129–131 °C; IR 1670, 1718 cm^{-1}; ^1H NMR δ 1.31 (s, 9 H), 2.3–3.0 (m, 4 H), 3.00 (sl br s, 6 H); HRMS, m/z 241.1125, calcd for $C_{12}H_{19}NO_2S$ 241.1137.

3,5-Dimethyl-2-[(dimethylthiocarbamoyl)oxy]-2-cyclopenten-1-one (21). The procedure used for the preparation of **3** was repeated, replacing cyclotene by 3,5-dimethyl-1,2-cyclopentanedione and stirring 3 h at room temperature. The crude product was chromatographed on silica gel and crystallized from ether, giving white crystals: mp 47–48 °C; IR 1720, 1665, 1540 cm^{-1}; ^1H NMR δ 1.23 (d, J = 7 Hz, 3 H), 1.98 (sl br s, 3 H), 2.2–3.0 (m, 3 H), 3.30 (s, 3 H), 3.40 (s, 3 H). Anal. Calcd for $C_{10}H_{15}NO_2S$: C, 56.32; H, 7.08. Found: C, 56.32; H, 7.10.

Preparative Runs Involving Diosphenol Dimethylthiocarbamates. 5-Chloro-3-methyl-2-cyclopenten-1-one (4). A 12.9-g (65-mmol) sample of **3** was added, in one portion, to a boiling solution of 27.3 g (650 mmol) lithium chloride in 325 mL of acetic acid, and the resulting solution was heated at reflux for 1 h. The reaction mixture was poured into 2 kg of ice–water and neutralized with solid potassium bicarbonate. The mixture was extracted with two 1-L portions of methylene chloride. Drying and evaporation gave a thick liquid, which was chromatographed on 350 g of silica gel packed in cyclohexane/ethyl acetate (2:1), giving ca. 3.5 g of a pale liquid. Vacuum distillation afforded pure material: bp 69–70 °C (0.35 mm); IR 1714, 1626 cm^{-1}; ^1H NMR δ 2.17 (s, 3 H), 2.3–2.8 (m, 2 H), 4.22 (dd, J = 6.5, 3 Hz, 1 H), 5.92 (narr m, 1 H); ^{13}C NMR δ 19.2, 43.4, 53.9, 127.7, 176.3, 201.7; HRMS, m/z 130.0186, calcd for C_6H_7ClO 130.0186.

The title compound is hitherto unreported; its ^{13}C NMR spectrum is very similar to that reported[6e] for 5-bromo-3-methyl-2-cyclopenten-1-one.

2-Chloro-3-methyl-2-cyclopenten-1-one (5). A 1.99-g (10 mmol) sample of **3** was added, in one portion, to a boiling solution of 4.2 g (100 mmol) lithium chloride in 50 mL of acetic acid, and the resulting solution was heated at reflux for 16 h. Workup as above gave 1.0 g of a thick dark liquid, which was chromatographed on 70 g of silica gel packed in cyclohexane/ethyl acetate (2:1), giving 230 mg (18%) of **5**, which was recrystallized from pentane to give white crystals: mp 37–38 °C; IR 1714, 1621 cm^{-1}; ^1H NMR δ 2.13 (s, 3 H), 2.3–2.8 (m, 4 H); HRMS, m/z 130.0178, calcd for C_6H_7ClO 130.0186.

The title compound has been reported without physical or spectral data.[9]

3-(Chloromethyl)-2-cyclopenten-1-one (8) and 5-Acetoxy-3-methyl-2-cyclopenten-1-one (9). A 70-g (350-mmol) sample of **3** was added, in one portion, to a boiling solution of 147 g (3.5 mol) of lithium chloride in 1.5 L of acetic acid, and the resulting solution was heated at reflux for 3 h. Workup as above gave ca. 30 g of a dark liquid, which was chromatographed on 600 g of silica gel packed in cyclohexane/ethyl acetate (6:1), giving first, 12.2 g of a mixture of **4** and **5**, then 1.5 g of crude **8**, and finally 2.0 g of pure **9**. Vacuum distillation of crude **8** afforded material, bp 67–68 °C (0.4 mm), which was further purified by chromatography on 50 g of silica gel packed in cyclohexane/ethyl acetate (6:1), giving 1.0 g of pure **8**: IR 1713, 1681, 1626 cm^{-1}; ^1H NMR δ 2.36–2.74 (m, 4 H), 4.30 (s, 2 H), 6.06 (narr m, 1 H). Compound **9** had the following spectra: IR 1782, 1744, 1718, 1620 cm^{-1}; ^1H NMR δ 2.10 (2 s, 6 H), 2.6–3.3 (m, 2 H), 5.04 (dd, J = 5, 1 Hz, 1 H), 5.95 (narr m, 1 H).

3-*tert*-Butyl-5-chloro-2-cyclopenten-1-one (18a). A 120-mg (0.5 mmol) sample of **17** was added to a boiling solution of 210 mg (5 mmol) of lithium chloride in 2.5 mL of acetic acid, and the resulting solution was heated at reflux for 3 h. Workup as in the preparation of **4** gave 0.1 g of an oil, which was chromatographed on 15 g of silica gel packed in cyclohexane/ethyl acetate (3:1), giving 39 mg (45%) of **18a** (oil) followed by 38 mg of a 9:1 mixture of **19** and **20** (as determined by NMR and GC comparison with an authentic mixture). Compound **18a** had the following spectra, closely analogous to **4**: IR 1719, 1601 cm^{-1}; ^1H NMR δ 1.20 (s, 9 H), 2.64 (A part of ABMX, $|J_{ab}|$ = 16 Hz, J_{am} = 3 Hz, J_{ax} = 1.5 Hz, 1 H), 3.15 (B part of ABMX, $|J_{ab}|$ = 16 Hz, J_{bm} = 6.5 Hz, J_{bx} = 1.5 Hz, 1 H), 4.24 (M part of ABMX, dd J_{bm} = 6.5, J_{am} = 3 Hz, 1 H), 5.94 (X part of ABMX, t, J_{ax} = J_{bx} = 1.5 Hz, 1 H); ^{13}C NMR δ 28.3, 35.5, 38.8, 54.2, 124.6, 188.0, 202.9. Anal. Calcd for $C_9H_{13}ClO$: C, 62.62; H, 7.59. Found: C, 62.63; H, 7.43; HRMS, m/z 172.0647, calcd for $C_9H_{13}ClO$ 172.0655.

5-Bromo-3-*tert*-butyl-2-cyclopenten-1-one (18b). The procedure used above was followed, replacing lithium chloride by lithium bromide and heating for only 1.5 h. Workup and chromatography gave 45 mg (42%) of **18b** (oil): IR 1714, 1699, 1601 cm^{-1}; ^1H NMR δ 1.20 (s, 9 H), 2.88 (A part of ABMX, $|J_{ab}|$ = 18 Hz, J_{am} = 3 Hz, J_{ax} = 1.5 Hz, 1 H), 3.30 (B part of ABMX, $|J_{ab}|$ = 18 Hz, J_{bm} = 6 Hz, J_{bx} = 1.5 Hz, 1 H), 4.32 (M part of ABMX, dd, J_{bm} = 6, J_{am} = 3 Hz, 1 H), 5.93 (X part of ABMX, t, J_{ax} = J_{bx} = 1.5 Hz, 1 H).

The spectrum of this substance is clearly different from that of 4-bromo-3-*tert*-butyl-2-cyclopenten-1-one reported by Garbisch.[5c]

2,4-Dimethyl-4-[(dimethylcarbamoyl)thio]-2-cyclopenten-1-one (24). A 230-mg (1-mmol) sample of **21** was added to a boiling solution of 420 mg (10 mmol) of lithium chloride in 5 mL of acetic acid, and the resulting solution was heated at reflux for 1.5 h. Workup as in the preparation of **4** gave 0.11 g of an oil, which was chromatographed on 15 g of silica gel packed in cyclohexane/ethyl acetate (3:1), giving 79 mg (37%) of **24**: mp 60–62 °C; IR 1712, 1656 cm^{-1}; ^{1}NMR δ 1.72 (s, 3 H), 1.77 (d, J = 1.5 Hz, 3 H), 2.54, 2.81 (AB q, $|J_{ab}|$ = 19 Hz, 2 H), 2.92 (s, 6 H), 7.38 (t, J = 1.5 Hz, 1 H); ^{13}C NMR δ 9.9, 27.7, 36.6, 49.8, 51.4, 140.7, 160.8, 166.8, 206.2; MS, m/z 213 (21, $M^{\cdot+}$), 109 (78, $M^{\cdot+}$ – $Me_2NC(=O)S$), 81 (49, 109 – CO), 72 (100, Me_2NCO^+); HRMS, m/z 213.0814, calcd for $C_{10}H_{15}NO_2S$ 213.0824.

Interconversion of 4 and 8. A solution of 1.17 g (9 mmol) of **4** and 780 mg (90 mmol) of lithium chloride in 45 mL of acetic acid was heated at reflux as the appearance of **8** was monitored by GC. During this reaction, neither **5** nor 2-chloro-4-methyl-2-cyclopenten-1-one was observed. (An authentic sample of the latter compound was made by treatment of 2-[(dimethylthiocarbamoyl)oxy]-4-methyl-2-cyclopenten-1-one with lithium chloride in acetonitrile/acetic acid.) After 2 h the reaction was worked up as usual, and the crude product was chromatographed on 120 g of silica gel packed in cyclohexane/ethyl acetate (6:1), giving **4** followed by **8**. Similarly, a solution of 261 mg (2 mmol) of **8** and 840 mg (20 mmol) of lithium chloride in 10 mL of acetic acid was heated at reflux for 7 h when GC analysis showed partial conversion to **4**.

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Registry No. **3**, 110874-84-5; **4**, 110874-85-6; **5**, 73923-18-9; **6**, 91240-27-6; **7**, 110874-86-7; **8**, 110874-87-8; **9**, 55444-07-0; **17**, 110874-94-7; **18a**, 110874-95-8; **18b**, 110874-91-4; **19**, 110874-96-9; **20**, 110874-97-0; **21**, 110874-93-6; **24**, 110874-92-5; $Me_2NC(S)Cl$, 16420-13-6; Me_2NCOCl, 79-44-7; 2-chloro-4-methyl-2-cyclopenten-1-one, 110874-88-9; 2-[(dimethylthiocarbamoyl)oxy]-4-methyl-2-cyclopenten-1-one, 110874-89-0; 3-butyl-1,2-cyclopentanedione, 110874-90-3; 3-methyl-1,2-cyclopentanedione, 765-70-8.

(9) Boya, M.; Marquet, J.; Moreno-Manas, M.; Prior, M. *Ann. Quim.* **1979**, *75*, 920.

^{13}C Kinetic Isotope Effects in the Acid-Catalyzed Disproportionation and Rearrangements of 4,4′-Dichloro[2,2′,6,6′-$^{13}C_4$]hydrazobenzene

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In acid solution, 4,4′-dichlorohydrazobenzene (**1**) undergoes disproportionation into 4-chloroaniline (**2**) and 4,4′-dichloroazobenzene (**3**) and also rearrangement to an *o*- and *p*-semidine (**4** and **5**, respectively) (Scheme I).

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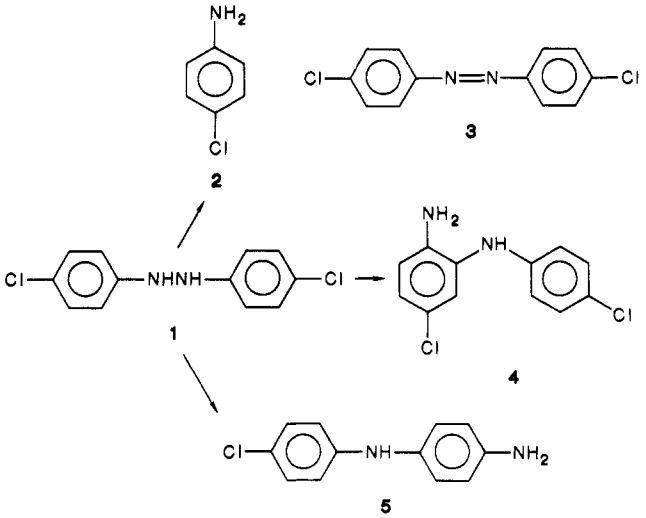
Table I. Yields[a] of Products in the Acid-Catalyzed Reaction of [$^{13}C_4$]-1

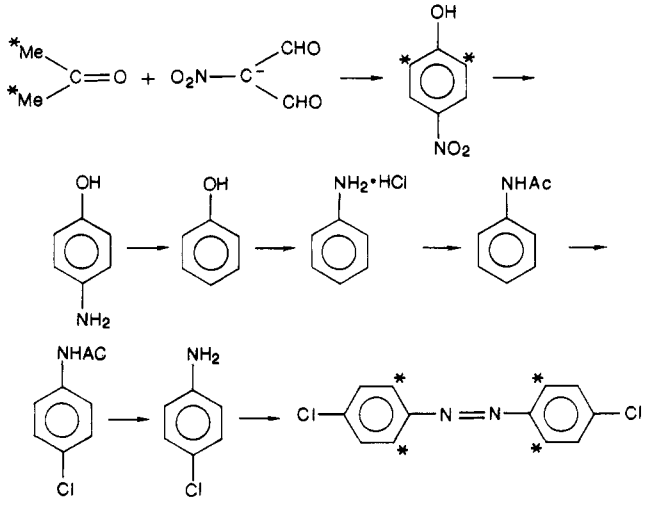
run	% convn A[b]	% convn B[c]	% 2	% 4	% 5	% 3 C[d]	% 3 D[e]	3 (C) × 100/(2 + 5)	total recov, %
1	27.8	24.5	7.0	3.2	2.1	12.2	72.2		96.7
	100	92.2	25.1	16.1	11.6	39.5		107.6	92.2
2	21.3	19.2	5.9	2.3	2.0	9.0	78.7		97.9
	100	94.7	25.3	15.9	12.8	40.7		106.8	94.7
3	16.1	15.0	4.9	1.9	1.3	6.9	83.9		98.9
	100	94.5	25.6	15.2	13.1	40.6		104.9	94.5

[a] Expressed as percent of 1 converted into product. The yields of 2, 4, and 5 were measured, in reality, with the isolation of their trifluoroacetyl derivatives 7, 8, and 9, respectively. [b] Based on the amount of 3 recovered after air oxidation of unreacted 1. [c] Sum of yields of 2, 3 (C), 4, and 5. [d] Filtered from acid solution. [e] Recovered after air oxidation of unreacted 1.

Scheme I

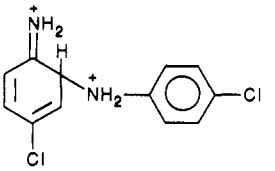


Scheme II



Recently, we reported the quantitative analysis and separation of these products from reaction of 1 in 60% aqueous dioxane solution at 0 °C and the heavy-atom kinetic isotope effects (KIE) in their formation.[1] That is, KIE were measured for the reactions of [^{15}N,$^{15}N'$]-1, [2-^{14}C]-1, and [4,4'-$^{13}C_2$]-1. Although substantial ^{15}N KIE were found for *all* of the reactions, no carbon KIE was found for *any* of them. These results meant that no evidence for concertedness could be found for any of the reactions. It was pointed out at the time that, in principle, concertedness in an *o*-semidine rearrangement was forbidden by the conservation of orbital symmetry. On the other hand, a concerted *p*-semidine rearrangement could occur, although in the case of 1 we could not find evidence for one. Finally, it was noted that disproportionation of a hydrazoarene occurs via the rate-determining formation of a quinoidal intermediate, and that in the case of 1 such an intermediate was not likely to have been formed in a concerted way.

In our earlier work, we used [2-^{14}C]-1 as the isotopic labeling specifically suitable for measuring the KIE of the *o*-semidine rearrangement. In that type of labeling, only one of the four ortho positions in a given molecule of 1 is likely to be labeled with ^{14}C. In that case, there is an intramolecular competition, threefold in favor of ^{12}C, in an *o*-semidine rearrangement, so that a statistical correction is needed in calculations of the intermolecular competition from which the KIE is customarily expressed. The arithmetic of the correction then leads to a magnification of the errors in the KIE measurement. Thus, the KIE for the *o*-semidine rearrangement of [2-^{14}C]-1 was 0.9989 ± 0.0093.[2] The KIE for disproportionation, which was also measured in reaction of [2-^{14}C]-1, was 1.0012 ± 0.0082.[2] The *o*-semidine result, that is, a KIE close to 1.000, meant that a KIE for N–C bonding could not be detected. The disproportionation result meant that the quinoidal intermediate of the *o*-semidine rearrangement (i.e., 6) might also be the intermediate in disproportionation.



6

We were disappointed that the errors in our ^{14}C KIE were substantially larger than the KIE themselves. The rearrangement of 1 is the only case in which the KIE of an *o*-semidine rearrangement has been measured, and, therefore, we have been concerned to obtain a more reliable measurement of the *o*-semidine KIE, one that was not complicated by intramolecular competition. We have now been able to do this with the use of [2,2',6,6'-$^{13}C_4$]-1. The KIE was obtained from measuring isotope abundances by whole-molecule-ion mass spectrometry. Further, because it was necessary to separate all products of reaction, as in our earlier work, we have been able to measure isotope abundances for the *p*-semidine rearrangement and for disproportionation of [2,2',6,6'-$^{13}C_4$]-1, too. They confirm the earlier measurements, namely, that no evidence for concerted reactions can be found.

(1) Rhee, E. S.; Shine, H. J. *J. Am. Chem. Soc.* **1986**, *108*, 1000.

(2) Rhee, E. S.; Shine, H. J. *J. Am. Chem. Soc.* **1987**, *109*, 5052, a correction.

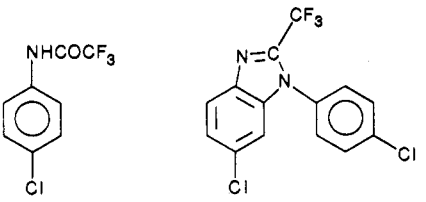
Table II. ^{13}C Kinetic Isotope Effects (KIE) in the Acid-Catalyzed Reactions of 4,4'-Dichlorohydrazobenzene (1)[a]

run	F[b]	KIE[c]		
		o-semidine	p-semidine	disprop
1	0.278	0.9957 ± 0.0055	0.9986 ± 0.0018	0.9968 ± 0.0077
2	0.213	0.9974 ± 0.0053	0.9972 ± 0.0041	
3	0.161	0.9957 ± 0.0028	0.9960 ± 0.0077	1.0038 ± 0.0048
av[d]		0.9963 ± 0.0045	0.9973 ± 0.0045	1.0003 ± 0.0063

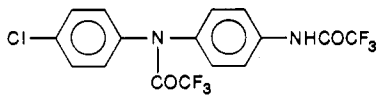
[a] ^{13}C labeling in the 2,2',6,6'-positions. [b] A, Table I. [c] Measured from isotope abundances, obtained by whole-molecule-ion mass spectrometry in the products 8, 9, and 7, respectively.

Results and Discussion

Labeled 4,4'-dichloroazobenzene, [2,2',6,6'-$^{13}C_4$]-3, hereafter called [$^{13}C_4$]-3, was prepared as shown in Scheme II, in overall 5% yield based on [1,3-$^{13}C_2$]acetone. The [$^{13}C_4$]-3 was diluted by crystallization with unenriched 3 and was reduced as needed to [$^{13}C_4$]-1. Rearrangements and isolation of products were carried out as described earlier.[1] The results of three runs are tabulated (Table I) in the same way as earlier and correspond very well with our earlier ones.[1] The yields of 4-chloroaniline (2) and o- and p-semidine (4 and 5, respectively) given in Table I are in reality, as earlier, the yields of isolated trifluoroacetyl derivatives, namely 7, 8, and 9. Isotope abundances were



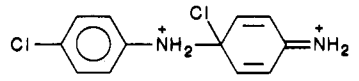
7 8



9

measured with these derivatives, too. This required that M/(M + 2) ratios be measured with 7 and M/(M + 4) ratios with 8 and 9. Because 7 contains a chlorine atom, it was necessary to choose which chlorine-containing isotope would represent the parent in our measurements of $^{13}C_2$ enrichments. We chose $C_8H_5NOF_3{}^{35}Cl$ as the parent and measured mass ratios 223/225 for determining ^{13}C KIE. Similarly, we chose the ^{35}Cl isotope when working with 8 and 9, measuring as M/(M + 4) for 8 the ratios 330/334, and for 9 the ratios 410/414. Calculations of KIE are given in Table II.

The calculations show that the KIE are close enough to unity as to rule out our considering bond formation as a significant part of the rate-determining process in any of the reactions. p-Semidine rearrangement cannot, itself, in this case, show a KIE because the para positions of 1 were not enriched with ^{13}C. Measurement of $^{12}C/^{13}C$ abundances in 9 can only reflect, therefore, any changes of that ratio in 1 that may have occurred as a result of the o-semidine rearrangement. Our best conclusion is that in neither case have we detected, within experimental error, a change in the $^{12}C/^{13}C$ ratio and, hence, a KIE. As discussed earlier,[1] disproportionation can occur via one of several quinoidal intermediates. In the present work the only chance that a KIE would be found in disproportionation lies in there being a KIE in the o-semidine rearrangement, and that, of course, turns out not to be the case. Earlier,[1] we argued from product distributions that disproportionation occurred via the quinoidal intermediate 10 of the p-semidine rearrangement. The data in the present work, as summarized in column 9, Table I, support that view again. That is, that 3 is formed not only in disproportionation but also in the reductive removal of Cl^+ from 10 by 1.[1]



10

The large amount of information about the family of benzidine rearrangements that is now known to us holds that each member is intramolecular. Among the family, are the diphenyline[3,4] and the o-semidine rearrangements, for each of which our KIE results are in accordance with a nonconcerted process.[5] Nonconcertedness of these two rearrangements would be in accord with theory, since, respectively, they are [3,5]- and [1,3]-sigmatropic rearrangements. How, then, do such rearrangements occur intramolecularly? A definite answer to that question cannot now be given and remains yet another of the enigmatic, kaleidoscopic parts of the benzidine rearrangements awaiting solution. Certainly, we can propose that a π-complex is involved, and yet, this leaves us with another of the benzidine enigmas, namely, why, in such cases, intramolecularity should persist.

Experimental Section

The procedures for preparing 1 by reduction of 3, for reaction of 1 in 60% aqueous dioxane, and for the separation, isolation, and trifluoroacetylation of products were described earlier.[1]

Synthesis of [2,2',6,6'-$^{13}C_4$]-1. The source of ^{13}C labeling was [1,3-$^{13}C_2$]acetone, obtained from ICN-Kohler and shown by mass spectrometric analysis[7] to be at least 96% $^{13}C_2$. Steps in the synthesis of [$^{13}C_4$]-1 are shown in Scheme II. All of the steps are from the literature and will not be described here in detail. Conversion of 6.0 g of acetone gave 7.1 g (51%) of p-nitrophenol,[8] mp 108–110 °C. This was reduced with hydrazine hydrate and Pd/C to 3.1 g (80%) of p-aminophenol, mp 183–186 °C, and the latter was deaminated ($NaNO_2$, H_3PO_2, Cu_2O) to give, after vacuum distillation, 1.5 g (54%) of labeled phenol. The phenol was converted into aniline by the method of Scherrer and Beatty,[9,10] and the aniline was isolated as its hydrochloride (1.44 g, 72%). The hydrochloride of the aniline was then converted into acetanilide (51%), which was chlorinated as described earlier.[1] Chlorination gave 510 mg (53%) of p-chloroacetanilide, mp

(3) Shine, H. J.; Zmuda, H.; Park, K. H.; Kwart, H.; Horgan, A. G.; Brechbiel, M. *J. Am. Chem. Soc.* **1982**, *104*, 2501.
(4) Kupczyk-Subotkowska, L.; Shine, H. J.; Subotkowski, W.; Zygmunt, J. *Gazz. Chim. Ital.*, in press.
(5) We acknowledge here the *caveat* that bond formation may, in fact, be part of a concerted process but nevertheless, because of the cancellation of opposing effects, may lack a demonstrable KIE.[6] Consequently, our finding in the present case of rearrangement of 1, as well as in the diphenyline rearrangement, does not prove, but is consistent with, the nonconcertedness of these reactions. This point has been discussed earlier.[4]
(6) Fry, A. In *Isotope Effects in Chemical Reactions*; Collins, C. J., Bowman, N. S., Eds.; Van Nostrand Reinhold: New York, 1970; pp 364–414.
(7) Analysis by Midwest Center for Mass Spectrometry, a regional NSF facility, Department of Chemistry, University of Nebraska, Lincoln, NE.
(8) Swartz, G. L.; Gulick, W. M., Jr. *J. Labelled Compd.* **1975**, *11*, 525.
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179–180 °C, and 390 mg of a mixture of *o*- and *p*-chloroacetanilide, containing mostly the ortho isomer. The mixture was dechlorinated by heating overnight in ethanol (40 mL) solution with 0.5 mL of hydrazine hydrate and 100 mg of 10% Pd/C and gave 270 mg of acetanilide. The recovered acetanilide was rechlorinated, giving 170 mg of *p*-chloroacetanilide, mp 179–180 °C. The total conversion of acetanilide into *p*-chloroacetanilide was, thus, 70.5%. The *p*-chloroacetanilide was hydrolyzed to 488 mg (95%) of *p*-chloroaniline, mp 66–69 °C, and this was oxidized by MnO_2 into [2,2′,6,6′-$^{13}C_4$]-**3**, giving 412 mg (86%) of product, mp 187–188 °C after column chromatography on silica gel. The [$^{13}C_4$]-**3** (400 mg) was recrystallized with 7.6 g of unenriched **3** for use in preparing **1** for KIE studies.

KIE Measurements. The trifluoroacetyl derivatives **7–9** were used for measurements of relative abundances of the M and (M + 2) ions in **7** and the M and (M + 4) ions in **8** and **9**. Whole-molecule-ion abundances were measured with a Hewlett-Packard mass spectrometer, Model 5995, in the SIM mode, and KIE were calculated as described earlier.[1] The number of scans in each of the 25 blocks of scans was approximately 60 for **7**, approximately 140 for **8**, and approximately 100 for **9**. Each ratio of abundances was measured three or four times and then averaged. The KIE results are given in Table II.

Acknowledgment. We thank the Robert A. Welch Foundation (Grant No. D-028) and the National Science Foundation (Grant No. CHE 86-12031) for generous support.

A New Method for Predicting Isomerization Barriers in Sterically Congested Alkenes from the First Correct Barrier Measurement in Solution: (*Z*)-2,2,3,4,5,5-Hexamethyl-3-hexene

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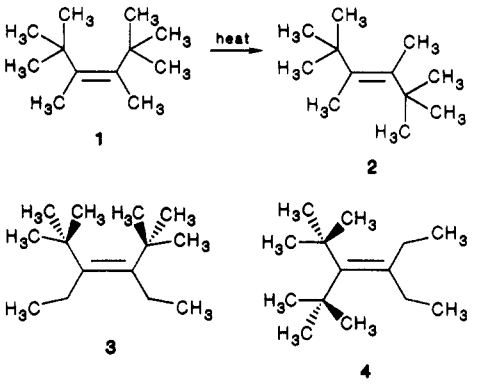
Although considerable effort has been expended to determine thermal isomerization barriers in simple alkenes,[1] investigations in solution were fraught with difficulties. All reported values have eventually been found to be erroneous. Although steric congestion should lower such barriers, little is known regarding the magnitude of those effects. The development of the low valent titanium coupling reaction of ketones, such as the McMurry reagent,[2] has made available a large variety of sterically congested alkenes.[3,4] The first, correct, solution phase measurement of a thermal, *Z*/*E* isomerization barrier in a sterically congested alkene, (*Z*)-2,2,3,4,5,5-hexamethyl-3-hexene (**1**) is reported below along with a method for predicting the quantitative effects of steric congestion on such barriers. Predictions of barriers are made for **3** and **4**.

Results

A mixture of alkenes **1** and **2** was prepared by the low valent titanium induced coupling of pinacolone.[5] Pure samples of **1** (93.6%) and **2** (98.7%) were obtained by GLC fractionation of the mixture. In the absence of vinylic hydrogens, the distinction between **1** and **2** was not trivial. The published procedures assumed that the intensity of the Raman scatterings from **1** and **2** were identical or that



1 **2**

3 **4**

2 was formed because it was the *E* isomer. Since twisting of the double bond can dramatically attenuate the Raman intensity, the first assumption was questionable. As might have been expected, neither IR spectrum showed a recognizable C=C stretching band. The NOE enhancement, which should have been greater for **2**, was essentially the same for both **1** and **2**. This surprising result was understood by inspection of models. Apparently, the nonbonded repulsions in **1** pushed the *tert*-butyl groups sufficiently close to the methyl groups to create a significant NOE effect. Likewise, the highest frequency C–H stretching vibrations in the IR spectrum of **1** showed abnormally high bands, 3040–3050 cm^{-1}, for both isomers rather than just for **1**.[6] Eventually, the stereochemical assignment had to rely upon the observation that **1** isomerized to **2** upon heating. Force field calculations (vida infra) and many other examples of *Z*/*E* isomerizations demonstrated that **1** should be significantly more strained than **2**. The only impurities detected in **1** were its isomer

1 **5**

2 (1.7%) and an unidentified material (4.7%), which remained unchanged (vida infra) during the reaction. A preliminary pyrolysis experiment revealed **1** readily isomerized at temperatures below 165 °C in nitrobenzene-d_5. Careful NMR analysis, however, demonstrated that the isomerization product was not **2** but rather 2-*tert*-butyl-3,4,4-trimethyl-1-pentene (**5**). Since this isomerization was known to occur under conditions of Lewis acid catalysis,[7a] all traces of polar, acidic substances were avoided (vide infra). Under those conditions and in the absence of exposure to air, pyrolysis of **1** in tetradecane lead to reluctant isomerization to **2**. The reverse reaction, **2** to **1**, was not observable at 225 °C. The presence of varying concen-

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(1) For a general review of alkene isomerizations, see: Saltiel, J.; Charlton, J. L. *Rearrangements in the Ground and Excited States*; DeMayo, P., Ed.; Academic: New York, 1980; p 25.
(2) (a) For a review, see: Lai, Y.-H. *Org. Prep. Proced. Int.* **1980**, *12*, 361. (b) McMurry, J. E. *Acc. Chem. Res.* **1983**, *16*,405.
(3) See the series of papers Sterically Congested Olefins, I–XI; Part XI: Lenoir, D.; Malwitz, D.; Meyer, B. *Tetrahedron Lett.* **1984**, *25*, 2965.
(4) (a) Lenoir, D.; Gano, J. E.; McTague, J. *Tetrahedron Lett.* **1986**, *27*, 5339. (b) Michalczyk, M. J.; West, R.; Michl, J. *Organometallics* **1985**, *4*, 826.
(5) Pure **1** has not been reported, but the isomeric mixture has been prepared: Rice, J. E.; Okamoto, Y. *J. Org. Chem.* **1982**, *47*, 4189. See also: Lenoir, D. *Chem. Ber.* **1978**, *111*, 411 for preparation of **2**.
(6) Ermer, O.; Lifson, S. *Tetrahedron* **1974**, *30*, 2425.
(7) (a) This isomerization was instantaneous in the presence of iodine in pentane. (b) Fieser, M.; Fieser, L. *Reagents for Organic Synthesis*; Wiley-Interscience: New York, 1974; Vol. 4, p 503.

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