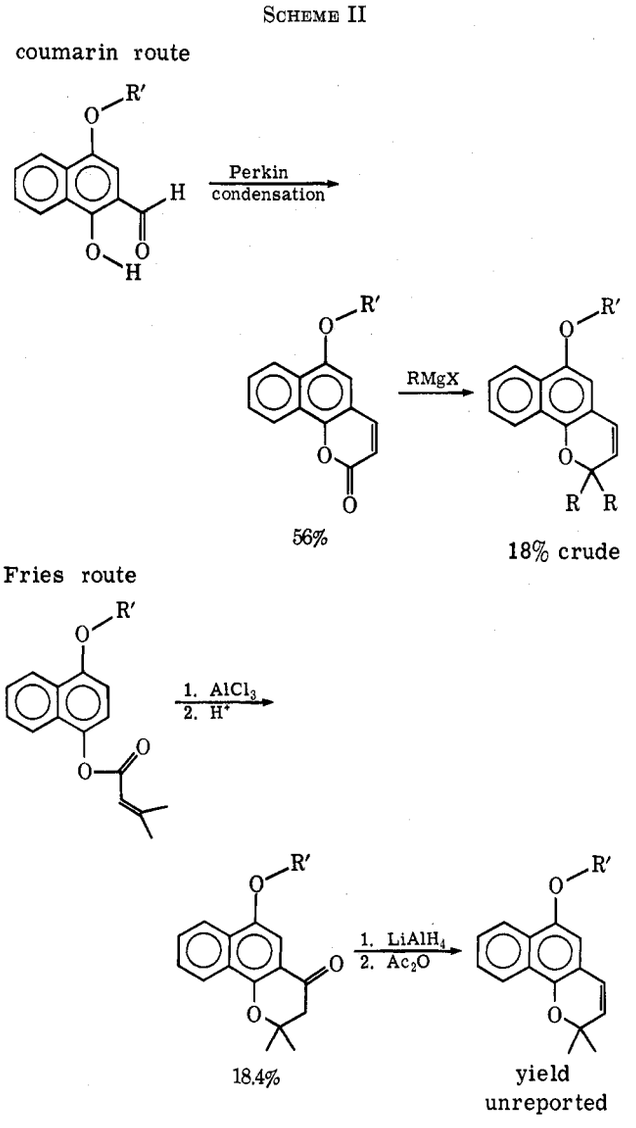
(3) D. McHale and J. Green, *Chem. Ind. (London)*, 1867 (1962).

(4) (a) C. C. Lee, F. C. G. Hoskin, L. W. Trevoy, L. B. Jaques, and J. W. Spinks, *Can. J. Chem.*, **31**, 769 (1953); (b) O. Isler and K. Doebel, *Helv. Chim. Acta*, **27**, 225 (1954).

outstanding (45% is the maximum isolated yield reported). In addition, column chromatography is generally required in the first and last steps, and finally, the resultant pyranol has not been isolated as such but is trapped as an acetate or phosphate ester. Because of these considerations and also because initial results using this approach were disappointing, a more efficient synthetic route to the pyranol **11** and its derivatives was sought.

Two other potential approaches are embodied in syntheses of lapachenole (Schme II).[5] The coumarin

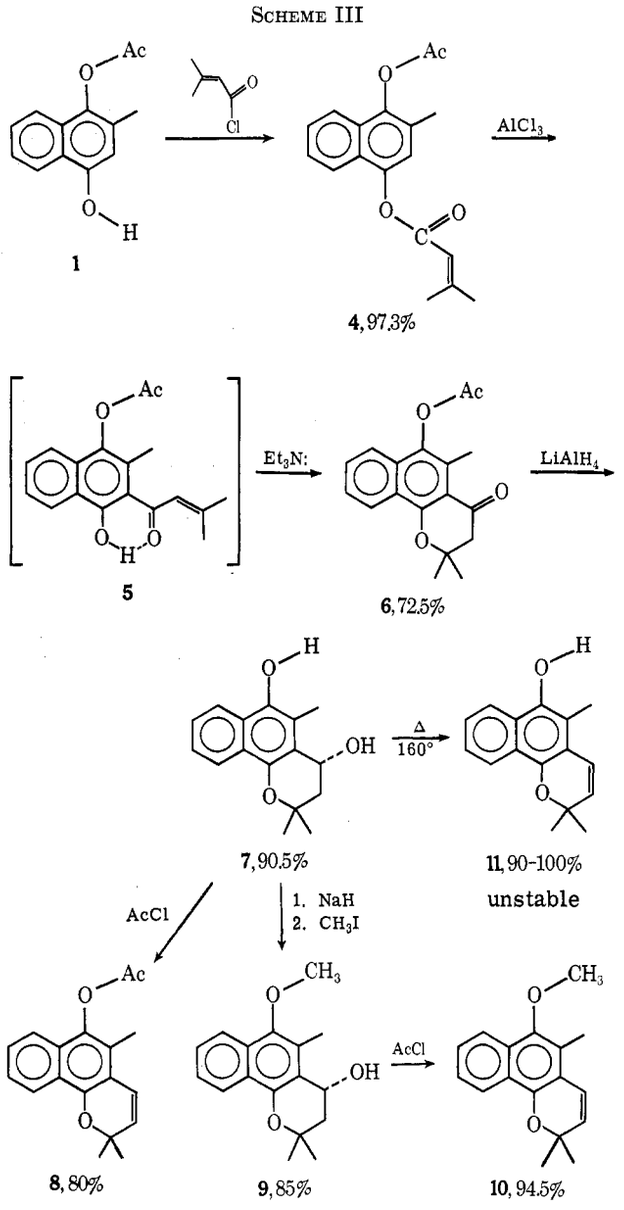
SCHEME II



route lacks appeal because of nonregiospecificity in the Grignard step. The Fries route has no obvious flaws, but the reported yields are poor. Nevertheless, this route appeared to have promise and was investigated. The analogous series of reactions illustrated in Scheme III can now be recommended as affording the desired naphthopyranyl compounds in good yield (51–64%). Five steps (six for the ether **9**), instead of the three used in the conventional procedure, are required. However, the yields in each step are high with the new route, at least in the present instances, and one of the steps requires no purification procedure. The other steps in-

(5) R. Livingstone and R. B. Watson, *J. Chem. Soc.*, 3701 (1956).

SCHEME III



volve purification by recrystallization. The new method thus may have some distinct advantages and it is hoped that it will prove equally applicable to the syntheses of higher isoprenologs of the 2*H*-naphtho[1,2-*b*]pyran system.

Reduction of the readily isolated Fries product **5** by lithium aluminum hydride gives 2-(γ,γ-dimethylallyl)-3-methylnaphthoquinone[6] in 36% yield, thus providing another potential route of entry into the vitamin K_1 series. Use of lithium aluminum deuteride gives specifically methylene dideuterated quinone. No attempts were made to optimize the yield, so it is quite possible that the 36% yield can be considerably improved. However, at this point the method appears somewhat inferior to the conventional Friedel–Crafts alkylation approach.[4]

Experimental Section

Melting points were determined without correction, using a Mel-Temp apparatus. Infrared spectral measurements utilized

(6) R. Mamont, R. Cohen, R. Azerad, and M. Vilkas, *Bull. Soc. Chim. Fr.*, 2513 (1965).

a Beckman IR-5, nmr spectra a Varian A-60, spectrometer unless otherwise noted. A consolidated Electrodynamics 21–102 spectrometer was used for obtaining mass spectra.

4-Acetoxy-3-methyl-1-naphthyl-β,β-dimethyl Acrylate (4).—A stirring solution of 26.05 g (0.12 mol) of menadiol-1-acetate[7] and 17.2 g (0.145 mol) of β,β-dimethylacryloyl chloride[8] in 200 ml of chloroform was refluxed for 2.5 hr under nitrogen and cooled to 25°, followed by addition of 200 ml of water. The customary work-up afforded a viscous oil. Crystallization from hexane gave 35.0 g (97.3%) of **4** as white crystals: mp 101–103°; ir ($CHCl_3$) ν 1755, 1735 cm^{-1}; nmr ($CDCl_3$) τ 8.02 (d, 3 H, J = 1.2 Hz), 7.77 (d, 3 H, J = 1.0 Hz), 7.72 (s, 3 H), 7.61 (s, 3 H), 3.93 (m, 1 H), 2.86 (broad s, 1 H), and 2.34 (m, 4 H). Two recrystallizations from ether increased the melting point to 103–104.5°.

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08. Found: C, 72.59; H, 6.26.

3-(3-Methyl-2-butenoyl)-4-hydroxy-2-methyl-1-naphthyl Acetate (5).—To a mechanically stirred suspension of aluminum chloride (14.3 g, 0.107 mol, 4 equiv) in 100 ml of methylene chloride was added, over a 10-min period, a solution of 8.0 g (0.0268 mol) of **4** in 50 ml of methylene chloride. The reaction was monitored by ir and continued until, after about 2.0 hr, the 1735-cm^{-1} absorption was replaced by the 1635-cm^{-1} absorption of the enol. Only a small amount of the cyclized ketone **6** was detectable by a peak at 1685 cm^{-1}. The reaction mixture was then poured onto a mixture of 600 g of ice and 100 ml of hydrochloric acid, stirred for 15 min, and separated. The aqueous layer was extracted four times with 100-ml portions of methylene chloride and the combined organic phases were worked up in the usual way. There was obtained 8.28 g of crude **5** as an orange gum: ir ($CHCl_3$) ν 1755, 1635 cm^{-1}; nmr ($CDCl_3$) τ 8.04 (d, 3 H, J = 1.25 Hz), 7.83 (d, 3 H, J = 1.0 Hz), 7.65 (s, 3 H), 7.58 (s, 3 H), 4.45 (m, 1 H), 2.5 (m, 3 H), 1.53 (m, 1 H), and −3.08 (s, 1 H). Purification of this intermediate was not attempted in view of its facile cyclization.

6-Acetoxy-3,4-dihydro-2,2,5-trimethyl-2*H*-naphtho[1,2-*b*]pyran-4-one (6).—A solution of 35.0 g (0.117 mol) of crude **5** in 100 ml of benzene containing 19.7 ml (0.141 mol) of triethylamine was stirred for 12 hr at room temperature. Evaporation of the solvent and recrystallization from hexane gave 25.3 g (72.5%, based on **4**) of **6**. Two further recrystallizations from ether afforded 16.2 g of **6** as yellow crystals: mp 142–143°; ir (CS_2, IR-7) ν 1765, 1683 cm^{-1}; nmr ($CDCl_3$) τ 8.49 (s, 6 H), 7.59 (s, 3 H), 7.45 (s, 3 H), 7.24 (s, 2 H), 2.54 (m, 3 H) and 1.73 (m, 1 H); mass spectrum m/e 298 (M), 255.

Anal. Calcd for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08. Found: C, 72.43; H, 5.87.

3,4-Dihydro-4,6-dihydroxy-2,2,5-trimethyl-2*H*-naphtho[1,2-*b*]pyran (7).—A solution of 8.0 g (0.0268 mol) of **6** in 400 ml of ether was added gradually to a suspension of 4.8 g (0.126 mol) of lithium aluminum hydride in 200 ml of ether. After a 6-hr period the excess hydride was destroyed by slow addition of 10 ml of 95% ethanol and then by addition of water until bubbling ceased. The ethereal solution was decanted from the solids, the latter were leached with ether, and the combined ether phases were washed and evaporated. The solid residue was stirred with hexane, washed with hexane, and air dried, yielding 5.88 g (90.5%) of **7** as tan crystals, mp 153–155° dec. Two recrystallizations from acetone–carbon tetrachloride gave white crystals of **7**: mp 138–140°; ir (KBr, IR-7) ν 3410 cm^{-1} (s); nmr (10% DMSO-d_6–$CDCl_3$) τ 8.57 (s, 3 H), 8.53 (s, 3 H), 7.89 (d, 2 H), 7.54 (s, 3 H), 6.06 (d, 1 H), 5.08 (m, 1 H), 2.63 (m, 2 H), and 1.92 (m, 2 H); mass spectrum m/e 240 ($M - H_2O$).

Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.39; H, 7.02. Found: C, 74.61; H, 7.11.

2,2,5-Trimethyl-2*H*-naphtho[1,2-*b*]pyranyl-6 Acetate (8).—A solution of 10.05 g (0.039 mol) of diol **7** in 50 ml of acetyl chloride was stirred for 25 min at room temperature and then concentrated to a dark solid. Benzene (75 ml) was added and the solution was refluxed for 12 hr, cooled, treated with Darco G-60, filtered through Super-Cel, and finally evaporated under reduced pressure. Crystallization from hexane afforded 9.15 g (80% yield) of **8** as tan crystals, mp 115–118°. Two recrystallizations from ether–hexane gave **8** as white crystals: mp 121.5–122.5°; ir ($CHCl_3$) ν 1750 cm^{-1}; nmr ($CDCl_3$) τ 8.54 (s, 6 H), 7.80 (s, 3 H), 7.63 (s, 3 H), 4.4, 3.48 (q, 2 H, J = 10.0 Hz), 2.54 (m, 3 H), and 1.84 (m, 1 H); mass spectrum m/e 282 (M).

Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.84; H, 6.55.

3,4-Dihydro-6-methoxy-2,2,5-trimethyl-2*H*-naphtho[1,2-*b*]pyran-4-ol (9).—To a cooled (5°) solution of 1.06 g (4.1 mmol) of **7** in 35 ml of DMF under nitrogen was added 0.21 g (4.6 mmol) of sodium hydride dispersion. The mixture was stirred for 10 min after the gas evolution subsided, followed by addition of 1.98 g (0.014 mol) of methyl iodide. After stirring for 0.5 hr the reaction mixture was poured into 200 ml of water and 100 ml of chloroform and worked up in the usual way. The product crystallized from hexane (0.912 g, 85% yield) as tan crystals: mp 127–129°; nmr (10% DMSO-d_6–$CDCl_3$) τ 8.57 (s, 3 H), 8.53 (s, 3 H), 7.92 (d, 2 H, J = 4.5 Hz), 7.52 (s, 3 H), 6.20 (s, 3 H), 5.1 (m, 1 H), 2.58 (m, 2 H), and 1.96 (m, 4 H); mass spectrum m/e 272 (M), 254, 239.

6-Methoxy-2,2,5-trimethyl-2*H*-naphtho[1,2-*b*]pyran (10).—A solution of 4.55 g (0.0167 mol) of **9** in 40 ml of acetyl chloride was stirred for 0.5 hr at room temperature. Concentration of the dark solution gave a solid to which was added 150 ml of benzene and the solution was refluxed for 12 hr. After cooling to 25°, the solution was diluted with 200 ml of water and worked up as usual. The resultant dark oil was chromatographed on 100 g of silica gel. The hexane eluates were combined and evaporated, affording 4.0 g (94.5%) of **10**, a viscous, yellow oil which crystallized upon standing: nmr ($CDCl_3$) τ 8.55 (s, 6 H), 7.63 (s, 3 H), 6.2 (s, 3 H), 4.48, 3.43 (q, 2 H, J = 10.0 Hz), 2.58 (m, 2 H), and 1.92 (m, 2 H); mass spectrum m/e 254 (M). An analytical sample was prepared by repeated chromatography on basic alumina (hexane).

Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.36; H, 7.07.

2,2,5-Trimethyl-2*H*-naphtho[1,2-*b*]pyran-6-ol (11).—A sample of 0.258 g (1.0 mmol) of the diol **7** was heated for 15 min at 160° under nitrogen and evaporated for 1 hr *in vacuo* at 50°, affording alcohol **11**: ir ($CHCl_3$) ν 3600, 3400 cm^{-1}; nmr (10% DMSO-d_6–$CDCl_3$) τ 8.62 (s, 6 H), 7.7 (s, 3 H), 4.46, 3.49 (q, 2 H, J = 10.0 Hz), 2.75 (m, 2 H), 2.52 (broad s, 1 H), and 1.99 (m, 2 H). Not appreciable amounts of impurities were noted in the nmr spectrum. Further attempts at purification resulted in oxidative decomposition of the pyranol **11**.

2-(γ,γ-Dimethylallyl)-3-methyl-1,4-naphthoquinone (3).—A solution of 8.0 g (26.8 mmol) of enol **5** dissolved in 100 ml of anhydrous ether was added slowly to 8.0 g (0.211 mol) of lithium aluminum hydride suspended in 150 ml of ether. The mixture was stirred overnight at room temperature, the excess hydride was decomposed with a minimum amount of water, and the ether supernatant was worked up as described earlier. The 10, 20, and 40% benzene–hexane eluates of an alumina chromatography were combined after ir examination, giving 2.32 g (36.1%) of **3**: ir ($CHCl_3$) ν 1660 cm^{-1} (vs); nmr ($CDCl_3$) τ 8.31 (d, 3 H, J = 1.25 Hz), 8.22 (d, 3 H, J = 1.0 Hz), 7.83 (s, 3 H), 6.35 (broad d, 2 H, J = 7.0 Hz), 4.97 (broad t, 1 H, J = 7.0 Hz), and 2.17 (multiplet, 4 H).

Registry No.—**3**, 957-78-8; **4**, 34638-45-4; **5**, 34638-46-5; **6**, 34638-47-6; **7**, 34638-48-7; **8**, 16511-15-2; **9**, 34638-50-1; **10**, 34638-51-2; **11**, 34638-52-3.

(7) B. R. Baker, T. H. Davies, L. McElroy, and G. H. Carlson, *J. Amer. Chem. Soc.*, **64**, 1096 (1942).

(8) W. Bridge, R. G. Heys, and A. Robertson, *J. Chem. Soc.*, 283 (1937).

A Convenient Synthesis of Benzocyclobutene

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Received January 31, 1972

In connection with current studies on strained heterocyclic systems, we required a supply of benzocyclobutene (**2**).[2] The preferred pathways to this compound

(1) Based on the Honors theses, Williams College, of S. J. Basta (1972) and P. M. Wege (1971).

(2) For a recent review of benzocyclobutene and its derivatives, see I. L. Klundt, *Chem. Rev.*, **70**, 471 (1970).