Table I. Nmr and Activation Parameters for *tert*-Butyl Rotation in 2-*tert*-Butyl 1,3-Diheteroatomic Rings

Compd	Chemical shifts of *t*-Bu peaks at slow exchange, Hz, 60 MHz	$\Delta G^{\ddagger}$, kcal/mol (temp, °C)	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
1[a]	65.1 (6 H), 78.8 (3 H)	9.6 ± 0.1 (−83.5)	9.9 ± 0.3	1.4 ± 2.0
2[b]	75.0 (3 H), 65.0 (6 H)	10.6 ± 0.1 (−70.2)		
3[b]	63.1 (6 H), 59.1 (3 H)	7.5 ± 0.2 (−133.2)		
4[b]	62.8 (3 H), 62.3 (3 H), 59.7 (3 H)	9.8 ± 0.1 (−101.2)		
5[b]	65.0 (3 H), 56.5 (3 H), 54.5 (3 H)	7.0 ± 0.2 (−139.6)		
6[a]	60.5 (3 H), 54.2 (6 H)	8.7 ± 0.1 (−109.8)		
7[b]	58.5 (6 H), 52.6 (3 H)	7.5 ± 0.1 (−124.7)	7.5 ± 0.3	0 ± 2.0

[a] 5% v/v in CH_2CHCl. [b] 5% v/v in $CBrF_3$.

Perusal of Table I reveals some expected and some unusual trends. First, we have completed the line-shape analysis at several temperatures for **1** and **7** revealing very small entropies of activation ($\Delta S^{\ddagger}$) for *tert*-butyl rotation. Thus, it may be assumed in this series that the free energy of activation ($\Delta G^{\ddagger}$) is a good estimate of the enthalpy of activation ($\Delta H^{\ddagger}$) for *tert*-butyl rotation. The higher barriers to *tert*-butyl rotation in **2** and **4** as compared to **3** and **5**, respectively, are clearly consistent with not unexpected increased nonbonded repulsions in the eclipsed transition state involving methyl as compared to hydrogen. The barriers to *tert*-butyl rotation for the two essentially strain-free 6-rings (**1**, **6**) reveal sulfur to be more effective than oxygen in hindering *tert*-butyl rotation. This observation obviously could be rationalized by the larger van der Waals radius for sulfur leading to enhanced repulsions in **1** as compared to **6** in the eclipsed transition state and is consistent with a greater preference of sulfur for the equatorial *vs.* the axial position in monosubstituted cyclohexanes, *e.g.*, SCD_3 ($\Delta G°_{ae} = -1.07$ kcal/mol at −79°)[7] and OCD_3 ($\Delta G°_{ae} = -0.55$ kcal/mol at −82°).[7] However, the higher barrier in **1** as compared to **6** could also be due in part to a larger SCS angle (*ca.* 115°)[8] in **1** rendering the sulfurs in close proximity to *tert*-butyl in **1** as compared to **6** in which the OCO angle (*ca.* 111°) is smaller.[9]

Ostensibly, the nonbonded repulsions hindering *tert*-butyl rotation should be similar in **6** and **7**, but the barrier in **7** is significantly lower than that in **6**. Whether one assumes the 5-ring conformation in **7** to be the half-chair or envelope,[4] examination of models and vector analysis indicate that incorporation of the CH_2CH_2 fragment into the 5-ring requires a "pinning back" of the oxygen atoms, *i.e.*, a closing of the angle γ in **7** as compared to the OCO angle in **6**. A corollary effect to the closing of the angle γ in **7** is an opening of the angle θ in **7** (geminal dialkyl effect[10]). The net result of these bond angle adjustments is to move the oxygen atoms and methyl group in **7** further away from *tert*-butyl and lower the barrier as compared to **6**. This trend is analogous to *tert*-butyl rotation in *tert*-butylcyclopentane ($\Delta G^{\ddagger} \sim 6.0$ kcal/mol at −155°),[11] *tert*-butylcyclohexane ($\Delta G^{\ddagger} \sim 6.3$ kcal/mol at −150°),[11] and *tert*-butylcycloheptane ($\Delta G^{\ddagger} = 7.4$ kcal/mol at −126°).[11] A similar analysis of **2** indicates that despite the smaller preferred CSC bond angle (100°)[8] and longer C–S bond length (1.82 Å)[8] as compared to the preferred COC bond angle (111°)[9] and shorter C–O bond length (1.43 Å),[9] there results a pinning back of the sulfur atoms in the preferred half-chair form of **2**[4] to an even greater extent than the oxygen atoms in **7**. Presumably, this would lead to bond angle adjustments (α and β in **2**) analogous to those in **7**. However, the "anomalously" higher barrier in **2** as compared to **1** is a reversal of the trend in **6** and **7** as well as in the *tert*-butylcycloalkanes. The rationale for this behavior is not totally clear. Predictably, the barrier to *tert*-butyl rotation in **4** is between **2** and **7**.

Thus, it is clear that conformational adjustments in rings dictated by bond angle and bond length requirements can have a profound and not necessarily consistent effect on the conformational dynamics of attached substituents.

Acknowledgment. We are grateful to the National Science Foundation (GP-18197) for support and to Dr. S. J. Weininger for stimulating suggestions.

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[8] C. H. Bushweller, *Int. J. Sulfur Chem.*, **5**, 75 (1970).

[9] E. L. Eliel, *Accounts Chem. Res.*, **3**, 1 (1970).

[10] T. C. Bruice and W. C. Bradbury, *J. Amer. Chem. Soc.*, **90**, 3808 (1968), and references therein.

[11] F. A. L. Anet, M. St. Jacques, and G. N. Chmurny, *ibid.*, **90**, 5243 (1968).

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Hydrogen-Bonded Complex Formation as Evidenced by Solvatochromic Shifts

Sir:

Enhanced bathochromic shifts for 4-nitroaniline (**1**) relative to *N*,*N*-diethyl-4-nitroaniline (**2**) [$-\Delta\Delta\nu$(**1**–**2**)] and for 4-nitrophenol (**3**) relative to 4-nitroanisole (**4**) [$-\Delta\Delta\nu$(**3**–**4**)] on going from cyclohexane to a series of alcohol solvents have been represented[1] as arising from hydrogen bonding *by* **1** and **3** *to* the alcohols, with the magnitudes of the $-\Delta\Delta\nu$ values considered to be measures of relative solvent proton affinities. Good linear correlations were noted between the $-\Delta\Delta\nu$ values and σ^* values of R in ROH.

We wish now to report that, on going from cyclohexane to a number of non-self-associating solvents of various types, $-\Delta\Delta\nu$(**1**–**2**) and $-\Delta\Delta\nu$(**3**–**4**) values show good linear correlation with pK_{HB} values (logarithms of formation constants)[2] and excellent linear correlation with Δ values (limiting F nmr shifts)[3] for hydrogen-

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[1] R. R. Minesinger, E. G. Kayser, and M. J. Kamlet, *J. Org. Chem.*, **36**, 1342 (1971).

[2] R. W. Taft, D. Gurka, L. Joris, P. von R. Schleyer, and J. W. Rakshys, *J. Amer. Chem. Soc.*, **91**, 4801 (1969).

[3] D. Gurka and R. W. Taft, *ibid.*, **91**, 4794 (1969).

bonded complex formation by the same bases with *p*-fluorophenol, as reported by Taft and coworkers. The data are assembled in Table I and the $-\Delta\Delta\nu(\mathbf{1}\text{–}\mathbf{2})$ *vs.* pK_{HB} results are plotted in Figure 1.

Table I. Enhanced Bathochromic Shifts Compared with pK_{HB} and Δ Values

No.	Solvent	$-\Delta\Delta\nu$-(**1**–**2**), kK	$-\Delta\Delta\nu$-(**3**–**4**), kK	pK_{HB}[a]	Δ, ppm[b]
5	Hexamethylphosphoramide	2.91	2.04	3.56	3.71
6	Triethyl phosphate	2.31	1.67	2.73	
7	Dimethyl sulfoxide	2.20	1.60	2.53	2.71
8	Dimethylacetamide	2.15	1.71	2.38	2.86
9	*N*-Methylpyrrolidone	2.20	1.61	2.37	2.91
10	Dimethylformamide	2.09	1.66	2.06	2.72
11	Triethylamine	1.98		1.91	2.66
12	Pyridine	1.97	1.52	1.88	2.49
13	Dimethylbenzylamine	1.72		1.58	2.33
14	Tributylamine	1.89		1.57	2.50
15	Butyrolactone	1.40	1.06	1.33	
16	Tetrahydrofuran	1.63	1.28	1.26	2.00
17	Tetrahydropyran	1.53		1.23	
18	2-Butanone	1.53		1.18	2.02
19	Acetone	1.51		1.18	
20	Ethyl acetate	1.42	1.18	1.08	1.85
21	Acetonitrile	1.15	0.91	1.05	1.88
22	Dibutyl ether	1.43	1.35	1.02	
23	Diethyl ether	1.48	1.30	0.98	1.88
24	Ethyl benzoate	1.26		0.88	
25	Dibenzyl ether	1.23		0.72	1.70
26	Dioxane	1.13	0.96	0.71	1.45
27	Ethyl chloroacetate	1.00	0.85	0.69	
28	Anisole	0.75	0.64	0.02	
29	Cyclopentanone	1.60		(1.16)[c]	
30	Trichloroacetone	0.47		(−0.17)[c]	

[a] Reference 2. [b] Reference 3. [c] Estimated value based on pK_{HB} for closely related compound.

The correlation equations are

$$\mathrm{p}K_{\mathrm{HB}} = 1.551[-\Delta\Delta\nu(\mathbf{1}\text{–}\mathbf{2})] - 1.087 \qquad (1)$$

with $n = 26$, r (the correlation coefficient) = 0.981, and sd (the standard deviation) = 0.16 pK_{HB} unit

$$\Delta(\mathrm{ppm}) = 1.260[-\Delta\Delta\nu(\mathbf{1}\text{–}\mathbf{2})] - 0.074 \qquad (2)$$

with $n = 15$,[4] $r = 0.991$, and sd = 0.08 ppm

$$\mathrm{p}K_{\mathrm{HB}} = 2.297[-\Delta\Delta\nu(\mathbf{3}\text{–}\mathbf{4})] - 1.460 \qquad (3)$$

with $n = 16$, $r = 0.938$, and sd = 0.34 pK_{HB} unit, and

$$\Delta = 2.121[-\Delta\Delta\nu(\mathbf{3}\text{–}\mathbf{4})] - 0.694 \qquad (4)$$

with $n = 10$,[4] $r = 0.986$, and sd = 0.12 ppm.

Deviations from eq 1 and 3 for specific compounds are generally in the same directions as were noted by Gurka and Taft[3] in their log K_f *vs.* F nmr shift correlation, *i.e.*, bases of large steric requirements (compounds **14**, **22**, and **23** of Table I) tend to deviate in the direction indicating that both the $-\Delta\Delta\nu$ and the F nmr Δ values have smaller dependence on steric requirements than do the equilibrium constants. The parallelism is most notable with tributylamine (**14**), which Gurka and Taft excluded from their correlation because of excessive deviation, and which showed a large deviation in the same direction from the correlation line in Figure 1, but whose data point falls almost directly on the F nmr Δ *vs.* $-\Delta\Delta\nu(\mathbf{1}\text{–}\mathbf{2})$ correlation line (eq 2).

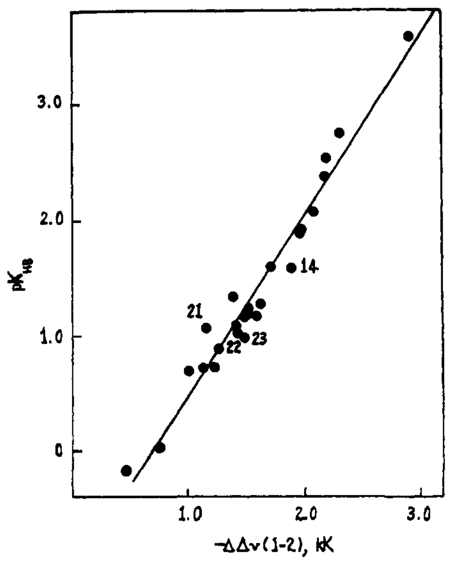

Figure 1. pK_{HB} values of solvents plotted against enhanced bathochromic shifts for 4-nitroaniline (**1**) relative to *N*,*N*-diethyl-4-nitroaniline (**2**).

By comparing the Δ value for complete proton transfer with limiting Δ values for hydrogen-bonded complex formation, Gurka and coworkers[5] estimated that the latter process involves a 10–25% extent of proton transfer. The $-\Delta\Delta\nu(\mathbf{3}\text{–}\mathbf{4})$ values in Table I, compared with a value of 7.63 kK for complete ionization [a 6.62 kK difference in $\nu_{\mathrm{max}}^{\mathrm{H_2O}}$ between 4-nitrophenoxide and 4-nitrophenol added to the 1.01 kK $-\Delta\Delta\nu(\mathbf{3}\text{–}\mathbf{4})$ value[1] for water], leads to similar estimates for extents of proton transfer in hydrogen-bonded complexes with **3**.

That our $-\Delta\Delta\nu$ results, determined in the neat solvents, correlate so well with properties determined by Taft, *et al.*, in dilute $\mathrm{CCl_4}$ solutions indicates that hydrogen-bond strengths to non-self-associating acceptors are little influenced by medium effects. This accords well with the striking finding by Arnett, *et al.*, that enthalpies of complex formation are very nearly the same in dilute $\mathrm{CCl_4}$ solutions as in the pure bases.[6]

As has already been pointed out,[3] however, bases capable of higher order complexing may show significant medium (or dilution) effects. In common with water, as recently demonstrated by Gordon,[7] dimers or polymers of alcohols and primary and secondary amines should be significantly more basic than corresponding monomers. Several primary amines, for which pK_{HB} values have been reported[2] or could be estimated, showed $-\Delta\Delta\nu(\mathbf{1}\text{–}\mathbf{2})$ values which were 0.4–0.7 kK higher than required by eq 1, probably because of significant higher order association in the neat solvents. In a subsequent paper we shall report on $-\Delta\Delta\nu$ and apparent pK_{HB} values of alcohols, and the effects of dilution on $-\Delta\Delta\nu$ values as a probe for higher order association.

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(4) The data for acetonitrile (**21**) were excluded from the correlations leading to eq 2 and 4 because the deviations were more than three times the sd.

(5) D. Gurka, R. W. Taft, L. Joris, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 89, 5957 (1967).

(6) E. M. Arnett, L. Joris, E. Mitchell, T. S. S. R. Murty, T. M. Gorrie, and P. von R. Schleyer, *ibid.*, 92, 2364 (1970).

(7) J. E. Gordon, *ibid.*, 94, 650 (1972).

The $-\Delta\Delta\nu$(1–2) correlations reported here represent the first linear free energy relationships involving N–H acids and the pK_{HB} scale.[8]

[8] NOTE ADDED IN PROOF. The pK_{HB} scale has very recently been applied to hydrogen-bonded complex formation with 5-fluoroindole; J. Mitsky, L. Joris, and R. W. Taft, *ibid.*, **94**, 3442 (1972).

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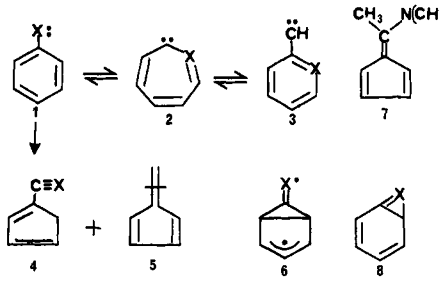
On the Mechanism of the Ring Contraction of Phenylcarbene to Fulvenallene. A Carbon-13 Labeling Study

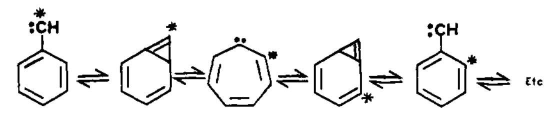
Sir:

Two facts have emerged from recent studies on the properties of arylcarbenes generated in the gas phase. Firstly, phenylcarbene (**1a**) undergoes ring contraction[1a,2] yielding fulvenallene (**5**) and ethynylcyclopentadiene (**4a**) at temperatures ⩾600°. The mechanism for the ring contraction is thought to involve bond formation between C_2 and C_6 giving a prefulvene type intermediate[3] **6a**. Secondly, phenylcarbene rapidly interconverts[1a,1c,2] with cycloheptatrienylidene (**2a**) at temperatures ⩽600° by way of the bicyclic intermediate **8a**. The cycloheptatrienylidene (**2a**) may revert to phenylcarbene in two ways giving **1a** or **3a**, thereby permitting a series of degenerate rearrangements, which will eventually result in a uniform distribution of the label X over all positions of phenylcarbene except C_1. This process is outlined in Scheme I and is valid only for the case in which hydrogen shifts are absent. This scheme was proposed by Jones and coworkers[7] and has been used to account for the isomerization of *m*- and *p*-tolylcarbenes to *o*-tolylcarbene and methylphenylcarbene. This has been subsequently verified by Hedaya[8,9] using ^{13}C labeling studies.



a, X = CH
b, X = N

Scheme I



Direct[10] gas-phase generation of cycloheptatrienylidene under conditions which bring about ring contraction in phenylcarbene does not, however, result in formation of fulvenallene. This led Hedaya[1] and Wentrup[2] to the conclusion that the ring contraction route and the ring expansion route are two separate, competing pathways. We were surprised therefore to learn that under the conditions in which phenylcarbene yields fulvenallene, *p*-tolylcarbene did not yield methylfulvenallenes but instead gave products resulting from the intramolecular trapping of *o*-tolylcarbene and methylphenylcarbene. Evidently the rearrangement of *p*-tolylcarbene *via* Scheme I must be proceeding at a greater rate than that of ring contraction to methylfulvenallenes. If the methyl group has no profound effect on the relative rates of ring contraction and ring expansion it follows that, in the case of phenylcarbene, we are forced to conclude that a similar series of degenerate rearrangements (Scheme I) involving ring expansion should precede ring contraction, *i.e.*, these are not separate competing pathways. This conclusion is at variance with that reached by Hedaya[1] and Wentrup[2] and therefore we decided to test this by an appropriate labeling experiment.

The dry sodium salt of benzaldehyde tosylhydrazone[11] labeled at the aldehydic carbon[12] with 92% excess ^{13}C was heated at 90° and the phenyldiazomethane led directly into the furnace[13] at 770° and 0.05 mm. The crude mixture of fulvenallene and its isomer **4a** was converted to 6-dimethylamino-6-methylfulvene (**7**) with ethanolic dimethylamine at −30° and the product[14] was examined by 22.63-MHz ^{13}C nmr.[16]

The pulsed Fourier transform spectrum (^{1}H broad-band decoupling) of the enamine **7** (Figure 1) shows that enrichment at every carbon atom of fulvenallene has occurred. Tentative assignments of the signals[16] are: a, C_7 (methyl); b, NCH_3 (natural abundance);[17] c and e–g, C_1, C_2, C_3, and C_4 (tertiary ring carbons); d, C_5 (quaternary ring carbon); and h, C_6 (quaternary carbon).[18] It is evident from the spectrum that both

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[1] (a) P. O. Schissel, M. E. Kent, D. J. McAdoo, and E. Hedaya, *J. Amer. Chem. Soc.*, **92**, 2147 (1970); (b) J. A. Myers, R. C. Joines, and W. M. Jones, *ibid.*, **92**, 4740 (1970); (c) this pathway has been postulated in order to rationalize certain arylcarbene rearrangements occurring in the solution phase: G. G. Vander Stouw, *Diss. Abstr.*, **25** (12), 6974 (1965) (*Chem. Abstr.*, **63**, 13126b (1965)), under the direction of H. Shechter.

[2] C. Wentrup and K. Wilczek, *Helv. Chim. Acta*, **53**, 1459 (1970).

[3] For the related ring contraction of phenylnitrene (**1b**) to cyanocyclopentadiene (**4b**) see ref 4–6.

[4] W. D. Crow and C. Wentrup, *Tetrahedron Lett.*, 4379 (1967).

[5] E. Hedaya, M. E. Kent, D. W. McNeil, F. P. Lossing, and T. McAllister, *ibid.*, 3415 (1968).

[6] W. D. Crow and C. Wentrup, *ibid.*, 5569 (1968).

[7] W. J. Baron, M. Jones, Jr., and P. P. Gasper, *J. Amer. Chem. Soc.*, **92**, 4739 (1970).

[8] E. Hedaya and M. E. Kent, *ibid.*, **93**, 3283 (1971).

[9] For the related interconversion between phenylnitrene (**1b**) and 2-, 3-, and 4-pyridylcarbenes see (a) W. D. Crow and C. Wentrup, *Tetrahedron Lett.*, 6149 (1968); (b) W. D. Crow, M. N. Paddon-Row, and D. S. Sutherland, *ibid.*, in press.

[10] *I.e.* from the tosylhydrazone salt of tropone.

[11] G. M. Kaufman, J. A. Smith, G. G. Vander Stouw, and H. Shechter, *J. Amer. Chem. Soc.*, 87, 935 (1965).

[12] The labeled benzaldehyde was obtained from Merck Sharp and Dohme, Canada Ltd., and the position of the label was verified by mass spectrometry.

[13] W. D. Crow and R. K. Solly, *Aust. J. Chem.*, **19**, 2119 (1966).

[14] The properties of compound 7 were in agreement with those reported[15] for 6-dimethylamino-6-methylfulvene. The overall yield of 7 based on the tosylhydrazone salt was 14%.

[15] A. P. Downing, W. D. Ollis, and I. O. Sutherland, *J. Chem. Soc. B*, 111 (1969), and ref 11 therein.

[16] The solvent was $CDCl_3$, the signal of which occurred at 68.3 ppm. The chemical shifts of the resonances relative to $CDCl_3$ are: (a) +57.2; (b) +33.3; (c) −38.5; (d) −39.2; (e) −40.6; (f) −42.2; (g) −43.2; (h) −80.2.

[17] This signal is considerably enhanced by the nuclear Overhauser effect and is yet less intense than those of the quaternary carbon atoms C_5 (d) and C_6 (h) (the signals of which cannot be significantly enhanced by this effect). It is evident, therefore, that enrichment of C_5 and C_6 has occurred.

[18] Assignments were made on the basis of chemical-shift data[19]