89-2; **8b**, 20931-91-3; **10b**, 62166-69-2; **11**, 62166-70-5; **12**, 31429-31-9; **18**, 62166-71-6; TCNE, 670-54-2.

References and Notes

(1) B. C. Mc Kusick, R. E. Heckert, T. L. Cairns, D. D. Coffman, and H. F. Mower, *J. Am. Chem. Soc.*, **80**, 2806 (1958).
(2) F. Kröhnke and H. H. Steuernagel, *Ber.*, **96**, 486 (1963).
(3) C. M. Camaggi and R. Leardini, to be published.
(4) R. C. Kerber and T. J. Ryan, *Tetrahedron Lett.*, **10**, 703 (1970).
(5) R. R. Schmidt, *Angew. Chem., Int. Ed. Engl.*, **12**, 212 (1973).
(6) S. Nishida, I. Maritani, and T. Teraji, *Chem. Commun.*, 501 (1970).
(7) C. M. Camaggi, M. Tiecco, and A. Tundo, *J. Chem. Soc. B*, 680 (1968).
(8) S. Patai, Ed., "The Chemistry of Amidines and Imidates", Wiley, New York, N.Y., 1975.

Rapid and Unequivocal Determination of Syn–Anti Stereochemistry for Toluenesulfonylhydrazones and Other Imine Derivatives via Carbon-13 Nuclear Magnetic Resonance Spectroscopy. A Synthetic Adjunct

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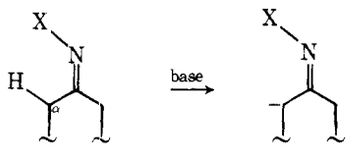
Received February 10, 1977

Measurement of the ^{13}C NMR chemical shift differences between the α carbons of ketone and imine derivatives (toluenesulfonylhydrazones, dimethylhydrazones, and oximes) provides a convenient and reliable means of assigning imine stereochemistry. It has been found that carbons syn to the imine "X" moiety are shifted to higher field (Δ syn α = 12–15 ppm) than are carbons anti to the imine "X" moiety (Δ anti α' = 3–6 ppm).

α-Metalated imine derivatives (**2a–c**), including dimethylhydrazones,[1] oximes,[2] and toluenesulfonylhydrazones,[3] are becoming increasingly important intermediates in organic synthesis. The deprotonation reactions of these imines (**1a–c**) exhibit a substantial preference for selective removal of α hydrogens which are syn to the imine X group (**1a–c** → **2a–c**).

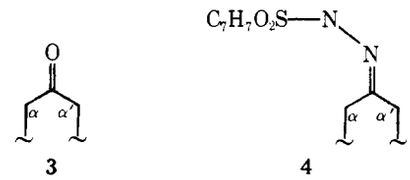


1a, X = $N(CH_3)_2$ 2a, X = $N(CH_3)_2$
b, X = OH b, X = O^-
c, X = $NHSO_2C_7H_7$ c, X = $N^-SO_2C_7H_7$

Utilization of this directing effect in a synthetically rational manner clearly requires an unambiguous method for the determination of syn–anti stereochemistry for imine derivatives of unsymmetrical ketones.

In connection with several synthetic projects in the area of tosylhydrazone chemistry,[3a,b] it became apparent that the traditional ^1H NMR spectral methods for assigning syn and anti isomers, such as differential solvent shifts[4a] (including benzene, a medium in which tosylhydrazones are only sparingly soluble) and lanthanide shift reagent studies,[4b,c] were neither uniformly unambiguous nor particularly convenient.

Several literature reports on the ^{13}C NMR spectra of hydrazones[5] and oximes[6] have indicated a substantial chemical shift difference between the syn and anti carbons α to the imine moiety. We have measured the ^{13}C NMR of a large number of imine derivatives (Tables I–V) based on the hypothesis that the major factor responsible for affecting chemical shift differences between syn and anti carbons is a steric compression effect,[7] which results in upfield shifts for syn α carbons. We have also measured the ^{13}C NMR of the parent ketone in each case. Comparison of the chemical shift differences between the ketone (**3**) and its imine derivative (**4**) *for each α carbon* readily shows that α carbons syn to the tosylhydrazone moiety are substantially shifted upfield (Δ syn α = 12–15 ppm) by comparison to the ketone, while α carbons



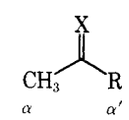
3 4

Δ syn α = (δ ketone 3 for C_α) – (δ hydrazone 4 for C_α)
Δ anti α' = (δ ketone 3 for $C_{\alpha'}$) – (δ hydrazone 4 for $C_{\alpha'}$)

anti to the tosylhydrazone moiety are shifted upfield only slightly (Δ anti α' = 3–6 ppm) (Tables I–IV).

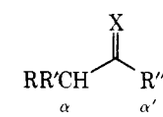
These observations can be qualitatively explained by postulating that the small upfield shift of the anti carbons is primarily due to an inductive effect resulting from the electronegativity difference between ketone and tosylhydrazone. The larger upfield shift of the syn α carbons results from a combination of the inductive effect *plus* a steric compression effect[6b,7] which, in turn, results in additional shielding. Use of this comparison of ketone and tosylhydrazone shifts allows the ketone to serve as an "internal standard"; therefore, the primary structural contributions to the chemical shift which are present both in the ketone and the tosylhydrazone tend to cancel out. The only major effect remaining is that which results from, and hence defines, the hydrazone stereochemistry.

Inspection of Tables I–IV for the structural types **5–11** demonstrates the validity of this approach. Table V indicates



5

a, R = Me
b, R = CH_2Cl
c, R = CH_2Br
d, R = CH_2OAc
e, R = Et
f, R = CH_2Ph
g, R = CH_2CO_2Me
h, R = CH_2CO_2tBu
i, R = *t*-Bu
j, R = Ph



6

a, R = H; R′ = Me; R″ = Et
b, R = R′ = Me; R″ = *i*-Pr
c, R = R′ = Me; R″ = Ph
d, R = R′ = Me; R″ = CH_2CO_2Et
e, R = H; R′ = Et; R″ = CH_2CO_2Et
f, R = H; R′ = Me; R″ = $CH(Me)CO_2Me$

Table I. Tosylhydrazones of Methyl Ketones, 5 (X = $NNHSO_2C_7H_7$)

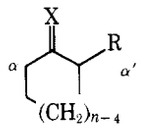
Registry no.	Hydrazone	δα	δα′	Δ syn α	Δ anti α′	Δ anti α	Δ syn α′
3900-79-6	**5a**[e] syn α	17.1	25.3	13.6	5.3		
	anti α	25.3	17.1			5.3	13.6
62460-87-1	**5b** syn α	13.6	48.0	13.4	1.0		
62460-88-2	**5c** syn α	14.2	35.5	12.9	−0.7		
62460-89-3	**5d** syn α	13.4	67.0	12.6	1.4		
62460-90-6	**5e**[a] syn α	15.6	32.0	13.8	4.9		
62460-91-7	anti α[d]	23.5	22.5			5.9	14.4
62460-92-8	**5f**[a] syn α	15.1	45.1	14.1	5.9		
62460-93-9	anti α	24.1	36.9			5.1	14.1
62460-94-0	**5g**[a] syn α	16.0	44.0	14.1	5.8		
62460-95-1	anti α	24.7	37.9			5.4	11.9
62460-96-2	**5h**[a] syn α	16.0	45.5	14.0	6.0		
62460-97-3	anti α	24.6	39.8			5.4	11.7
62460-98-4	**5i** syn α	11.8	38.8	12.9	5.5		
62460-99-5	**5j**[e] syn α	13.5	137.4	13.0	−0.2[b]		
62461-00-1	**11** syn α	15.5	*c*	14.7			

[a] Syn and anti isomers were obtained as unequal mixtures which allowed assignment of chemical shifts. The syn methyl isomer always predominated. [b] Included for completeness but not applicable in direct comparison. [c] Could not be determined from several peaks. [d] Due to the low percentage of this isomer, it was not possible to unequivocally assign δα and δα′. [e] Reference 5 reports **5a** (X = NNHPh) has δα = 15.1 ppm and δα′ = 24.8 ppm for syn α while **5j** (X = NNHPh) has δα = 12.5 ppm.

Table II. Tosylhydrazones of Acyclic Ketones, 6 (X = $NNHSO_2C_7H_7$)

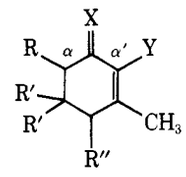
Registry no.	Hydrazone	δα	δα′	Δ syn α	Δ anti α′	Δ anti α	Δ syn α′
28495-72-9	**6a** syn α	22.7	29.4	12.8	6.8		
	anti α	29.4	22.7			6.1	12.8
17530-00-6	**6b** syn α	28.4	30.5	10.5	8.4		
	anti α	30.5	28.4			8.4	10.5
62461-01-2	**6c** anti α	36.4	132.4			−1.0	4.0[b]
62461-02-3	**6d** anti α	36.9	35.7			4.3	11.5
62461-03-4	**6e** anti α	40.3	37.5			4.6	11.9
62461-04-5	**6f**[a] syn α	21.7	46.7	13.0	5.8		
62461-05-6	anti α	27.5	41.2			7.2	11.3

[a] Syn and anti isomers were obtained as an unequal mixture with the anti α isomer predominating. [b] Included for completeness but not applicable in direct comparison.



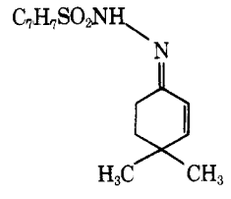
7

a, n = 6; R = H
b, n = 6; R = Me
c, n = 6; R = *t*-Bu
d, n = 6; R = CO_2Me
e, n = 5; R = H
f, n = 7; R = H
g, n = 8; R = H



8

a, R = R′ = R″ = H; Y = H
b, R = R″ = H; R′ = Me; Y = H
c, R = R′ = H; R″ = CO_2Et; Y = H
d, R = *i*-Pr; R′ = R″ = H; Y = H
e, R = R″ = H; R′ = Me; Y = OMe



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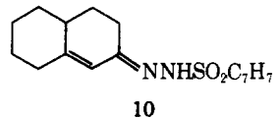

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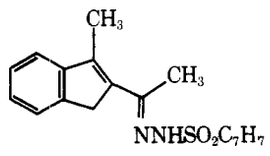
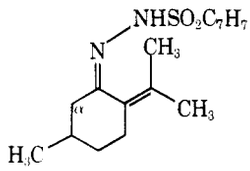


11

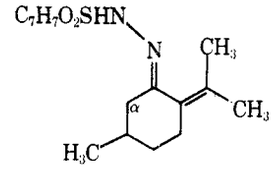
that the same procedure also appears to be generally applicable for oximes and dimethylhydrazones.

Verification of the accuracy of the method was provided by examination of tosylhydrazones **12** and **13**, whose stereochemistry has recently been established by x-ray crystallography.[3h] Consistent assignments were also obtained for other compounds including **1i** (X = $NHSO_2C_7H_7$),[4a] **1j** (X = $NHSO_2C_7H_7$),[8] and **8b** (X = NOH).[9]



12

(Δ syn α = 14.7 ppm)



13

(Δ anti α = 6.0 ppm)

The observed chemical shift effects do not seem to be universally applicable to phenyl ketones, i.e., the phenyl α carbons are shielded considerably less than aliphatic or vinyl carbons (vide supra) so that comparison of alkyl phenyl ketone imine derivatives (**5j** and **6c**) must be made with the alkyl portion.

Another limitation can occur in those occasional cases where difficulty is encountered in assigning the chemical shifts for the α carbons. Since the α carbons usually occur downfield of the potentially crowded aliphatic region for both the ketone and the imine derivatives, this situation seldom occurs. Furthermore, an imine derivative should yield a substantially

Table III. Tosylhydrazones of Cycloalkanones, 7 (X = $NNHSO_2C_7H_7$)

Registry no.	Hydrazone	$\delta\alpha$	$\delta\alpha'$	Δ syn α[a]	Δ anti α'	Δ anti α	Δ syn α'[a]
4545-18-0	**7a** syn α	26.9	35.2	$\geq$15.0	6.7		
	anti α	35.2	26.9			6.7	$\geq$15.0
63269-90-9	**7b** syn α	24.5	39.2	$\geq$15.4	6.2		
63269-91-0	anti α	*b*	31.8				13.6
63269-92-1	**7c** syn α	24.8	54.1	$\geq$19.5	6.2		
63269-93-2	**7d** syn α	26.8	50.9	14.8[c]	6.3[c]		
63269-94-3	anti α	33.3	41.7			8.3	15.5
61515-13-7	**12** syn α	36.2		14.7			
61515-14-8	**13** anti α	44.9				6.0	
17529-98-5	**7e** syn α	28.1	33.5	10.2	4.8		
	anti α	33.5	28.1			4.8	10.2
56382-69-5	**7f** syn α	30.4	37.0	$\geq$13.5	6.9		
	anti α	37.0	30.4			6.9	$\geq$13.5
2567-85-3	**7g** syn α	28.0	36.2	$\geq$14.0	5.8		
	anti α	36.2	28.0			5.8	$\geq$14.0

[a] Uncertainty in Δ syn values arises from ambiguity in chemical shift assignment of the respective carbon; however, the values assigned are the best guesses and are correct to within 3 ppm. [b] This isomer was <20% of the mixture and the α carbon signal was apparently hidden under the signals of the more predominant isomer. [c] This compound is a mixture of the enehydrazine form as well as syn and anti isomers. There is uncertainty in both $\delta\alpha$ and $\delta\alpha'$. These values are correct to $\pm$1.0 ppm.

Table IV. Tosylhydrazones of Cyclohexenones, 8 (X = $NNHSO_2C_7H_7$)

Registry no.	Hydrazone	$\delta\alpha$	$\delta\alpha'$	Δ syn α	Δ anti α'	Δ anti α	Δ syn α'
61530-89-0	**8a**[b] syn α	23.5	122.8	$\leq$13.5[a]	4.0		
61530-88-9	anti α	31.4	113.5			$\geq$5.6[a]	13.3
62505-87-7	**8b**[c] syn α	37.0	122.0	13.8	3.5		
62505-85-5	anti α	45.9	112.5			4.9	13.0
62461-11-4	**8c** syn α	20.9	125.4	13.4	3.1		
62560-50-3	**8d** anti α	45.9	113.0			5.7	13.9
62461-12-5	**8e**[b] syn α	38.3	*d*	13.9			
62461-13-6	anti α	46.7	*d*			5.5	
62461-14-7	**9** syn α	21.1	124.6	15.0	2.2		
62461-15-8	**10** syn α	22.8	121.0	$\leq$15.2[a]	3.3		
62461-16-9	anti α	*e*	111.0				13.3

[a] Uncertainty arises from ambiguity in chemical shift assignment of the respective carbon atom; however, the values given are accurate within 2.0 ppm. [b] Syn and anti isomers were obtained as unequal mixtures with the syn α isomer predominating. [c] The anti α isomer could be obtained in >90% purity by fractional crystallization; however, equilibration occurred during data acquisition. [d] Due to ambiguity in the spectra of ketone (δ 142.8 and 148.5 ppm) we could not assign the chemical shifts of the hydrazone (δ 130.5 and 145.6 ppm for syn α and δ 131.5 and 145.7 ppm for anti α). [e] There were too many peaks to even make a good guess at the chemical shift.

Table V. Comparison of ^{13}C Chemical Shifts of Tosylhydrazones, Oximes, and Dimethylhydrazones [a,d]

Registry no.	Compd		$\delta\alpha$	$\delta\alpha'$	Δ syn α	Δ anti α'	Δ anti α	Δ syn α'
	5e (X = $NNHSO_2C_7H_7$)	syn α	15.6	32.0	13.8	4.9		
		anti α	23.5	22.5			5.9	14.4
	7a (X = $NNHSO_2C_7H_7$)	syn α	26.9	35.2	$\geq$15.0[b]	6.7		
		anti α	35.2	26.9			6.7	$\geq$15.0[b]
	8b (X = $NNHSO_2C_7H_7$)	syn α	37.0	122.0	13.8	3.5		
		anti α	45.9	112.5			4.9	13.0
10341-63-6	**5e** (X = NOH)	syn α	13.3	29.2	16.1	7.7		
10341-59-0		anti α	19.2	21.9			10.2	15.0
100-64-1	**7a** (X = NOH)	syn α	25.6	32.2	$\leq$16.3[b]	9.7		
		anti α	32.2	25.6			9.7	$\leq$16.3[b]
3968-96-5	**8b**[c] (X = NOH)	syn α	35.0	118.8	15.8	6.7		
3968-95-4		anti α	41.1	112.6			9.7	12.9
19885-65-5	**5e** (X = $NN(CH_3)_2$)	syn α	16.0	32.2	13.4	4.7		
62461-17-0		anti α	22.1	24.6			7.3	12.3
10424-93-8	**7a** (X = $NN(CH_3)_2$)	syn α	28.7	36.0	$\geq$13.2[b]	5.9		
		anti α	36.0	28.7			5.9	$\geq$13.2[b]
62461-19-2	**8b** (X = $NN(CH_3)_2$)	syn α	38.8	123.1	12.0	4.7		
62461-20-5		anti α	46.1	115.8			2.4	9.7

[a] Reference 5 reports that the semicarbazone of **5e** (syn α) gives $\delta\alpha$ = 15.3 and $\delta\alpha'$ = 31.9 ppm. [b] Uncertainty is due to ambiguity in assigning respective carbon atoms. The values shown are correct within 3 ppm. [c] We were able to obtain a pure sample of the anti isomers by fractional crystallization, mp 100–102 °C (lit. 102–104 °C).[9b] [d] Syn and anti isomers were unequal mixtures with syn α isomer predominating.

different shift increment (Δ syn α and Δ anti α′ or Δ anti α and Δ syn α′) for each of two α carbons, making it possible to assign stereochemistry even in cases where only either δα or δα′ are known. For example, with enone derivatives, such as **10** (Table IV), there is great ambiguity in assignment of δα; however, the stereochemistry of the major isomer can be clearly established from the chemical shift (δα′ = 121.0, Δ anti α′ = 3.3) of the α′ carbon alone. Another obvious advantage is that only one isomer of the syn–anti pair is needed for comparison. The large body of empirical data in Tables I–V should be of substantial assistance in making subsequent stereochemical assignments for new imine derivatives.

It should be also noted that the five carbons of the toluenesulfonyl group fall within such a narrow range that assignment of other peaks in these areas should cause no problems (144.1–143.6, 136.1–135.4, 129.7–129.3, 128.4–128.7, and 21.7–21.5 ppm).[10]

Experimental Section

Natural abundance, ^{1}H-decoupled ^{13}C NMR spectra were obtained with a Varian CFT-20 instrument in $CDCl_3$ with Me_4Si as internal reference. Fourier transform spectra were obtained using 4000- and 5000-Hz spectral widths. A pulse angle of 45° was used with a pulse delay of 1 s. Chemical shift assignments of ketones were made by analogy to known systems.[11] Single frequency off-resonance ^{1}H-decoupled spectra were obtained when unambiguous assignment of resonances could not be made from the fully ^{1}H-decoupled spectrum.

The *p*-toluenesulfonylhydrazones **5–10** (X = $NNHSO_2C_7H_7$) were prepared by either of two general methods from the ketone **5–10** (X = O) and *p*-toluenesulfonylhydrazide.[12]

The following hydrazones (X = $NNHSO_2C_7H_7$) were prepared in ether:[13] **5a**;[14] **5b** (mp 123–125 °C dec); **5c** (mp 114–116 °C dec); **5d** (mp 106–107 °C); **5e**;[15] **5f**;[14] **5g** (mp 128–130 °C); **5h** (mp 115–118 °C); **5i** (mp 158–160 °C); **6a** (mp 101–103 °C); **6d** (mp 77–78 °C); **6e** (oil); **6f** (mp 91–93 °C); **8a** (mp 131–141 °C dec); **8d** (mp 111–113 °C);[16] **10** (mp 139–141 °C).

All others were prepared in ethanol:[14] **5j**;[14] **6b** (mp 78–95 °C);[16] **6c** (mp 105–108 °C);[16] **7a–c**;[17] **7d** (mp 129–132 °C); **7e–g**;[17] **8b**;[18] **8c** (mp 157–159 °C); **8e**;[19] **9**;[20] **12**; and **13**.[3h]

The dimethylhydrazones **5e**,[21] **7a**,[21] and **8b** (X = $NNMe_2$)[22] and oximes **5e**,[23] **7a**,[23] and **8b** (X = OH)[9b] were prepared by standard procedures.

Ketones **5c**,[24] **6f**,[25] **7d**,[25] **8e**,[19] **9**,[26] and **10**[27] (X = O) were prepared by published procedures. **11** and the corresponding ketone were graciously provided by Professor H. A. Morrison and Dr. F. Palensky of this department. All other ketones were obtained from commercial sources.

Acknowledgments. We wish to thank Dr. J. B. Grutzner for his invaluable comments during the conceptualization phase of this work. We wish to thank the National Science Foundation for the institutional grant (7842) under which the CFT-20 ^{13}C NMR instrument was obtained. This investigation was supported by Grant CA-19689-01, awarded by the National Cancer Institute, DHEW.

Registry No.—**5b** (X = O), 67-64-1; **5c**)x , o), 598-31-2; **5d** (X = O), 592-20-1; **5g** (X = O), 105-45-3; **5h** (X = O), 1694-31-1; **5i** (X = O), 75-97-8; **6a** (X = O), 96-22-0; **6d** (X = O), 7152-15-0; **6e** (X = O), 3249-68-1; **6f** (X = O), 17422-12-7; **7d** (X = O), 41302-34-5; **8a** (X = O), 1193-18-6; **8c** (X = O), 487-51-4; **8d** (X = O), 89-81-6; **10** (X = O), 1196-55-0.

References and Notes

(1) (a) E. J. Corey and D. Enders, *Tetrahedron Lett.*, 3 (1976); and (b) E. J. Corey, D. Enders, and M. G. Bock, *ibid.*, 7 (1976); (c) E. J. Corey and D. Enders, *ibid.*, 11 (1976); (d) E. J. Corey and S. Knapp, *ibid.*, 4687 (1976); (e) for related work with chiral hydrazones see D. Enders and H. Eichenauer, *Angew. Chem., Int. Ed. Engl.*, **15**, 549 (1976); (f) D. Enders and H. Eichenauer, *Tetrahedron Lett.*, 191 (1977).

(2) (a) T. A. Spencer and C. W. Leong, *Tetrahedron Lett.*, 3889 (1975); (b) W. G. Kofron and M. K. Yeh, *J. Org. Chem.*, **41**, 439 (1976); (c) M. E. Jung, P. A. Blair, and J. A. Lowe, *Tetrahedron Lett.*, 1439 (1976); (d) R. E. Lyle, J. E. Saavedra, G. G. Lyle, H. M. Fribush, J. L. Marshall, W. Lijinsky, and G. M. Singer, *ibid.*, 4431 (1976); (e) R. R. Fraser and K. L. Dhawan, *J. Chem. Soc., Chem. Commun.*, 674 (1976); (f) C. A. Park, C. F. Beam, E. M. Kaiser, R. J. Kaufman, F. E. Henoch, and C. R. Hauser, *J. Heterocycl. Chem.*, **13**, 449 (1976); (g) R. M. Sandifer, L. M. Shaffer, W. M. Hollinger, D. C. Reames, and C. F. Beam, *ibid.*, **13**, 607 (1976).

(3) (a) C. A. Bunnell and P. L. Fuchs, manuscript in preparation; (b) D. H. Lloyd and P. L. Fuchs, unpublished results; (c) R. H. Shapiro, *Org. React.*, **23**, 405 (1976), and references cited therein; (d) R. H. Shapiro, M. F. Lipton, K. J. Kolonko, R. L. Buswell, and L. A. Capuano, *Tetrahedron Lett.*, 1811 (1975); (e) J. E. Stemke and F. T. Bond, *ibid.*, 1815 (1975); (f) P. C. Traas, H. Boelens and H. J. Takken, *ibid.*, 2287 (1976); (g) J. E. Stemke, A. R. Chamberlin and F. T. Bond, *ibid.*, 2947 (1976); (h) W. G. Dauben, G. T. Rivers, W. T. Zimmerman, N. C. Yang, B. Kim, and J. Yang, *ibid.*, 2951 (1976); (i) R. M. Sandifer, S. E. Davis, and C. F. Beam, *Synth. Commun.*, **6**, 339 (1976); (j) E. Vedejs and W. T. Stolle, *Tetrahedron Lett.*, 135 (1977); (k) R. T. Taylor, C. R. Degenhardt, W. P. Melega, and L. A. Paquette, *ibid.*, 159 (1977).

(4) (a) G. J. Karabatsos and C. E. Osborne, *Tetrahedron*, **24**, 3361 (1968), and references cited therein; (b) K. D. Berlin and S. Rengaraju, *J. Org. Chem.*, **36**, 2912 (1971); (c) M. Zinic, M. Stromar, and D. Kolbah, *Hem. Ind.*, **28**, 15 (1974).

(5) N. Naulet, M. L. Filleux, G. J. Martin, and J. Pornet, *Org. Magn. Reson.*, **7**, 326 (1975).

(6) (a) Reference 5; (b) G. C. Levy and G. L. Nelson, *J. Am. Chem. Soc.*, **94**, 4897 (1972); (c) Z. W. Wolkowski, E. Vauthier, B. Gonbeau, H. Sauvaitre, and J. A. Musso, *Tetrahedron Lett.*, 565 (1972); (d) M. Gurudata, *Can. J. Chem.*, **50**, 1956 (1972).

(7) N. K. Wilson and J. B. Stothers, *Top. Stereochem.*, **8**, 1 (1974).

(8) G. J. Karabatsos and R. A. Taller, *J. Am. Chem. Soc.*, **85**, 3624 (1963).

(9) (a) G. Slomp and W. J. Wechter, *Chem. Ind. (London)*, 41 (1962); (b) R. H. Mazur, *J. Org. Chem.*, **26**, 1289 (1961).

(10) The >C═N carbon atom in tosylhydrazones is generally found 47–50 ppm upfield of the corresponding >C═O carbon for aliphatic derivatives. For conjugated systems the difference is 40–45 ppm upfield.

(11) (a) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York and London, 1972; (b) for cyclohexenones see J. Torri and M. Azzaro, *Bull. Soc. Chim. Fr.*, 1633 (1974); (c) for pulegone see M. Jautelat, J. B. Grutzner, and J. D. Roberts, *Proc. Natl. Acad. Sci. U.S.A.*, **65**, 288 (1970).

(12) Purchased from Aldrich Chemical Co. and Eastman Chemicals.

(13) P. L. Fuchs, *J. Org. Chem.*, **41**, 2935 (1976).

(14) W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952).

(15) C. H. DePuy and D. H. Froemsdort, *J. Am. Chem. Soc.*, **82**, 634 (1960).

(16) Boron trifluoride etherate was used as a catalyst.

(17) C. E. Sachs and P. L. Fuchs, *Synthesis*, 456 (1976).

(18) W. G. Dauben, M. E. Lorber, N. D. Vietmeyer, R. H. Shapiro, J. H. Duncan, and K. Tomer, *J. Am. Chem. Soc.*, **90**, 4762 (1968).

(19) K. M. Patel and W. Reusch, *Synth. Commun.*, **5**, 27 (1975).

(20) W. Kirmse and L. Ruetz, *Justus Liebigs Ann. Chem.*, **726**, 30 (1969).

(21) G. R. Newkome and D. L. Fishel, *J. Org. Chem.*, **31**, 677 (1966).

(22) G. Stork and J. Benaim, *J. Am. Chem. Soc.*, **93**, 5938 (1971).

(23) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds", Wiley, New York, N.Y., 1967.

(24) P. A. Levene, "Organic Syntheses", Collect. Vol. IV, Wiley, New York, N.Y., 1963, p 88.

(25) A. P. Krapcho, J. Diamanti, C. Cayen, and R. Bingham, "Organic Syntheses", Collect. Vol. V, Wiley, New York, N.Y., 1973, p 198.

(26) (a) E. L. Eliel and C. A. Lukach, *J. Am. Chem. Soc.*, **79**, 5986 (1957); (b) E. D. Bergmann, and R. Corett, *J. Org. Chem.*, **23**, 1507 (1958).

(27) G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Am. Chem. Soc.*, **85**, 207 (1963).

(28) Postdoctoral Research Associate.