(i) Desulfurization with $LiAlH_4$. A blue-violet solution of 217 mg (2.03 mmol) of 2,2′-bipyridyl and 559 mg (2.03 mmol) of $(C_8H_{12})_2Ni$ in 15 mL of THF was admixed with 77 mg (2.03) of $LiAlH_4$. The solution foamed slightly, and a distinct reddening of the initially blue-violet color was noted. After 48 h at 55 °C the usual protolytic workup showed the presence of 93% of biphenyl and 5% of the starting thiophene.

In an identical run, the reaction mixture was treated after 48 h with CH_3CO_2D. The isolated biphenyl consisted of 95% of undeuterated, 2% of 2-deuterated, and 3% of 2,2′-dideuterated hydrocarbon.

In a control run, dibenzothiophene and $LiAlH_4$ in THF at 55 °C for 48 h gave <1% of biphenyl upon workup.

(j) Desulfurization with $LiAlD_4$. A reaction identical with that in section i, except that $LiAlD_4$ was substituted for $LiAlH_4$, gave upon workup with CH_3CO_2H a mixture of 60% undeuterated biphenyl, 25% of 2-deuteriobiphenyl, and 15% of 2,2′-dideuteriobiphenyl.

Desulfurizations of the Dimethyldibenzothiophenes 9 and 10. Under strictly comparable conditions, both the 2,8- and the 3,7-dimethyl isomers of dibenzothiophene were individually treated with 2 molar equiv of $(C_8H_{12})_2Ni$ and 2,2-bipyridyl in THF, as described in section c above. The 2,8-isomer (**9**) yielded 83% of the starting thiophene and 12% of only *m*,*m*′-bitolyl, which contained no trace of any *p*,*p*′-bitolyl: NMR (neat) δ 2.25 (s, 6 H), 6.7–7.13 (m, 8 H); IR (neat) 3020 (s), 2910 (s), 1610 (s), 1480 (s), 1170 (w), 1150 (w), 1130 (w), 890 (m), 770 (vs), 700 (vs). These spectral data were identical with those of an authentic sample.

The 3,7-isomer (**10**) gave a maximum of 3% of *p*,*p*′-bitolyl containing no detectable amount of the *m*,*m*′-isomer. Its NMR and IR spectra were superimposable upon those of an authentic sample.

Cleavage of Biphenylene (6). The interaction of 0.93 mmol of $(C_8H_{12})_2Ni$ and 0.78 mmol of biphenylene in 8 mL of THF for 20 h at 50 °C gave upon workup with 6 N HCl only unreacted biphenylene. However, a reaction of 0.5 mmol of biphenylene with 0.58 mmol each of $(C_8H_{12})_2Ni$ and 2,2′-bipyridyl in 7 mL of THF gave, after 20 h at 50 °C and workup with a sequence of $LiAlH_4$ (reaction time of 10 min) and then H_2O, a mixture of 40% of biphenyl and 60% of **6**.

Acknowledgment. We are appreciative of the support of this research by the Federal Government, initially by the Energy Research and Development Administration and subsequently by the Department of Energy under Grants DE-AC22-79ET14879 and DE-FG22-81PC40782.

Registry No. **1**, 1295-35-8; **2**, 132-65-0; **3**, 92-52-4; **5**, 55425-72-4; **6**, 259-79-0; **9**, 1207-15-4; **10**, 1136-85-2; **16**, 612-75-9; **17**, 613-33-2; H, 1333-74-0; $LiAlH_4$, 16853-85-3; 4,4′-dibromobiphenyl, 92-86-4; 3,7-dibromodibenzothiophene 5,5-dioxide, 83834-12-2; 3,7-dibromodibenzothiophene, 83834-10-0; 3,7-dilithiodibenzothiophene, 86456-51-1; 2,8-dibromodibenzothiophene, 31574-87-5; 2,8-dilithiodibenzothiophene, 86456-52-2; nickel(II) chloride, 7718-54-9; nickel(II) acetylacetonate, 3264-82-2; triethylaluminum, 97-93-8; 1,5-cyclooctadiene, 111-78-4; 1,3-butadiene, 106-99-0; 2,2′-dideuteriobiphenyl, 16327-75-6; 2,2′-diiodobiphenyl, 2236-52-4; 2,2′-dilithiobiphenyl, 16291-32-0; 2-biphenylylmagnesium bromide, 82214-69-5; 2-deuteriobiphenyl, 4819-96-9; 2,2′-bipyridyl, 366-18-7; 4-(dimethylamino)pyridine, 1122-58-3; ethylenediamine, 107-15-3; 1,10-phenanthroline, 66-71-7; pyridine, 110-86-1; hexamethylphosphorus triamide, 680-31-9; *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, 110-18-9; 1,8-bis(dimethylamino)naphthalene, 20734-58-1; *N*,*N*′-dimethylpiperazine, 106-58-1.

Electrochemical Oxidation of Benzophenone Hydrazones

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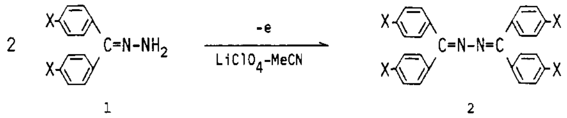
The anodic oxidation of benzophenone hydrazones (**1**) was found to give several products, depending upon the electrolysis conditions employed such as electrode material, temperature, and electrolyte composition. For example, the oxidation using a platinum anode at room temperature in $LiClO_4$–MeCN afforded exclusively benzophenone azines (**2**), whereas in NaOMe–MeOH benzophenone dimethyl acetals (**3**) were formed as the main products. On the other hand, the oxidation using a graphite anode in refluxing MeOH containing NaOMe gave diphenylmethyl methyl ethers (**4**), along with diphenylmethanes (**5**). When the analogous electrolysis was conducted in the presence of methacrylic acid derivatives, corresponding diphenylcyclopropanes (**7**) were obtained in relatively high yields.

The oxidation of ketone hydrazones has been extensively studied by using various oxidizing agents[1] and utilized in a wide variety of synthetic processes;[2] however, only a limited amount of work has been accomplished on the electrochemical oxidation of hydrazones. The only available report has shown that the anodic oxidation of keto arylhydrazones in aqueous acetonitrile gives the parent ketone, whereas with a cyclic hydrazone such as 3,5,5-trimethyl-2-pyrazoline, a rearranged product, i.e., 3,3-dimethylbutan-2-one, is formed.[3]

In this paper, we report the results of macroscale electrolysis of benzophenone hydrazones (**1**) under various

Scheme I[a]



[a] For **1** and **2**: a, X = H; b, X = Me; c, X = OMe; d, X = Cl.

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(1) For the reports on the oxidation of benzophenone hydrazones, see: (a) Curtius, Th.; Rauterberg, F. *J. Prakt. Chem.* **1891**, *44*, 192. (b) Barakat, M. Z.; Abdel-Wahab, M. F.; El-Sadr, M. M. *J. Chem. Soc.* **1956**, 4685. Particularly, the oxidative conversion into diazo compounds has received considerable attention, see: (c) Eistert, B.; Regitz, M.; Heck, G.; Schwall, H. "Methoden der Organishen Chemie (Houben-Weyl)"; Georg Thieme Verlag: Stuttgart, 1968; Vol. 10/4, p 574. (d) Nakagawa, N.; Onoue, H.; Minami, K. *Chem. Commun.* **1966**, 730. (e) Adamson, J. R.; Bywood, R.; Eastlick, D. T.; Gallagher, G.; Walker, D.; Wilson, E. M. *J. Chem. Soc., Perkin Trans 1* **1975**, 2030.

(2) For example: (a) Walborsky, H. M.; Hornyak, F. M. *J. Am. Chem. Soc.* **1955**, *77*, 6026. (b) Jones, W. M.; Glenn, T. H.; Baarda, D. G. *J. Org. Chem.* **1963**, *28*, 2887. (c) Impastato, E. J.; Barash, L.; Walborsky, H. M. *J. Am. Chem. Soc.* **1959**, *81*, 1514. (d) Aboderin, A. A.; Delpierre, G. R.; Fruton, J. S. *Ibid.* **1965**, *87*, 5468. (e) Bywood, R.; Gallagher, G.; Sharma, G. K.; Walker, D. *J. Chem. Soc., Perkin Trans. 1* **1975**, 2019.

(3) Lin, E.-C.; Mark, M. R. V. D. *J. Chem. Soc., Chem. Commun.* **1982**, 1176.

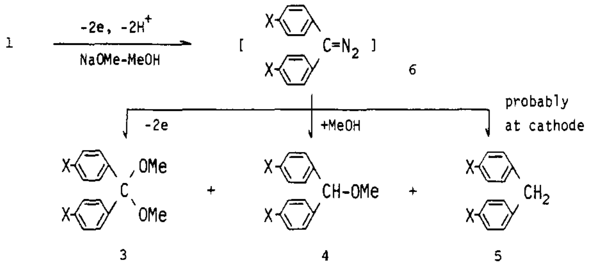
0022-3263/83/1948-2968$01.50/0

Table I. Anodic Oxidation of 1 with Pt Anode in $LiClO_4$-MeCN[a]

hydrazone	$E_{1/2}$,[b] V vs. SCE	applied potl, V vs. SCE	product	yield,[c] %	mp, °C (found)
1a	0.83	0.7-2.0	2a	84	163-164[d]
1b	0.77	0.7-1.8	2b	81	191-192[e]
1c	0.67	0.5-2.0	2c	73	180-181[d]
1d	0.88	0.8-2.0	2d	88	228-230[d]

[a] Anolyte: hydrazone (15 mmol) in MeCN (80 mL) containing $LiClO_4$ (48 mmol). Anode: Pt. Constant current: 0.5 A. Electron release: 0.5 F/mol. Temperature: ca. 17 °C. Electrolyzed in a divided cell. [b] Read from the current-potential curves. The measurements were carried out in 0.1 M $LiClO_4$-MeCN with Pt electrodes at 17 °C. The concentration of 1 was 2×10^{-3} M and the scan rate was 7 V/s. [c] Isolated yield based on 1. [d] Reference 12. [e] Reference 14.

Scheme II[a]



[a] For 3-5: a, X = H; b, X = Me; c, X = OMe; d, X = Cl.

conditions and their application to a direct preparation of diphenylcyclopropane derivatives.

Results and Discussion

Preparative electrolyses were carried out either in a divided cell at room temperature or in an undivided cell at elevated temperatures under a constant current until almost all of the starting material 1 was consumed. The electrode material employed was platinum or graphite.

At first, 1 was subjected to electrolysis by using a platinum anode in $LiClO_4$–MeCN at room temperature. In this system, 1 underwent predominantly anodic oxidation involving evolution of nitrogen gas and gave good yields of ketazines 2 (Scheme I, Table I), this is also the product formed when 1 is oxidized with I_2, MnO_2, and so on.[1a,b] In each case, most of the starting material was converted into 2 at the stage where only about 0.5 F of electricity was passed per mole of 1, and essentially pure 2 separated out on concentrating the anolyte. Analogous results were also obtained by using a graphite anode.

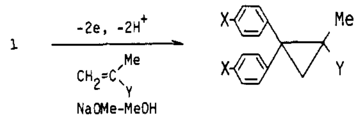
On the other hand, electrooxidation in NaOMe–MeOH yielded little 2 but gave mainly three types products; benzophenone dimethyl acetals 3,[4] diphenylmethyl methyl ethers 4, and diphenylmethanes 5 (Scheme II). The relative yields of these compounds were greatly affected by the electrolysis conditions. Generally, a platinum anode, low temperature, and an excess amount of NaOMe favored the production of 3, while elevated temperatures tended to involve formation of a byproduct such as benzophenone formal azine.[5] Probably, anodic oxidation of methoxide ion or methanol to formaldehyde followed by dehydration of 1 with the aldehyde was allowed to proceed under such conditions. A graphite anode, high temperature, and a small amount of NaOMe facilitated formation of 4 and 5, but no formal azine was formed.

Table II. Anodic Oxidation of 1 with Pt Anode in NaOMe-MeOH[a]

hydrazone	applied potl, V vs. SCE	product	yield,[b] %	mp, °C (found)
1a	0.7-1.2	3a	70 (70)	108-109[c]
1b	0.6-1.2	3b	54 (51)	92-93
1c	0.6-0.8	3c	49 (47)	106-108[d]
1d	0.9-1.0	3d	77 (75)	72-74

[a] Anolyte: hydrazone (15 mmol) in MeOH (80 mL) containing NaOMe (30 mmol). Anode: Pt. Constant current: 0.5 A. Electron release: 3.7 F/mol. Temperature: ca. 17 °C. Electrolyzed in a divided cell. [c] By VPC analysis. Values in parentheses are isolated yields based on 1. In all cases, small amounts of 4 and 5 were also formed. [c] Reference 15. [d] Reference 16.

Scheme III



7a, X = H, Y = COOMe
b, X = Me, Y = COOMe
c, X = OMe, Y = COOMe
d, X = Cl, Y = COOMe
e, X = H, Y = CN
f, X = H, Y = $CONH_2$

Tables II and III show the results of the oxidation of some para derivatives of 1 under the various conditions for the production of compounds 3–5. In electrolysis with a platinum anode at room temperature, 1 at more anodic oxidation potentials gave high yields of 3. In contrast, in boiling methanol with a graphite anode, 1, which gave low yields of 3 under the foregoing conditions, afforded 4 in high yields. When a graphite electrode was used for both the anode and the cathode, the yields of 5 were increased; however, they did not exceed 40%, because they always were accompanied by the formation of considerable amounts of 4. The influence of the cathode material on the the product yields indicates that cathodic reduction is also involved in the production of 5. In fact, almost no 5 was produced when electrolysis was performed in a divided cell.

In all electrolyses in this medium, the electrolyte assumed a wine-red or purple color. The visible spectrum of the electrolyzed solution of 1a exhibited a characteristic absorption at 525 nm, which strongly suggested the presence of an intermediate diphenyldiazomethane (6).[1e] (The other isolated products were transparent in this region.) The diazo compound 6 is known to react with boiling methanol to give 4a,[6] and electrolytic reduction of 6 may produce 5a.[7] Moreover, it was found that the anodic oxidation of 6 in NaOMe–MeOH at room temperature afforded 3a in a yield of ca. 85% at the stage where 2 F of electricity was passed per mol of 6. We, therefore, firmly believe that the products 3–5 obtained in the present experiment were derived from 6, generated by anodic oxidation of 1, although the intermediate 6 could not be isolated.

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(4) The products 3 are obtainable with some difficulty from benzophenones by conventional methods including the use of orthoesters in the presence of acid catalysts, see: Taylor; E. C.; Chiang, C.-S. *Synthesis* **1977**, 467.

(5) The structure of the formal azine was identified by comparison with the authentic sample prepared from 1a and formaldehyde according to Curtius's method (ref 1a).

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Table III. Anodic Oxidation of 1 in Boiling NaOMe-MeOH[a]

hydrazone	electrode material +	electrode material −	electron release, F/mol	% yield of products[b] 3	4	5
1a	C	Pt[c]	6.2	2	57 (55)	12
1b			5.4	15	59 (52)	4
1c			4.4	16	77 (70)[d]	trace
1d			4.6	12	19 (15)	29
1a	C	C[e]	4.4	3	32	40 (37)
1b			4.5	11	33	29 (25)
1c			2.9	11	36	27 (27)
1d			2.8	7	15	35 (33)

[a] Electrolyte: hydrazone (15 mmol) in MeOH (80 mL) containing NaOMe (7.5 mmol). Temperature: ca. 70 °C. [b] By VPC analysis. Values in parentheses are isolated yields based on 1. [c] Electrolyzed in an undivided cell with C anode and Pt cathode and a constant current of 0.2 A. [d] The purity was ca. 92% according to VPC analysis. [e] Electrolyzed in an undivided cell with C anode and C cathode and a constant current of 0.5 A.

Table IV. Electrolytic Preparation of Diphenylpropanes from 1 and Methacrylic Acid Derivatives[a]

hydrazone	CH_2=C(Me)Y, Y =	electron release, F/mol	product	material yield,[b] %	mp, °C (found)
1a	COOMe	2.3	7a	61	90-92[c]
	CN	3.1	7e	53	142-144[c]
	$CONH_2$	2.7	7f	55	146-148 (sublimed)[c]
1b	COOMe	2.4	7b	68	80-82
1c		2.4	7c	62	93-95
1d		2.5	7d	42	116-118

[a] Electrolyte: hydrazone (60 mmol) and CH_2=C(Me)Y (120 mmol) in MeOH (80 mL) containing NaOMe (5 mmol). Constant current: 0.5 A. Temperature: ca. 55 °C. Electrolyzed in an undivided cell with C anode and Pt cathode. [b] Isolated yield based on 1. [c] Reference 2a.

One of the typical reactions of 6 involves diphenylmethylene addition to the double bond of an electrophilic olefin to yield a diphenylcyclopropane derivative (7).[2a-c] Thus we next attempted a direct preparation of 7 by means of the electrolytic oxidation of 1 in the presence of substituted ethylenes (Scheme III). The reaction was carried out by employing a graphite anode-platinum cathode system. Moreover, the amount of NaOMe was minimized, and the reaction temperature was maintained at ca. 55 °C in order to suppress the formation of undesirable byproducts such as 3-5 or oligomers of ethylenes.

As is shown in Table IV, the expected reaction smoothly took place with methacrylic acid derivatives. Products 7 are usually prepared by a two-step process consisting of an oxidation of 1 to 6 followed by addition of 6 to ethylenes.[2a-c] The most common oxidizing agent used in this process is mercury(II) oxide,[1c,8] while silver oxide[1c,9] or peroxides[1d,e] have also been employed. However, they have some disadvantages in terms of cost of the metal oxides and the disposal of the liberated metals. The present method seems preferable in that compounds 7 can be prepared directly from 1. Moreover, oxidizing agents are unnecessary, and the yields are relatively high. However, it was not applicable to ethylenes that are susceptible to an addition of methanol in the presence of NaOMe.[10]

Experimental Section

Melting and boiling points are uncorrected. Infrared spectra (IR) were recorded on a JASCO IRA-I grating spectrophotometer. Visible spectra were recorded on a Shimazu MPS-5000 multipurpose recording spectrophotometer. ^1H NMR spectra were obtained on an Hitachi 20-A spectrometer. Chemical shifts are reported in units downfield from Me_4Si internal standard. Mass spectra were measured on an Hitachi EPI-G2 spectrometer. Elemental analyses were performed in our laboratory. Gas-liquid chromatography (VPC) was carried out on an Hitachi 163 gas chromatograph using a 2-m glass column packed with FFAP on Chromosorb W AW and a 1-m stainless steel column packed with SE-30 on Uniport B. Electrolysis apparatus used was similar to that previously described.[11]

Benzophenone hydrazones were prepared from anhydrous hydrazine and the corresponding benzophenone by literature methods[8,12] and were recrystallized several times from ethanol. The melting points of these hydrazones were in good agreement with previously reported values.[8,12,13]

Macroscale electrolyses were performed in a 100-mL cylindrical flask equipped with a concentric cylindrical glass filter as the cathode compartment, which can also be used as an undivided cell by removal of the filter. A cylindrical platinum net (4.5 cm in height, 11.0 cm in circumference) or two carbon plates (5.0 cm × 2.0 cm) were used as the anode, and the cathode was a platinum coil or a carbon plate similar to that of the anode. The cell was externally cooled with water or heated in a water bath, and the electrolyte was stirred by a magnetic stirring bar. Under the conditions of elevated temperatures, a reflux condenser was connected to the cell.

Electrolysis of 1 in $LiClO_4$-MeCN (General Procedure). A solution of 15 mmol of 1 in 80 mL of acetonitrile containing 48 mmol of lithium perchlorate was electrolyzed with a platinum anode in a divided cell at a constant current of 0.5 A. A few minutes after initiation of the electrolysis, crystals of 2 appeared, and at the end of 24 min, the anode potential sharply increased to over 2.0 V vs. SCE, which indicated the completion of the reaction. Total electron release was 7.5 mF.

The product 2 was collected by filtration and rinsed with cold methanol. Additional 2 could be recovered by concentration of the filtrate. Identification of products was accomplished by determination of mixture melting points and by comparison of their IR spectra with those of authentic samples prepared by

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(8) Smith, L. I.; Howard, K. L. "Organic Syntheses"; Wiley: New York, 1955; Collect Vol. III, p 351.

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(11) Chiba, T.; Okimoto, M.; Nagai, H.; Takata, Y. *J. Org. Chem.* **1979**, *44*, 3519.

(12) Szmant, H. H.; McGinnis, C. *J. Am. Chem. Soc.* **1950**, *72*, 2890.

(13) Staudinger H.; Goldstein, J. *Ber. Dtsch. Chem. Ges.* **1916**, *49*, 1923.

literature methods.[1a,12,14] Product yields and the melting points are listed in Table I.

Electrolysis of 1 in NaOMe–MeOH at Room Temperature (General Procedure). A solution of 15 mmol of 1 in 80 mL of methanol containing 30 mmol of sodium methoxide was electrolyzed with a platinum anode in a divided cell at a constant current of 0.5 A for 3 h. The anolyte slowly became wine-red, and an evolution of nitrogen gas was observed as the electrolysis proceeded.

The resulting anolyte was concentrated to one-fourth its volume under reduced pressure and allowed to stand at room temperature. The precipitated product 3 was filtered and rinsed with a small amount of cold methanol. Analytical samples were purified by recrystallization from methanol and compared with authentic samples prepared by Mackenzie's method.[15,16] Acid-catalyzed hydrolysis of 3 also gave the corresponding benzophenone and methanol.

4,4′-Dimethylbenzophenone dimethyl acetal (3b): plates, mp 92–93 °C; IR (KBr) 1060, 1090 cm^{-1} (dimethyl acetal); ^{1}H NMR (CCl_4) δ 2.26 (s, 6, CH_3), 3.00 (s, 6, CH_3O), 6.95, 7.26 (d, d, 8, J = 8 Hz, Ph); mass spectrum, m/e (relative intensity) 256 (M^+, 3), 226 (19), 225 ($M^+ - 31$, 100), 210 (31), 165 ($M^+ - 91$, 14), 119 (60). Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.68; H, 7.77.

4,4′-Dichlorobenzophenone dimethyl acetal (3d): prisms, mp 73–74 °C; IR (KBr) 1050, 1080 cm^{-1} (dimethyl acetal); ^{1}H NMR (CCl_4) δ 3.02 (s, 6, CH_3O), 7.26 (ca. d, 8, Ph); mass spectrum, m/e (relative intensity) 298 ($M^+ + 2$, 2), 296 (M^+, 3), 267 (65), 265 ($M^+ - 31$, 100), 185 ($M^+ - 111$, 16), 139 (34). Anal. Calcd for $C_{15}H_{14}O_2Cl_2$: C, 60.62; H, 4.75; Cl, 23.86. Found: C, 60.73; H, 4.82; Cl, 23.85.

Electrolysis of 1 in Boiling NaOMe–MeOH (General Procedure). Into an undivided cell equipped with a reflux condenser, two carbon-plate anodes, and a platinum cathode were placed 15 mmol of 1 and 80 mL of methanol containing 7.5 mmol of sodium methoxide. The solution was refluxed in a water bath and electrolyzed at constant current of 0.2 A for 6.4–9.0 h (4.4–6.2 F/mol). The electrolyte soon turned deep-red or purple.

After completion of the reaction, yields of the products were determined by gas chromatography using an internal standard. Then the solvent was removed under reduced pressure and the residue was treated with water. The oily layer was extracted into benzene, shaken with concentrated hydrochloric acid, washed with aqueous sodium bicarbonate and water, dried with anhydrous magnesium sulfate, and chromatographed on a column of silica gel.

Analogous electrolysis was performed by using a carbon anode–carbon cathode system at constant current of 0.5 A in order to obtain 5 effectively. Structures of products were comfirmed by comparison of their physical and spectral data with those of authentic samples or with literature data.

4a and 5a. In this case, the benzene extracts were distilled under reduced pressure prior to chromatography. The fraction with bp 90–120 °C (2 mmHg) was eluted with hexane to give **5a** as a thick oil, which solidified on cooling. **Diphenylmethane (5a)**: mp 24–25 °C.[17] Continued elution with 4:6 hexane–benzene gave **4a** as a thick oil, which solidified on cooling. **Diphenylmethyl methyl ether (4a)**: mp 25–27 °C, bp 105 °C (2 mmHg).[18]

4b and 5b. After evaporation of the solvent, the residue was passed through a column. Elution with 9:1 hexane–benzene gave **5b** which later solidified. **Bis(4-methylphenyl)methane (5b)**: mp 27–29 °C.[19] Continued elution with benzene gave **4b** as an oil, which solidified on standing. **Bis(4-methylphenyl)methyl methyl ether (4b)**: mp 49–51 °C;[17,20] IR (neat) 1095 cm^{-1} (aliphatic CH_3O); ^{1}H NMR (CCl_4) δ 2.17 (s, 6, CH_3), 3.16 (s, 3, CH_3O), 4.99 (s, 1, >CH—), 6.88, 7.07 (d, d, 8, J = 8 Hz, **Ph**); mass spectrum, m/e (relative intensity) 226 (M^+, 57), 211 ($M^+ - 15$, 21), 195 ($M^+ - 31$, 100), 135 (71), 119 (50). Anal. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 84.77; H, 7.90.

4c and 5c. Elution with 1:3 hexane–benzene gave **5c** as a white solid. **Bis(4-methoxyphenyl)methane (5c)**: leaflets from methanol, mp 50–51 °C.[21] Since **4c** was decomposed on silica gel or by treatment with acid; a distillation with Kügelrohr apparatus was attempted but compound **4c** could not be isolated in analytically pure form. The spectroscopic and elemental analysis data are reported for 93% pure material that was obtained by the distillation at the air-bath temperature of 220 °C and the pressure of 2 mmHg. **Bis(4-methoxyphenyl)methyl methyl ether (4c)**:[20] IR (neat) 1250 (aromatic CH_3O), 1095 cm^{-1} (aliphatic CH_3O); ^{1}H NMR (CCl_4) δ 3.18 (s, CH_3O), 3.56 (s, CH_3O), 4.98 (s, >CH—), 6.64, 7.07 (d, d, J = 9 Hz, Ph); mass spectrum, m/e (relative intensity) 258 (M^+, 30), 242 (66), 228 (69), 227 ($M^+ - 31$, 79), 197 (29), 135 (100). Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.39; H, 7.02. Found: C, 74.35; H, 7.02.

4d and 5d. Elution with 3:1 hexane–benzene gave **5d** as a thick oil, which solidified on standing. **Bis(4-chlorophenyl)methane (5d)**: plates from ethanol, mp 52–53 °C.[22] Then, **4d** was eluted with 1:3 hexane–benzene. **Bis(4-chlorophenyl)methyl methyl ether (4d)**: rod-like crystals from methanol, mp 84–85 °C; IR (KBr) 1090 cm^{-1} (aliphatic CH_3O); ^{1}H NMR (CCl_4) δ 3.24 (s, 3, CH_3O), 5.04 (s, 1, >CH—), 7.15 (ca. s, 8, Ph); mass spectrum, m/e (relative intensity) 268 ($M^+ + 2$, 26), 266 (M^+, 40), 237 (52), 235 ($M^+ - 31$, 80), 231 ($M^+ - 35$, (44), 155 ($M^+ - 111$, 100), 139 (88). Anal. Calcd for $C_{14}H_{12}OCl_2$: C, 62.94; H, 4.53; Cl, 26.54. Found: C, 63.07; H, 4.40; Cl, 26.54.

Electrolysis of 1 in the Presence of Methacrylic Acid Derivatives (General Procedure). Following the same apparatus as described above, a mixture of 60 mmol of 1, 120 mmol of methacrylic acid derivative and 80 mL of methanol containing 5 mmol of sodium methoxide was electrolyzed at constant current of 0.5 A at ca. 55 °C. The electron release was 2.3–3.1 F per mol of 1.

After the reaction, the solvent was evaporated, and the residue was treated with water, followed by extraction with ether. The ether extracts were dried with anhydrous magnesium sulfate, concentrated, and chromatographed on a column of silica gel. The products were identified either by direct comparison with authentic samples prepared by an alternative method[2a] or by IR, NMR, and mass spectra.

For the isolation of **7a**, **7b**, and **7d**, 4:1 hexane–ether, and for **7c** 1:1 hexane–ether, was used as the eluent. In each case, **7** was eluted after elution of a small amount of **5**. For **7e** and **7f**, the electrolyte was allowed to stand overnight, and the precipitated product was collected by filtration, followed by washing with methanol.

Methyl 1-methyl-2,2-bis(4-methylphenyl)cyclopropanecarboxylate (7b): pale yellow plates from methanol, mp 83–84 °C; IR (KBr) 1725, 1145 cm^{-1} (ester); ^{1}H NMR (CCl_4) δ 1.11 (s, 3, CH_3), 1.28, 2.05 (d, d, 2, J = 5 Hz, CH_2), 2.17 (s, 6, CH_3), 3.21 (s, 3, $COOCH_3$), 6.87, 7.16 (dd, dd, 8, J = 8 and 3 Hz, Ph); mass spectrum, m/e (relative intensity) 294 (M^+, 4), 279 ($M^+ - 15$, 9), 262 ($M^+ - 32$, 12), 235 ($M^+ - 59$, 87), 234 (100), 219 (31), 143 (40). Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.40; H, 7.48.

Methyl 1-methyl-2,2-bis(4-methoxyphenyl)cyclopropanecarboxylate (7c): fine needles from methanol, mp 94–95 °C; IR (KBr) 1720, 1140 (ester), 1250 cm^{-1} (aromatic CH_3O); ^{1}H NMR (CCl_4) δ 1.12 (s, 3, CH_3), 1.25, 2.12 (d, d, 2, J = 4.5 Hz, CH_2), 3.23 (s, 3, $COOCH_3$), 3.58 (s, 6, CH_3O), 6.60, 7.14 (dd, dd, 8, J = 9 and 4 Hz, Ph); mass spectrum, m/e (relative intensity) 326 (M^+, 63), 267 ($M^+ - 59$, 31), 226 (100). Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.42; H, 6.70.

Methyl 1-methyl-2,2-bis(4-chlorophenyl)cyclopropanecarboxylate (7d): prisms from methanol, mp 118–119 °C; IR (KBr) 1710, 1150 cm^{-1} (ester); ^{1}H NMR (CCl_4) δ 1.13 (s, 3, CH_3), 1.32, 2.18 (d, d, 2, J = 5 Hz, CH_2), 3.29 (s, 3, $COOCH_3$), 7.16 (ca. d, 8, Ph); mass spectrum, m/e (relative intensity) 336 ($M^+ + 2$,

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2), 334 (M^+, 3), 287 (65), 286 (77), 285 ($M^+ - 59$, 100), 284 (93), 239 (42). Anal. Calcd for $C_{18}H_{16}O_2Cl_2$: C, 64.49; H, 4.81; Cl, 21.15. Found: C, 64.60; H, 4.79; Cl, 21.16.

Registry No. **1a**, 5350-57-2; **1b**, 55816-25-6; **1c**, 20114-55-0; **1d**, 5463-11-6; **2a**, 983-79-9; **2b**, 5895-68-1; **2c**, 5831-42-5; **2d**, 50482-89-8; **3a**, 2235-01-0; **3b**, 86456-47-5; **3c**, 2186-93-8; **3d**, 6861-53-6; **4a**, 1016-09-7; **4b**, 18939-92-9; **4c**, 2186-95-0; **4d**, 55702-41-5; **5a**, 101-81-5; **5b**, 4957-14-6; **5c**, 726-18-1; **5d**, 101-76-8; **7a**, 6975-21-9; **7b**, 86456-48-6; **7c**, 35525-34-9; **7d**, 86456-49-7; **7e**, 56701-20-3; **7f**, 86456-50-0; $CH_2{=}C(Me)COOMe$, 80-62-6; $CH_2{=}C(Me)CN$, 126-98-7; $CH_2{=}C(Me)CONH_2$, 79-39-0.

Molecular Orbital Study on the Gas-Phase Nucleophilic Displacement on Acyl Chlorides

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The mechanism of the nucleophilic displacement is investigated by molecular orbital (MO) calculations. The minimum-energy paths of two gas-phase reactions, (a) $F^- + CH_3COCl \rightarrow CH_3COF + Cl^-$ and (b) $Cl^- + CH_3COCl \rightarrow CH_3COCl + Cl^-$, are sought by geometry optimization. The stable tetrahedral intermediate is not found in the reaction and the bond interchange ($X^-\cdots CO{-}Cl \rightarrow X{-}CO\cdots Cl^-$) takes place in the concerted fashion. The path is interpreted in terms of the frontier orbital theory. The presence or the absence of the double-well potential is discussed in relation to the basicity of X^-.

The attack of a nucleophile at a carbonyl center plays an important role in many organic and biochemical reactions, and is extensively investigated because of its contribution to the enzymatic catalysis in reactions of carboxylic acids.[1] While these studies have been made in solution, recent development of ion cyclotron resonance (ICR) spectroscopy makes it possible to observe the gas-phase ion–carbonyl compound reactions. Such solvent-free data reveal the intrinsic reactivity of the carbonyl compound which is determined solely by the electronic and structural nature of the reagent and the carbonyl substrate. The reaction is believed to proceed through the tetrahedral intermediate. Asubiojo and Brauman have argued that the tetrahedral structure is located not at the energy minimum but at the saddle point of the gas-phase reaction on the basis of kinetic data for many nucleophilic displacements.[2] To shed light on many disputable points for tetrahedral intermediacy in the gas phase, we present here an ab initio MO calculation for the nucleophilic displacement between a halide ion and an acetyl chloride. To our knowledge, the theoretical research of such realistic reactions has not been made, although some model reactions (e.g., $H^- + H_2C{=}O$[3]) were traced. The potential energy profile obtained here is compared with that deduced experimentally, and the factor of initiating the reaction is analyzed in terms of the frontier orbital theory.

Method of Calculation

The electronic structure and the minimum-energy path are investigated by the standard closed-shell SCF wave function with the 4-31G + p + p′ basis set. The diffuse p and p′ GTOs, of which exponents are 0.09 and 0.07, are added to the F and Cl atoms, respectively. This augmentation by the sufficiently diffuse orbitals is needed to describe the spread out electron distribution of F^- and Cl^- and to obtain the reliable total energy (E_T).[4] The quality of the basis set is indicated in Table I, in which some calculated enthalpy changes are presented and compared with the experimental data.

Table I. Quality of the Basis Set[a]

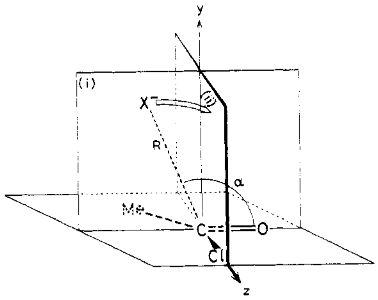
basis set	total energy (E_T) + 700, au: $CH_3COCl + F^-$	total energy (E_T) + 700, au: $CH_3COF + Cl^-$	enthalpy change, kcal/mol
exptl			−39.4[b]
3-21G	−7.544 66	−7.751 86	−130.0
3-21G + p + p′	−7.702 49	−7.792 61	−56.5
4-31G	−10.343 08	−10.460 15	−73.5
4-31G + p + p′	−10.423 97	−10.511 06	−54.6

[a] The geometry used in the calculation is taken from the standard value proposed by Pople. [b] Taken from ref 2.

The geometry optimization in the course of the reaction is made in terms of the internal coordinates to the accuracy of 0.001 Å for the bond length and 0.01 degree for the angle. The GAUSSIAN 70 program is used for the present MO calculation.[5]

Results of Optimization

At the early stage of the reaction, X^- approaches the substrate from the backside of the carbonyl group in plane i as was investigated by Stone and Erskine.[6] The stable structure (π complex) is completed in plane i with (a) *R*



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