ISSN 0300-9580 JCPKBH(10) 2071–2268(1994)

JOURNAL OF THE CHEMICAL SOCIETY

Perkin Transactions 2

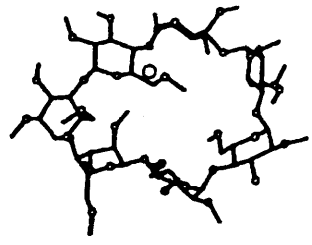
Physical Organic Chemistry

CONTENTS

Perkin Communications

2071 **Unusual $^1C_4$ conformation of a methylglucose residue in crystalline permethyl-β-cyclodextrin monohydrate**

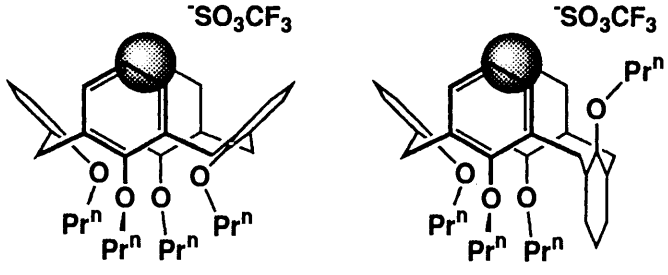
Mino R. Caira, Vivienne J. Griffith, Luigi R. Nassimbeni and Bosch van Oudtshoorn



Articles

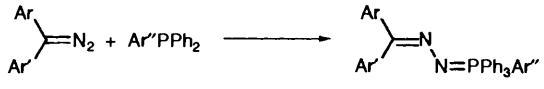
2073 **NMR spectroscopic and X-ray crystallographic studies of calix[4]arene·Ag^+ complexes. Influence of bound Ag^+ on C_{2v}–C_{2v} interconversion in *cone*-calix[4]arenes**

Atsushi Ikeda, Hirohisa Tsuzuki and Seiji Shinkai



2081 **Substituent effects in the reaction of triphenylphosphine with diazodiphenylmethane: the interpretation of a U-shaped Hammett correlation in an elementary biphilic reaction**

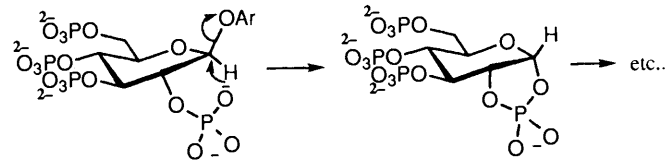
Donald Bethell, Raymond Bourne and Madzlan Kasran



Substituent effects on the reaction rate give rise to a U-shaped Hammett plot (Ar, Ar') but a linear correlation (Ar''), confirming that the conformation of the aryl groups in the diazoalkane controls the reactivity

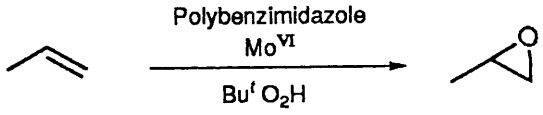
2085 **Nucleophilic catalysis of glycoside hydrolysis. The hydrolysis of 4-nitrophenyl α- and β-D-glucopyranoside tetraphosphates**

Patrick Camilleri, Rosie F. D. Jones, Anthony J. Kirby and Roger Strömberg



2091 **Alkene epoxidations catalysed by molybdenum(VI) supported on imidazole-containing polymers. Part 3. Epoxidation of oct-1-ene and propene**

Matthew M. Miller, David C. Sherrington and Sidney Simpson



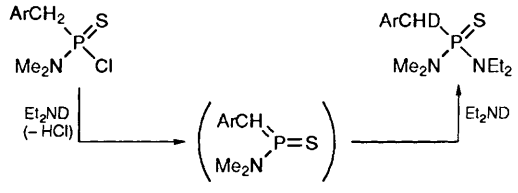
2097 **Is the collision induced loss of methanol from deprotonated 4-methoxybut-1-yne in the gas phase a charge remote reaction?**

Suresh Dua and John H. Bowie

The loss of methanol from deprotonated 4-methoxybut-1-yne occurs by (*i*) a stepwise process involving the acetylenic π electrons and (*ii*) a 1,2-elimination process

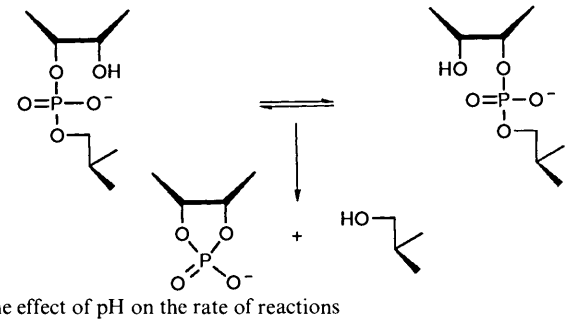
2101 **Nucleophilic substitution in benzylic thiophosphinyl and thiophosphonyl chlorides: the contribution of elimination–addition pathways with methylenethioxophosphorane (thiophosphene) intermediates**

Michael P. Coogan and Martin J. P. Harger



2109 **Hydrolysis and isomerization of the internucleosidic phosphodiester bonds of polyuridylic acid: kinetics and mechanism**

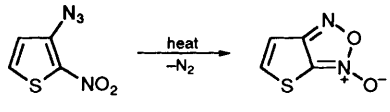
Satu Kuusela and Harri Lönnberg



The effect of pH on the rate of reactions

2115 **Factors affecting the rates of thermal decomposition of azidothiophenes**

Leonard K. Dyall, Peter M. Suffolk, Wim Dehaen and Gerrit L'abbé



It is argued from rate measurements on model compounds that the endocyclic sulfur atom causes the observed high thermolysis rate, by conjugative stabilization of a nitrene

2119 **Photolysis of 2,4-dihydroxy-2,4-dimethylpentan-3-one studied by quantitative time-resolved CIDNP and optical spectroscopy**

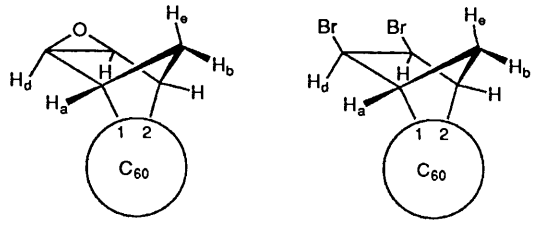
Michael Salzmann, Yuri P. Tsentalovich and Hanns Fischer

$$HO(CH_3)_2CCOC(CH_3)_2OH \xrightarrow{h\nu}$$
$$HO(CH_3)_2C\dot{C}O + \dot{C}(CH_3)_2OH \longrightarrow$$
$$CO + 2(CH_3)_2\dot{C}OH \longrightarrow \text{Products}$$

Reaction and relaxation rates

2125 **Bicyclopentene addend on [60]fullerene: epoxidation and *cis*-bromine addition**

Mohamed F. Meidine, Anthony G. Avent, Adam D. Darwish, G. John Langley, Wyn Locke, Osamu Ohashi, Harold W. Kroto, Roger Taylor and David R. M. Walton



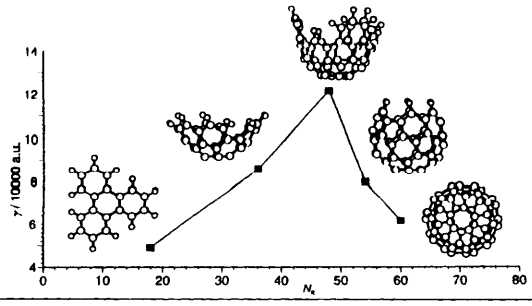
2129 **1,2-Carbon to nitrogen migrations. Part 2. *Ab initio* study on the rearrangement of (α-methylazo)alkyl isocyanates**

Romano T. Kroemer, Hubert Gstach, Klaus R. Liedl and Bernd M. Rode

Ab initio calculations on the rearrangement of (α-methylazo)alkyl isocyanates (R = Me, Et, Pr^i)

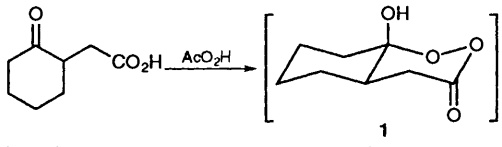
2137 **The relationship between structure and second hyperpolarisability in conjugated hydrocarbons**

Robert Thomas



2141 **Conformationally restricted Criegee intermediates: evidence for formation and stereoelectronically controlled fragmentation**

Sosale Chandrasekhar and Chandra Deo Roy

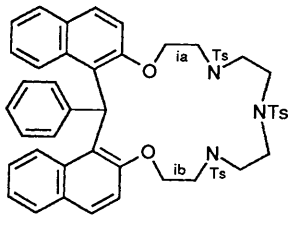


1

Migration of the secondary rather than the tertiary centre occurs in the fragmentation of **1**

2145 **A detailed study defining the extent of preorganization of an aza macrocycle containing the phenyldinaphthomethane subunit (a three bladed propeller) using dynamic NMR and molecular dynamics**

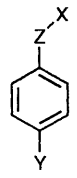
Paul J. Cooper, M. N. Stuart Hill and Joyce C. Lockhart



Propeller crowns with nitrogen donors have been modelled with molecular dynamics and the results together with a detailed assessment of the solution conformations observed through low temperature ^{13}C NMR spectroscopy give a very detailed picture of the types of movement possible for these compounds and their relative rates, and of the extent of preorganization

2149 **Remote substituent effects on polar and non-polar covalent bonds**

Mats Jonsson, Johan Lind, Gábor Merényi and Trygve E. Eriksen



The variation in Z–X bond dissociation energy with 4-substituent has been studied using semiempirical quantum chemical methods

2155 **An extended form of the Evans–Polanyi equation: a simple empirical relationship for the prediction of activation energies for hydrogen-atom transfer reactions**

Brian P. Roberts and Andrew J. Steel

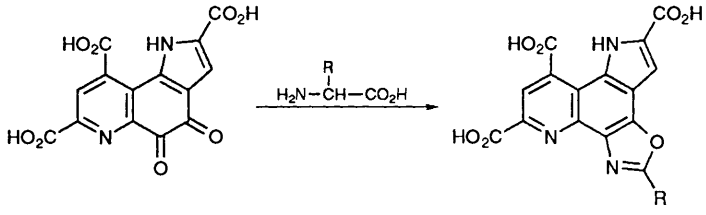
$A^{\bullet} + H\text{–}B \longrightarrow A\text{–}H + B^{\bullet}$

$E_a = E_o f + \alpha\Delta H^{\circ}(1 - d) + \beta\Delta\chi_{AB}^2 + \gamma(s_A + s_B)$

Correlation coefficient = 0.988, standard error in E_a(calc.) = ± 2.0 kJ mol^{-1} for 65 reactions in both gas and liquid phases

2163 **Kinetic analysis of oxazolopyrroloquinoline formation in the reaction of coenzyme PQQ with amino acids by capillary zone electrophoresis**

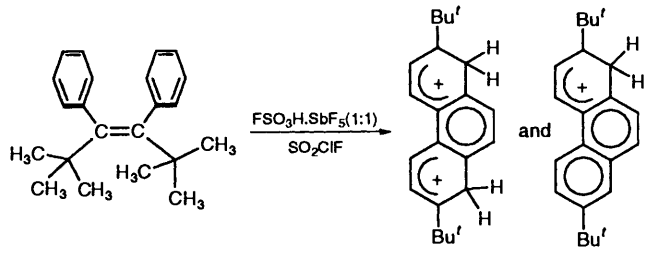
Yukihiro Esaka, Yasuo Yamaguchi, Masashi Goto and Kenji Kano



Kinetics of the OPQ formation from PQQ and three amino acids was studied with the aid of capillary zone electrophoresis

2169 **Electrophilic chemistry (protonation, nitration, bromination) of crowded (*Z*)-2,2,5,5-tetramethyl-3,4-diphenylhex-3-ene; formation of phenanthrenium ions by facial ring protonation/transannular cyclization in superacid media; *p,p*-dinitration and *p,p*-dibromination with $NO_2^+BF_4^-$ and Br_2–SO_2**

Kenneth K. Laali, James E. Gano, Charles W. Gundlach IV and Dieter Lanoir



2175 **Oxygen transfer from Ph_4PHSO_5 to manganese porphyrins: kinetics and mechanism of the formation of the oxo species in homogeneous solution**

Sandro Campestrini, Fulvio Di Furia, Gilles Labat and Fabiola Novello

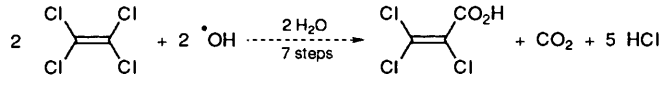
$$Mn(Porph)(Im)_x \xrightarrow[ClCH_2CH_2Cl \text{ or } CH_3CN]{Ph_4PHSO_5} Mn(O)(Porph)(Im)$$

$x = 1,2$

A stopped-flow kinetic study on the formation of the oxo species of various manganese porphyrins by Ph_4PHSO_5 oxidation in homogeneous solution is reported and a very short-lived intermediate or a simple bimolecular mechanism is suggested

2181 **Reaction of the OH radical with tetrachloroethene and trichloroacetaldehyde (hydrate) in oxygen-free aqueous solution**

Ralf Mertens and Clemens von Sonntag



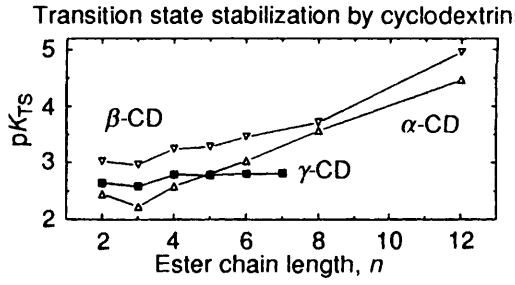
2187 **Aromatic nucleophilic substitution reactions of some 2-L-3-nitro-5-X-thiophenes with piperidine and aniline in methanol. Substituent constants for the thiophene system**

Giovanni Consiglio, Vincenzo Frenna, Caterina Arnone, Elisabetta Mezzina and Domenico Spinelli

Kinetic data have been obtained and used to calculate a series of optimized 'thiophene' σ_T values. Susceptibility constants of the various sets have been analysed in the framework of the reactivity–selectivity principle

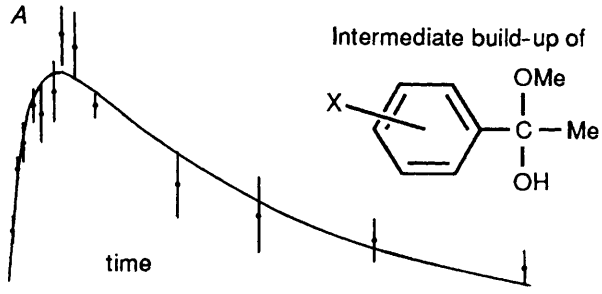
2191 **The kinetics of cleavage of nitrophenyl alkanoates by γ-cyclodextrin and by 'dimethyl-β-cyclodextrin' in basic aqueous solution**

Oswald S. Tee and Timothy A. Gadosy



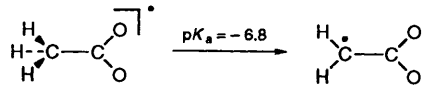
2199 **Hemiacetals of acetophenone. Aromatic substituent effects in the H^+- and general-base-catalysed decomposition in aqueous solution**

Robert A. McClelland, Karen M. Engell, Truels S. Larsen and Poul E. Sørensen



2207 **Radicals and ions of formic and acetic acids: an *ab initio* study of the structures and gas and solution phase thermochemistry**

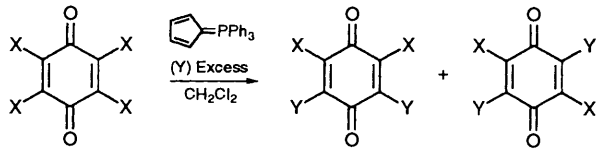
Dake Yu, Arvi Rauk and David A. Armstrong



$\Delta_f G^\circ$(g)	−152	−301
$\Delta_f G^\circ$(aq)	−162	−201

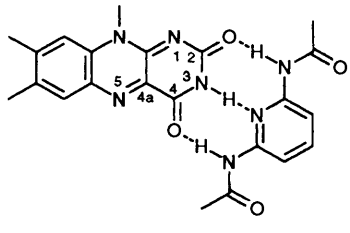
2217 **Kinetics and mechanism of the addition of triphenylphosphoniocyclopentadienide to tetrahalo-*p*-benzoquinones. Part III. The disubstitution of chloranil and bromanil**

Francisco Pérez Pla, C. Dennis Hall, Rosa Valero and Manuel Pons



2229 **Synthesis of 2,6-diamidopyridine derivatives and their functions as flavin receptors in chloroform**

Norio Tamura, Keita Mitsui, Tatsuya Nabeshima and Yumihiko Yano



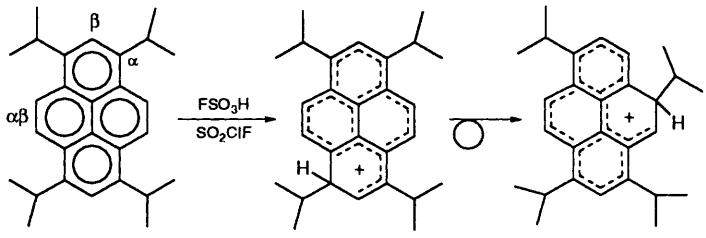
2239 **Substituent effects on the structures and energies of isocyanates and imines by *ab initio* molecular orbital calculations**

Michael A. McAllister and Thomas T. Tidwell

The structures and energies of substituted isocyanates and imines have been examined by *ab initio* molecular orbital calculations

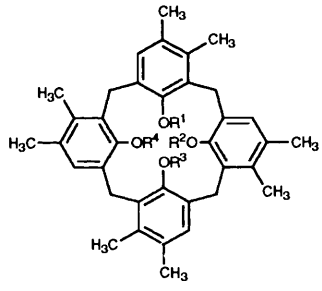
2249 **^{13}C, ^{1}H and two-dimensional NMR studies of charge distribution in sterically congested persistent cycloalkyl- and alkyl-pyrenium ions generated by protonation in superacid media**

Kenneth K. Laali and Poul Erik Hansen



2259 **Molecular modelling study of a dissymmetric calix[4]arene and its methyl ethers**

Iris Thondorf, Grit Hillig, Wolfgang Brandt, Jörg Brenn, Alfred Barth and Volker Böhmer



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Forthcoming Articles in *Perkin Transactions 2*

Nucleophilicity towards a vinylic carbon atom: rate constants for the addition of amines to the 1-methyl-4-vinylpyridinium cation in aqueous solution **C. K. M. Heo** and **J. W. Bunting**

Nucleophilicity towards a saturated carbon atom: rate constants for the aminolysis of methyl 4-nitrobenzenesulfonate in aqueous solution. A comparison of the n and N_+ parameters for amine nucleophilicity **J. W. Bunting, J. M. Mason** and **C. K. M. Heo**

Conformational analysis. Part 23. A lanthanide-induced shift investigation of some cyclic and acyclic sulfoxides
R. J. Abraham, L. Pollock and **F. Sancassan**

Solvent independent transition state structures. Part 3. Sulfonyl transfer reactions
R. M. Tarkka, W. K. C. Park, P. Liu, E. Buncel and **S. Hoz**

Bond-stretch isomerism and the fullerenes **S. J. Austin, J. Baker, P. W. Fowler** and **D. E. Manolopoulos**

Keto–enol tautomerism of phenacylpyrazine: acid catalysis with protonation at nitrogen
A. R. E. Carey, S. Eustace, R. A. More O'Ferrall, M. G. Murphy and **B. A. Murray**

^{1}H- and ^{13}C-NMR spectra of α-heterocyclic ketones and assignment of keto, enol and enaminone tautomeric structures
R. A. More O'Ferrall and **B. A. Murray**

Equilibrium constants for ionisation and enolisation of 2-phenylacetylfuran **A. Fontana** and **R. A. More O'Ferrall**

Reaction of gaseous sulfur mustard with zeolite 13X **A. J. Bellamy**

Triazene drug metabolites. Part 14. Kinetics and mechanism of the acid catalysed hydrolysis of 3-alkoxymethyl-3-alkyl-1-aryltriazenes **L. Fernandes, A. P. Francisco, J. Iley** and **E. Rosa**

Solvato- and halo-chromic behaviour of some iminomerocyanines **C. Machado, M. Da G. Nascimento** and **M. C. Rezende**

Metal ion-promoted hydrolysis of polyuridylic acid **S. Kuusela** and **H. Lönnberg**

Relevance of third-derivative cross-interaction coefficients in Hammett-type treatments of nucleophilic substitution reactions
D. N. Kevill and **M. J. D'Souza**

Photoinduced electron transfer reactions of chloranil with benzodioxoles
B.-Z. Yan, Z.-G. Zhang, H.-C. Yuan, L.-C. Wang and **J.-H. Xu**

A semiempirical study of the solvent effect on the Menshutkin reaction **U. Maran, T. A. Pakkanen** and **M. Karelson**

One- and two-electron reduction potentials of peroxyl radicals and related species **G. Merényi, J. Lind** and **L. Engman**

The effective 'size' of the tris(trimethylsilyl)silyl group in several molecular environments
J. Frey, E. Schottland, Z. Rappoport, D. Bravo-Zhivotovskii, M. Nakash, M. Botoshansky, M. Kaftory and **Y. Apeloig**

Reactivity of 1-iodoadamantane with carbanions by the $S_{RN}1$ mechanism **R. A. Rossi, A. B. Pierini** and **G. L. Borosky**

Gas phase basicities of 1,3-benzazoles: benzimidazole, benzoxazole, benzothiazole, benzoselenazole and benzotellurazole
R. Notario, M. Herreros, E. Ballesteros, M. Essefar, J. L. M. Abboud, I. D. Sadekov, V. I. Minkin and **J. Elguero**

^{13}C, ^{2}H coupling constants and ^{2}H-induced ^{13}C NMR isotope chemical shifts in deuteriated cyclohexanes: application for measurements of conformational equilibrium isotope effects **V. A. Uvarov, V. A. Chertkov** and **N. M. Sergeyev**