Table V. Results of Statistical Analysis of Experimental and Calculated Ionization Potentials[a]

model	compd	I	a	b	n	s	r
conjugation	butadienes + benzenes	I_1	0.828	1.451	15	0.427	0.588
		I_2	0.739	2.665	15	0.306	0.929
		I_3	0.732	3.041	7	0.208	0.881
inductive	butadienes	I_1	1.101	0.875	8	0.114	0.968
		I_2	0.462	5.751	8	0.159	0.831
	benzenes	I_1	0.954	0.339	7	0.129	0.942
		I_2	0.743	2.339	7	0.093	0.926
		I_3	0.408	6.636	7	0.135	0.848
heteroatom	ethylenes	I_1	0.992	0.075	6	0.082	0.996
	butadienes	I_1	0.869	1.117	8	0.066	0.975
		I_2	0.760	2.491	8	0.019	0.874
	benzenes	I_1	0.709	2.498	7	0.075	0.964
		I_2	0.617	3.402	7	0.079	0.923
		I_3	0.986	0.156	7	0.022	0.923

[a] Least-squares method. I_{exp} (eV) = aI_{calcd} (eV) + b. The other parameters are defined as follows: a, slope; b, intercept; n, number of points; s, standard error; r, correlation coefficient. With the exception of the first correlation (first line), all other data are significant on a 1% probability level.

eigenvector coefficients are obtained upon the choice of an initial set of parameters, and the final parameters are found after iteration to a self-consistent solution.

Table I summarizes the values of ionization potentials of various methyl-substituted ethylenes, butadienes, and benzenes and the respective literature sources as well as the calculated values obtained in the present study. The results of the calculations for the conjugation, inductive, and heteroatom models of the methyl group are given in Tables II–IV, respectively. In all cases, the final parameter values are those obtained after 20 iterations. The Coulomb integrals reflect the electron-donating character of the methyl group and its inductive effect, and the resonance integrals reflect its conjugative ability.[33]

The data obtained for the conjugation model (Table II) indicate that, instead of the hitherto accepted Coulomb integral for the H_3 pseudoatom, $\alpha_Z = \alpha - 0.5\beta$, a value of $\alpha - 2.3\beta$ should be used. The value of the resonance integral between the carbon atom and the H_3 pseudoatom of the methyl group remains almost unchanged, $\beta_{YZ} = 3.1\beta$, as compared to the originally suggested value, $\beta_{YZ} = 3.0\beta$. Statistical analysis of the results using the least-squares method for the regression line between experimental and calculated ionization potentials shows a poor correlation for the first ionization potentials but a very satisfactory correlation for the second and third ionization potentials (Table V). In the case of the inductive model, a satisfactory correlation is obtained both for methylated butadienes and for methylbenzenes (Table V). The optimum value of the Coulomb integral seems to be $\alpha_{\mathrm{C(Me)}} = \alpha - 0.6\beta$ rather than the originally proposed $\alpha_{\mathrm{C(Me)}} = \alpha - 0.5\beta$ (Table III).

The optimum values of the Coulomb and resonance integrals for the heteroatom model vary, depending on the structural type of the compounds studied (Table IV). This point should be emphasized and considered by anyone who wishes to calculate properties by using these parameters. Attempts to treat the individual groups of hydrocarbons (ethylenes, butadienes, benzenes) as a single group or to combine two groups into one lead to much poorer correlations and thus are generally unacceptable. However, our results and our previous experience indicate that the heteroatom model is the best generally applicable model of the methyl group. This can be seen from a comparison of the calculated and experimental ionization potentials summarized in Table I. We recommend the use of the heteroatom model and these parameters in future applications of this type.

Acknowledgment. This work was supported by the Robert A. Welch Foundation, Houston, TX. A.S.S. thanks the Robert A. Welch Foundation for a postdoctoral fellowship. Generous amounts of computer time were provided by the University of Texas at El Paso.

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[33] W. C. Herndon and C. Párkányi, *Tetrahedron*, 34, 3419 (1978).

Synthetic Methods and Reactions. 85.[1] Reduction of α-Halo Ketones with Sodium Iodide/Chlorotrimethylsilane

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Received February 8, 1980

Recently we reported[2] the reduction of α-halo ketones to their parent ketones by using sodium iodide and trimethyl(ethyl)amine–sulfur dioxide or pyridine–sulfur trioxide complexes in acetonitrile solution. Although open-chain aliphatic α-halo ketones were reduced at room temperature by using either of these reagents, α-halocycloalkanones needed prolonged heating to effect the reduction. We, therefore, were interested in finding other reagents, effective under less severe conditions and with shorter reaction times. We report now that, indeed, such a reagent has been found in chlorotrimethylsilane/sodium iodide in acetonitrile solution, which meets the above requirements and can be employed effectively for the reduction of both α-haloalkanones as well as α-halocycloalkanones (see Table I). Although there are several methods[2-4] available to bring about such conversions, we consider the present method a useful addition to them. Chlorotrimethylsilane/sodium iodide is readily available, is inexpensive, and gives excellent yields in simple and easy to carry out reactions under mild conditions.

In general, α-halogenated aliphatic ketones, upon treatment with sodium iodide and chlorotrimethylsilane in acetonitrile solution at room temperature, yield the corresponding parent ketones in 80–94% yield in 3–5 h. α-Halogenated cycloalkanones are reduced, however, at room temperature in the presence of excess of sodium iodide, and ketones are obtained in 75–98% yield in 8–12 h. 2-Chlorocyclopentanone and 2-chlorocyclohexanone are exceptions and require more time (ca. 48 h). The mechanism of the reduction may be represented as in Scheme I.

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[1] For part 84, see G. A. Olah, S. C. Narang, and G. F. Salem, *Synthesis*, in press.

[2] G. A. Olah, Y. D. Vankar, and A. P. Fung, *Synthesis*, 59 (1979), and references cited therein.

[3] Tein-Yan Luh, C. Lai, K. L. Lei, and S. W. Tam, *J. Org. Chem.*, 44, 641 (1979).

[4] H. Alper and L. Patee, *J. Org. Chem.*, 44, 2568 (1979).

[5] "Handbook of Chemistry and Physics", 55th ed., CRC Press, Cleveland, OH, 1974–1975.

[6] "Dictionary of Organic Compounds", Oxford University Press, New York, 1965.

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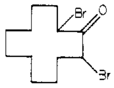
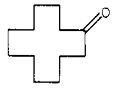
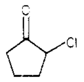
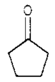
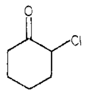
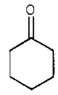
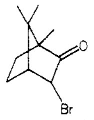
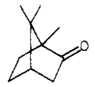
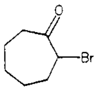
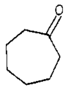
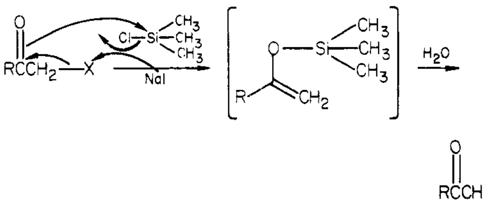
Table I. Reduction of α-Halo Ketones with Sodium Iodide/Chlorotrimethylsilane

substrate	ketone	amount (mmol) of reagent[c]		t, h/temp[d]	yield,[a,b] %	mp or bp/torr, °C	lit.[5,6] mp or bp/torr, °C
		$ClSi(CH_3)_3$	NaI				
$PhC(O)CH_2Br$	$PhC(O)CH_3$	15	15	5/rt	91	82/12	79/10
$PhC(O)CHBrPh$	$PhC(O)CH_2Ph$	15	15	3/rt	94	60.2	60-61
$PhC(O)CH_2Cl$	$PhC(O)CH_3$	15	15	4/rt	89	80-82/12	79/10
p-$PhPhC(O)CH_2Br$	p-$PhPhC(O)CH_3$	15	15	3/rt	93	120.5	120-121
		40	60	12/rt 2/reflux	98 98	60.7	59-61
		20	30	48/rt 3/reflux	75 78	128-129/760	130/760
		20	30	48/rt 3/reflux	72 78	48-49/15	47/15
		20	30	12/rt 2/reflux	89 87	176.8	175-179
$C_3H_7C(O)CH(Cl)C_3H_7$	$C_3H_7C(O)CH_2C_3H_7$	15	15	10/rt	85	50-52/15	70/26
$C_3H_7C(O)CH(Br)C_3H_7$	$C_3H_7C(O)CH_2C_3H_7$	15	30	8/rt	88	50-52/15	70/26
		20	30	8/rt	88	31-32/0.28	180/760

[a] Yields of the isolated products of ⩾99% purity as determined by TLC (benzene as eluent) and IR and NMR spectroscopy. [b] All physical data including IR and NMR spectra were consistent with the literature data. [c] In every case 10 mmol of substrate was used. [d] rt is room temperature.

Scheme I



Experimental Section

(A) General Procedure for Reduction of α-Halogenated Aliphatic Ketones. To a solution of corresponding α-halo ketone (10 mmol) in dry acetonitrile (15 mL) is added a solution of sodium iodide (15 mmol) dissolved in acetonitrile (15 mL) at room temperature, and the mixture is stirred for 5 min. A solution of chlorotrimethylsilane (15 mmol) in acetonitrile (5 mL) is then added to the above mixture, and this is stirred at room temperature until the reaction is completed (monitored by TLC and NMR spectroscopy). The reaction mixture is then poured into a 10% aqueous solution of sodium thiosulfate, which removes the iodine liberated in the reaction and discharges the brown color of the solution. The colorless mixture is extracted with ether (3 × 25 mL), washed with water (2 × 25 mL) followed by brine (15 mL), and dried over anhydrous sodium sulfate. Evaporation of the solvent under vacuum gives almost pure reduced product, which is further purified by distillation or recrystallization and identified by physical and spectral characteristics.

General Procedure for Reduction of α-Halogenated Cycloalkyl Ketones. To a magnetically stirred solution of the corresponding α-halocycloalkyl ketone (10 mmol) in dry acetonitrile is added a solution of sodium iodide (30 mmol) in acetonitrile (20 mL), and the mixture is stirred for 5 min. A solution of chlorotrimethylsilane (20 mmol) in acetonitrile (5 mL) is then added to the above mixture while stirring is continued at room temperature until completion of the reaction. The workup is done according to the same procedure as that described previously for α-halogenated aliphatic ketones.

Acknowledgment. Support of our work by the National Institutes of Health and the National Science Foundation is gratefully acknowledged.

Registry No. 2-Bromoacetophenone, 70-11-1; 2-bromo-2-phenylacetophenone, 1484-50-0; 2-chloroacetophenone, 532-27-4; 2-bromo-4′-phenylacetophenone, 135-73-9; 2,12-dibromocyclododecanone, 24459-40-3; 2-chlorocyclopentanone, 694-28-0; 2-chlorocyclohexanone, 822-87-7; 3-bromo-2-bornanone, 76-29-9; 5-chloro-4-octanone, 24251-73-8; 5-bromo-4-octanone, 61539-87-5; 2-bromocycloheptanone, 766-65-4; acetophenone, 98-86-2; 2-phenylacetophenone, 451-40-1; 4′-phenylacetophenone, 92-91-1; cyclododecanone, 830-13-7; cyclopentanone, 120-92-3; cyclohexanone, 108-94-1; camphor, 76-22-2; 4-octanone, 589-63-9; cycloheptanone, 502-42-1; sodium iodide, 7681-82-5; chlorotrimethylsilane, 75-77-4.

Synthetic Methods and Reactions. 86.[1] Novel Synthesis of *N*-(1-Adamantyl)amides from Adamantane

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Received February 8, 1980

Recently we reported[2] a convenient and mild Ritter-type synthesis of amides from alkyl(arylalkyl) halides using $NO^+PF_6^-$ as the halide-abstracting reagent in the presence of nitriles. A similar reaction has been reported to take

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[1] For part 85, see G. A. Olah, M. Arvanaghi, and Y. D. Vankar, *J. Org. Chem.*, previous paper in this issue.

[2] G. A. Olah, B. G. B. Gupta, and S. C. Narang, *Synthesis*, 274 (1979). Also see B. G. Balaram Gupta, Ph.D. Thesis, University of Southern California, 1979.

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