selectivity than chlorination and thus should enhance the formation ratio of the ±*sc* to the *ap* form[5] if the chloro group participates in stabilizing the transition state. Contrariwise, the ratio should be almost invariant if the steric factor dominates. In the event, bromination of **1** with bromine by irradiation gave an ±*sc*:*ap* ratio of 5.6. ±*sc*-9-(2-Bromo-1,1-dimethylethyl)-1,2,3,4-tetrachlorotriptycene was obtained 90% pure: $^1$H NMR ($CDCl_3$) $\delta$ 2.14 (3 H, s), 2.36 (3 H, s), 4.39 (2 H, apparent s), 6.10 (1 H, s), 6.95-8.15 (8 H, m). Chlorination with chlorine by irradiation may also be used for the diagnosis, since chlorination with sulfuryl chloride is known to be slightly more selective than chlorination with chlorine.[6] Again, if the steric effect is a dominating factor, chlorination with chlorine should give an almost invariant ±*sc*:*ap* ratio, whereas, if the participation of the chloro group is important in eq 1, the ±*sc*:*ap* ratio should be diminished. We found that the actual reaction gave an ±*sc*:*ap* ratio of 2.0 which is the statistical value; i.e., the participation hypothesis is verified.

A competitive reaction of **1** and 9-*tert*-butyltriptycene (**3**) allows comparison of the reactivities of the methyl groups concerned. If the reactivity of a methyl group in **1** is suppressed relative to that of a methyl in **3**, it may mean that disfavorable steric and/or electronic effects are present in **1**. Relative reactivities of the ±*sc* and the *ap* methyls in **1** were 1.0 and 0.7, respectively, in chlorination with sulfuryl chloride, taking one of the three methyl groups in **3** as a standard. The retardation may not be taken as evidence of the steric effect, if one considers the fact that chlorine atoms are electron-demanding radicals.[7,8] We feel it is informative that the competitive bromination between **1** and **3** gives the relative reactivities of 2.6 and 0.9 for the ±*sc* and the *ap* methyls, respectively.

It has now become clear that identical substituents may react at different rates to produce different rotamers. We conclude from the data shown above that, among three methyls in a *tert*-butyl group of **1**, the ±*sc* methyls are more reactive toward halogen radicals because of chloro-group participation. Other substituents which delocalize the odd electron should enhance the reactivities of the ±*sc* methyls as well.

Finally, the rotational isomers of **2** were found to react quite differently toward Lewis acids, as were the behaviors in chromatography on alumina: ±*sc*-**2** was destroyed by addition of $TiCl_4$ to its solution, whereas $SbCl_5$ was required to destroy *ap*-**2**. The details will be reported elsewhere.

**Acknowledgment.** We acknowledge the receipt of a grant from Toray Science Foundation which supported this work.

## References and Notes

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(2) $^1$H NMR spectral data of ±*sc*-**2** were obtained by subtracting the signals due to *ap*-**2** from those of a ±*sc*-*ap* mixture ($CDCl_3$): $\delta$ 2.11 (3 H, s), 2.30 (3 H, s), 4.89 (2 H, br s), 6.02 (1 H, s), 6.5-8.0 (8 H, m).

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(5) Tedder, J. M. *Q. Rev.* **1960,** *14*, 336-356.

(6) Fuller, A. E.; Hickinbottom, W. J. *J. Chem. Soc.* **1965,** 3235-3238.

(7) Chlorine atoms generated from sulfuryl chloride are known to abstract hydrogen more slowly from electron-poor methyls than from electron-rich methyls: (a) Helden, R. van; Kooyman, E. C. *Recl. Trav. Chim. Pays-Bas* **1954**, *73*, 269-278. (b) Walling, C. S.; Miller, B. *J. Am. Chem. Soc.* **1957,** *79*, 4181-4187.

(8) Although the reaction of 9-allyl-1,2,3,4-tetrachlorotriptycene and 9-allyl-1,4-dimethyltriptycene with bromine is considered to occur from similar conformations, their relative reactivities are 0.47 and 0.74, respectively, when 9-allyltriptycene is taken as a standard: Hatakeyama, S.; Mitsuhashi, T.; Ōki, M. *Bull. Chem. Soc. Jpn.*, in press.

**Tsutou Morinaga, Shigetaka Seki, Hiromi Kikuchi**
**Gaku Yamamoto, Michinori Ōki***
*Department of Chemistry, Faculty of Science*
*The University of Tokyo, Tokyo 113, Japan*

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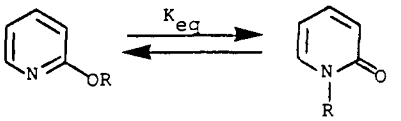
## Photoelectron-Determined Core Binding Energies and Predicted Gas-Phase Basicities for the 2-Hydroxypyridine ⇌ 2-Pyridone System

*Sir:*

Much attention has been devoted to the gas-phase tautomerism established between 2-hydroxypyridine (**1a**) and 2-pyridone (**2a**, eq 1).[1] In solution the equilibrium position of **1a** ⇌ **2a** lies far to the right,[2] while in the gas phase **1a** is slightly favored.[1,3] As part of our continuing interest in the application of X-ray photoelectron spectroscopy (X-ray PES) to tautomeric equilibria,[4] we have investigated the $N_{1s}$ and $O_{1s}$ binding energies for **1** and **2** as well as that of the analogous 2-hydroxypyridine *N*-oxide (**3a**) and *N*-ethoxy-2-pyridone (**4b**) (eq 2) with the intent of observing core ionizations from those species present in the gas phase. These data allow one to unambiguously confirm the position of the **1a** ⇌ **2a** equilibrium found recently by Beak[1b] and show that the equilibrium for **3a** ⇌ **4a** lies (within the limits of detection of this technique) completely on the side of **4a**. Moreover from a correlation of $N_{1s}$ binding energies for a series of 2-X-pyridines with existing gas-phase basicities, one can estimate the gas-phase basicity of **1a**.



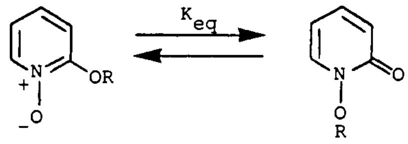
(1)

1a R = H
b R = $CH_3$

2a R = H
b R = $CH_3$

$K_{eq}$ (soln.) = 910[2]

$K_{eq}$ (gas) = 0.4 ± 0.25[1b]



(2)

3a R = H
b R = $CH_2CH_3$

4a R = H
b R = $CH_2CH_3$

For ease of visualization, the $N_{1s}$ and $O_{1s}$ ionization regions of **1a** ⇌ **2a** obtained at 130 °C[5] are presented in Figure 1, while the binding energies for those and related derivatives are compiled in Table I. Relative to pyridine (BE = 404.94 eV)

**Table I.** $O_{1s}$ and $N_{1s}$ Binding Energies (BE) for Compounds **1-4**[a]

| compd | binding energy, eV[b] $N_{1s}$ | binding energy, eV[b] $O_{1s}$ |
|---|---|---|
| pyridine | 404.94 (404.82)[c] | |
| 2-hydroxypyridine (**1a**) | 404.96 | 539.45 |
| 2-methoxypyridine (**1b**) | 404.68 | 538.91 |
| 2-pyridone (**2a**) | 406.61 | 536.66 |
| *N*-methyl-2-pyridone (**2b**) | 406.33 | 536.36 |
| *N*-hydroxy-2-pyridone (**4a**) | 408.07[d] | 540.08 (O—H)<br>537.01 (C=O) |
| *N*-ethoxy-2-pyridone (**4b**) | 407.41 | 539.58 (OEt)<br>536.49 (C=O) |
| pyridine *N*-oxide | 408.65[d] | 536.00[d] |

[a] Each BE is the average of at least three determinations and has a precision of ±0.03 eV unless otherwise noted. [b] Calibrated against a Ne auger line with 804.56-eV kinetic energy (T. D. Thomas and R. W. Shaw, *J. Elect. Spectrosc.*, **5**, 1081 (1974)). [c] Reference 7e. [d] Precision ±0.10 eV.

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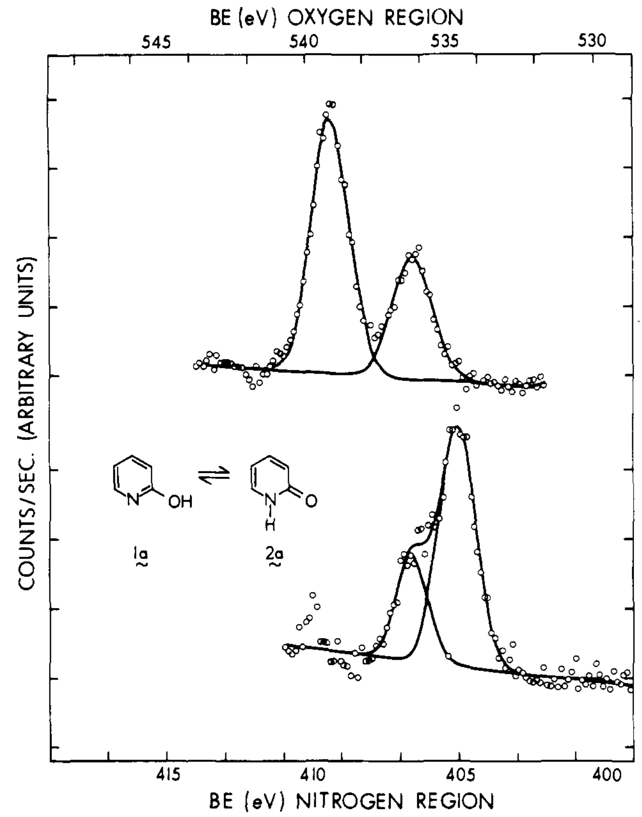


**Figure 1.** Unrestricted computer deconvolution of the $N_{1s}$ and $O_{1s}$ ionization regions of **1a** $\rightleftarrows$ **2a** at 130 °C. The ratio of the two N peaks and O peaks is 0.48 ± 0.05.

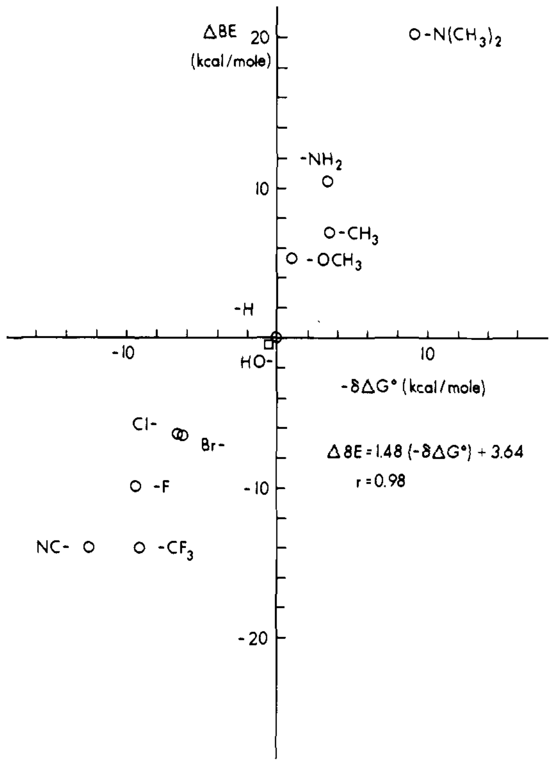
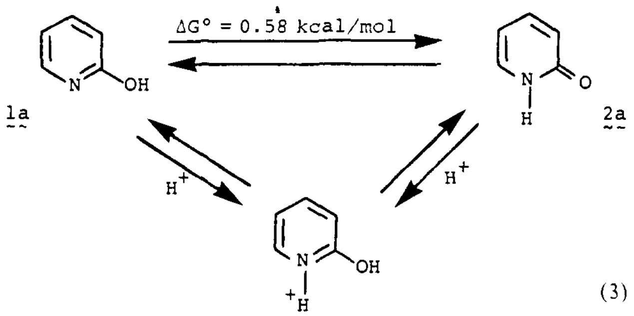


**Figure 2.** A plot of the change in $N_{1s}$ binding energy (ΔBE in kilocalories/mole) against change in gas-phase basicity [$-\delta\Delta G°$ in kilocalories/mole) of a series of 2-substituted pyridines relative to pyridine fitting the equation $\Delta BE = 1.58(-\delta\Delta G°) + 3.64$ ($r = 0.98$)]. Basicities are from ref 9.

the $N_{1s}$ of pyridones **2b** and **2a** are more difficult to ionize by 1.42 and 1.67 eV, respectively. On the other hand **1b** is easier to ionize than pyridine by 0.26 eV while **1a** is more difficult by 0.02 eV. Separate computer deconvolution of both the $N_{1s}$ and $O_{1s}$ regions of Figure 1, assuming equal ionization cross sections for **1a** $\rightleftarrows$ **2a**, shows that $K_{eq}$ for eq 1 is 0.48 ± 0.05 at 130 °C with the hydroxy form (**1a**) clearly dominating. This corresponds to a $\Delta G°$ for eq 1 of 0.58 ± 0.08 kcal/mol in excellent agreement with the $\Delta G°$ of 0.8 kcal/mol at 132 °C found by Beak.[1b]

For the **3a** $\rightleftarrows$ **4a** equilibrium, the assignment of the dominant species is not so straightforward. The $O_{1s}$ and $N_{1s}$ ionization regions show only two and one band, respectively, indicative of one dominant gas-phase species (we conservatively estimate that 5–10% of another species would be observable). Comparison of the separation between the $O_{1s}$ ionizations for the blocked derivative **4b** (3.09 eV) and that found for **3a** $\rightleftarrows$ **4a** 3.07 eV) suggests that in both cases the oxygens are of similar charge type so that the equilibrium lies on the side of **4a**.[6a] Additional support for the assignment comes from a comparison of the differences in the $N_{1s}$ BE for pyridine and its *N*-oxide (ΔBE = 3.71 eV). One might reasonably assume a similar ΔBE in passing from **2a** to **3a** which should yield an estimated $N_{1s}$ BE of 408.67 eV for the latter. That the observed BE for **3a** $\rightleftarrows$ **4a** is less than this by some 0.6 eV would indicate that the species giving rise to this ionization does not have such a positive nitrogen and is therefore more compatible with **4a**.[6b]

From eq 3, one sees that protonation of **1a** and **2a** must occur at different sites (N and O, respectively) but lead to the same species. From the cycle however, the gas-phase basicities for **1a** and **2a** cannot differ by more than 0.58 kcal/mol even though their $N_{1s}$ binding energies differ by some 1.65 eV. This provides conclusive evidence for the suggestions[7a,d-f] that correlations between $N_{1s}$ binding energies and basicities can only be valid when the site of protonation is the nitrogen. Such correlations have been established between various homologous bases provided that the site of protonation remains the same and that geometry changes accompanying protonation are not substantially different between the various bases.[7a,f,g] For the homologous series of 2-substituted pyridines [2, X = CN, $CF_3$, F, Cl, Br, H, $OCH_3$, $CH_3$, $NH_2$, $N(CH_3)_2$][8] the correlation with existing gas-phase basicities[9] is illustrated in Figure 2. When plotted on the same graph the $N_{1s}$ binding energy of **1a** (but not **2a**) is very close to that of pyridine itself. Although there are certain discrepancies in the graph (notably for 2-CN and 2-$CF_3$ which have identical BE's but different basicities), if the correlation between BE and $\Delta G°$ is valid for **1a**, one expects its gas-phase basicity to be similar to that of pyridine.[10] It would then appear that, provided that suitable reference compounds are available for comparison, estimates can be made for materials where conventionally determined basicities are lacking.[11]



(3)

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structed the heated inlet assembly, and to Professors P. Kebarle and R. W. Taft for helpful discussions and providing the gas-phase basicities, respectively.

## References and Notes

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(3) From ref 1b, $\Delta G°$(**1a** $\rightleftarrows$ **2a**) = 0.8 kcal/mol at 132 °C.

(4) (a) R. S. Brown, *J. Am. Chem. Soc.*, **99**, 5497 (1977); (b) R. S. Brown, A. Tse, and R. C. Haddon, *ibid.*, **101**, 3157 (1979).

(5) (a) Spectra were determined on a MacPherson 36 ESCA spectrometer with a heated inlet assembly, the details of which will be published. (b) **1a (1b)** was a commercial sample purified by distillation. (c) **2b** was prepared by $CH_3I$-catalyzed rearrangement of **1b** according to the procedure of P. Beak, J. Bonham, and J. T. Lee, *J. Am. Chem. Soc.*, **90**, 1569 (1968).

(6) (a) It would clearly be desirable to investigate the other blocked derivative **3b** for comparison. Unfortunately, under the conditions of the experiment, heating of **3b** caused it to rearrange cleanly to **4b** and the spectrum which was finally obtained showed only **4b** and no other species. (b) J. N. Gardner and A. R. Katritzby, *J. Chem. Soc.*, 4375 (1957), estimate from analysis of solution-phase IR and UV data that the pyridone form (**4a**) dominates.

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(8) R. S. Brown and A. Tse, unpublished results. Full results and analysis for the 2-, 3-, and 4-substituted pyridines will be published.

(9) Corrected gas-phase basicities were generously provided by Professor R. W. Taft.

(10) Since the difference in gas-phase basicities for **1a** and **2a** is given here as 0.58 kcal/mol, the differences in proton affinity should also be small. The PA of pyridine (relative to that of $NH_3$ (202.3 kcal/mol)[1d] is given as 217.4 kcal/mol,[1d] and, according to Figure 1, should be close to that for **1a**. For a series of oxygen bases, Benoit and Harrison[7g] have established a correlation between PA and $O_{1s}$ ionization energies given as PA (eV) = $-0.792$ BE($O_{1s}$) + 434.6. For **2a** [BE($O_{1s}$) = 536.66 eV]; the predicted PA is 220.6 kcal/mol which, considering the extrapolation, is in gratifyingly close agreement with that expected for **1a**.

(11) NOTE ADDED IN PROOF. A recent UV PES investigation of the **1a** $\rightleftarrows$ **2a** equilibrium shows that there are at least six overlapping bands with ionization energies of <11 eV. Deconvolution of the bands gives a $\Delta G°$ (**1a** $\rightleftarrows$ **2a**) of 0.90 kcal/mol at 110 °C [C. Guimon, G. Garrabe, and G. Pfister-Guillouzo, *Tetrahedron Lett.*, 2585 (1979)].

**R. S. Brown,* A. Tse, J. C. Vederas**
*Department of Chemistry, University of Alberta*
*Edmonton, Alberta, Canada T6G 2G2*

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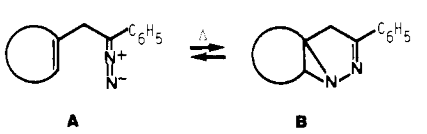
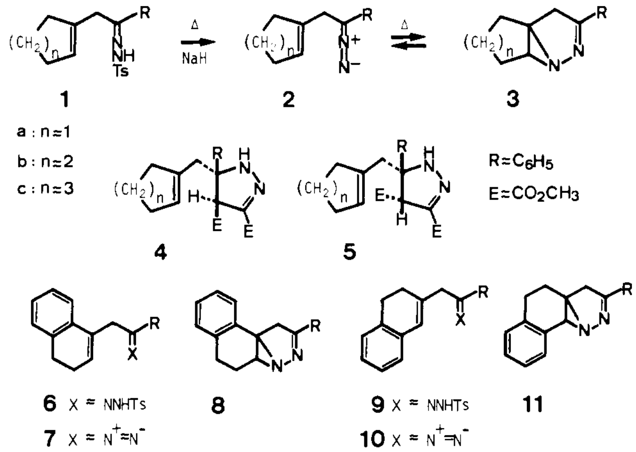
## Intramolecular 1,1-Cycloaddition Reactions of Diazomethanes to C=C Double Bonds[1]

*Sir:*

Recently, Padwa[2] and Steglich[3] reported that both photochemically[2] and thermally[3] generated 2-allyl-substituted nitrile ylides underwent a *carbene*-type intramolecular 1,1 cycloaddition to give 2-azabicyclo[3.1.0]hex-2-enes. In connection with those findings and our recent report[4] on a novel cyclization of allyldiazomethane derivative derived from thermal decomposition of the sodium salt of $\alpha$-(1,3,5-cycloheptatrien-3-yl)acetophenone to 10-phenyl-1,11-diazatricyclo[6.3.0.0$^{4,6}$]undeca-2,8,10-triene, it was of interest to explore the generality of intramolecular cyclizations of 2-allyl-substituted diazomethanes in which steric restrictions oppose the parallel-plane approach which gives normal 1,3-dipolar adducts, 2,3-diazabicyclo[3.1.0]hex-2-enes. Herein we report our first observation of a formal *nitrene*-type 1,1 cycloaddition of 2-allyl-substituted diazomethanes A leading to 1,2-diazabicyclo[3.1.0]hex-2-enes B.



Decomposition of the sodium salt of tosylhydrazone **1a** (mp 123 °C)[7] in refluxing carbon tetrachloride immediately developed a red coloration which gradually faded during refluxing. Upon cooling to room temperature the color faded completely and **3a** (mp 91 °C) was isolated in 73% yield. The structure of **3a** was unequivocally determined by its spectral properties: *m/e* (rel intensity) 198 ($M^+$, 62), 170 (45), 169 (35), 155 (52), 142 (90), 141 (100); $\nu_{max}^{KBr}$ 3040, 2950, 1560, 1495, 1445, 760, 690 cm$^{-1}$; $\lambda_{max}^{EtOH}$ 253.4 nm (log $\epsilon$ 4.09); $^1H$ NMR ($\delta$ units in toluene-$d_8$), 1.2~2.2 (m, 7 H), 2.72 (d, 1 H, $J$ = 17.3 Hz), 2.91 (d, 1 H, $J$ = 17.3 Hz), 7.0~7.2 (m, 3 H), 7.6~7.8 (m, 2 H). Similarly, decomposition of **1b** (mp 127 °C) and **1c** (mp 120 °C) under the same conditions gave the corresponding aziridines **3b** (mp 71.5 °C)[8] and **3c** (mp 65~67 °C)[9] in 72 and 86% yields, respectively. Dihydronaphthalene derivative **6** (mp 138 °C) also afforded a quantitative yield of the air-sensitive **8**.[10] The isomer **9** (mp 159 °C dec), on the other hand, afforded in quantitative yield **10**,[11] which was found, however, to cyclize slowly to **11** (mp 93.5~95 °C)[12] in 50% yield when allowed to stand at −23 °C.



The generation of diazomethanes as intermediates in the formation of aziridines was substantiated in the case of **2c**[13] by the formation of the usual 1,3-dipolar adducts,[14] **4c** (58%) and **5c** (18%), and suppression of the yield of **3c** (20%) when **1c** was decomposed in the presence of dimethyl fumarate. Also, the reversibility of the 1,1 cycloaddition between diazomethanes and aziridines was directly observed by temperature-dependent $^1H$ NMR analyses of these aziridines.[15] Thus, upon heating a solution of **3a** in toluene-$d_8$ at 101 °C for 10 min in the probe or **3b** at 85 °C, new absorptions appeared due to **2a** and **2b** both in the $^1H$ NMR[16] and IR ($\nu_{max}^{neat}$ 2040 cm$^{-1}$) spectra, indicating the formation of the following mixtures, respectively: **2a** (13%) and **3a** (87%) and **2b** (24%) and **3b** (76%). The absorptions due to **2a** and **2b** disappeared upon cooling to room temperature, cleanly reproducing the spectra of **3a** and **3b**. Separate heating of a mixture of **7** (9%) and **8** (91%) at 30 or at 90 °C for 10 min in carbon tetrachloride gave mixtures composed, respectively, of 13% **7** and 87% **8** at 30 °C and 50% **7** and 50% **8** at 90 °C. The latter mixture, when cooled to 30 °C, gave nearly the same composition (10% **7** and 90% **8**) as the starting one. Diazomethane **10**, on the other hand, cyclized rather slowly to **11**; a mixture composed of **10** (74%) and **11** (26%) obtained by heating of **11** at 80 °C for 10 min slowly changed its composition to 45% **10** and 55% **11** after 30 days at room temperature. During the above $^1H$ NMR analyses, neither an intermediate such as a 2,3-di-

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