Tetrahedron Vol. 41, No. 8, pp. 1509 to 1516, 1985
Printed in Great Britain.

0040–4020/85 $3.00 + .00
Pergamon Press Ltd.

SUBSTITUENT EFFECTS ON THE RATE OF CARBENE FORMATION BY THE PYROLYSIS OF RIGID ARYL SUBSTITUTED DIAZOMETHANES

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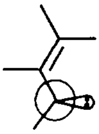
(*Received in USA* 15 *December* 1983)

Abstract—Rate constants for the pyrolysis of 1-diazo-4,4-dimethyl-1,4-dihydronaphthalenes, **4a–4e**, have been measured in methanol: 6% triethylamine. In contrast to non-rigid cases, like diphenyldiazomethanes, where all *para* substituents show a rate increase compared to hydrogen, these rates show a linear Hammett correlation for para substituents with $\sigma^+ = -0.84$. This observation is rationalized by a non-linear process for loss of nitrogen leading directly to the ground-state singlet of the carbene, **17**. This carbene is then trapped to give the ether **11**.

As is well recognized, diazo compounds serve as useful precursors for carbenes by either photochemical or thermal decomposition.[1,2] Recently we have been examining in some detail the kinetics of the thermal decomposition of a variety of vinyldiazo compounds[3,4] in an attempt to learn about the electronic structure of the carbene generated. Vinyl carbenes, in their planar geometry, have four readily accessible electronic configurations; singlets **1** (2π or σ^2)[5,6] and **2** (4π or p^2) and both a singlet and a triplet corresponding to **3** (3π or σp). Both MO calculations[5–7] and ESR results [8,9] indicate that the triplet **3** is normally the most stable of these states but it is not necessarily the first formed intermediate in decomposition reactions of diazo compounds. For singlet states, normally **1** is the most stable, **3** the next and **2** the least stable. The thermal decomposition should be easier to interpret than the photochemical process because the starting material, transition state and the initially formed carbene will all be in the singlet state. The question of which of the three singlets is generated is not so easy to answer.



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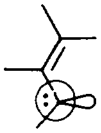

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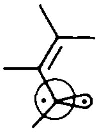

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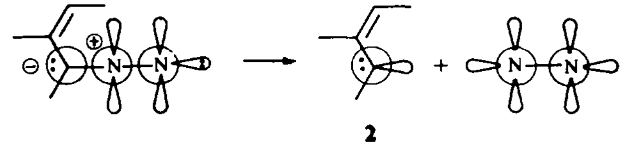
As indicated in Eq. 1 the loss of nitrogen from a vinyldiazo compound in the linear mode (using the terminology developed by Woodward and Hoffmann[10] for cheletropic reactions) leads directly to the carbene **2**, the doubly excited singlet. This carbene should be converted rapidly and exothermically to the more stable **1** but the transition state for the thermal process should reflect the development of an electronic configuration like **2** if the reaction follows this "forbidden" pathway. If the loss of nitrogen from the diazo compound occurs in the nonlinear mode, the ground state singlet **1** will be generated directly and the process will be "allowed". In fact MO calculations[11] for the loss of nitrogen from diazomethane indicate that the activation barrier for loss of nitrogen disappears if the restriction of the linear geometry is removed. To our knowledge there are no experimental results that address this problem of orbital symmetry.

The kinetics for the thermal loss of nitrogen from a series of ring substituted diphenyldiazomethanes have been measured.[12,13] Substitution in the *para* position gives rate acceleration compared to hydrogen for both electron-donating and electron-withdrawing substituents. This leads to a parabolic Hammett plot with the two arms having slopes of $\rho^+ \simeq -0.9$ for electron-donating substituents and $\rho^- \simeq 0.4$ for electron-withdrawing ones.[14] A similar parabolic plot is observed for a smaller series of phenylvinyldiazomethanes.[4]

Curved Hammett plots have been observed before in benzylic systems[16] and usually indicate a change in mechanism as the substituent changes. However, in the case of the pyrolysis of diazo compounds, a different explanation is possible. A late transition state with considerable singlet carbene character, i.e. one orbital electron-deficient and one orbital electron-rich, is proposed; freedom of rotation of the aryl ring then allows conjugation with either orbital depending on the substituent.[4,12,13] However, this explanation would be applicable for either singlet state, **1** or **2**, of the carbenes. In fact, the rate data might also be accounted for by initial generation of a carbene with considerable radical character like **3**. The recent development of a $\sigma^{\bullet}$ scale for radical stability[17] indicates that most *para* substituents (the exceptions are F, CF_3 and $OCOCH_3$) are radical stabilizing and should be rate accelerating relative to hydrogen in reactions involving radical intermediates.



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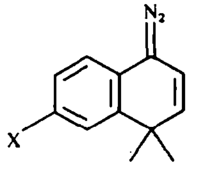


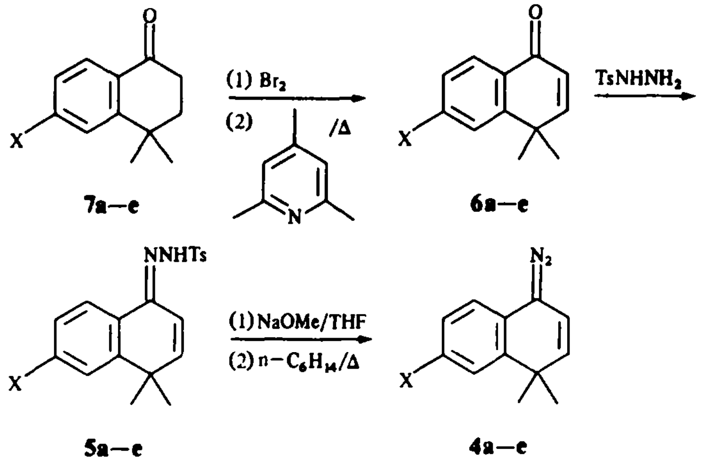
4a–e

4a X = CH_2O
4b X = CH_2
4c X = H
4d X = Br
4e X = NO_2

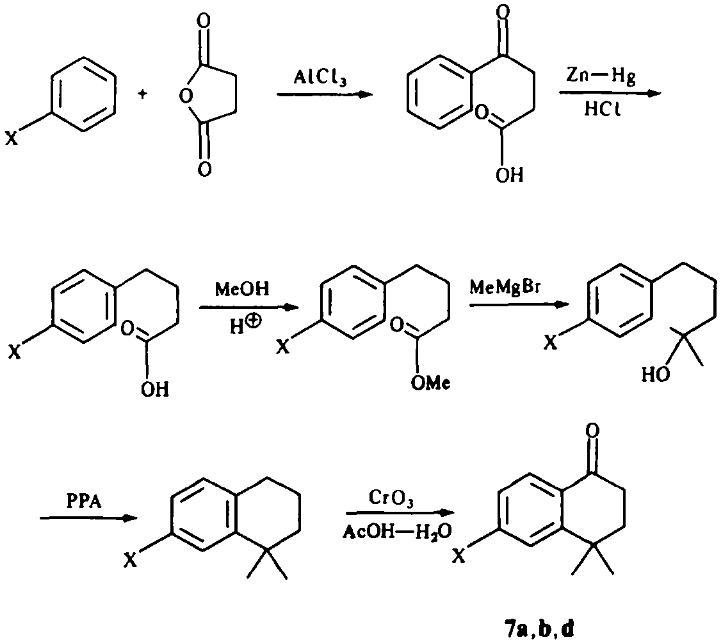
In order to examine these questions concerning the connection between substituent effects, carbene structure and orbital symmetry for the pyrolysis of diazo compounds, we have measured the thermal kinetics for the loss of nitrogen from the series of compounds, **4a**–**4e**. In these rigid examples the substituents on the aryl ring are directly conjugated with only the p or π type orbital at the carbene center and their rate effects should be more easily rationalized.

RESULTS

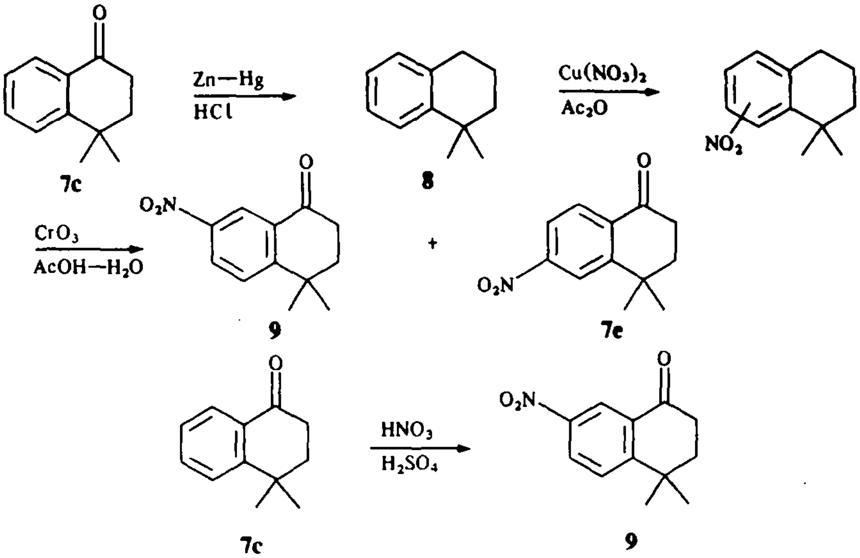
Synthesis of the diazo compounds, **4a**–**4e**. All of the diazo compounds were prepared by pyrolysis of the corresponding sodium salts of the tosylhydrazones, **5a**–**5e**, in refluxing hexane. Since the diazo compounds themselves are thermally unstable, this had to be done quite carefully to get reasonable yields. In fact samples of the diazo compounds were always contaminated to some extent by products of their decomposition (by NMR analysis less than 10%). Quite pure samples can be obtained at low conversions. Details of this procedure and the spectral data for **4a**–**4e** are given in the Experimental Section. The tosylhydrazones were prepared from the enones, **6a**–**6e**. The unsubstituted enone, **6c**, is known and was prepared by the literature procedure.[18] The enones were prepared by bromination/dehydrobromination of the corresponding ketones, **7a**–**7e**. The procedures are outlined in



Scheme 1. Synthesis of diazo compounds **4a**–**e**.



Scheme 2. Synthesis of tetralones **7a**, **7b** and **7d**.

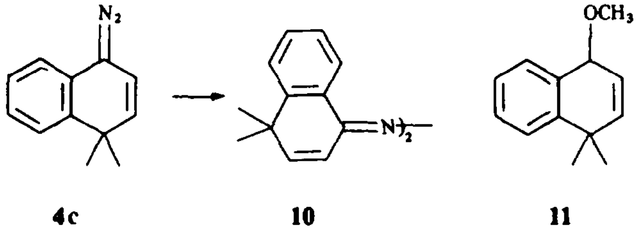


Scheme 3. Synthesis of 6- and 7-nitrotetralones.

Scheme 1. The ketones, **7a**, **7b** and **7d** were prepared by the sequence outlined in Scheme 2; **7a** is a known compound.[19] The nitro compound, **7e**, was prepared by separation of the mixture obtained by nitration of **8** followed by reoxidation as in Scheme 3. That **7e** was in fact the 6-nitro isomer was confirmed by independent preparation of **9** by nitration of **7c**. The position of the nitro group as *meta* or *para* to the carbonyl was established by the very good comparison of the UV spectra with both *meta* and *para* nitroacetophenone and benzophenone. Full details of these procedures are given in the Experimental Section.

Kinetics of the thermal decomposition of the diazo compounds, **4a**–**4e**. The thermal decomposition of 10^{-3}–10^{-4}M solutions of the diazo compounds in 6% triethylamine in methanol at 61° was monitored spectrophotometrically using an ampule technique described previously.[3,4] The first order rate constants are from ln $(A-A_\infty)$ plots and are the average of at least two runs from each of two different samples of the diazo compound. Correlation coefficients were always greater than 0.99. The values obtained and the mean deviations ($s^{-1} \times 10^4$) are: **4a**, 10.4 ± 0.7; **4b**, 3.9 ± 0.2; **4c**, 2.2 ± 0.1; **4d**, 1.70 ± 0.05; **4e**, 0.50 ± 0.02. Details are given in the Experimental Section.

Products of the thermal decomposition of the diazo compounds, **4c**. Pyrolysis of **4c** in hexane gave as the principal product (>60%) the azine, **10**. At high concentrations (0.2 M) in methanol, **10** was still the major product and less than 10% of the ether, **11**, was



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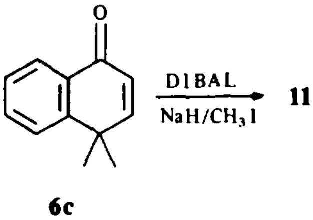

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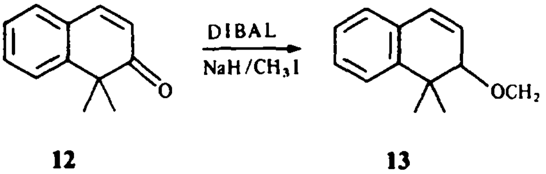


(4)

formed. However, at low concentrations (10^{-3}–10^{-4}M) in methanol the ether **11** was the only product (by NMR). More than 5% of the isomeric ether **13** would have been easily detected. The structure of **11** was demonstrated by independent synthesis from **6c** as shown in Eq. 3. Because we had thought that the isomeric ether **13** would also be a product, it was synthesized from the known enone, **12**,[20] as shown in Eq. 4.

DISCUSSION

The main objective of this work was to examine the thermal decomposition of diazomethanes by comparing the kinetics of the rigidly conjugated cases, **4a**–**4e**, with those of the non-rigid examples reported earlier, in particular the diphenyldiazomethanes.[12,13] As shown in the Results, the total range of rate constants for **4a**–**4e** is only about a factor of 20 as the substituent changes from the electron-donating methoxy group to the electron-withdrawing nitro group. This is quite different from the diphenyldiazomethanes where the range is about a factor of 5 but both methoxy and nitro are faster than hydrogen. These rate effects are quite small for a process involving *para* substitution in a benzylic system. This is a reflection of the fact that the rate determining step involves loss of nitrogen and carbene formation; that is, a neutral starting material gives two neutral fragments. The substituent effects are a result then of changes in charge distribution as the reaction proceeds rather than the creation or destruction of charged species.

A Hammett plot of the rate data for **4a**–**4e** is shown in Fig. 1 versus the σ^+ substituent constants[21] and gives $\rho^+ = -0.84$ ($r = 0.998$). The correlation is worse if other substituent constants are used: σ gives $\rho = -1.10$ ($r = 0.93$) and σ^- gives $\rho^- = -0.71$ ($r = 0.88$).[22] The rate data cannot be accounted for by radical character in the transition state since all *para* groups should be rate accelerating by the $\sigma^\cdot$ scale. The linear correlation with σ^+ again emphasizes the difference in substituent effects on the rates for the loss of nitrogen in the rigid systems, **4**, as compared to the diphenyldiazomethanes[12,13] where the electron-donating substituents do correlate with σ^+ ($\rho = -0.9$) but the electron-withdrawing substituents correlate with σ^- ($\rho = 0.4$) and the final plot is therefore parabolic.

Kinetic differences are, of course, a result of changes in ground state to transition state energies. Normally, in Hammett type correlations, substitution effects are attributed entirely to transition state changes since there is the formation of a charged intermediate. For the loss of nitrogen from diazomethanes, this is not true and both ground state and transition state effects must be assessed carefully. The linear σ^+ correlation with a negative slope for the rates of decomposition of **4** indicates that positive charge is increasing in an orbital directly conjugated to the substituent. In Eq. 5, the diazo compound is shown in its two major resonance forms, **14** and **15**, and the intermediate carbene in the two most probable singlet states, **16** (p^2 resulting from linear loss of nitrogen) and **17** (σ^2 resulting from non-linear loss of nitrogen). The σp state (see Introduction) is excluded based on the very poor correlation of the kinetic results with $\sigma^\cdot$. The rigid geometry of all of these structures forces the substituent, X, to conjugate only with the π orbital at the diazo and carbene carbon.

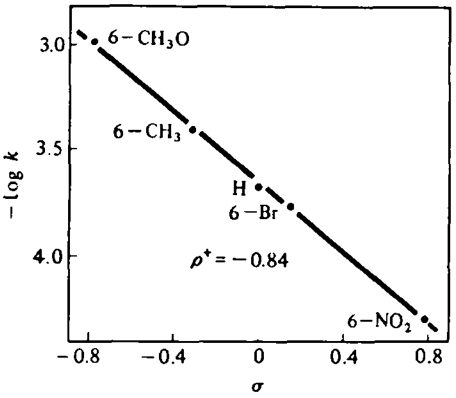
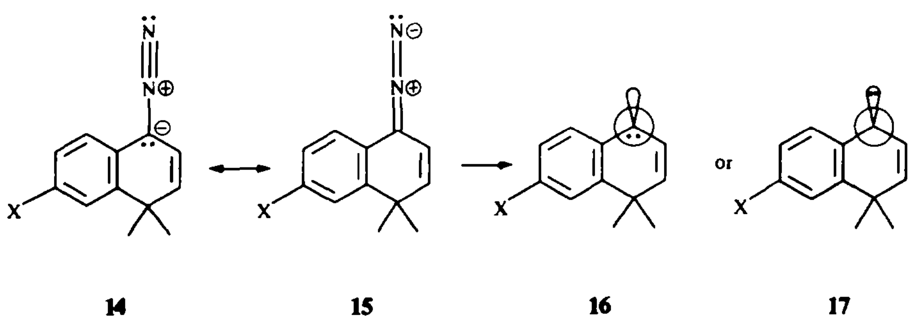


Fig. 1. Hammett plot for the thermal decomposition of diazo compounds **4a**–**e**.

An examination of **14** reveals that the π system is electron rich and that electron-withdrawing substituents should stabilize **14** and **15**. Since, in fact the reaction rate becomes slower for electron-withdrawing substitutions, it seemed possible that this ground state stabilization effect could be important in determining the relative rates. However, if this were true, the reaction rates should correlate with σ^- since it is an electron-rich orbital that conjugates with the substituent. As stated above the correlation with σ^- is significantly poorer. Moreover, if a two parameter correlation is used ($\log k = \rho^-\sigma^- + \rho^+\sigma^+$) the first term should reflect this ground state effect. This does in fact lead to a slight improvement in the correlation ($r = 0.999$ compared with $r = 0.998$ with just σ^+) but the values of $\rho^- = -0.07$ and $\rho^+ = -0.91$ indicate the minor importance of the first term. Shechter[12] has, by an analysis of ^{13}C chemical shifts of the diazo carbon in diphenyldiazomethanes, reached the similar conclusion that ground state effects are unimportant in



(5)

14 **15** **16** **17**

accounting for rate changes in the dediazotation reaction.

If ground state effects are unimportant, then the kinetic results reflect changes in transition state energies as a function of the substituent. The explanation for the σ^+ correlation is then simply that the intermediate formed in the rate-determining step is the carbene in its ground singlet state, σ^2, **17**. This state has an electron deficient π orbital in direct conjugation with the substituent. The allowed pathway by orbital symmetry is therefore a non-linear[10] loss of nitrogen.

The contrast between the kinetic behavior of the rigid diazo compound, **4**, and the non-rigid diphenyldiazomethanes[12,13] also demonstrates that the explanation for the parabolic Hammett behaviour is likely correct. That is, the freedom of rotation of the aryl ring allows conjugation with either the electron-deficient or the electron-rich orbital at the carbenic C. In fact, if the carbene is of the σ^2 type, conjugation with the electron-deficient π orbital should be more effective than conjugation with the electron-rich σ orbital because the geometry for the overlap is better. In agreement with this ρ value on the σ^+ side of hydrogen (i.e. electron-donating groups) is larger (-0.9) than on the σ^- side of hydrogen (-0.4).

Finally, a brief discussion about the products formed from the reaction is necessary. At high concentrations of the diazo compound, **4**, in either methanol or hexane, pyrolysis gives good yields of the azine, **10** (Eq. 2). This, of course, introduces second order terms into the kinetics and complicates the determination of the rate of carbene formation. However, if the concentration of the diazo compound is less than 10^{-3} M in methanol, then the only product observed (by NMR) was the ether **11** (Eq. 2). More than 5% of the isomeric ether **13** would have been easily detected. In fact **13** is the more stable of the two isomers since it is formed quantitatively from **12** by refluxing in methanol. This process is presumably catalyzed by trace acid impurities in methanol since addition of triethylamine to the methanol stops isomerization.

A variety of pathways have been proposed in the past for the reaction of singlet carbenes in alcohol solvents including direct insertion into the O—H bond, protonation of the carbene by the alcohol to give a carbocation,[23] attack on the carbene C by the nucleophilic oxygen of the alcohol to give a zwitterion[23] and trapping of the carbene by the oligomers of the alcohol.[24] Which of these pathways occurs is dependent on the structure of the carbene. For vinyl carbenes, allylic cations are known to form in some cases.[25] For the σ^2 carbene **17** generated from **4** this would lead to the two ethers **11** and **13**, Eq. 6. Since **13** is the more stable of the two ethers and since it is not formed, it seems unlikely that the cation **18** is present unless **18** is simply attacked in the kinetic sense preferentially at the less hindered carbon giving **11**. The other possibility is that the carbene **17** simply reacts by direct insertion into the O—H bond of methanol or methanol oligomers.

EXPERIMENTAL

60 MHz NMR spectra were recorded on a Varian T-60 spectrometer using TMS as the internal standard. 80 MHz NMR were recorded on a Varian CFT-20 spectrometer. Chemical shifts are reported as δ-values. IR spectra were recorded on a Perkin–Elmer 237 B or 238 B grating spectrometer using NaCl plates and are reported in wavenumbers, calibrated against the 1620 cm^{-1} polystyrene absorption. Mass spectra (70 eV) were recorded on a Dupont CEC-21-104 mass spectrometer and are reported as m/e (relative intensity). Other than the molecular ion peak (if it was observed), only peaks greater in intensity than 10% of the base peak are reported. Exact mass determinations were done on a Dupont CEC-21-110B mass spectrometer. UV spectra, recorded as absorbance against wavelength (in nanometers) were run on a Varian Cary 219 spectrometer using 1.0 cm quartz cuvettes. Melting points (in °) were taken on a Fisher–John apparatus or a Thermolyne hot-stage microscope and are uncorrected.

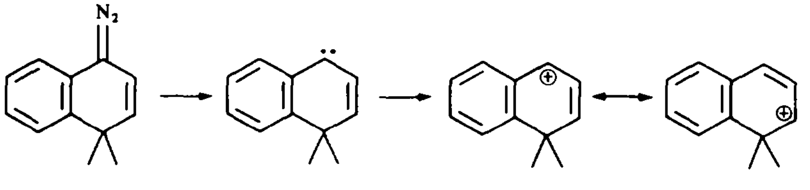
Combustion analysis were performed by Microanalysis Laboratory Ltd., Toronto, Ontario.

All kinetic or constant temperature studies were done in a Haake-(FK-10) thermostated bath controlled to within ±0.1° of the required temperature. Triethylamine used for the kinetic studies was freshly distilled over KOH.

4,4-Dimethyl-6-methoxytetralone, **7a**. The ketone was prepared by the procedure of Miller and Gutierrez[19] as outlined in Scheme 1; m.p.: 39–42° (reported previously as an oil), NMR ($CDCl_3$): 1.35 (6H, s), 1.85–2.08 (2H, m), 2.55–2.78 (2H, m), 3.85 (3H, s), 6.68–8.07 (3H, m).

3-(4-Methylbenzoyl)propanoic acid. In a 2 l 3-neck flask equipped with two reflux condensers and a mechanical stirrer were placed 68 g (0.75 mol) of succinic anhydride, 92 g (1.0 mol) of toluene and 310 ml of benzene. The mixture was stirred and 200 g of anhyd $AlCl_3$ was added all at once followed by heating at reflux for 0.5 hr. Heating was stopped and the mixture cooled by ice. Water (300 ml) was added dropwise to the flask. The water and benzene were removed azeotropically and then MeOH was added to remove, by azeotrope, the excess of toluene. The solution was then transferred to a 2 l beaker to which 20 ml of conc HCl was added. The ppt was filtered off with a Buchner funnel. The ppt was then added to 134 g of Na_2CO_3, dissolved in 1500 ml of water and boiled for 1 hr. The soln was filtered and acidified with HCl. The acid so obtained was filtered and was added to 1 l of 10% NaOH aq. The mixture was boiled for 1 hr, cooled, filtered and acidified. The ppt so obtained was filtered and dried in a vacuum desiccator overnight. The yield was 90 g (62%); m.p.: 128–129°, NMR ($CDCl_3$): 2.4 (3H, s), 2.68–2.88 (2H, m), 3.18–3.4 (2H, m) 7.18 (1H, bs), 7.26 (2H, d, J = 8 Hz), 7.88 (2H, d, J = 8 Hz).

3-(4-Bromobenzoyl)propanoic acid. In a 2 l flask equipped with a condenser and a mechanical stirrer were placed 136 g (1.5 mol) of succinic anhydride and 650 ml of bromobenzene. With stirring, 400 g of anhyd $AlCl_3$ was added at once and the mixture heated in an oil bath at 90° for 5 hr. The soln was cooled and worked-up as above. The yield was 170 g (44%); m.p.: 115–117°; NMR (DMSO): 2.55–2.77 (2H, m), 3.2–3.4



(6)

4 **17** **18**

(2H, m), 7.57–8.07 (4H, m); IR ($CHCl_3$): 800, 1225, 1700, 1725, 2400, 3000 cm^{-1}.

4-(4-Methylphenyl)butanoic acid. A mixture of 158 g of amalgamated Zn, 85.6 g (0.48 mol) of the 3-(4-methylbenzoyl)propanoic acid and 400 ml conc HCl, was placed in a 1 l flask with a reflux condenser. The mixture was refluxed for 15 hr and then 160 ml of conc HCl was added. The mixture was refluxed for an additional 2 hr and then cooled and filtered. The filtrate was extracted with 6 × 100 ml of diethyl ether, dried over $MgSO_4$, filtered and the solvent evaporated. Distillation at 124°/3 mm gave 49.5 g (58%) of the desired acid which crystallized on standing; m.p.: 47–48°; NMR ($CDCl_3$): 1.7–2.77 (6H, m), 1.92 (3H, s), 7.03 (4H, m), 9.67 (1H, bs).

4-(4-Bromophenyl)butanoic acid. The procedure was similar to the one used above, b.p. 185–190°/1.5 mm. The product again crystallized on standing. The solid was used without any further purification: yield 70%; m.p.: 83–86°; NMR ($CDCl_3$): 1.75–2.83 (6H, m), 6.87–7.12 (4H, m), 11.6 (1H, s).

Methyl 4-(4-methylphenyl)butanoate. To a 250 ml round-bottom flask was added 30 g (0.169 mol) of the acid, 28 ml of MeOH, 90 ml of benzene and 0.1 g of *p*-toluenesulphonic acid. The soln was refluxed for 18 hr, cooled, neutralized with $NaHCO_3$ and extracted with ether. The combined organic layers were washed with water until neutral then dried. Evaporation *in vacuo* gave an oil which was distilled (84–86°/1.5 mm); yield: 23.4 g (67%); NMR ($CDCl_3$): 1.83 (3H, s), 1.57–2.33 (6H, m), 3.47 (3H, s), 6.87–6.93 (4H, m).

Methyl 4-(4-bromophenyl)butanoate. By the same method as above, 79 g (0.33 mol) of the acid gave 83.5 g (100%) of the ester on distillation (90°/0.05 mm); NMR ($CDCl_3$): 1.67–2.78 (6H, m), 3.55 (3H, s), 6.78–7.35 (4H, m).

2-Methyl-5-(4-methylphenyl)-2-pentanol. MeMgI was prepared using 5.75 g of Mg and 34.1 (0.24 mol) of MeI dissolved in 100 ml of anhyd diethyl ether. Methyl 4-(4-methylphenyl)-butanoate, 22.6 g (0.109 mol) was then added to the Grignard reagent dropwise with mechanical stirring. After 24 hr of stirring at room temp a sat soln of NH_4Cl aq was added dropwise. The mixture was extracted with diethyl ether three times. The combined organic extracts were washed with water until neutral and dried. Evaporation of the solvent gave 20.6 g (100%) of the desired alcohol which was used without further purification; NMR ($CDCl_3$): 1.12 (6H, s), 1.33–1.93 (4H, m), 2.18 (3H, s), 2.3–2.67 (2H, m), 3.03 (1H, bs, exchangeable), 6.83–6.98 (4H, m).

2-Methyl-5-(4-bromophenyl)-2-pentanol. The procedure was similar to that described above; NMR ($CDCl_3$): 1.15 (6H, s), 1.55 (4H, m), 2.42–2.78 (3H, m), 6.87 (4H, bs).

6-Methyl-4,4-dimethyltetralin and 6-bromo-4,4-dimethyltetralin. The alcohols (25 g), were placed in a round-bottom flask and to this was added 50 g of polyphosphoric acid. The resulting mixture was allowed to stand at 50–55° for 9 hr. The mixture was then cooled to room temp and then poured over ice-water. The soln was then extracted four times with diethyl ether. The combined organic layers were washed with water until neutral and then dried. Evaporation of the solvent gave a brown oil which was chromatographed on a silica gel column using n-hexane as eluent. Yields were in the range of 80–85%. For 6-methyl; NMR ($CDCl_3$): 1.27 (6H, s), 1.57–1.9 (4H, m), 2.28 (3H, s), 2.57–2.87 (2H, m), 6.87–7.2 (3H, m). For 6-bromo; NMR ($CDCl_3$): 1.25 (6H, s), 1.6–2.0 (4H, m), 2.57–2.9 (2H, m), 6.93–7.4 (3H, m).

4,4-Dimethyl-6-methyl-1-tetralone, **7b**. In a 100 ml 3-necked round-bottom flask equipped with a mechanical stirrer and a dropping funnel are placed 6.6 g (0.038 mol) of the 6-methyltetralin in 80 ml of glacial AcOH. The soln was cooled to 10°. A soln of CrO_3, 6.06 g (0.061 mol), in minimum amount of warm water (8.6 ml) and 35 ml of glacial AcOH, was introduced into the dropping funnel and two drops of this soln were added to the mixture. At this time the mixture was cooled to 0° and the rest of the CrO_3 soln added dropwise maintaining the temp at 0–5°. After the addition was complete, the mixture was stirred at 0° for 24 hr. The mixture was then diluted with 100 ml of ice-water and then extracted with ether, five times. The combined organic layers were then washed with 5% NaOH aq until the aqueous layers were alkaline. The organic layer was then washed with water until neutral and then dried. Removal of the solvent gave a heavy oil which was chromatographed on silica gel using CH_2Cl_2 as eluent; yield 6.0 g (84%); NMR ($CDCl_3$): 1.4 (6H, s), 1.9–2.13 (2H, m), 2.42 (3H, s), 2.6–2.87 (2H, m), 7.0–8.0 (3H, m); IR ($CHCl_3$): 1330, 1345, 1365, 1390, 1610, 1685, 3000 cm^{-1}; high resolution mass spectrum calc (*m/e*) for $C_{13}H_{16}O$, 188.1201; found 188.1195.

Preparation of 4,4-dimethyl-6-bromo-1-tetralone, **7d**. The tetralone was prepared by a similar method as described above; yield 70%; NMR ($CDCl_3$): 1.37 (6H, s), 1.87–2.17 (2H, m), 2.6–2.87 (2H, m), 7.13–8.1 (3H, m); IR (neat): 760, 1280, 1325, 1360, 1382, 1425, 1595, 1685, 2960 cm^{-1}; high resolution mass spectrum calc (*m/e*) for $C_{12}H_{13}OBr$, 252.0150; found 252.0146.

4,4-Dimethyl-7-nitrotetralone, **9**. In a 250 ml 3-necked round-bottom flask equipped with a mechanical stirrer and an ice-salt bath are placed 36 ml of conc H_2SO_4. When the temp cooled to 0°, 20 g (0.115 mol) of 4,4-dimethyltetralone was added dropwise maintaining the temp of the soln below 5°. After the addition was complete the soln was cooled to $-7°$ and ice-cold mixture of conc HNO_3 (9.2 ml) and conc H_2SO_4 (14 ml) added dropwise keeping the temp between $-5°$ and 0°. After the addition was complete, the soln was stirred for another 10 min at 0°. Then the soln was poured over a mixture of 200 g of ice and 200 ml of water. A ppt appeared. The ppt was collected on a Buchner funnel, dissolved in a minimum amount of hot EtOH and then poured into an equal volume of water. The ppt thus obtained was once again filtered and recrystallized in EtOH to give 13 g (52%) of the desired nitrotetralone: m.p.: 160–161°; NMR ($CDCl_3$): 1.47 (6H, s), 1.95–2.2 (2H, m), 2.67–3.05 (2H, m), 7.58 (1H, d, J = 8 Hz), 8.28 (1H, dd, J = 8 Hz, 3 Hz), 8.7 (1H, d, J = 3 Hz); IR ($CHCl_3$): 1340, 1525, 1610, 1690, 2960 cm^{-1}; UV (MeOH): λ_{max} 231 (14,600).

1,1-Dimethyltetralin, **8**. 4,4-Dimethyltetralone, **7c** (20 g, 0.115 mol), was placed in a 250 ml round-bottom flask and 38 g of amalgamated Zn was added. The mixture was refluxed for 16 hr, cooled and filtered. The filtrate was extracted four times with ether. The combined ether extracts were washed with water and then with sat $NaHCO_3$ aq; dried, and the solvent evaporated. The residual oil was chromatographed over silica gel using n-hexane as eluent: yield 14 g (76%); NMR ($CDCl_3$): 1.22 (6H, s), 1.58–1.88 (4H, m), 2.42–2.78 (2H, m), 6.78–7.25 (4H, m).

4,4-Dimethyl-6-nitrotetralone, **7e**. To a soln of 4.0 g (0.025 mol) of the 1,1 dimethyltetralin dissolved in 200 ml of Ac_2O held at 0°, was added 4.3 g of powdered cupric nitrate trihydrate. The soln was stirred magnetically at 0° for 1 hr and then for 3 hr at room temp. The mixture was then poured over ice in a 1 l beaker and allowed to stand overnight to hydrolyse all the Ac_2O. The soln was stirred occasionally and more ice was added when the soln temp went above room temp. The mixture was then extracted twice with $CHCl_3$. The combined organic extracts were then washed several times with water and finally with $NaHCO_3$ aq. The organic extract was then filtered and the solvent evaporated to give a yellow oil. Chromatography of the oil on silica gel using 3 : 1 hexane–CH_2Cl_2 gave a mixture of nitrotetralins; yield: 3.0 g (58%).

In a 250 ml 3-necked round-bottom flask equipped with a mechanical stirrer and a dropping funnel was placed 7.0 g (0.034 mol) of the mixture of nitrotetralins dissolved in 50 ml of glacial AcOH and 6 ml of water. The soln was cooled to 10°. A soln of CrO_3, 15.0 g (0.15 mol) dissolved in 10 ml of warm water (50–60°) and 40 ml of glacial AcOH was introduced into the dropping funnel and then added dropwise. After the addition was complete, the mixture was stirred at 10° for 36 hr. The mixture was then poured into ice-water and extracted with $CHCl_3$. The combined organic extracts were washed with water and then with $NaHCO_3$ aq and again with water. The soln was dried over $MgSO_4$. Removal of the solvent *in vacuo* gave an oil which solidified on standing. Chromatography on silica gel using benzene as eluent gave the unoxidized tetralins (3.2 g overall) followed by **7e** (0.7 g) and **9** (1.1 g). For **7e**, m.p.: 170–171°; NMR ($CDCl_3$): 1.43 (6H, s), 1.92–2.2 (2H, m), 2.63–2.9 (2H, m), 7.9–8.17 (3H, m); IR ($CHCl_3$): 1345, 1530, 1700 cm^{-1}; UV (MeOH): λ_{max} 265 (11,600); high resolution mass spectrum calc (*m/e*) for $C_{12}H_{13}NO_3$, 219.0895; found 219.0894.

Enones, **6a–6e**. Enone, **6c**, is a known compound.[18] The other enones were made by a similar procedure from the tetralones. Since the nitrotetralone was insoluble in carbon tetrachloride the bromination was carried out in $CHCl_3$. No attempts were made to purify the α-bromotetralones. Reflux of the bromotetralones in γ-collidine gave the enones. Overall yield from the tetralones to enones were in the range of 40–50%. The enones were purified over alumina (basic, activity I) using hexane:$CHCl_3$ as eluent. The enones were identified only by NMR spectrum and were used without further purification. **6a**; NMR ($CDCl_3$): 1.48 (6H, s), 3.9 (3H, s), 6.33 (1H, d, J = 10 Hz), 6.85 (1H, d, J = 10 Hz), 6.90 (2H, m), 8.12 (1H, m); **6b**; NMR (CCl_4): 1.43 (6H, s), 2.37 (3H, s), 6.15 (1H, d, J = 10 Hz), 6.67 (1H, d, J = 10 Hz), 6.88–7.23 (2H, m), 7.8–7.93 (1H, m); **6c**; NMR ($CDCl_3$): 1.48 (6H, s), 6.4 (1H, d, J = 10 Hz), 6.94 (1H, d, J = 10 Hz), 7.38–7.63 (2H, m), 8.2 (1H, m); **6d**; NMR ($CDCl_3$): 1.47 (6H, s), 6.3 (1H, d, J = 10 Hz), 6.84 (1H, d, J = 10 Hz), 7.2–7.57 (2H, m), 8.12 (1H, m); **6e**; m.p.: 184–186°; NMR ($CDCl_3$): 1.55 (6H, s), 6.33 (1H, d, J = 10 Hz), 6.92 (1H, d, J = 10 Hz), 8.08–8.33 (3H, m).

Tosylhydrazones, **5a–5d**. Equimolar amounts of the enone and tosylhydrazine were refluxed in MeOH (15–20 ml per gram of the enone) for 3–4 hr. The mixture was cooled and evaporation of the solvent gave an oil which was chromatographed using $CHCl_3$ as eluent. The gums obtained were crystallized in a suitable solvent to give pure tosylhydrazones: **5a** (25%), from MeOH; m.p.: 187–190°; NMR ($CDCl_3$): 1.37 (6H, s), 2.42 (3H, s), 3.85 (3H, s), 6.36 (1H, d, J = 10 Hz), 6.57 (1H, d, J = 10 Hz), 6.9–8.18 (8H, m); IR ($CHCl_3$): 910, 990, 1030, 1060, 1075, 1150, 1230, 1245, 1320, 1375, 1605, 2920, 3225 cm^{-1}; mass spectrum: 370 (7), 211 (12), 210 (81), 182 (20), 181 (100), 167 (18), 166 (36), 151 (15), 138 (35), 123 (35), 91 (17), 90 (31). (Found: C, 65.11; H, 5.89; N, 7.32; S, 8.61. Calc for $C_{20}H_{22}N_2SO_3$: C, 64.84; H, 5.99; N, 7.56; S, 8.65%.)

Compound **5b** (37%), from EtOH; m.p.: 184–186°; NMR ($CDCl_3$): 1.35 (6H, s), 2.35 (3H, s), 2.39 (3H, s), 6.28 (1H, d, J = 10 Hz), 6.46 (1H, d, J = 10 Hz), 6.96–7.98 (8H, m); IR ($CHCl_3$): 920, 1010, 1080, 1160, 1320, 1375, 1600, 2940, 3190 cm^{-1}; mass spectrum: 354 (12), 199 (69), 171 (43), 170 (100), 169 (12), 156 (43), 155 (61), 92 (13), 91 (37). (Found: C, 67.62; H, 6.22; N, 7.83; S, 9.11. Calc for $C_{20}H_{22}N_2SO_2$: C, 67.77; H, 6.26; N, 7.90; S, 9.05%.)

Compound **5c** (58%), from benzene:hexane; m.p.: 150–151°; NMR ($CDCl_3$): 1.28 (6H, s), 2.33 (3H, s), 6.28 (1H, d, J = 10 Hz), 6.63 (1H, d, J = 10 Hz), 7.15–8.2 (8H, m), 8.5 (1H, bs, exchangeable); IR ($CHCl_3$): 910, 1000, 1085, 1160, 1325, 1375, 1605, 1650, 2970, 3220 cm^{-1}; mass spectrum: 340 (25), 185 (100), 157 (42), 156 (88), 155 (23), 142 (55), 141 (78). (Found: C, 66.85; H, 6.10; N, 8.10; S, 9.31. Calc for $C_{19}H_{20}N_2SO_2$: C, 67.03; H, 5.92; N, 8.23; S, 9.42%.)

Compound **5d** (57%), from benzene:hexane; m.p.: 158–161°; NMR ($CDCl_3$): 1.33 (6H, s), 2.33 (3H, s), 6.22 (1H, d, J = 10 Hz), 7.07–8.1 (8H, m); IR (KBr): 670, 770, 930, 1010, 1040, 1085, 1170, 1335, 1355, 1400, 1600, 1650, 2970, 3220 cm^{-1}; mass spectrum: 339 (19), 185 (11), 184 (78), 158 (28), 157 (100), 156 (17), 142 (35), 141 (66), 115 (18), 91 (23). (Found: C, 54.61; H, 4.39; N, 6.32; S, 7.61; Br, 19.11. Calc for $C_{19}H_{19}N_2SO_2Br$: C, 54.42; H, 4.57; N, 6.68; S, 7.65; Br, 19.06%.)

Tosylhydrazone, **5e**. To 0.2 g (0.92 mmol) of the enone dissolved in 1 ml of hot $CHCl_3$ was added 0.17 g (0.92 mmol) of tosylhydrazine dissolved in 2 ml of MeOH. The soln was allowed to reflux with magnetic stirring for 5.5 hr. The soln was cooled and the solvent was evaporated. To the residual gum 1 ml of MeOH was added and the soln was cooled to 0°. A ppt was obtained which was filtered on a Buchner funnel and washed twice with MeOH and then recrystallized from $CHCl_3$:hexane; yield 60–70%; m.p.: 182–184°; NMR (acetone-d$_6$): 1.47 (6H, s), 2.35 (3H, s), 6.35 (1H, d, J = 10 Hz), 6.73 (1H, d, J = 10 Hz), 7.05–8.18 (8H, m); IR ($CHCl_3$): 1170, 1350, 1530, 3020, 3220 cm^{-1}; mass spectrum: 385 (12), 325 (28), 277 (24), 230 (28), 203 (67), 202 (100), 201 (16), 186 (42), 172 (31), 171 (14), 170 (21), 157 (15), 156 (81), 155 (86), 154 (47), 153 (69), 152 (49), 151 (15), 143 (53), 142 (12), 141 (36), 140 (36), 139 (75), 129 (34), 128 (65), 127 (40), 123 (14), 115 (42), 108 (26), 107 (31), 92 (55), 91 (69), 89 (24), 77 (28). (Found: C, 59.50; H, 4.92; N, 10.73; S, 8.52. Calc for $C_{19}H_{19}N_3SO_4$: C, 59.21; H, 4.97; N, 10.90; S, 8.32%.)

Diazo compounds, **4a–4e**. The tosylhydrazone (0.5 g) was dissolved in anhyd THF in a 100 ml round-bottom flask and NaOMe (50% excess) was quickly added. The soln was stirred magnetically for 15 min. The solvent was then evaporated *in vacuo* and to the tosylhydrazone salt so obtained was added 75 ml of n-hexane. The flask was then equipped with a water condenser and then the flask was plunged into an oil-bath maintained at 90–100° for 4–5 min. The flask was then taken out of the oil-bath and immediately placed in an ice-cold water bath. When the temp of the soln fell below room temp the supernatant liquid was filtered off into a round-bottom flask immersed in ice-cold water. The solvent was evaporated on a rotary evaporator at room temp. The whole process was repeated once again with the left over tosylhydrazone salt. The combined samples of the diazo compound were taken up in 10 ml of n-pentane and filtered to remove any solid particles: yield 15–20%. The diazo compounds were identified by their color, IR (2020–2040 cm^{-1}) and NMR spectra only: **4a**; NMR (CCl_4): 1.38 (6H, s), 3.82 (3H, s), 5.12 (1H, d, J = 10 Hz), 6.1 (1H, d, J = 10 Hz), 6.73–7.25 (3H, m); **4b**; NMR ($CDCl_3$): 1.28 (6H, s), 2.23 (3H, s), 5.09 (1H, d, J = 10 Hz), 5.98 (1H, d, J = 10 Hz), 6.65–7.2 (3H, m); **4c**; NMR (CCl_4): 1.37 (6H, s), 5.15 (1H, d, J = 10 Hz), 6.02 (1H, d, J = 10 Hz), 6.76–7.4 (4H, m); **4d**; NMR ($CDCl_3$): 1.38 (6H, s), 5.17 (1H, d, J = 10 Hz), 6.04 (1H, d, J = 10 Hz), 7.06–7.42 (3H, m); **4e**; NMR (C_6D_6): 1.39 (6H, s), 4.72 (1H, d, J = 10 Hz), 5.3 (1H, d, J = 10 Hz), 6.08 (1H, d, J = 9 Hz), 7.63 (1H, dd, J = 9 Hz, 2 Hz), 8.03 (1H, d, J = 2 Hz).

Kinetics of the thermal decomposition of the diazo compounds, **4a–4e**. Solns (10^{-3}–10^{-4}M) of a fresh sample of the diazo compound were made in 6% Et_3N in MeOH and the samples were sealed in 5 ml ampoules (10–12 per kinetic run). Since diazo compounds decompose in visible light, these were wrapped in aluminum foil. The ampoules were then placed in a constant temp bath at 61° for the kinetic run and taken out at the appropriate times and immediately quenched in ice-cold water. The absorbance of the solns was then measured. The wavelength used for monitoring the rate of disappearance of diazo compounds **4a–4d** was 280 nm and 415 nm for **4e**.

Products of the thermal decomposition of diazo compound, **4c**. Pyrolysis of **4c** (0.35 g, 1.9 mmol) in 100 ml of n-hexane after chromatography over alumina (neutral, activity I) gave 0.21 g (60%) of azine, **10**, 0.04 g (10%) of the enone, **4c**, and several other unidentified products (in all, 12%). The diazo compound, **4c** (90 mg, 0.49 mmol), was allowed to react in 2 ml of CH_3OD (0.25 molar in diazo sample) at room temp for 30 hr. From the NMR 90% of the product was azine and less than 10% was a methoxy derivative. A 10^{-3}M soln of the diazo compound after reflux in MeOH–Et_3N gave a quantitative conversion to the ether, **11**. The diazo compound, **4c** (5×10^{-3} molar in CD_3OD), was degassed in an NMR tube by three freeze–thaw-pump cycles. The tube was then sealed and the NMR spectra were recorded before and after the pyrolysis (61°). The concentration of the azine, **10**, was found to be identical before and after the pyrolysis. No enone, **4c**, was detected. Spectral properties of azine, **10**: m.p.: 177–179°; NMR ($CDCl_3$): 1.42 (12H, s), 6.15–7.4 (12H, m); IR ($CHCl_3$): 1300, 1350, 1365, 1385, 1460, 1550, 1640, 2950 cm^{-1}; mass spectrum: 340 (12), 325 (12), 127 (100); high resolution mass spectrum calc (*m/e*) for $C_{24}H_{24}N_2$, 340.1940; found 340.1932.

Preparation of the ether, **13**. To 1 g (5.8 mmol) of the enone **12** dissolved in benzene was added 3.6 g (25 mmol) of diisobutylaluminum hydride (25% soln in toluene). The soln was stirred for 2 hr and then cautiously added to cold MeOH and then filtered. The filtrate, on evaporation of solvent, gave the desired vinyl alcohol: NMR ($CDCl_3$): 1.17 (3H, s), 1.32 (3H, s), 2.22 (1H, bs, exchangeable), 3.9 (1H, bs) AB system, with first-order coupling of one proton to the proton at 3.9: 5.95 (1H, dd, J = 10 Hz, 4 Hz), 6.42 (1H, d, J = 10 Hz), 7.0–7.38 (4H, m).

The alcohol so obtained was dissolved in anhyd THF and then 20 g of NaH (57% oil dispersion) was added followed by 11 g of MeI. The mixture was stirred at room temp for 16 hr and then poured over MeOH. Evaporation of the solvent followed by quick filtration over alumina (basic, activity I) using hexane : benzene gave 0.45 g (41%) of the ether: NMR ($CDCl_3$): 1.27 (3H, s), 1.30 (3H, s), 3.33 (3H, s), 3.63 (1H, d, J = 4 Hz), 6.0 (1H, dd, J = 4 Hz, 10 Hz), 6.47 (1H, d, J = 10 Hz), 6.93–7.3 (4H, m).

Preparation of the ether **11**. The enone, **6c** (1 g, 5.8 mmol) was dissolved in 15 ml of benzene and 4 ml of diisobutylaluminium hydride (25% soln in toluene) was added dropwise with magnetic stirring. After the addition was complete, the soln was stirred for 2 hr and then poured over MeOH with caution. Hot filtration followed by evaporation of the solvent gave a heavy oil which had a satisfactory NMR for the desired alcohol: ($CDCl_3$), 1.27 (3H, s), 1.37 (3H, s), 2.18 (1H, d, exchangeable), 4.93 (1H, m), 5.78 (2H, m), 6.98–7.47 (4H, m).

The alcohol (0.8 g) so obtained was dissolved in 10 ml of anhyd THF. NaH (57% oil dispersion, 2 g) was placed over a Buchner funnel and washed with n-hexane to get rid of the mineral oil. The NaH was then quickly poured into the alcohol soln. The soln was stirred for 10 min and then 4.5 g of MeI was added. The soln was then stirred overnight, poured into ice slowly and then extracted with CH_2Cl_2 twice. The organic layer was dried over $MgSO_4$. Filtration followed by evaporation of the solvent gave the desired ether: yield 0.45 g (41%); NMR (CCl_4): 1.25 (3H, s), 1.33 (3H, s), 2.93 (3H, s), 4.9 (1H, m), 5.72 (2H, m), 6.93–7.3 (4H, m). Attempts at further purification of the ether by column chromatography (alumina, basic) using benzene : hexane as eluent led to isomerization to the ether **13**.

Acknowledgements—This research was supported by a grant from the National Science and Engineering Research Council of Canada, a Dalhousie Faculty of Graduate Studies Award to N. C. Mathur and an NSERC Summer Student Award to K. M. Young.

REFERENCES

[1] W. J. Barton, M. R. DeCamp, M. E. Henrick, M. Jones Jr., R. H. Lewin and M. B. John, *Carbenes* (Edited by M. Jones and R. A. Moss), Vol. 1, p. 1. Wiley-Interscience, New York (1973).

[2a] W. Ando, p. 341; [b] D. S. Wulfman, G. Linstrumelle and C. F. Cooper, *The Chemistry of Diazonium and Diazo Groups* (Edited by J. Patai), p. 821. Wiley, New York (1978).

[3] J. A. Pincock and N. C. Mathur, *J. Org. Chem.* **47**, 3699 (1982).

[4] J. A. Pincock and K. P. Murray, *Can. J. Chem.* **57**, 1403 (1979).

[5] J. H. Davis, W. A. Goddard and R. G. Bergman, *J. Am. Chem. Soc.* **99**, 2427 (1977).

[6] R. Hoffmann, G. D. Zeiss and G. W. Van Dine, *J. Am. Chem. Soc.* **90**, 1485 (1968).

[7] A. Sevin and L. Arnaud-Danon, *J. Org. Chem.* **46**, 2346 (1981).

[8] D. R. Arnold, R. W. Humphreys, W. J. Leigh and G. E. Palmer, *J. Am. Chem. Soc.* **98**, 6225 (1976).

[9] R. S. Hutton, M. L. Manion, H. D. Roth and E. Wasserman, *J. Am. Chem. Soc.* **96**, 4680 (1974).

[10] R. B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry*, p. 152. Verlag Chemie, GmbH, Weisheim, Germany (1970).

[11] J. Lievin and G. Verhaegen, *Theor. Chim. Acta* **45**, 269 (1977).

[12] R. J. Miller and H. Shechter, *J. Am. Chem. Soc.* **100**, 7920 (1978).

[13] R. J. Miller, L. S. Yang and H. Shechter, *J. Am. Chem. Soc.* **99**, 938 (1977).

[14] Shechter[12] has correlated this data using the two parameter separation of inductive and resonance effects.[15]

[15] E. Ehrenson, R. T. C. Brounlee and W. R. Taft, *Prog. Phys. Org. Chem.* **10**, 1 (1973).

[16] For instance, J. P. Richard and W. P. Jencks, *J. Am. Chem. Soc.* **104**, 4689 (1982).

[17a] J. M. Dust and D. R. Arnold, *J. Am. Chem. Soc.* **105**, 1221 (1983); [b] J. M. Dust and D. R. Arnold, *Ibid.* Erratum to appear (1983).

[18] R. T. Arnold, J. S. Buckley Jr. and J. Richter, *J. Am. Chem. Soc.* **69**, 2322 (1947).

[19] R. B. Miller and C. G. Gutierrez, *J. Org. Chem.* **43**, 1569 (1978).

[20] E. N. Marvell and J. L. Stephenson, *J. Am. Chem. Soc.* **77**, 5177 (1955).

[21] K. B. Wiberg, *Physical Organic Chemistry*, p. 410. Wiley, New York (1964).

[22] Using the two parameter separation of inductive and resonance effects gives $\log(k/k_H) = -0.80\ \sigma_I^- + 0.87\ \sigma_R^+$ with f = 0.036.

[23] W. Krimse, K. Loosen and H. Sluma, *J. Am. Chem. Soc.* **103**, 5935 (1981).

[24] D. Griller, M. T. H. Liu and J. C. Scaiano, *J. Am. Chem. Soc.* **104**, 5549 (1982).

[25] J. A. Pincock, R. Morchat and D. R. Arnold, *J. Am. Chem. Soc.* **95**, 7536 (1973).