Extrusion Reactions in an RF Plasma. Production of Benzocycloalkenes

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Ketones and lactones were reacted in a 13.56 MHz discharge at flow rates of about 1 mmol/min. The reaction products were collected in a cold trap and identified using NMR, mass spectroscopy, and gas chromatography. The ketone reactants and major products were: 2-indanone/benzocyclobutene; 2-tetralone/indane; dihydrocoumarin/benzofuran; 1-indanone/styrene; 1-tetralone/allylbenzene. The effects of power, flow rate, added argon, pumping speed, and glass wool packing on the reaction rate and the yield of benzocyclobutene from 2-indanone were studied. Phthalide produced a complex mixture including benzocyclopropene. 3-Phenylphthalide led to fluorene, and 3,3-diphenylphthalide gave 9-phenylfluorene.

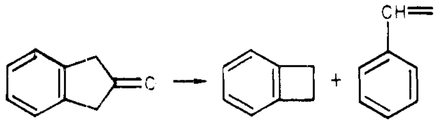
Recent work on reactions in the plasma generated by a radiofrequency discharge is of interest to organic chemists. In these processes a vaporized organic compound is flowed through the discharge region and electron impact events within this region initiate chemical reactions. Substantial quantities (grams) of products result, and some unusual transformations are observed.[1] In particular, a number of rather selective reactions involving extrusion of carbon monoxide or carbon dioxide have been discovered.[2]

This work follows on an initial olfactory detection of benzocyclopropene from the plasmolysis of phthalide. A number of ketones and lactones were then studied as potential precursors to benzocycloalkenes, and the results are summarized in this paper.

Results and Discussion

Decarbonylations. Plasmolyses were performed using a similar apparatus to that described previously,[3] which had dual reactant inlets. The reactant alone or the reactant and argon flowed through the plasma zone. The flow rates of the reactant and argon were independently controlled. Energy was supplied by an inductively coupled 13.6 MHz radiofrequency generator. The products were collected in a cold trap and analyzed by gas chromatography (GC), mass spectroscopy (MS), and nuclear magnetic resonance spectroscopy (NMR).

The reaction of 2-indanone (1) in the radiofrequency discharge gave benzocyclobutene (7) and styrene (8) as the major products. Small amounts of *o*-xylene and ethylbenzene (<1% yield) were also detected. The yield of 7 based on reacted 1 decreased under conditions which gave high conversion. This yield was, however, improved substantially by the addition of argon into the reaction system. At argon flow rates of 1 mmol/min, yields up to 50% were obtained. These results are summarized in Table I. As a representative example, about 2 g of 1 was reacted in a period of 10 min. The products from three such runs were combined and distilled to give approximately 1 g of 7 by distillation. Even though these reactions are not clean, a one-step synthesis for 7 from commercially available 1 is of synthetic interest because most preparative methods for 7 involve several steps or start from commercially unavilable compounds. Flash pyrolysis[4d] of 1 does seem a useful alternative. At 800–850 °C for 1 h with a flow rate of 0.038 mmol/min, 1 was reported to give 0.1–0.16 g of 7 (44–64% yield).[4d] Although decarbonylations are often observed photochemically, 7 has not been isolated from the photolysis of 1.[5] Phenyl- or diphenyl-substituted benzocyclobutene was only isolated in the photolysis of 1-phenyl- or 1,3-diphenyl-2-indanone.[5]



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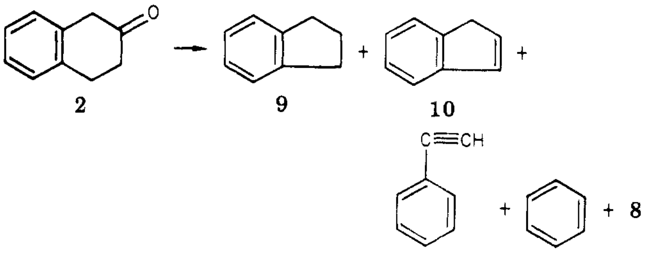
Plasmolysis of 1,2,3,4-tetrahydronaphthalen-2-one (2) gave indan (9) and indene (10) as the major products.



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Phenylacetylene (11), styrene, and benzene were also produced in amounts of 0.1–5%. Higher power and lower flow rate gave a higher yield of 10, and it is suggested that 10 was produced by the secondary plasmolysis of the product 9.[1]

Dihydrocoumarin is a readily available oxygen analogue of 2, and it was of interest to see if a useful method for the production of the benzofurans could be obtained. In the radiofrequency discharge, decarbonylation did take place, giving 2,3-dihydrobenzofuran (12) and benzofuran (13). A large number of other products, 8, 11, ethyl benzene (14), toluene (15), and benzene, were also obtained in a yield less than 2%. Again, the dehydrogenation of 12 in the discharge was confirmed to give 13 as a major product (Table III).

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(1) For a review, see J. R. Hollahan and A. T. Bell, Ed., "Techniques and Applications of Plasma Chemistry", Wiley, New York, 1974; H. Suhr, *Angew. Chem., Int. Ed. Engl.*, 11, 781 (1972).

(2) H. Suhr and R. I. Weiss, *Angew. Chem.*, **82**, 295 (1970); H. Suhr and G. Kruppa, *Justus Liebigs Ann. Chem.*, **744**, 1 (1971); H. Suhr and A. Szabo, *ibid.*, **752**, 37 (1971); A. Szabo and H. Suhr, *ibid.*, **749** (1977).

(3) M. Tezuka and L. L. Miller, *J. Am. Chem. Soc.*, **99**, 5832 (1977); **100**, 4201 (1978).

(4) (a) For a review, see I. L. Klundt, *Chem. Rev.*, **70**, 471 (1970). (b) For recent papers, see W. S. Trahanovsky and P. W. Mullen, *J. Am. Chem. Soc.*, **94**, 5911 (1972); R. J. Spangler and J. Ho Kim, *Synthesis*, 107 (1973); E. Cuthbertson and D. D. MacNicol, *Tetrahedron Lett.*, 1893 (1975); (c) C. R. Flynn and J. Michl, *J. Am. Chem. Soc.*, **95**, 5802 (1973); (d) G. Schaden, *Z. Naturforsch.*, **32**, 805 (1977).

(5) G. Quinkert, K. Opitz, W. W. Eiersdorff, and J. Weinlich, *Tetrahedron Lett.*, 1863 (1963); G. Quinkert, J. Palmowski, H-P. Lorenz, W. W. Diersdorff, and M. Finke, *Angew. Chem., Int. Ed. Engl.*, **10**, 198 (1971); A. Padwa, D. Dehm, T. Oine, and G. A. Lee, *J. Am. Chem. Soc.*, **97**, 1837 (1975).

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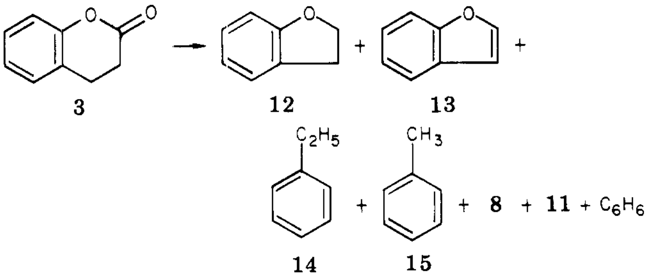
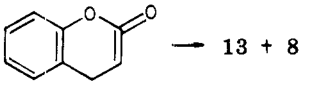


$$\mathbf{12} \rightarrow \mathbf{13} + \mathbf{8} + \mathbf{11} + \mathbf{14} + \mathbf{15} + C_6H_6$$

Plasmolysis of coumarin (**4**) gave a similar decarbonylation reaction. Products **13** (7–9% yield) and **8** (~2%) were obtained at 30–40% conversion at 20–40 W with a flow rate of 0.3–2.0 mmol/min.



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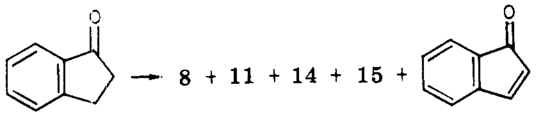
1-Indanone (**5**) and 1,2,3,4-tetrahydronaphthalen-1-one (**6**) are isomers of **1** and **2** and could produce **7** and **9**. This was not observed. Instead, the reaction of **5** in the discharge resulted in the formation of products such as **8**, **11**, **14**, **15**, 1-indenone (**16**), and benzene. Only a trace of **7** was detected by GC–mass spectroscopy. The results under various conditions are indicated in Table IV. In this plasmolysis, a large effect of the addition of argon was not observed. Plasmolysis of **6** produced small amounts of **9** and **10**, but the major product was allylbenzene (**17**) (Table II).



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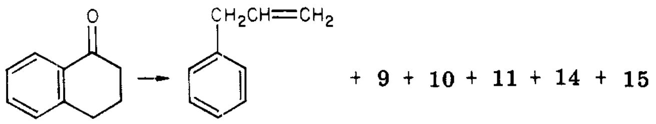

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The effects of power (*P*) and flow rate (*r*) on conversion and yield are seen in the tables. Consider first the reaction of **1** (Table I) without added argon. As expected, higher *P* gave higher conversion, and as shown in runs 1–4, where the flow rate was relatively constant, conversion was approximately proportional to *P*. It is also clear from these runs that the yield of benzocyclobutene (**7**) based on reacted **1** dropped as conversion increased. This is attributed to destruction of initially formed **7**. **1** does not have an especially high reaction rate, and decomposition of initially formed products will take place under most conditions. It may, indeed, be true that styrene comes from **7**. Note that the high styrene yields correspond to low yields of **7**. The dependence of conversion on flow rate is not so clear. The scatter apparent from 40 W runs shown in Table I contrasts with observations made earlier for a number of other reactions where conversion was proportional to r^{-1}. The difference appears to be due in part to the pumping system used here (see below). As evidence for this conclusion, see runs 13, 14, and 15 made using a higher capacity pumping system. It can be seen that the conversion responds more regularly to r^{-1}. The yield of **7** based on reacted **1** also goes up more regularly with *r* in these runs.

The effects of argon on the results are of particular interest since we have previously not seen such results. To be specific the experiment follows: **1** is being pumped through at about 2 mmol min^{-1} and the plasma zone is about 5 cm long. Argon is then admitted and the following observations are made: (1) The plasma zone decreases in length to about 3 cm. (2) The luminosity of this region is intensified. (3) The flow rate of **1** decreases to 1.2 mmol/min. These observations contrast with out previous experience where added argon had a minimal effect on the appearance of the plasma and the flow rate of organics. The difference in these experiments arises from a limited pumping capacity in the experiments with **1**. Thus, at the lower pumping speeds employed, the added argon increases the total pressure dramatically. This leads to a short, hot zone in which the energetics are partially determined by the argon. We turn now to comparisons of conversions and yield with and without argon. Compare runs 5 and 6 and compare runs 8 and 9. In each case the flow rate of **1** and the power are the same. In the runs with added argon, the conversion is lower and the yield based on reacted **1** is substantially higher. This is consistent with the shorter plasma zone giving less reaction and less destruction of initially formed **7**. A comparison of power yields does illustrate that argon generally increases the reaction efficiency. This is useful from a synthetic viewpoint, but the effect is too small to interpret mechanistically.

As a consequence of the observed effects of argon, it was of interest to determine if "wall effects" were important in determining yields of products or reaction rates. In particular it might be suspected that hot products would be stabilized by collision with the walls of the tube. This was tested by placing glass wool in the reactor. This will increase the surface area enormously and effectively decrease the distance from any reactive intermediate to the wall. In this experiment the plasma glow was observed to be quite irregular as expected. Brightly luminescent areas were seen in small pockets in the glass wool. Dimmer areas appeared in larger pockets and, of course, many areas where the glass wool was firmly packed gave no light. The rate of reaction and the product yield were, however, not substantially affected in comparison to runs with **1** alone (see runs 5 and 7; 8 and 10; 21 and 22).

The mechanism of decarbonylation is certainly of interest, but no definitive evidence is available. Such reactions are quite common in both photochemistry[6] and mass spectroscopy,[7] as might be expected considering the extreme stability of the carbon monoxide molecule which is extruded. In a plasma, reactions are initiated by electron impact and could involve either ions[8] or excited neutrals.

The specificity for formation of benzocycloalkenes for the various reactants can be understood in terms of the stability of the intermediate radicals or ions which could be formed. From the compounds **1**, **2**, **3**, and **4**, stable benzyl or phenoxy radicals such as A are possible. The radicals should rapidly eliminate carbon monoxide to give the stable biradicals (or *o*-xylylene[4,9] from **1**) which ring close to produce **7**, **9**, **12**, and **13**. On the other hand,

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[6] D. O. Cowan and R. L. Drisko, "Elements of Organic Photochemistry", Plenum Press, New York, 1976, p 162.

[7] F. W. McLafferty, "Interpretation of Mass Spectra", 2nd ed., W. A. Benjamin, London, 1973, p 427.

[8] In the mass spectra of **1**–**6**, the most abundant peaks are $M^+ - CO$, and the parent peaks appear in a range of relative intensities 40–90%. J. G. Grasseli and W. M. Ritchey, Ed., "Atlas of Spectral Data and Physical Constants for Organic Compounds", 2nd ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1975; E. Stenhagen, S. Abrahamsson, and F. W. McLafferty, Ed., "Atlas of Mass Spectral Data", Wiley, New York, 1969.

[9] M. P. Cava and A. A. Deana, *J. Am. Chem. Soc.*, 81, 4266 (1959); M. P. Cava, A. A. Deana, and K. Muth, *ibid.*, 81, 6458 (1959); K. Alder and M. Fremery, *Tetrahedron*, 14, 190 (1961); F. R. Jensen, W. E. Coleman, and A.-J. Birlin, *Tetrahedron Lett.*, 15 (1962).

Table I. Plasmolysis of 2-Indanone (1)

expt no.	r,[a] mmol min^{-1}	P,[b] W	conversion of 1, %	% yield of products[c] 7	% yield of products[c] 8	power yield[d] of 7[h]
1	1.54	20	29	30	1	67
2	1.68	40	52	19	3	42
3	1.54	60	56	13	2	19
4	1.39	80	67	11	15	13
5	0.66	40	42	29	3	20
6	0.75[e]	40	34	54	6	34
7	0.88[f]	40	61	16	6	22
8	2.02	40	44	23	1	51
9	2.15[e]	40	26	51	2	71
10	2.03[f]	40	47	21	1	50
11	1.77	40	53	23	4	54
12	2.78	40	27	41	0.8	77
13	1.03[g]	40	76	21	6	41
14	1.55[g]	40	54	31	3	65
15	2.09[g]	40	45	34	2	80
16	0.14	10	50	15	2	11
17	0.60	60	57	12	4	7
18	1.90[e]	20	25	44	2	105
19	1.44[e]	60	53	39	8	50
20	2.20[e]	80	45	19	8	24
21	2.78	40	27	41	0.8	77
22	2.87[f]	40	17	41	2	50

[a] Flow rate of the reactant. [b] Applied power. [c] Based on reacted starting material. [d] $r \times$ (conversion of 1) $\times$ (yield of 7). [e] Argon was added at a flow rate of 0.5–1.0 mmol/min. [f] Reactor tube was packed with glass wool. [g] Higher pumping speed employed. [h] $\times 10^{-4}$, mmol min^{-1} W^{-1}.

Table II. Plasmolysis of 1,2,3,4-Tetrahydronaphthalen-2-one (2) and 1,2,3,4-Tetrahydronaphthalen-1-one (6)

compd no.	P,[a] W	r,[b] mmol min^{-1}	conversion, %	% yield of products[c] 9	% yield of products[c] 10
2[d]	20	1.63	21	40	3
	40	1.21	30	37	9
	60	0.73	34	18	12
6[d,e]	20	2.16	47	0.7	0.3
6[f]	40	0.53	63	3	6

[a] Applied power. [b] Flow rate of the reactant. [c] Based on reacted starting material. [d] Argon was added at a flow rate of 0.5–1.0 mmol/min. [e] 17 formed in 3% yield. [f] 17 formed in 12% yield.

Table III. Plasmolysis of Dihydrocoumarin (3)

P,[a] W	r,[b] mmol min^{-1}	conversion of 3, %	% yield of products[c] 12	% yield of products[c] 13
20	1.14	29	20	1
40	2.09	76	8	0.4
20[d]	0.20	48	9	2
40[d]	0.33	60	9	2
20[e]	0.60	57		6

[a] Applied power. [b] Flow rate of the reactant. [c] Based on reacted starting material. [d] Argon was added at a flow rate of 0.5–1.0 mmol/min. [e] Plasmolysis of dihydrobenzofuran (12).

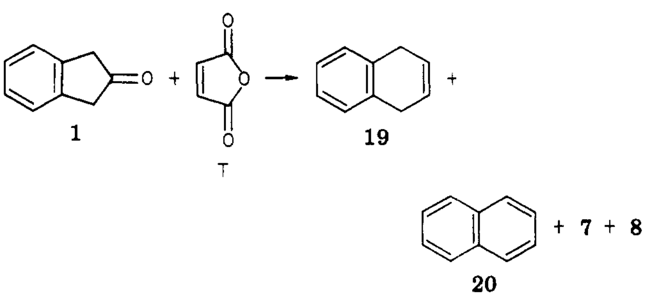
Table IV. Plasmolysis of 1-Indanone (5)

P,[a] W	r,[b] mmol min^{-1}	conversion of 5, %	% yield of products[c] 8	% yield of products[c] 11
20	2.9	39	6	0.4
40	0.92	56	19	4
80	0.62	77	16	0.6
20[d]	0.75	38	10	0.6
40[d]	1.01	53	21	3
60[d]	1.24	63	14	4
80[d]	1.10	53	14	7

[a] Applied power. [b] Flow rate of the reactant. [c] Based on reacted starting material. [d] Argon was added at a flow rate of 0.5–1.0 mmol/min.

compounds 5 and 6 cannot directly produce benzyl radicals. The alternative benzoyl radicals B and C from 5 and 6 could, however, eliminate carbon monoxide to give nonstabilized radicals D and E, which in turn decompose or disproportionate intramolecularly to give 8 and 17 as products (Scheme I).

It seemed possible that the intermediacy of 18 could be established by trapping it with maleic anhydride.[9] Experiments in which maleic anhydride was held in the cold trap during the reaction of 1 did not, however, produce the Diels–Alder adduct. When a mixture of 1 and maleic anhydride was reacted together in the radiofrequency discharge, small amounts of 1,4-dihydronaphthalene (19) and naphthalene (20) were detected in the reaction mixture



by GC–mass spectroscopy. Product 19 could be produced by the Diels–Alder reaction of 18 with acetylene. It is known that the latter arises from loss of carbon monoxide and carbon dioxide from maleic anhydride.[2,10,11]

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(10) B. Beijer and H. Suhr, *Justus Liebigs Ann. Chem.*, 1614 (1977).

(11) G. Rosskamp and H. Suhr, *Justus Liebigs Ann. Chem.*, 1478 (1975).

Table V. Products from Phthalide

			% yield of product[a]					
P, W	*r*, mmol min^{-1}	conversion, %	**21**	**22**	C_6H_6	**15**	**23**	**24**
20	2.5	17	16	8	20	13	16	10
40	3.4	19	12	2	26	16	13	7
60	3.7	40	8	1	28	17	10	5

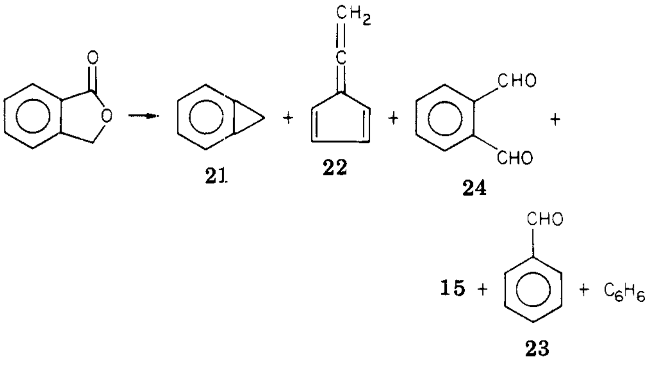
[a] Yields based on reacted starting material, measured as a fraction of the total GC integral.

Table VI. Products from 3-Phenylphthalide and 3,3-Diphenylphthalide

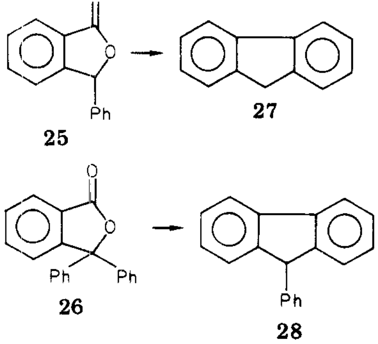
				% yield of products[a]		
reactant	*r*, mmol min^{-1}	*P*, W	conversion, %	**27**	**28**	**29**
25	1.2	10	50	74		6
25	1.8	40	64	66		10
26	0.8	5	15		91	3
26	3.5	20	24		83	6

[a] Yields based on reacted starting material, measured as a fraction of the total GC integral.

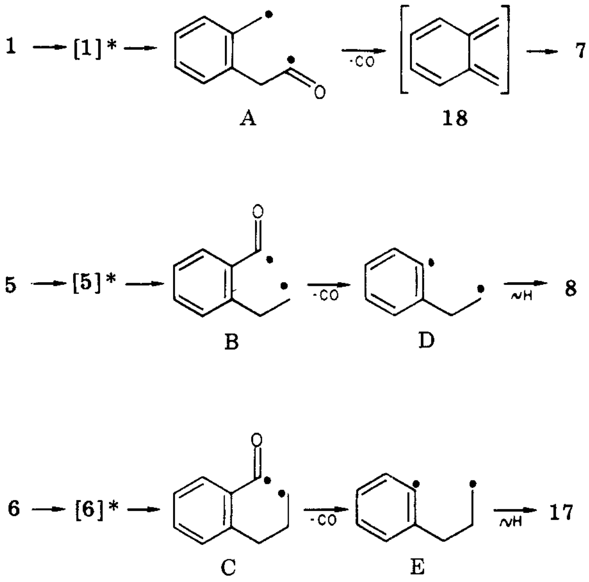
Decarboxylations. As suggested in the introduction, extrusion of carbon dioxide from phthalide, indeed, leads to benzocyclopropene (**21**). This product, as well as the isomeric allene (**22**), was isolated by GC and identified spectrally. A large number of other products including benzene, toluene, benzaldehyde (**23**), and phthalaldehyde (**24**) were also produced in this reaction. The yields of these products are found in Table V. Smaller amounts of biphenyl, fluorene, and bibenzyl were also identified by GC–MS. It will be seen that relative yields varied with reaction conditions, but because of the complexity of the mixture no attempt was made to maximize yields of the strained products or to understand the variation.



Much cleaner extrusion reactions were achieved using 3-phenylphthalide (**25**) and 3,3-diphenylphthalide (**26**). In each of these cases, the predominant product was the corresponding fluorene, along with a small amount of fluorenone (**29**) and benzene.



Scheme I[a]



[a] An asterisk indicates an excited state or ions formed by electron impact.

These hydrocarbon products can be rationalized as above, using diradical precursors to the products.[13] In the case of phthalide, an initially formed diradical has several possible fates, among them ring closure to **21**. The similarity of the product mixture to that obtained by flash pyrolysis[12,13] is quite good and is consistent with product-forming steps involving neutrals. The formation of fluorene **27** from 2-phenylphthalide **25** and **28** from **26** is similarly rational in terms of diradical product precursors.

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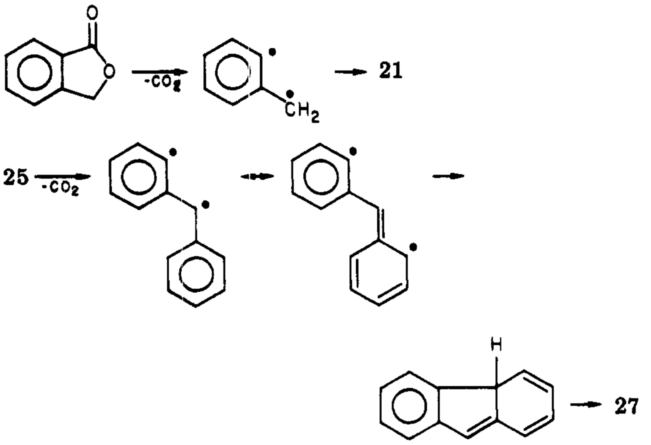
(12) P. Schissel, M. E. Kent, D. J. McAdoo and E. Hedaya, *J. Am. Chem. Soc.*, **92**, 2148 (1970); E. Hedaya and M. E. Kent, *J. Am. Chem. Soc.*, **92**, 2149 (1970).

(13) K. Wentrup and P. Muller, *Tetrahedron Lett.*, 2915 (1973).

(14) H. Günther, G. Jikeli, H. Schmickler and J. Presien, *Angew. Chem., Int. Ed. Engl.*, **12**, 762 (1973).



In summary, these plasma reactions demonstrate that extrusion of carbon monoxide or carbon dioxide can provide a direct route to benzocyclobutene or benzocyclopropene. The major reaction products are generally rationalizable in terms of schemes involving diradical intermediates as product precursors, but the mechanisms are in fact unknown.

Experimental Section

All reactants were commercial samples whose purity was ascertained by GC. Authentic samples of products were also commercially available except for **7**, **21**, **22**, and **28**.

Plasmolysis experiments were carried out in a double walled reactor tube (300 × 25 mm i.d.), which had dual reactant inlets as described previously.[3] Argon gas was added through one of those inlets. When the reaction was carried out without the addition of argon, one of the inlets was closed with a stopper. The dual inlets and an upper portion of the reactor were heated with heating tape to prevent condensation. The glow discharge was generated by a radiofrequency generator at 13.6 MHz (Tegal Model 100) with inductive coupling (copper coil, 10 turns in 100 mm) through a tunable Collins filter. The applied power (*P*) was measured with a built-in wattmeter, and in every case the circuit was balanced so that the reflected power was negligible. Flow rate (*r*) was calculated from the amount of material lost from the reactant reservoir and the elapsed time during plasmolysis. Except where noted in the text, experiments with reactants **1**–**6** employed a pumping system with a small diameter outlet from the cold trap. This restricted the pumping capacity as noted. Removal of this restriction led to a reduction in pressure in the plasma zone, especially when the total pressure was relatively high with argon as diluent gas. An accurate measure of this change was not made. After the plasmolysis, the inner wall of the reactor and the inlets were washed with 30–40 mL of acetone. Acetone solution was concentrated with a rotatory evaporator and then analyzed.

Analysis of products was generally carried out by GC, using an internal standard. The column was 10% silicon gum rubber SE-30 on Chromosorb W 80/100 mesh, 2 or 3 m, and dimethyl phthalate or acetophenone were standards. In the case of **1**, NMR was also employed using *tert*-butyl chloride or diphenylmethane as internal standards, since **7** seemed to be decomposed through the GC column. Absorptions of a vinyl proton of **8** at δ 5.75, methylene protons of **1** at δ 3.54, methylene protons of **7** at δ 3.15, methyl protons of *tert*-butyl chloride at δ 1.62, and methylene protons of diphenylmethane at δ 3.94 were used for analysis. Identification of other products was achieved by GC by comparison with authentic samples and was confirmed by GC–MS. Benzocyclobutene (**7**) was isolated from the reaction of **1** by a distillation, and its ^{1}H and ^{13}C NMR spectra were consistent with published data:[4b,11] ^{1}H NMR (CDCl$_3$) δ 3.18 (s, 4), 7.11 (m, 4); ^{13}C NMR (CDCl$_3$) δ 29.8, 122.7, 126.8, 146.1.

Benzocyclopropene (**21**) and allene **22** were collected by GC and identified from comparison of their ^{1}H, ^{13}C NMR, and mass spectra with literature values. **21**: ^{1}H NMR (CDCl$_3$) δ 3.18 (s, 2 H), 7.22 (s, 4 H). **22**: ^{1}H NMR (CDCl$_3$) δ 5.30 (s, 2 H), 6.42 (s, 4 H).

Acknowledgment. This work was supported by the National Science Foundation and a NATO Cooperative Research Grant.

Registry No. **1**, 615-13-4; **2**, 530-93-8; **3**, 119-84-6; **4**, 91-64-5; **5**, 83-33-0; **6**, 529-34-0; **7**, 694-87-1; **8**, 100-42-5; **9**, 496-11-7; **10**, 95-13-6; **11**, 536-74-3; **12**, 496-16-2; **13**, 271-89-6; **15**, 108-88-3; **17**, 300-57-2; **21**, 4646-69-9; **22**, 27041-32-3; **23**, 100-52-7; **24**, 643-79-8; **25**, 87-41-2; **26**, 596-29-2; **27**, 86-73-7; **28**, 789-24-2; **29**, 486-25-9; C_6H_6, 71-43-2.

Electroreductive Elimination of Phenolic Hydroxyl Groups and a New Synthesis of Olivetol[1]

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The replacement of phenolic hydroxyl groups by hydrogen was achieved through the electrochemical reduction of aryl diethyl phosphates. The mechanism of the initiation step was proposed to be one-electron transfer into not the phosphate group but the aromatic nucleus. This new reduction was applied to the synthesis of olivetol.

Organic synthesis often requires the elimination of hydroxyl groups from phenolic compounds, and two methods have already been exploited. One of them is based on the reduction of aryl ethers[2] or aryl phosphates[3] with alkali metals in ammonia and the other is the hydrogenolysis.[4]

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[1] Electroorganic Chemistry. 39.

[2] (a) W. H. Pirkle and J. L. Zabriskie, *J. Org. Chem.*, **29**, 3124 (1964); (b) P. A. Sartoretto and F. J. Sowa, *J. Am. Chem. Soc.*, **59**, 603 (1937); (c) Y. K. Sawa, N. Tsuji, and S. Maeda, *Tetrahedron*, **15**, 144, 154 (1961).

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