for 5 min and poured into ten times its volume of distilled water. The resulting white precipitate was filtered, dried, and recrystallized twice from dry ethanol to yield pure **4** (~30–50% yield). *Anal.* Calcd for $C_{21}H_{15}N_3O_7$ (**4a**): C, 59.86; H, 3.59; N, 9.97. Found: C, 59.78; H, 3.69; N, 9.81. Calcd for $C_{12}H_{11}N_3O_9$ (**4b**): C, 42.24; H, 3.25; N, 12.31. Found: C, 42.20; H, 3.22; N, 12.17.

**Registry No.**—NBS, 128-08-5; **4a**, 30388-22-8; **4a** 2,4-DNP, 30388-23-9; **4b**, 30338-24-0.

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## Pyrolysis of Phenylalkenylidenecyclopropanes[1]

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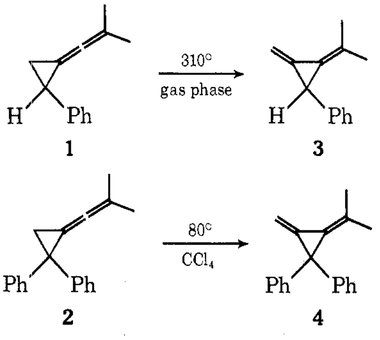
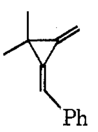
Dimethylenecyclopropanes have been found to be the products of the thermal rearrangement of alkenylidenecyclopropanes in both the parent[3] and methylated[4] systems. Because of the nature of the substitution of these compounds, little or no choice exists in the substitution pattern of the products. To probe this question, we have heated the mono- and diphenylalkenylidenecyclopropanes **1** and **2** and find that the phenyl groups always remain on the cyclopropane ring and do not migrate to the double bonds.[5]



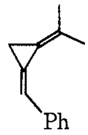
Pyrolysis of **1**[6] in a flow system at 310° under vacuum gives only **3** and starting material in the ratio 2.6:1. Compound **3** was identified by its elemental analysis and nmr spectrum in $CCl_4$: multiplets at $\delta$ 1.82 (3 H, methyl), 1.94 (3 H, methyl), 2.85 (1 H, benzyl cyclopropyl), 5.11 (1 H, vinyl), 5.34 (1 H, vinyl), and 6.9–7.2 (5 H, aryl). The chemical shift of the methyl signals leaves no doubt that it is the double bond and not the three-membered ring that bears the methyl groups. A broad band in the infrared spectrum at 1795 $cm^{-1}$ confirms the methylenecyclopropane structure.[7,8]

Compound **2** is less volatile than **1** and was therefore rearranged to **4** in $CCl_4$ solution at 80°. **2** was made by an adaptation of the method of Hartzler[6] and was identified by its mass spectrum and nmr spectrum in $CCl_4$: singlets at $\delta$ 1.82 (6 H, methyls) and 2.13 (2 H, cyclopropyls) and a multiplet at 7.1–7.5 (10 H, aryl). A band in the infrared spectrum at 2005 $cm^{-1}$ is appropriate for an allene.[9] Compound **4** was similarly identified by its mass spectrum and nmr spectrum in $CCl_4$: broad singlets at $\delta$ 2.09 (6 H, methyls), 5.50 (1 H, vinyl), and 5.64 (1 H, vinyl) and a multiplet at 7.2–7.7 (10 H, aryl). Again, a band in the infrared spectrum at 1795 $cm^{-1}$ is typical of methylene cyclopropanes.[7,8]

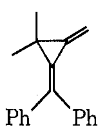
The potential products **5–8** are not formed in significant amounts, as appropriate signals do not appear in the nmr spectra of the crude products. At first glance this may seem strange, but, if the mechanism of these changes involves perpendicular diradicals, as is generally thought,[10,11] it is understandable. The diradicals **9** and **10** should be the most stable ones available, and they must lead to **3** and **4**, and cannot give the others. At higher temperatures many other compounds are formed, and we hope to report on these at a later time.



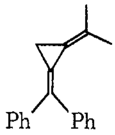
**5**



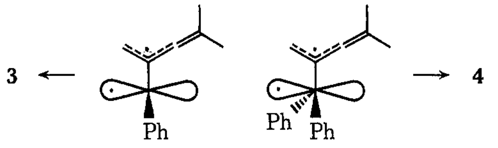
**6**



**7**



**8**



**9** **10**

### Experimental Section

**General.**—Nmr and infrared spectra were recorded on Varian Associates A-60A and Perkin-Elmer 237B instruments, respectively. Mass spectra were measured on an AEI MS-9 mass spectrometer.[12] Gas chromatographic analyses were performed on a Varian Aerograph A-90P instrument using a 5-ft 10% Dow-Corning 550 silicone oil on 60–80 mesh Chromosorb P column operated at 150° with a He flow rate of 100 ml/min.

**Pyrolysis of 1.**—Compound **1**, 1-(2-methylpropenylidene)-2-phenylcyclopropane, was prepared by the method of Hartzler[6] and purified by bulb-to-bulb distillation immediately before use. The pyrolysis apparatus consisted of a 20-cm length of 14-mm quartz tube heated by chromel wire. Temperatures in the tube varied by a maximum of 6° over its length. The temperature reported is the maximum in the tube. In a typical run

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[1] We thank the National Science Foundation for support of this work through Grant GP-12759.

[2] National Science Foundation Predoctoral Fellow, 1967–1971.

[3] R. Bloch, P. LePerchec, and J.-M. Conia, *Angew. Chem.*, **82**, 910 (1970).

[4] D. R. Paulson, J. K. Crandall, and C. A. Bunnell, *J. Org. Chem.*, **35**, 3708 (1970).

[5] The rearrangement of **1** to **3** at 130° in solution has been noted by T. B. Patrick, E. C. Haynie, and W. J. Probst, *Tetrahedron Letters*, 423 (1971), and, in passing, by I. H. Sadler and J. A. G. Stewart, *Chem. Commun.*, 1588 (1970).

[6] H. D. Hartzler, *J. Amer. Chem. Soc.*, **83**, 4990 (1961).

[7] J. T. Gragson, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *ibid.*, **75**, 3344 (1953).

[8] R. F. Bleiholder and H. Shechter, *ibid.*, **86**, 5032 (1964).

[9] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, Wiley, New York, N. Y., 1958.

[10] W. von E. Doering and H. D. Roth, *Tetrahedron*, **26**, 2825 (1970).

[11] J. J. Gajewski, *J. Amer. Chem. Soc.*, **90**, 7178 (1968).

[12] We thank the National Science Foundation for providing the funds for the purchase of this instrument through Grant GP-5200.

80 μl of **1** was placed in a reservoir at the cold end of the tube and a 0.1-mm vacuum was applied through a trap cooled to −78°. Gentle warming was applied to the sample to facilitate distillation into the hot tube. Collection of the major product gave a colorless liquid: ir 3070, 3060, 3015, 2960, 2915, 2895, 2835, 1795, 1745, 1600, 1490, 1360, 855, and 690 cm$^{-1}$.

*Anal.* Calcd for $C_{18}H_{14}$: C, 91.71; H, 8.29. Found: C, 91.53; H, 8.17.

**Synthesis of 2.**—To a slurry of 6.12 g (0.054 mol) of potassium *tert*-butoxide and 18 g (0.1 mol) of 1,1-diphenylethylene in 75 ml of *n*-pentane held at −10° was added dropwise a solution of 5.12 g (0.054 mol) of 3-chloro-3-methyl-1-butyne[13] in 20 ml of *n*-pentane. Following the addition the slurry was allowed to warm to room temperature and 100 ml of water was added. The layers were separated and the organic material was washed with five 150-ml portions of water, dried over anhydrous sodium sulfate, and concentrated at the water pump to give 21 g of a red oil. Chromatography of 2.0 g of the oil on silica gel using hexane as eluent led to the recovery of 1.5 g of 1,1-diphenylethylene and 0.3 g of **2**. A value of 246.140713 was obtained in a precise mass measurement (calcd for $C_{19}H_{18}$: 246.140844).

**Pyrolysis of 2.**—**2** (100 mg) was dissolved in 500 μl of $CCl_4$ and sealed in a medium-walled nmr tube under nitrogen. Heating the sample at 80° for 19 hr caused complete rearrangement to **4**, which was purified by chromatography on a 1 ft × 0.5 in. column of basic alumina: ir 3080, 3060, 3030, 2970, 2930, 2905, 1795, 1600, 1490, 1440, 1365, 1095, 1070, 855, 775, 750, and 685 cm$^{-1}$. A value of 246.140713 was obtained in a precise mass measurement.

**Registry No.**—**1**, 4544-23-4; **2**, 30800-74-9; **3**, 30896-86-7; **4**, 30800-58-9.

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[13] W. J. Bailey and C. R. Pfeifer, *J. Org. Chem.*, **20**, 95 (1955).

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# Mononitration of Methyl Abieta-8,11,13-trien-18-oate

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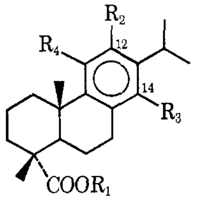
*Received March 29, 1971*

Aromatic substitution reactions on abieta-8,11,13-trien-18-oic acid, dehydroabietic acid (**1a**), and the corresponding methyl ester **1b** have been the subject of a number of investigations. Although monosulfonation at C-12,[1-3] monobromination at C-12,[4] and monoacetylation[2,5] at C-12 and at C-14 (75% C-12) have been reported, attempted mononitration has failed to produce the desired results, yielding instead the 12,14-dinitro derivative **1c**[6] and **1d**.[7] Also an attempt to produce a mononitro derivative *via* nitration of the 12-sulfonic acid and subsequent hydrolysis of the sulfonic acid group failed at the second step.[4] The 14-nitro derivative **1e** has been prepared from methyl 12,14-dinitroabieta-8,11,13-trien-18-oate (**1d**) by selective reduction of the 12-nitro group to the amine **1f** followed by deamination[4,8] and by nitration of the 12-amino compound **1g** followed by deamination.[4,9]



**1**

| | $R_1$ | $R_2$ | $R_3$ | $R_4$ |
|---|---|---|---|---|
| a | H | H | H | H |
| b | $CH_3$ | H | H | H |
| c | H | $NO_2$ | $NO_2$ | H |
| d | $CH_3$ | $NO_2$ | $NO_2$ | H |
| e | $CH_3$ | H | $NO_2$ | H |
| f | $CH_3$ | $NH_2$ | $NO_2$ | H |
| g | $CH_3$ | $NH_2$ | H | H |
| h | $CH_3$ | $NO_2$ | H | H |
| i | $CH_3$ | H | H | $NO_2$ |

The work cited indicates that the 12 position is more reactive than the 14 position. We, therefore, decided to investigate anew the feasibility of direct mononitration of methyl abieta-8,11,13-trien-18-oate (**1b**). We hoped to obtain the 12-nitro derivative **1h**, which we believe would be a useful synthetic intermediate. We were encouraged also by the advent of positionally selective nitration procedures in recent years. Acetic acid, for instance, is the solvent of choice for positionally selective nitrations of fluoranthene[10] and naphthalene[11] (mixed acids), acenaphthene[12] (nitric acid), and octaethylporphyrin[13] (fuming nitric acid). Nitric acid in nitromethane is also positionally selective.[11] Mechanistic considerations have been discussed[11,14] but will not be reviewed here.

We attempted mononitration of **1b** with the above procedures and found, uniformly, that under the usual mild conditions no reaction occurred. By increasing time or temperature complex mixtures were obtained which were relatively free of both starting material and the desired product, as shown by the aromatic region of their nmr spectra. The conclusion reached was that the substrate **1b** was not sufficiently reactive toward these reagents under the usual conditions.

The more reactive but still selective[15,16] nitrating agent acetyl nitrate provided a procedure which yields a mixture of the 12-nitro and 14-nitro derivatives, **1h** and **1e**, respectively. A convenient separation of the mixture by one fractional crystallization in methanol gave a first fraction of almost pure 14-nitro derivative **1e** (20% yield). The 14-nitro derivative **1e** was identical with a sample prepared by the method of Zeiss.[8] This one-step synthesis (20%) compares well in terms of con-

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[1] Numbering systems used in the past have been translated into the presently accepted system.

[2] L. F. Fieser and W. P. Campbell, *J. Amer. Chem. Soc.*, **60**, 2631 (1938).

[3] T. Hasselstrom and J. D. McPherson, *ibid.*, **60**, 2340 (1938).

[4] W. P. Campbell and M. Morgana, *ibid.*, **63**, 1838 (1941).

[5] L. F. Fieser and W. P. Campbell, *ibid.*, **61**, 2528 (1939).

[6] L. F. Fieser and W. P. Campbell, *ibid.*, **60**, 159 (1938).

[7] E. S. Hansen and H. H. Zeiss, *ibid.*, **77**, 1643 (1955).

[8] H. H. Zeiss, U. S. Patent 2,803,645 (1957); *Chem. Abstr.*, **52**, 2921 (1958).

[9] The assignment of one nitro group of the dinitro compound (**1c** and **1d**) at C-12 was unambiguous.[2,4] Locating the second nitro group at C-14 was based on the expectation of normal meta orientation. Hansen and Zeiss[7] have pointed out that this assignment is reasonable but not beyond question.

[10] A. Streitwieser, Jr., and R. C. Fahey, *J. Org. Chem.*, **27**, 2352 (1962).

[11] P. G. E. Alcorn and P. R. Wells, *Aust. J. Chem.*, **18**, 1377 (1965).

[12] A. Davies and K. D. Warren, *J. Chem. Soc. B*, 873 (1969).

[13] R. Bonnett and G. F. Stephenson, *J. Org. Chem.*, **30**, 2791 (1965).

[14] G. A. Olah, S. J. Kuhn, S. H. Flood, and J. C. Evans, *J. Amer. Chem. Soc.*, **84**, 3687 (1962).

[15] G. Powell and F. R. Johnson, "Organic Syntheses," Collect. Vol. II, A. H. Blatt, Ed., Wiley, New York, N. Y., 1955, p 449.

[16] M. L. Scheinbaum, *Chem. Commun.*, 1235 (1969).