149.2 (^{2}D) and 174.2 nm (^{2}P), serves as the resonance lamp. Since both transitions have a common upper state, one or the other multiplet must be isolated in a given experiment; i.e., for N(^{2}P) detection, a Suprasil-2 quartz window passes 174.2- but blocks 149.2-nm radiation, and for N(^{2}D) a band rejection filter (Acton Research Corp.) passes only 149.2-nm radiation. Since the fluorescence is emitted at both multiplets, the signal is monitored at a wavelength other than that used to excite the fluorescence with a resultant improvement in scattered light suppression. A 0.5-m vacuum monochromator (Jarrell-Ash, Model 84-110) and solar blind photomultiplier (EMR, Model 541-GX) are used to measure the resonance absorption or fluorescence signals at the downstream end of the 2.5-cm i.d. flow tube. Absorption of radiation by Cl_2 at 149.2 and 174.2 nm was found to be negligible over the range of concentrations used.

Atomic species are produced in a microwave discharge 26 cm upstream of the fluorescence cell in flowing Ar ($\sim$3 Torr) containing $\sim$1% N_2. Cl_2 ($\leq$1% in Ar) is added 14 cm upstream of the cell through a multiperforated, fast-mixing glass loop. Typical Cl_2 concentrations range from 8 to 80×10^{12} cm^{-3} for the fast metastable reactions and from 1 to 25×10^{14} for the slow N(^{4}S) reaction. Reaction times are 4.5 ms for the metastable and 50 ms for the ground-state reaction. Earlier experiments in which the discharge atom source was moved had shown that metastables are efficiently removed by surface deactivation whereas N(^{4}S) persists with negligible loss. For the metastable reactions it is important to know whether laminar flow is established in the reaction region,[5] since fully laminar flow introduces a factor of 1.6 by which the "plug-flow" rate constant must be multiplied for species whose concentration near the surface is zero. Our flow conditions are intermediate between plug- and laminar flow for M = Ar, whereas for M = He they are calculated to be purely laminar.[5] This was confirmed by studies of N(^{2}D and ^{2}P) with O_2 which gave consistent k's when factors of 1.3 and 1.6 were used for M = Ar and He, respectively. The metastable + Cl_2 rate constants reported here use the factor 1.3, but, since its total range is 1.0 to 1.6, a maximum error of 30% may be incurred.

Accurately linear plots of $\ln I_F$ vs. $[Cl_2]$ (I_F = resonance fluorescence signal) for six series of experiments, each consisting of five to six different Cl_2 additions, gave $k_{2D} = (3.60 \pm 0.4) \times 10^{-11}$ cm^3 s^{-1}, where the k's are the slopes multiplied by 1.3 and divided by the average reaction time, t. The individual experiments gave rate constants of 3.53, 4.19, 3.17, 3.68, 3.42, and 3.36×10^{-11} cm^3 s^{-1} with correlation coefficients of 0.970 to 0.998 for the least-squares fits of the linear $\ln I_F$ vs. $[Cl_2]$ plots. Similar experiments for N(^{2}P) gave $k_{2P} = 2.16 \pm 0.2 \times 10^{-11}$ cm^3 s^{-1} from individual values of 2.08, 2.12, 2.39, and 2.05×10^{-11} cm^3 s^{-1} with correlation coefficients of 0.990 to 0.998.

For the very much slower N(^{4}S) reaction, [N(^{4}S)] was monitored by the intensity of the (11, 7) band of the first positive system ($B^3\Pi - A^3\Sigma_u^+$) of N_2 whose intensity is known to be proportional to $[N]^2$ under these conditions.[6] It was also assumed that the reaction product, NCl, reacts rapidly with excess N(^{4}S) so that k_{4S} is given by $1/4t$ times the slope of the semilog plot of intensity vs. $[Cl_2]$. Because of the low flow velocity in these experiments, the N-metastable concentrations will have decayed to negligibly small values before Cl_2 is added to the flow. Three N(^{4}S) experiments gave $k_{4S} = 2 \times 10^{-15}$ cm^3 s^{-1}. This is likely to be an upper limit, since our brief investigation did not fully eliminate small changes in the surface properties of the flow tube that may contribute to the slow observed decay.

It has been shown[7] that a small amount of N(^{2}P) is produced from N(^{4}S) in the nitrogen afterglow, presumably by reaction of N(^{4}S) with $N_2(A^3\Sigma_u^+)$. The corresponding [N(^{2}P)] should therefore be proportional to $[N(^4S)]^2$, and relatively constant as a consequence of the slow decay of N(^{4}S). This steady-state [N(^{2}P)] is much smaller than that formed in the discharge source as evidenced by the measured linear semilog decay of [N(^{2}P)], without showing any leveling off, when the discharge source was moved along the flow tube.

Whether the observed removal of N(^{2}D or ^{2}P) by Cl_2 is due to quenching or chemical reaction is now also being investigated by monitoring the Cl-atom concentration in its $^2P_{3/2}$ and $^2P_{1/2}$ states by resonance absorption at 134.7 and 136.3 nm.[8] Early results indicate extensive reaction, i.e., a sharp rise of the Cl-absorption signal leveling off at a constant value as more Cl_2 is added. The Cl-atom yield, the $^2P_{1/2}$ to $^2P_{3/2}$ concentration ratio, and the contribution of the $NCl + N(^4S) \rightarrow N_2 + Cl$ reaction are still under investigation.

Potentially interfering reactions of N(^{2}D, ^{2}P) are easily shown to be much too slow to perturb the observed N-metastable decays. The present experiments thus provide species-selective, elementary reaction rate constants at 298 K, and they are easily extendable to higher and lower temperatures. They show the considerable power of the flow tube technique in the study of bimolecular reactions.

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References

(1) R. L. Love, J. M. Herrmann, R. W. Bickes, Jr., and R. B. Bernstein, *J. Am. Chem. Soc.*, **99**, 8316 (1977).
(2) K. S. Raworthy and L. F. Phillips, *Can. J. Chem.*, **42**, 2928 (1964).
(3) M. R. Grigor and L. F. Phillips, 11th Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pa., 1967, p 1171.
(4) C. L. Lin and F. Kaufman, *J. Chem. Phys.*, **55**, 3760 (1971).
(5) E. E. Ferguson, F. C. Fehsenfeld, and A. L. Schmeltekopf, *Adv. At. Mol. Phys.*, **5**, 1 (1969).
(6) M. F. Golde and B. A. Thrush, *Rep. Prog. Phys.*, **36**, 1285 (1973).
(7) M. F. Golde and B. A. Thrush, *Faraday Discuss. Chem. Soc.*, **53**, 233 (1972).
(8) M. A. Clyne and W. S. Nip, *J. Chem. Soc., Faraday Trans. 2*, **73**, 161 (1972); M. S. Zahniser and F. Kaufman, *Chem. Phys. Lett.*, **37**, 226 (1976).

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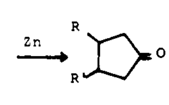
A Versatile Three-Carbon Annelation. Synthesis of Cyclopentanones and Cyclopentanone Derivatives from Olefins[1]

Sir:

Four-carbon annelation reactions have been extensively studied and are of general importance in the construction of complex organic molecules.[2] In contrast, there are few *generally useful* three-carbon annelation processes,[2,3] in spite of the widespread presence of the cyclopentane ring in many classes of natural products. In this communication, we present a simple, yet versatile, synthesis from olefins of cyclopentanones and various cyclopentanone derivatives, which we believe will offer an attractive alternative to existing three-carbon annelation methods.

The procedure (eq 1), formally a [3 + 2] cycloaddition, is



(1)

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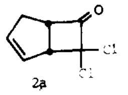
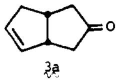
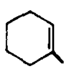
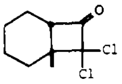
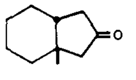
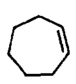
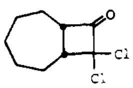
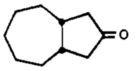
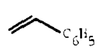
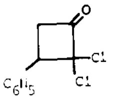
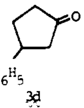
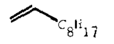
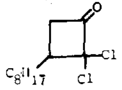
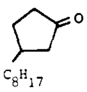
Table I. Formation of Cyclopentanones from Olefins

olefin	dichlorocyclobutanone	method,[a] % yield[b,c]	cyclopentanone	% yield[b,c]	overall yield[b,c] from olefin **1**
 **1a**	 **2a**	A, 88[d]	 **3a**	70[e]	62
 **1b**	 **2b**	B, 83[f]	 **3b**	71[g]	59
 **1c**	 **2c**	B, 85	 **3c**	64[h]	54
 **1d**	 **2d**	B, 88[i]	 **3d**	82[j]	72
 **1e**	 **2e**	B, 88	 **3e**	75[k]	66

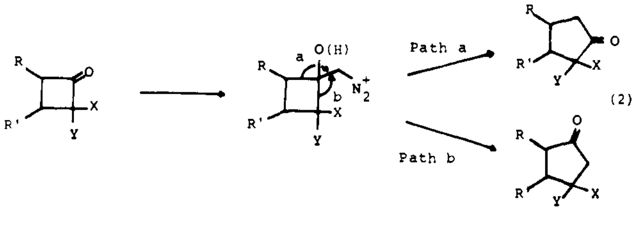
[a] Method A (ref 4c): $Cl_2CHCOCl$, Et_3N, pentane, reflux. Method B (ref 4d): Cl_3CCOCl, Zn–Cu, $POCl_3$, Et_2O, reflux. [b] Yields are for isolated pure products, except for **3a** where the yield is by calibrated VPC. [c] Reference 7. [d] Reference 4a,c. [e] J. D. Roberts and W. F. Gorham, *J. Am. Chem. Soc.*, **74**, 2278 (1952); L. A. Paquette, O. Cox, M. Oku, and R. Henzel, *ibid.*, **96**, 4892 (1974). [f] Reference 4d. [g] P. T. Lansbury and E. J. Nienhouse, *J. Am. Chem. Soc.*, **88**, 4290 (1966); B. E. Ratcliffe and C. H. Heathcock, *J. Org. Chem.*, **37**, 531 (1972); R. C. Clark and C. H. Heathcock, *ibid.*, **41**, 1396 (1976). [h] R. Granger, H. Orzalesi, and J. P. Chapat, *Bull. Soc. Chim. Fr.*, 1951 (1967); A. M. Islam and R. A. Raphael, *J. Chem. Soc.*, 3151 (1955); ref 3a. [i] Reference 4b,d. [j] H. A. Weidlich and G. H. Daniels, *Chem. Ber.*, **72**, 1590 (1939); ref 3a, 6. [k] K. Sakai, J. Ode, O. Oda, and N. Nakamura, *Tetrahedron Lett.*, 1287 (1972).

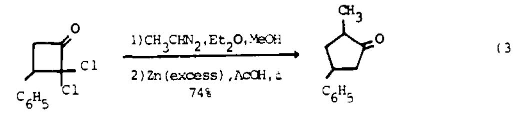
based on the finding that α,α-dichlorocyclobutanones, readily available cycloaddition adducts,[4] cleanly undergo very rapid, highly regioselective, one-carbon ring expansion reactions with diazomethane to produce the corresponding α,α-dichlorocyclopentanones. These, in turn, can be readily dechlorinated with zinc or subjected to other useful transformations (vide infra).

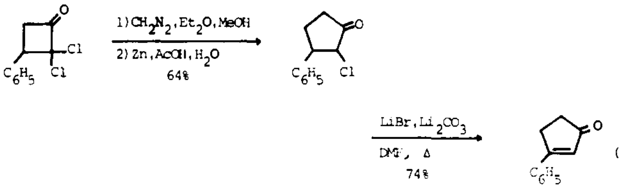
Table I presents the dichlorocyclobutanones **2a–e** that have been homologated and the cyclopentanones **3a–e** that have been obtained following dechlorination (same "pot") and chromatographic purification on silica gel. The following three-carbon annelation is representative and illustrates the simplicity of this method: 2,2-dichloro-3-phenylcyclobutanone (1.08 g, 5.0 mmol), readily secured from styrene via cycloaddition with dichloroketene,[4d] was treated with 40 mL of ethereal diazomethane (ca. 0.2 M, generated from Diazald[5]) followed by 2 mL of methanol. Immediately, a brisk evolution of nitrogen ensued. After 20 min, the remaining diazomethane was destroyed with a few drops of acetic acid and the solvent was evaporated. The resulting crude 2,2-dichloro-3-phenylcyclopentanone (IR 1770 cm^{-1}) was treated with 2.0 g of Zn powder in 7 mL of acetic acid at 70 °C for 1.5 h. The usual workup followed by purification on silica gel afforded 662 mg (82%) of pure 3-phenylcyclopentanone (semicarbazone; mp 181–182 °C, lit.[6] 181 °C).[7]

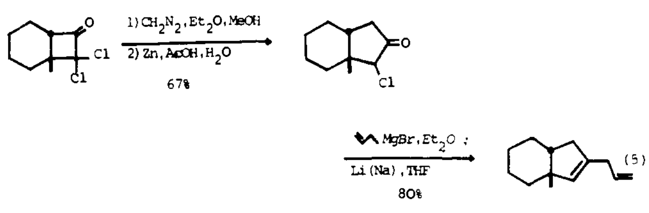
Previously, in the context of our work with 11-norprostaglandins,[8] we had examined the ring expansion reactions of certain alkyl-substituted cyclobutanones with diazomethane[9] (Et_2O, MeOH, room temperature) and found that, although the ring expansions proceeded quite cleanly to afford the corresponding cyclopentanones, there was not a high degree of regioselectivity in the migration (eq 2, X = Y = H, path a vs. path b).[10,11] As one might expect on the basis of electronic effects, however, that the presence of α-chlorine substituent(s) (X,Y = H,Cl or X = Y = Cl) not only accelerates the rate of this reaction, but also serves to favor path a over path b.[9,12,13] Epoxide formation is not significant, probably because of the strained nature of the four-membered ring,[14] in spite of the fact that epoxide formation generally increases with the introduction of negative substituents adjacent to the carbonyl.[9]

In our opinion, this annelation method offers several distinct advantages over existing procedures. The reaction sequence, which is operationally very simple and requires only inexpensive, commercially available reagents, affords products in overall yields *based on the starting olefins* that are in general









considerably higher than those obtainable using other methods. In addition, the mild reaction conditions should permit the presence of additional functionality in the substrate. Furthermore, and most importantly, the highly versatile intermediates in this synthesis offer the possibility of effecting a myriad of other synthetically important transformations in conjunction with those discussed above. For example, the α,α-dichlorocyclobutanones are transformed regioselectively and in high yield to α-substituted cyclopentanones (eq 3),[15] and the readily prepared α-chlorocyclopentanones can be easily converted to pure enones (eq 4)[16] and olefins (eq 5).[17] Of course, there are also numerous other possibilities.[18]

Extensions and applications of this work will be the subjects of future reports.

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References and Notes

(1) Contribution No. 39 from the Laboratoire de Chimie Organique, CERMO. For No. 38, see: P. Baret, E. Barreiro, A. E. Greene, J. L. Luche, M. A. Teixeira, and P. Crabbé, *Tetrahedron*, in press.

(2) See M. E. Jung, *Tetrahedron*, **32**, 3 (1976), and references cited.

(3) (a) M. E. Jung and J. P. Hudspeth, *J. Am. Chem. Soc.*, **99**, 5508 (1977); (b) Y. Hayakawa, K. Yokoyama, and R. Noyori, *ibid.*, **100**, 1791 (1978); (c) A. Marfat and P. Helquist, *Tetrahedron Lett.*, 4217 (1978); (d) T. Hiyama, M. Shinoda, and H. Nozaki, *ibid.*, 771 (1978); (e) E. J. Corey and D. L. Boger, *ibid.*, 13 (1978); (f) R. M. Jacobson, A. Abbaspour, and G. P. Lahm, *J. Org. Chem.*, **43**, 4650 (1978); R. M. Jacobson and G. P. Lahm, *ibid.*, **44**, 462 (1979); (g) B. M. Trost, Y. Nishimura, and K. Yamamoto, *J. Am. Chem. Soc.*, **101**, 1328 (1979), and references cited.

(4) (a) H. C. Stevens, D. A. Reich, D. R. Brandt, K. R. Fountain, and E. J. Gaughan, *J. Am. Chem. Soc.*, **87**, 5257 (1965); (b) W. T. Brady and O. H. Waters, *J. Org. Chem.*, **32**, 3703 (1967); W. T. Brady, *Synthesis*, 415 (1971); D. A. Bak and W. T. Brady, *J. Org. Chem.*, **44**, 107 (1979); (c) L. Ghosez, R. Montaigne, A. Roussel, H. Vanlierde, and P. Mollet, *Tetrahedron*, **27**, 615 (1971); R. A. Minns, *Org. Synth.*, **57**, 117 (1977); (d) L. R. Krepski and A. Hassner, *J. Org. Chem.*, **43**, 2879, 3173 (1978).

(5) *N*-Methyl-*N*-nitroso-*p*-toluenesulfonamide, Aldrich Chemical Co., Milwaukee, Wis.

(6) W. Borsche and W. Menz, *Chem. Ber.*, **41**, 190 (1908); W. Baker and W. G. Leeds, *J. Chem. Soc.*, 974 (1948).

(7) All compounds displayed spectral properties in full agreement with the assigned structures. Crystalline derivatives had melting points in accord with those reported in the literature. No attempt has been made to maximize any yield reported in this communication.

(8) A. E. Greene, J. P. Deprés, M. C. Meana, and P. Crabbé, *Tetrahedron Lett.*, 3755 (1976); A. E. Greene, J. P. Deprés, H. Nagano, and P. Crabbé, *ibid.*, 2365 (1977).

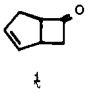
(9) For general reviews of the diazomethane ring expansion reaction, see: C. D. Gutsche, *Org. React.*, **8**, 364 (1954); G. D. Gutsche and D. Redmore, "Carbocyclic Ring Expansion Reactions", Academic Press, New York, 1968, Chapter IV; G. W. Cowell and A. Ledwith, *Q. Rev. Chem. Soc.*, **24**, 119 (1970); J. S. Pizey, "Synthetic Reagents 2", Wiley, New York, 1974, Chapter 2.

(10) For example, treatment of 11-nor-PGE_2 methyl ester with diazomethane in Et_2O–MeOH cleanly produced a ca. 2:1 mixture of methyl 15α-hydroxy-10-oxoprosta-5,13-dienoate and 11-deoxy-PGE_2 methyl ester, respectively, in 75% isolated yield.[8] In contrast to certain literature reports,[11a,b] we have found that, in general, diazomethane can quite effectively produce cyclopentanones from cyclobutanones in yields after purification of up to 75%.

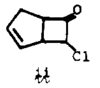
(11) For a frequently regioselective, one-carbon homologation of ketones, including *certain* cyclobutanones, using diazoacetic ester and triethyloxonium fluoroborate or boron trifluoride etherate, see: (a) W. L. Mock and M. E. Hartman, *J. Org. Chem.*, **42**, 459, 466 (1977); (b) D. Farcasiu, P. v. R. Schleyer, and D. B. Ledlie, *ibid.*, **38**, 3455 (1973), and references cited; (c) H. J. Liu and T. Ogino, *Tetrahedron Lett.*, 4937 (1973).

(12) B-W. Au-Yeung and I. Flemming, *J. Chem. Soc., Chem. Commun.*, 81 (1977). This is the only previous example of which we are aware of a ring expansion reaction of an α-chlorocyclobutanone using a diazoalkane. The directing effect of the α-chlorine substituent has also been used to advantage in the synthesis of γ-lactones: S. M. Ali and S. M. Roberts, *ibid.*, 887 (1975); B-W. Au-Yeung and I. Flemming, *ibid.*, 79 (1977); A. Hassner, H. W. Pinnick, and J. M. Ansell, *J. Org. Chem.*, **43**, 1774 (1978).

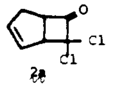
(13) In the only series examined, cyclobutanones i, ii, and **2a** afforded, re-



i



ii



2a

spectively, ca. 55:45, 90:10, and 95:5 mixtures of cyclopentanone **3a** and its isomer (cf. footnote *e* in Table I). We, therefore, chose to work with the more accessible dichlorides. In no case starting from the dichlorides **2** have we observed >5% of any isomeric impurity in the final product **3.**

(14) J. Jaz and J. P. Davreux, *Bull. Soc. Chim. Belg.*, **74**, 370 (1965); G. Fachinetti, F. Pietra, and A. Marsili, *Tetrahedron Lett.*, 393 (1971).

(15) J. A. Marshall and J. J. Partridge, *J. Org. Chem.*, **33**, 4090 (1968). A 4:1 mixture of stereoisomers is produced (which is the thermodynamic ratio).

(16) See C. Djerassi, "Steroid Reactions", Holden-Day, San Francisco, 1963, Chapter 4, and references cited.

(17) J. Barluenga, M. Yus, and P. Bernad, *J. Chem. Soc., Chem. Commun.*, 847 (1978).

(18) These include: oxidative cleavage [J. San Filippo, C-I. Chern, and J. S. Valentine, *J. Org. Chem.*, **41**, 1077 (1976)]; cuprate coupling [O. P. Vig, J. C. Kapur, and S. D. Sharma, *J. Indian Chem. Soc.*, **45**, 734, 1026 (1968); O. P. Vig, S. D. Sharma, and J. C. Kapur, *ibid.*, **46**, 167 (1969)]; epoxide formation [ref 16, Chapter 14]; Baeyer–Villiger oxidation [ref 12 and P. Wieland and K. Miescher, *Helv. Chim. Acta*, **32**, 1768 (1949)]; enone alkylation [M. A. Guaciaro, P. M. Wovkulich, and A. B. Smith, III, *Tetrahedron Lett.*, 4661 (1978)].

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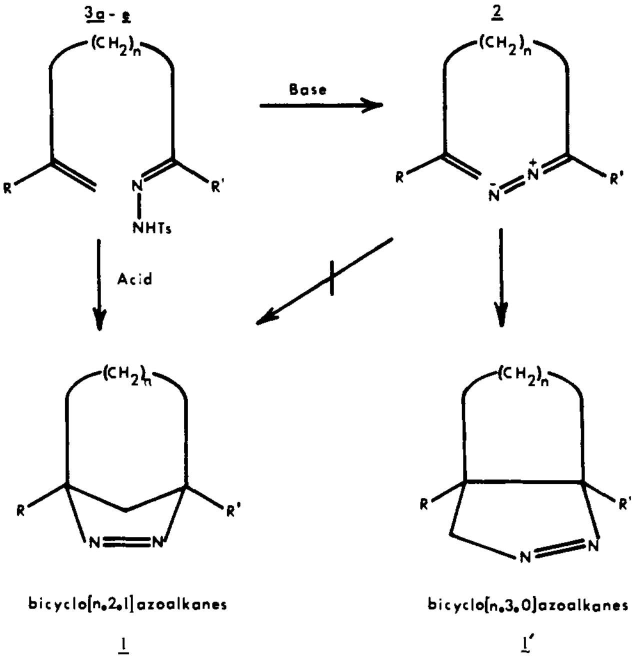
Cyclization of Olefinic Tosylhydrazones under Acidic Conditions. A Facile Synthesis of Bicyclic Azo Compounds

Sir:

Bicyclic azo compounds have attracted a great deal of interest during the past few years since they have been found to serve as stable analogues of prostaglandin endoperoxides,[1] to exhibit unusual electronic absorption properties,[2] and to serve as precursors for a wide variety of theoretically intriguing and synthetically useful biradicals.[3] We have become interested in bicyclo[*n*.2.1] azo compounds as starting materials for the synthesis of unusual bicyclic peroxides.[4] This report describes a facile synthesis of symmetrical and unsymmetrical azo compounds via a unique reaction of tosylhydrazones.

A particularly appealing route to bicyclo[*n*.2.1] azo compounds (**1**) would seem to be the intramolecular 1,3-dipolar cycloaddition of diazoalkenes (**2**) (Scheme I). However, previous workers[5] have only been able to realize dipolar additions of this type in low yields and then have only observed the bicyclo[*n*.3.0] adducts **1′**, rather than the desired bicyclo[*n*.2.1]

Scheme I



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