Anal. Calcd for $C_9H_{15}ClO_5$: C, 45.28; H, 6.29. Found: C, 44.92; H, 6.28.

2,2-Dichloro-3,3,4,4-tetramethoxycyclobutanone (1b). This adduct distilled at 57–58 °C (0.025 mm) to yield 5.48 g (85%) of product: IR 1815 cm^{-1} (neat); NMR δ 3.45 (s, 6 H), 3.55 (s, 6 H); mass spectrum, *m/e* (no M) 230 (M – 28).

Anal. Calcd for $C_8H_{12}Cl_2O_5$: C, 37.06; H, 4.63. Found: C, 36.81; H, 4.62.

2-Chloro-2-phenyl-3,3,4,4-tetramethoxycyclobutanone (1c). This cyclobutanone was produced as a white solid: mp 117–118 °C; 6.08 g (80%); IR 1805 cm^{-1} (CCl_4); NMR δ 2.98 (s, 3 H), 3.35 (m, 9 H), 7.08 (m, 5 H); mass spectrum, *m/e* 300 (M).

Anal. Calcd for $C_{14}H_{17}ClO_5$: C, 55.90; H, 5.65. Found: C, 55.92; H, 5.55.

Typical Procedure for the Hydrolysis of the 2-Chloro-3,3,4,4-tetramethoxycyclobutanones. A 1.0-g portion of the cycloadduct 1 was stirred at reflux for 5 h in 15 mL of 18% methanolic HCl solution. The solvent was then removed under vacuum, leaving the keto ester.

Methyl 4-Chloro-2,2-dimethoxy-3-oxopentanoate (2a). A 1.0-g (4.2 mmol) portion of **1a** was treated with the acid/methanol solution to yield a quantitative amount of the keto ester **2a**: IR 1770, 1750 cm^{-1} (neat); NMR δ 1.50 (d, 3 H, J = 5 Hz), 3.25 (s, 3 H), 3.40 (s, 3 H), 3.70 (s, 3 H), 4.75 (q, 1 H, J = 5 Hz); mass spectrum, *m/e* (no M) 193 (M – 31).

Anal. Calcd for $C_8H_{13}ClO_5$: C, 42.76; H, 5.79. Found: C, 42.70; H, 5.78.

Methyl 4,4-Dichloro-2,2-dimethoxy-3-oxobutanoate (2b). A 1.0-g (3.8 mmol) portion of **1b** was treated with the acid/methanol solution to give a quantitative yield of the keto ester **2b**: IR 1780, 1770 cm^{-1} (neat); NMR δ 3.35 (s, 6 H), 3.80 (s, 3 H), 6.45 (s, 1 H); mass spectrum, *m/e* (no M) 213 (M – 31).

Anal. Calcd for $C_7H_{10}Cl_2O_5$: C, 34.28; H, 4.08. Found: C, 34.46; H, 4.14.

Methyl 4-Chloro-2,2-dimethoxy-3-oxo-4-phenylbutanoate (2c). A 1.0-g (3.3 mmol) portion of **1c** was treated with the acid/methanol solution to give a quantitative amount of the ester **2c**: IR 1770, 1750 cm^{-1} (neat); NMR δ 3.25 (s, 3 H), 3.40 (s, 3 H), 3.62 (s, 3 H), 5.92 (s, 1 H), 7.30 (m, 5 H); mass spectrum, *m/e* (no M) 255 (M – 31).

Anal. Calcd for $C_{13}H_{15}ClO_5$: C, 54.45; H, 5.23. Found: C, 54.25; H, 5.31.

Typical Procedure for the Sodium Borohydride Reduction of the Cyclobutanones. To a stirred solution of 1.0 g of the cycloadduct 1 in 10 mL of anhydrous isopropyl alcohol was slowly added a 20% excess of sodium borohydride. The mixture was stirred at room temperature overnight. The alcohol was evaporated under vacuum and the residue shaken with 10 mL of 10% HCl. Extraction with two 10-mL portions of CCl_4, drying of the extract over $MgSO_4$, and evaporation of the solvent resulted in the solid alcohol. The alcohol was purified by sublimation.

2-Chloro-2-methyl-3,3,4,4-tetramethoxycyclobutanol (3a). The reduction of **1a** quantitatively produced **3a**, a white solid, which was isolated as a mixture of isomers melting at 47–51 °C: IR 3550 cm^{-1} (CCl_4); NMR δ 1.70 (s, 3 H), 2.68 (br s, 1 H), 3.3–3.45 (m, 12 H), 3.72, 3.88 (s, s, 1 H); mass spectrum, *m/e* 240 (M).

Anal. Calcd for $C_9H_{17}ClO_5$: C, 44.91; H, 7.06. Found: C, 44.65; H, 7.19.

2,2-Dichloro-3,3,4,4-tetramethoxycyclobutanol (3b). The reduction of **2a** also quantitatively produced **3a** as a white solid: mp 61–62 °C; IR 3550 cm^{-1} (CCl_4); NMR δ 3.40–3.55 (m, 12 H), 3.8 (br s, 1 H), 4.10 (s, 1 H); mass spectrum, *m/e* 260 (M).

Anal. Calcd for $C_8H_{14}Cl_2O_5$: C, 36.80; H, 5.40. Found: C, 36.87; H, 5.61.

2-Chloro-2-phenyl-3,3,4,4-tetramethoxycyclobutanol (3c). The reduction of **1c** quantitaviely produced **3c**, a white solid, which was isolated as an equal mixture of isomers: mp 71–74 °C; IR 3550 cm^{-1} (CCl_4); NMR δ 3.05, 3.35 (s, s, 1 H), 3.15 (s, 3 H), 3.25 (s, 3 H), 3.40 (s, 6 H), 4.3 (br s, 1 H), 6.9–7.4 (m, 5 H); mass spectrum, *m/e* (no M) 284 (M – 18).

Anal. Calcd for $C_{14}H_{19}ClO_5$: C, 55.55; H, 6.33. Found: C, 55.65; H, 6.18.

Procedure for Conversion of Cyclobutanols to 2-Substituted Semisquaric Acids. A 1.0-g portion of the cyclobutanol was heated at reflux in 15 mL of 18% methanolic HCl. The solvent was removed by evaporation, resulting in the isolation of the semisquaric acid. No further purification was necessary.

2-Methylsemisquaric Acid (1-Hydroxy-2-methyl-1-cyclobutene-3,4-dione, 4a). Hydrolysis of 1.0 g of the cyclobutanol **3a** yielded a quantitative amount of the acid derivative **4a**: mp 162–164 °C dec (lit.[7] mp 162–164 °C dec); the IR and NMR were identical with those found in the literature.

2-Phenylsemisquaric Acid (1-Hydroxy-2-phenyl-1-cyclobutene-3,4-dione, 4c). Hydrolysis of 1.0 g of the phenyl-substituted cyclobutanol **3c** also yielded a quantitative amount of the solid acid **4c**: mp 208–211 °C (lit.[8] mp 208–211 °C).

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Registry No. 1a, 74176-08-2; **1b**, 74176-09-3; **1c**, 74176-10-6; **2a**, 74176-11-7; **2b**, 74176-12-8; **2c**, 74176-13-9; *cis*-**3a**, 74176-14-0; *trans*-**3a**, 74176-15-1; **3b**, 74176-16-2; *cis*-**3c**, 74176-17-3; *trans*-**3c**, 74176-18-4; **4a**, 29769-75-3; **4c**, 708-10-1; tetramethoxyethylene, 1069-12-1; α-chloropropionyl chloride, 7623-09-8; dichloroacetyl chloride, 79-36-7; α-chlorophenylacetyl chloride, 2912-62-1.

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(7) Chickos, J. S. *J. Am. Chem. Soc.* **1970**, *92*, 5749.

(8) Smutny, F. J.; Caserio, M. C.; Roberts, J. D. *J. Am. Chem. Soc.* **1960**, *82*, 1793.

Addition of Hydrohalogenic Acids to Alkenes in Aqueous–Organic, Two-Phase Systems in the Presence of Catalytic Amounts of Onium Salts

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In previous works[1,2] we reported that lipophilic quaternary ammonium and phosphonium salts show a high catalytic activity in reactions promoted by hydrohalogenic acids in aqueous–organic two-phase systems such as the conversion of alcohols to the corresponding halides[1] and the cleavage of ethers.[2] Recently quaternary ammonium salts were shown to extract hydrohalogenic acids from their aqueous solutions into low-polarity organic solvents.[3]

We here report that, under phase-transfer conditions, aqueous HCl, HBr, and HI are easily added to carbon–carbon double bonds according to Markovnikov's rule. Classically this reaction is carried on with gaseous hydrogen halides in peroxide-free polar solvents in the presence of radical scavengers.[4] The reaction can be much more advantageously accomplished by stirring at 115 °C (bath temperature) a heterogeneous mixture of the alkene (1 mol), the catalyst (0.1 mol), and the appropriate aqueous hydrohalogenic acid (3–15 mol) (see eq 1). Under these

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(1) Landini, D.; Montanari, F.; Rolla, F. *Synthesis* **1974**, 37.

(2) Landini, D.; Montanari, F.; Rolla, F. *Synthesis* **1978**, 771.

(3) Dehmlow, E. V.; Slopianka, M. *Chem. Ber.* **1979**, *112*, 2765.

(4) For reviews of addition of hydrogen halides to carbon–carbon double bonds, see: (a) Gould, E. S. "Mechanism and Structure in Organic Chemistry"; Holt, Reinehart, and Winston: New York, 1959; p 519, 732; (b) Roedig, A. "Methoden der Organischen Chemie (Houben-Weyl)"; 4th ed.; E. Müller, ed.; G. Thieme Verlag, Stuttgart, 1960; Vol. 5, Part 4, p 13; (c) Stroh, R. *Ibid.* 1962; Vol. 5, Part 3, p 523. (d) Stacey, F. W.; Harris, J. F. *Org. React.* **1963**, *13*, 150; (e) Buheler, C. A.; Pearson, D. E. "Survey of Organic Chemistry"; Wiley-Interscience: New York, 1970; Vol. 1, p 356.

0022-3263/80/1945-3527$01.00/0

Table I. Reactions of Alkenes (1 mol) with Aqueous Hydrohalogenic Acids in the Presence of Hexadecyltributylphosphonium Bromide (0.1 mol) at 115 °C (Bath Temperature)

substrate	HHal (amt, mol)	t, h	% yield conv[c]	% yield isol	product[a,b]
1-hexene[d]	HBr (5)	1	94	88	2-bromohexane
1-octene	HCl (15)	50	90	75	2-chlorooctane
1-octene	HBr (5)	2	94	88	2-bromooctane
1-octene	HI (3)	0.25	97	90	2-iodooctane
1-dodecene	HBr (5)	2	94	86	2-bromododecane
1-tetradecene	HBr (5)	2	94	86	2-bromotetradecane[e]
1-hexadecene	HBr (5)	2	94	86	2-bromohexadecane[f]
2-hexene[d]	HBr (5)	2	94	86	bromohexanes[g]
7-tetradecene	HBr (5)	5	94	86	7-bromotetradecane[h]
1-bromoundec-10-ene	HBr (5)	1.5	96	91	1,10-dibromoundecane
undec-10-en-1-ol	HBr (5)	2	99	93	1,10-dibromoundecane
undec-10-enoic acid	HBr (5)	0.5	99	95	10-bromoundecanoic acid
methylenecyclohexane	HBr (5)	1	96	84	1-bromo-1-methylcyclohexane
cyclohexene[i]	HBr (5)	0.1	94	90	bromocyclohexane
styrene	HCl (5)	1	99	90	1-chloro-1-phenylethane
styrene	HBr (5)	0.2	99	93	1-bromo-1-phenylethane
1,1-diphenylethylene	HBr (5)	24	0[j]		1,1-diphenyl-1-bromoethane
(*E*)-stilbene	HBr (5)	24	0[k]		1,2-diphenyl-1-bromoethane
(*Z*)-stilbene	HBr (5)	1	0[k]		1,2-diphenyl-1-bromoethane

[a] The products were characterized by comparing IR, NMR, GC, boiling or melting point, and n_D data with those of authentic samples. [b] Satisfactory analytical data (±0.4% for C and H) were reported for all new compounds. [c] Conversion yields as determined by NMR. [d] At 70 °C (bath temperature). [e] New compound: bp 160-161 °C (8 mm); n^{19}_D 1.4606. [f] New compound: bp 154-155 °C (6 mm); n^{24}_D 1.4573. [g] 2:1 mixture of 2-bromohexane and 3-bromohexane (by NMR). [h] New compound: bp 164-165 °C (13 mm); n^{19}_D 1.4620. [i] At 90 °C (bath temperature). [j] From the crude compound only tars were isolated. [k] From the crude compound only (*E*)-stilbene was isolated.

conditions the halo derivatives are obtained in nearly quantitative yields (Table I).

$$R^1R^2C{=}CHR^3(org) + HHal(aq) \xrightarrow[\Delta]{Q^+X^-} R^1R^2C(Hal)CH_2R^3(org) \quad (1)$$

R^1 = alkyl, aryl; R^2 = H, alkyl; R^3 =
H, alkyl, aryl; Hal = Cl, Br, I; Q = $(alkyl)_4N$, $(alkyl)_4P$

The reaction rate is not affected by the nature of the onium salt, provided it is insoluble in the aqueous phase (hexadecyltributylphosphonium bromide, tetraoctylammonium bromide, trioctylmethylammonium chloride). Tetrabutylammonium bromide and triethylbenzylammonium chloride, on the contrary, show a very low catalytic activity, due to their appreciable solubility in water. As expected, reaction times increase with decreasing amounts of onium salt, and in the absence of the latter the reaction is much slower (Table II).

Other crucial factors are the nature of the acid and the molar ratio of acid to substrate, from the practical point of view the most convenient ratios being 3, 5, and 15 in the case of HI, HBr, and HCl, respectively. Under these conditions the reactivity sequence is HI > HBr > HCl, in spite of the different acid/substrate ratio we used (Table I). Attempts to increase the reactivity of hydrobromic and hydrochloric acid by adding catalytic amounts of iodide ions to the reaction mixture failed.

Table II also shows the effect of the temperature on the reaction of 1-dodecene with hydrobromic acid. When the addition is carried out at 80, 100, and 115 °C (bath temperature), comparable yields (93–95%) are obtained in 24, 6, and 2 h, respectively. In all cases the NMR analysis showed that in the reactions only halo derivatives according to Markovnikov's rule had been formed, the same products being obtained even in the presence of catalytic amounts of peroxides.

Table II. Effect of the Amount of Hydrobromic Acid and Catalyst in the Reaction of 1-Dodecene (1 mol) at 115 °C (Bath Temperature)

mol of 48% HBr	mol of catalyst	t, h	% conv[a,b]
2	0.1[c]	8	86
3.5	0.1[c]	3	94
5	0.1[c,d]	2[e]	94
5	0.05[c]	2.5	94
5	0.01[c]	6	94
5	0	2	5
5	0.1[f]	8	43
5	0.1[g]	8	16

[a] The percent conversion as determined by NMR analysis. [b] The remaining material was unreacted starting material. [c] Hexadecyltributylphosphonium bromide. [d] The same result was also obtained with tetraoctylammonium bromide and trioctylmethylammonium chloride. [e] The same conversion was observed in 6 and 24 h at 100 and 80 °C (bath temperature), respectively. [f] Tetrabutylammonium bromide. [g] Triethylbenzylammonium chloride.

α-Olefins react 2–3 times faster than internal olefins. Among arylethylene derivatives, styrene reacts with HBr and HCl, giving the corresponding 1-phenyl-1-haloethane in quantitative yields in 0.2 and 1 h, respectively. Under the same conditions, 1,1-diphenylethylene gives only tars.

(*E*)-Stilbene with hydrobromic acid gives no reaction, while (*Z*)-stilbene is quantitatively isomerized to (*E*)-stilbene in 1 h. In the latter case, NMR analysis shows that after 0.5 h the organic phase contains a mixture of starting material, 1,2-diphenyl-1-bromoethane and (*E*)-stilbene in comparable amounts, and after 1 h it contains only (*E*)-stilbene. These data suggest that the *Z* → *E* isomerization proceeds at least partially via addition–elimination of HBr.

Undec-1-en-11-ol gives both addition to the double bond and conversion of the hydroxy group to bromide,[2] the former being complete in 20 min and the latter within 2 h (by NMR analysis).

In the cases of 1-hexane, 2-hexane, and cyclohexene (1 mol), reaction times in the presence of the catalyst (0.1 mol) are only 1.5–3-fold faster than in its absence. At their reflux temperature the addition reaction is complete within 1, 2, and 0.1 h, respectively (Table I). This is likely due to the partial solubility of the substrate in the aqueous phase.

Experimental Section

NMR spectra were recorded on a Varian EM-390 90-MHz spectrometer in CCl_4 solutions with Me_4Si as internal reference. IR spectra were measured as films on a Perkin-Elmer 377 grating spectrophotometer. GC data were obtained on a PYE Series 104 chromatograph using a 3% SE-30 on Chromosorb column.

The general procedure for the preparation of 2-bromododecane is as follows. A mixture of 16.8 g of 1-docecene (0.1 mol), 55.5 mL of 48% hydrobromic acid (0.5 mol), and 5.1 g of hexadecyltributylphosphonium bromide (0.01 mol) is heated at 115 °C (bath temperature) with magnetic stirring for 2 h. After this time, NMR analysis shows a 94% conversion into 2-bromododecane. The organic layer is separated, the aqueous phase is extracted with dichloromethane, and the solvent is evaporated. The resulting oil is distilled to give 21.4 g (86.0%) of pure 2-bromododecane: bp 125–126 °C (9 mm); n^{22}_D 1.4594 [lit.[5] bp 125–130 °C (10 mm); n^{21}_D 1.4600]. By treatment of the distillation residue with petroleum ether 4.8 g (94.0%) of phosphonium bromide [mp 52–54 °C (lit.[6] mp 54 °C)] is recovered, which can be reused without further purification.

In the case of lower boiling alkenes, the reactions are carried out at the reflux temperature of the substrate.

Registry No. 1-Hexene, 592-41-6; 1-octene, 111-66-0; 1-dodecene, 112-41-4; 1-tetradecene, 1120-36-1; 1-hexadecene, 629-73-2; 2-hexene, 592-43-8; 7-tetradecene, 10374-74-0; 1-bromoundec-10-ene, 7766-50-9; undec-10-en-1-ol, 112-43-6; undec-10-enoic acid, 112-38-9; methylenecyclohexane, 1192-37-6; cyclohexene, 110-83-8; styrene, 100-42-5; (*E*)-stilbene, 103-30-0; (*Z*)-stilbene, 645-49-8; 2-bromohexane, 3377-86-4; 2-chlorooctane, 628-61-5; 2-bromooctane, 557-35-7; 2-iodooctane, 557-36-8; 2-bromododecane, 13187-99-0; 2-bromotetradecane, 74036-95-6; 2-bromohexadecane, 74036-96-7; 7-bromotetradecane, 74036-97-8; 1,10-dibromoundecane, 74036-98-9; 10-bromoundecanoic acid, 18294-93-4; 1-bromo-1-methylcyclohexane, 931-77-1; bromocyclohexane, 108-85-0; 1-chloro-1-phenylethane, 672-65-1; 1-bromo-1-phenylethane, 585-71-7; 1,1-diphenylethylene, 530-48-3; HBr, 10035-10-6; HCl, 7647-01-0; HI, 10034-85-2.

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(5) Maekawa, E. *Nagoya Kogyo Diagaku Gakuho* **1954**, *271*, 6; *Chem. Abstr.* **1956**, *50*, 11943.

(6) Starks, C. M. *J. Am. Chem. Soc.* **1971**, *93*, 195.

Optimum HMO Parameters for the Three Models of the Methyl Group[1a]

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Over the years, hyperconjugation has remained one of the controversial topics in theoretical organic chemistry. Although it has been well established that in many cases the presence or absence of a methyl or other alkyl groups attached to a π-electron system does not significantly alter its physical and chemical properties, there are situations in which the effect of the methyl group clearly manifests itself. Heats of hydrogenation and combustion of alkenes, the red shift of the longest wavelength absorption bands in the electronic absorption spectra of alkenes and methylated aromatic hydrocarbons (in alkenes, the red shift is about 5 nm per methyl group), and the ionization potentials of methylated π-electron hydrocarbons can serve as examples. Hyperconjugation is believed to arise from an overlap of σ bonds in the alkyl substituent with the π system, i.e., with a $2p_z$ orbital of the adjacent carbon atom. Thus, it is obvious that, at least in some cases, it is important to include the methyl group(s) in the calculations when a theoretical treatment of such systems is being carried out.

Chart I

Conjugation Model ($C—Y—Z = C—C{\equiv}H_3$)

$\alpha_C = \alpha - 0.1\beta$ $\beta_{C-Y} = 0.8\beta$
$\alpha_Y = \alpha$ $\beta_{Y-Z} = 3.0\beta$
$\alpha_Z = \alpha - 0.5\beta$

Inductive Model

$\alpha_{C(Me)} = \alpha - 0.5\beta$ $\beta_{C-Me} = 0$

Heteroatom Model

$\alpha_{C(Me)} = \alpha - 0.2\beta$ $\beta_{C-Me} = 0.7\beta$
$\alpha_{Me} = \alpha + 2.0\beta$

At present, there are three models of the methyl group available within the framework of the simple HMO method. In the conjugation (or hyperconjugation) model, the methyl group is approximated as a modified attached vinyl group, C–Y–Z, where C is the π-network carbon atom to which the methyl group is attached, Y is the sp^3-hybridized carbon atom of the methyl group, and Z represents the three hydrogen atoms of the methyl group considered together as a pseudoatom ($CYZ = CC{\equiv}H_3$). In this model, the sp^3 carbon atom of the methyl group contributes one electron into the delocalized π system as well as do the three hydrogen atoms together.[2-4]

Another simple model of the methyl group, which is called the inductive model and is due to Wheland and Pauling[5] and Longuet-Higgins,[6,7] neglects any possible conjugation between the methyl group and the π system and considers only its inductive effect alone. In this model, the methyl group itself does not explicitly appear in the calculation, and its effect is reflected in the modified value of the Coulomb integral of the carbon atom to which it is attached. Finally, in the heteroatom model of the methyl group, the methyl group is taken as a pseudoheteroatom, Me, representing a π-electron center and contributing a pair of electrons to the π system.[8,9] The heteroatom model of the methyl group was also used in the PPP method.[10,11]

The parameters suggested for the three models of the methyl group have been summarized by Streitwieser[12] as shown in Chart I (α_X and β_{XY} are the Coulomb and resonance integrals, respectively).

Although the above parameters have been widely employed,[13-21] no parameter study has been carried out to

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(1) (a) Presented at the 179th National Meeting of the American Chemical Society, Houston, TX, Mar 23–28, 1980. (b) On leave of absence from the Department of Chemistry, Faculty of Science, University of Cairo, Giza, Egypt.

(2) R. S. Mulliken, C. A. Rieke, and W. G. Brown, *J. Am. Chem. Soc.*, **63**, 41 (1941).

(3) C. A. Coulson, *Q. Rev., Chem. Soc.*, 1, 144 (1947).

(4) C. A. Coulson, "Valence", Oxford University Press, London, 1952, pp 310–314.

(5) G. W. Wheland and L. Pauling, *J. Am. Chem. Soc.*, **57**, 2086 (1935).

(6) H. C. Longuet-Higgins, *J. Chem. Phys.*, **18**, 383 (1950).

(7) H. C. Longuet-Higgins, *Proc. R. Soc.* (*London*), **207**, 121 (1951).

(8) F. A. Matsen, *J. Am. Chem. Soc.*, **72**, 5243 (1950).

(9) R. Stevenson, personal communication. Cf. F. H. Field and J. L. Franklin, "Electron Impact Phenomena", Academic Press, New York, 1957, p 124.

(10) R. Phan-Tan-Luu, Doctoral dissertation (Docteur ès Sciences), Université de Provence, Marseille, France, 1967.

(11) Y. Ferré, Doctoral dissertation (Docteur ès Sciences), Université de Provence, Marseille, France, 1972.

(12) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists", Wiley, New York, 1961, p 135.

(13) J. Kuthan, J. Paleček, J. Procházková, and V. Skála, *Collect. Czech. Chem. Commun.*, **33**, 3138 (1968).

(14) J. Kuthan and J. Procházková, *Collect. Czech. Chem. Commun.*, **34**, 1190 (1969).