

Figure 1. Translational energy releases ($T(H)$) following EI (70 eV) (—) and FI (---) against fractional metastable peak height (H).

distribution of this energy among the vibrational modes is unlikely to be the same. At its simplest, EI produces no change in geometry during ionization whereas FI occurs at the distorted geometry appropriate to the very high field conditions (10^9 to 10^{10} V m $^{-1}$) obtaining. Further, the time window for observable decompositions in the first field free region of our MS9 extends from 1×10^{-7} to 1.4×10^{-6} s for FI, but under EI it lies wholly in the microsecond time-frame (m/e 100 and 8 kV (FI), 4 kV (EI) accelerating voltages). This time difference gives important, mechanistically significant, information about the nature of the $k(E)$ vs. E curves.

The different methods used for the measurement of the translational energies released after EI and FI are being reported elsewhere.^{5,6} Both sets of measurements were made at the same relatively low energy resolution (1 in 800), this (10 eV) being less than the full width at half height for molecular ions under FI.⁷ The uncorrected⁷ peak widths^{5,6} at various fractional peak heights (H) were converted into energy releases⁸ and plotted against H in order to compare the FI and EI results.⁹

The loss of methane from 2-methylpropane, which is seemingly adequately described by the QET model,¹⁰ shows the same energy release after EI ($T_{EI}(H)$) and FI ($T_{FI}(H)$). Some other simple rearrangements show the same behavior. The loss of hydrogen cyanide from the molecular ion of benzonitrile is a further example where $T_{FI}(H) = T_{EI}(H)$. Measurements¹¹ suggest that an extra 0.6 eV excitation energy is required to raise $k(E)$ from 10^6 to 10^7 s $^{-1}$. This result in particular, those mentioned above, and others¹² indicate that shifting the observation time by an order of magnitude does not increase the translational energy release for a process with a reasonably steep $k(E)$ vs. E curve,¹¹ being consistent with a weak dependence of energy release on E .¹³

By contrast the formation (McLafferty rearrangement) of $[C_4H_8]^+$ from hexanal (Figure 1) and the formation of the $[M-CH_3]^+$ ion from hex-1-yne have $T_{FI}(H) > T_{EI}(H)$. The formation of the $[C_4H_8]^+$ ion from hexanal is a complex process involving an intermediate ion and three distinct rearrangement steps.^{14,15} The $[M-CH_3]^+$ ion from hex-1-yne probably has the cyclopentenyl structure,¹⁵ in which case its formation is associated with a very large kinetic shift.¹⁵ Both of these facts would suggest a complex mechanism. We attribute the larger energy release following FI in these and other cases to the shift to shorter observation times and suggest that this variation of kinetic energy release with lifetime is indicative of a very slow rise of $k(E)$ with E .

Unexpectedly, in other cases, for example, the loss of water from the molecular ions of cyclohexanol and pentan-1-ol, $T_{EI}(H)$ is considerably greater than $T_{FI}(H)$ and this would seem to indicate that, despite the formal similarity, the decomposition processes following EI and FI do not proceed over the same energy surfaces. In the case of cyclohexanol this

agrees with earlier work¹⁶ in which it has been suggested that loss of water after EI occurs through a high energy process involving acyclic isomers of the molecular ion, whereas the loss of water after FI is due to a low energy process. Examples in which there is a large energy release ($T_{EI}(0.5) > 200$ meV) after EI but a smaller one under FI are the loss of nitric oxide from *p*-nitrotoluene (although for the loss of NO from nitrobenzene $T_{EI}(H) = T_{FI}(H)$) and the loss of carbon dioxide from dimethyl acetylenedicarboxylate (Figure 1). Large energy releases are observed, however, after FI as exemplified by the loss of carbon monoxide from diphenyl ether where $T_{FI}(0.5) = 450$ meV = $T_{EI}(0.5)$. In general terms the most likely explanation of the cases where $T_{EI}(H)$ is considerably greater than $T_{FI}(H)$ would seem to lie in the existence of high energy processes occurring under electron impact which are not possible under FI. Among other reasons may be the existence of isolated vibronic states or possibly noninterconverting isomeric structure (e.g., cyclohexanol).

Acknowledgment. We gratefully acknowledge the Ramsay Memorial Trust (P.J.D.), The Central Research Fund, University of London (P.J.D. and A.G.L.), and technical assistance from Dr. M. A. Baldwin and Mr. R. P. Morgan. We thank Professor J. L. Holmes for suggesting a study of hex-1-yne.

References and Notes

- H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig, and H. Eyring, *Proc. Natl. Acad. Sci. U.S.A.*, **38**, 667 (1952).
- (a) J. F. Meagher, K. J. Chao, J. R. Barker, and B. S. Rabinovitch, *J. Phys. Chem.*, **78**, 2535 (1974); (b) S. Nordholm and S. A. Rice, *J. Chem. Phys.*, **62**, 157 (1975).
- H. M. Rosenstock, J. T. Larkins, and J. A. Walker, *Int. J. Mass Spectrom. Ion Phys.*, **11**, 309 (1973).
- H. M. Rosenstock, V. H. Dibeler, and F. N. Harlee, *J. Chem. Phys.*, **40**, 591 (1964).
- P. J. Derrick, R. P. Morgan, J. T. Hill, and M. A. Baldwin, *Int. J. Mass Spectrom. Ion Phys.*, **18**, 393 (1975).
- M. A. Baldwin, P. J. Derrick, and R. P. Morgan, *Int. J. Mass Spectrom. Ion Phys.*, accepted for publication.
- M. A. Baldwin, P. J. Derrick, and R. P. Morgan, *Org. Mass Spectrom.*, accepted for publication.
- R. G. Cooks, J. H. Beynon, R. M. Caprioli, and G. R. Lester "Metastable Ions", Elsevier, Amsterdam, 1973.
- The distributions in Figure 1 are therefore not the actual distributions of translational energy released during decomposition. See D. T. Terwilliger, J. H. Beynon, and R. G. Cooks, *Proc. R. Soc. London, Ser. A*, **341**, 135 (1974).
- P. J. Derrick, A. M. Falick, and A. L. Burlingame, *J. Chem. Soc., Faraday Trans. 1*, **71**, 1503 (1975).
- B. Andlauer and Ch. Ottinger, *Z. Naturforsch.*, **27**, 293 (1972).
- R. G. Cooks, K. C. Kim, T. Keough, and J. H. Beynon, *Int. J. Mass Spectrom. Ion Phys.*, **15**, 271 (1974).
- C. E. Klots, *J. Chem. Phys.*, **58**, 5364 (1973).
- R. P. Morgan and P. J. Derrick, *J. Chem. Soc., Chem. Commun.*, 836 (1974).
- J. L. Holmes and F. P. Lossing, personal communication, 1975.
- P. J. Derrick, J. L. Holmes, and R. P. Morgan, *J. Am. Chem. Soc.*, **97**, 4936 (1975).

Peter J. Derrick,* Alexander G. Loudon*

Christopher Ingold Laboratories, University College
London WC1H 0AJ, Great Britain

Received January 20, 1976

Stereoselective One-Pot Dialkylation of *gem*-Dihalocyclopropanes. A Simple Route to *dl*-Sesquicarene and *dl*-Sirenin

Sir:

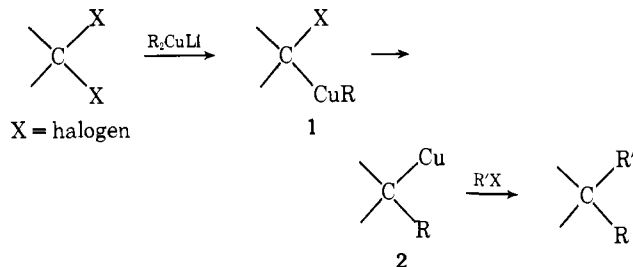
Double alkylation on the same carbon has been one of important synthetic problems.¹ The reaction of *gem*-dihalides with dialkylcuprates has proven to be a method of choice for this purpose, especially for dimethylation,² in which the intermediacy of a copper carbenoid of type **1** has been postulated.³ We wish to disclose that the reaction of *gem*-dihalocyclopropanes (**3**) with lithium dibutylcuprate proceeds as

Table I. Stereoselective Dialkylation of *gem*-Dibromocyclopropanes

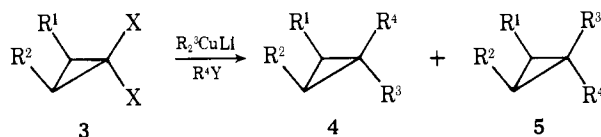
Entry	R ¹	R ²	R ³	R ⁴ - Y	Reaction temp °C	% yield ^{a,b}	4:5 ^c
1	Ph	H	<i>n</i> -Bu	Me-I	-40	100	80:20 ^d
2	Ph	H	<i>n</i> -Bu	Me-I	-78	64	86:14 ^d
3	Ph	H	<i>s</i> -Bu	Me-I	-78	43 ^e	>93:<7 ^f
4	Ph	H	<i>t</i> -Bu	Me-I	-55	20 ^g	100:0 ^f
5	Ph	H	<i>n</i> -Bu	Et-I	-48 ^h	65 ⁱ	51:49 ^j
6	Ph	H	<i>n</i> -Bu	CH ₃ CO-Br	-60	34 ^k	80:20 ^l
7	Ph	H	<i>n</i> -Bu	H-OEt ^m	-48	96 ⁿ	81:19 ^j
8	Ph	H ^o	<i>n</i> -Bu	Me-I	-60	71	41:59 ^d
9	-(CH ₂) ₄ -		<i>n</i> -Bu	Me-I	-48	82 ^p	>99:<1 ^q
10	<i>n</i> -C ₆ H ₁₃	H	<i>n</i> -Bu	Me-I	-48	50 ^r	76:24 ^q
11	PhCH ₂ OCH ₂	H	<i>n</i> -Bu	Me-I	-48	50 ^s	(70:30) ^t
12	6		<i>n</i> -Bu	Me-I	-48	78 ^u	100:0 ^q

^a Yield based on the sample purified by preparative TLC. ^b All the new compounds were identified spectrometrically and analytically. ^c Determined by gas chromatography and ¹H NMR. ^d The stereochemistry of the products was determined by ¹H NMR. The methyl signal of the isomer **4** appeared at δ 0.73, whereas that of **5** appeared at δ 1.18. Cf. K. Kitatani, T. Hiyama, and H. Nozaki, *J. Am. Chem. Soc.*, **97**, 949 (1975); C. H. Depuy, F. W. Breitbeil, and K. R. Debruin, *ibid.*, **88**, 3347 (1966). ^e Bp 84–92 °C (bath temperature) (23 mm). ^f The stereochemistry was determined by ¹H NMR in a similar manner described in the footnote *d*. ^g Bp 95–102 °C (bath temperature) (24 mm). ^h *m*-Xylene/dry ice bath. ⁱ Bp 87–95 °C (bath temperature) (27 mm). ^j The determination of the stereochemistry was based on the peak shape analysis of the *n*-butyl group in its ¹H NMR spectrum. ^k Bp 89–96 °C (bath temperature) (3.5 mm). ^l The acetyl group of the *cis* isomer **4** appeared at δ 1.61 and that of the *trans* isomer at δ 2.12. ^m Quenching with EtOH at -20°. ⁿ Bp 80–90 °C (bath temperature) (26 mm). ^o This is the reaction of 1,1-dichloro-2-phenylcyclopropane. The origin of the inverted stereochemistry is not certain. It should be remembered that the reaction of **6** proceeded with extreme selectivity of *exo*-attack followed by inversion. ^p Bp 100–106 °C (bath temperature) (15 mm). ^q The stereochemistry was unambiguously determined by independent synthesis of the authentic specimen (carbene addition to olefins). Details will appear in a full paper. ^r Bp 77–100 °C (bath temperature) (17 mm). The methyl signal appeared at δ 0.97. ^s Bp 98–105 °C (bath temperature) (2 mm). ^t The stereochemical assignment was not attained. ^u Bp 100–120 °C (bath temperature) (7 mm).

follows: (1) the initial halogen-copper exchange to afford **1**, (2) the consecutive alkyl migration under X⁻ elimination producing **2**, (3) the second alkylation by R'X. The unprecedented one-pot procedure gives dialkylcyclopropanes with greater facility than the previously reported two-step one.⁵



Lithium di-*n*-butylcuprate was prepared by treatment of *n*-butyllithium (10 mmol) in hexane (1.5 M) with cuprous iodide (5.0 mmol)⁶ suspended in ether (10 ml) at -40°. After 10 min 1,1-dibromo-2-phenylcyclopropane (1 mmol) dissolved in ether (1 ml) was added dropwise at this temperature. The solution was gradually warmed to -20° in 1 h, and treated with excess methyl iodide (1 ml). The mixture was further warmed to room temperature during 15 h. Workup afforded 1-butyl-1-methyl-2-phenylcyclopropane (bp 82–92 °C (bath temperature), 26 mm) in a quantitative yield. The stereochemical purity was assayed by GLC as shown in Table I (entry 1).



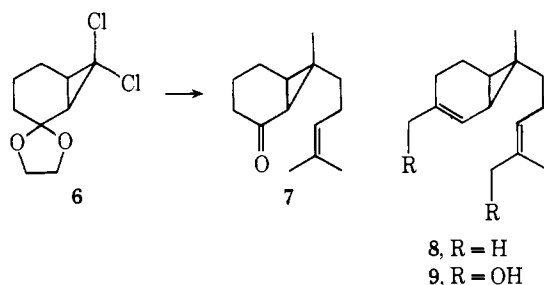
The success of the present unsymmetrical double alkylation as compared with dimethylation^{2,3} is ascribed to the different reactivity of the lithium dialkylcuprates.⁷ Therefore, *gem* di-alkylation was attained only by the oxidation (bubbling air) of a mixture of the intermediate **2** and excess di-*n*-butyl cuprate in a 34% yield (**4**, R¹ = Ph, R² = H, R³ = R⁴ = *n*-Bu).

The stereochemical consequence was independent of both

the period and temperature of aging of the intermediate **2**.⁸ In fact, it was found to depend upon factors below. Repeated reactions in various solvent systems (*n*-hexane, ether, tetrahydrofuran (THF), THF-hexamethylphosphoric triamide) indicated that ether gave the best results (yield and stereoselectivity).⁹ Preferably, the reaction of the cuprate with the dihalocyclopropane is carried out at -40° to -78°, while the second alkylation is carried out at -20°. An additional factor influencing the isomer distribution was the bulkiness of the alkyl group of the copper reagent.

Reaction of 1,1-dibromo-2-phenylcyclopropane with lithium di-*sec*-butylcuprate or di-*tert*-butylcuprate¹⁰ followed by the treatment with methyl iodide resulted mainly in the formation of **4** (R⁴ = Me) albeit in lower yields (entry 3, 4). Most remarkable was the reaction of 7,7-dihalonorcarane (entry 9) and its derivative (entry 12), which gave *endo*-methyl isomers (**4**) exclusively. With this observation in hand we extended the reaction to the preparation of a key intermediate **7** of *dl*-sesquicarene and *dl*-sirenin synthesis.¹¹

An ethereal solution of 4-methyl-3-pentenyllithium (12 mmol)¹² was added to cuprous iodide (6 mmol) and suspended in a mixture of *n*-hexane (15 ml) and ether (5 ml) at -78°. The resulting dark gray slurry was mixed with an ethereal solution of 7,7-dichloronorcaran-2-one ethylene acetal (**6**)¹³ (1.2 mmol) which was added slowly at -70°. The reaction mixture was gradually warmed to -20° during the period of 1 h, treated with excess methyl iodide, and allowed to stand for 16 h to warm to room temperature. Workup afforded an oil which was subsequently treated with THF-3 N sulfuric acid (1:1) at room temperature for 40 min. TLC purification (silica gel, dichloromethane, R_f 0.3–0.4) of the crude product gave a bicyclic ketone **7** (ir (neat) 1685 cm⁻¹, MS *m/e* 206 (M⁺), NMR δ 1.115 (*endo* Me)) in 44% yield. The stereochemistry was ascertained by methoxycarbonylation^{11a} of **7** affording a single stereoisomer. The methyl chemical shift (δ 1.02) of the product was strictly the same as that of the 7-*endo*-methyl keto ester and clearly different from that of 7-*exo*-methyl isomer (δ 1.14).^{11a} Transformation of **7** to *dl*-sesquicarene (**8**) and *dl*-sirenin (**9**) has been already established.^{11a}



References and Notes

- B. M. Trost and M. J. Bogdanowicz, *J. Am. Chem. Soc.*, **95**, 2038 (1973).
- (a) E. J. Corey and G. H. Posner, *J. Am. Chem. Soc.*, **89**, 3911 (1967); **90**, 5615 (1968); (b) G. H. Posner and D. J. Brunelle, *Tetrahedron Lett.*, 293 (1972); *ibid.*, 935 (1973); *J. Org. Chem.*, **38**, 2747 (1973).
- G. H. Posner, G. L. Loomis, and H. S. Sawaya, *Tetrahedron Lett.*, 1373 (1975).
- The resulting stereoselectivity is best explained by the assumption of the initial copper-halogen exchange occurring on the less hindered halogen followed by the S_N2 -type halogen-alkyl exchange under inversion.
- K. Kitatani, T. Hiyama, and H. Nozaki, *J. Am. Chem. Soc.*, **97**, 949 (1975).
- Commercially available cuprous iodide was purified according to the literature: G. H. Posner and J. J. Sterling, *J. Am. Chem. Soc.*, **95**, 3076 (1973).
- The reaction of **3** with lithium dimethylcuprate and lithium divinylcuprate proceeded similarly, whereas the one with lithium di-*n*-butylcuprate was apparently different. When 1,1-dibromo-2-phenylcyclopropane was treated with lithium dimethylcuprate in the absence of methyl iodide (-38° to 0° , 3 h, quenching with H_2O), a mixture of *rac*-1-bromo-1-methyl-*tert*-2-phenylcyclopropane and its diastereomer (57:43 ratio, 49% yield) was obtained besides a small amount of 1,1-dimethyl-2-phenylcyclopropane (17%). The reaction with lithium divinylcuprate (-78° to -70° , 1 h, quenching with MeI) also gave a mixture of *rac*-1-bromo-1-vinyl-*tert*-2-phenylcyclopropane and its diastereomer (72:28 ratio, 69% yield). In sharp contrast, however, no trace of 1-bromo-1-*n*-butyl-2-phenylcyclopropane was obtained in the reaction of 1,1-dibromo-2-phenylcyclopropane with lithium di-*n*-butylcuprate (entry 1, 2). Clearly, either bromine-methyl or bromine-vinyl exchange is predominant in the former cases over the preferred bromine-copper exchange in the lithium di-*n*-butylcuprate reaction.
- 1,1-Dibromo-2-phenylcyclopropane was treated with lithium di-*n*-butylcuprate (prepared at -48°) at -78° , and the reaction mixture was gradually warmed. Quenching the mixture with methanol at -48 , -21 , and -10° resulted in the formation of 1-butyl-2-phenylcyclopropane with 19:81 *cis/trans* ratio. This indicates that the species such as **2** is, at least, configurationally stable at the temperature examined.
- The addition of *n*-Bu₃P also decreased the stereoselectivity.
- C. R. Johnson and G. A. Dutra, *J. Am. Chem. Soc.*, **95**, 7777 (1973).
- (a) U. T. Bhalerao, J. J. Plattner, and H. Rapoport, *J. Am. Chem. Soc.*, **92**, 3429 (1970); (b) E. J. Corey and K. Achiwa, *Tetrahedron Lett.*, 1837, 3257 (1969); 2245 (1970); E. J. Corey, K. Achiwa, and J. A. Katzenellenbogen, *J. Am. Chem. Soc.*, **91**, 4318 (1969); (c) R. M. Coates and R. M. Freidinger, *Tetrahedron*, **26**, 3487 (1970); (d) K. Mori and M. Matsui, *ibid.*, **26**, 2801 (1970).
- The lithium reagent was prepared from the corresponding bromide and lithium dispersion containing ca. 5% sodium metal in ether at -10° . Cuprates prepared from Grignard reagents were tried without success. The C-MgX to C-Cu conversion requires the use of equimolar *n*-Bu₃P, which has, however, been found to be detrimental to the reaction of dihalocyclopropanes.
- The compound was obtained by dichlorocarbene addition (phase-transfer technique) to cyclohexenone ethylene acetal (71% yield) (*ir* (neat): 1107, 1020, 948, 784 cm^{-1} ; bp $88-90^\circ C/(1\text{ mm})$). Anal. Calcd for C₉H₁₂O₂Cl₂: C, 48.45; H, 5.42. Found: C, 48.70; H, 5.72.

Katuzi Kitatani, Tamejiro Hiyama,* Hitosi Nozaki

*Department of Industrial Chemistry, Kyoto University
Yoshida, Kyoto 606, Japan*

Received December 15, 1975

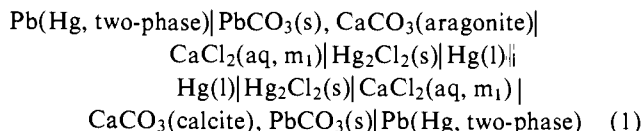
Determination of Gibbs Energies for Solid-Solid Phase Transitions in Electrochemical Double Cells without Liquid Junction: Calcite, Aragonite, and Vaterite

Sir:

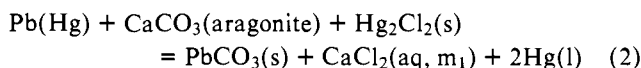
We have developed a novel electrochemical method for the study of solid-solid phase transitions of metal salts. The method involves the use of electrochemical double cells without liquid junction for which the solid-solid phase transition of interest is the net cell reaction. We report here the use of the method for the determination of the Gibbs energy of trans-

formation for the aragonite-to-calcite and vaterite-to-calcite phase transformations of CaCO₃. The aragonite-calcite phase transition is of special interest because of its potential use as a geobarometer,¹ and vaterite, aragonite, and calcite are found in the shells of various marine organisms.² Calcite is hexagonal with a density of 2.710 g cm⁻³ and a primary coordination of 9; aragonite is orthorhombic with a density of 2.944 and a primary coordination of 6; and, vaterite is pseudo-hexagonal with a density of 2.66.^{3,4} Aragonite is a high pressure form of CaCO₃, whereas vaterite is apparently metastable with respect to calcite and aragonite at 25 °C. The phase transformations are sluggish around room temperature and thermodynamic data for the transitions around 25 °C have been obtained primarily by indirect methods.

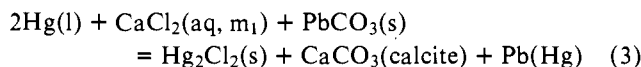
We have investigated the aragonite-calcite phase transition in the double cell



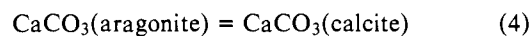
The cell reaction for the left half of the double cell is



whereas for the right half of the cell we have



If we use the same CaCl₂(aq) solution in both halves of the double cell, then the sum of reactions 2 and 3 yields for the net reaction of the double cell



A cell analogous to (1) but with vaterite in place of aragonite has the net cell reaction



For the net reactions given above $E_{\text{cell}} = E_{\text{tr}}^\circ$, and thus $\Delta \bar{G}_{\text{tr}}^\circ = -2FE_{\text{tr}}^\circ$; the voltage of the double cell should be independent of the CaCl₂(aq) concentrations. The double-cell technique yields $\Delta \bar{G}_{\text{tr}}^\circ$ directly, rather than as a small difference between two large numbers. Also, the double cell separates the two CaCO₃ phases such that crystals of the more stable phase are not in contact with the same cell electrolyte as those of the less stable phase, and therefore cannot catalyze the phase transformation of the less stable form.

Because of the sensitivity of the two-phase lead amalgam (~5 wt % Pb) to oxygen, the entire cell was set up on the high vacuum line; all cell components were introduced to the cell under oxygen-free conditions.⁵ The Pb(Hg)∥PbCO₃(s), CaCO₃(s)∥Ca²⁺(aq), and Hg(l)∥Hg₂Cl₂(s)∥Cl⁻(aq) electrodes were prepared as recommended in the literature.^{6,7} The calcite used in the cells was prepared from primary standard CaCO₃(s) which was covered with distilled water and held at 80 °C for several days. Synthetic aragonite was prepared according to the method described by Wray and Daniels.⁸ Synthetic vaterite was prepared according to Turnbull's⁴ method A1, except that the aging time was cut to 18 min; the sample was washed five times with distilled water and five times with absolute ethanol and then dried with an aspirator. The vaterite, aragonite, and calcite samples were authenticated by x-ray powder patterns and by the scanning electron microscope. Electron microprobe analysis showed that there were no impurities at the 0.01% level in our synthetic samples. All other chemicals used were reagent grade.

Emf measurements at $22 \pm 1^\circ C$ on cells of the type (1) at