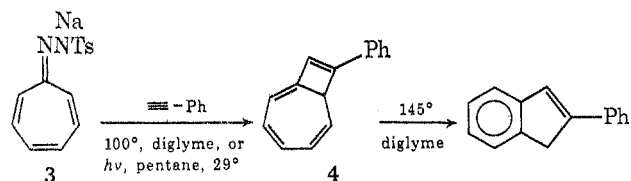


tion of cycloheptatrienyldiene (**1**) to carbon-carbon double bonds. Suitable acceptors include dimethylfumarate,¹ 1,3-pentadiene,² styrene,³ and ethylene.⁴ As a logical extension of this work as well as possible entry into the theoretically interesting⁵ spirononon-tetraene system **2**, we have now studied the addition of cycloheptatrienyldiene to phenylacetylene.



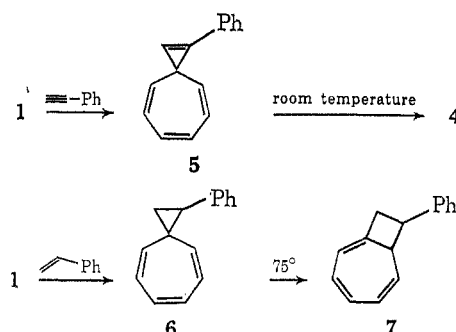
Either thermolysis (100°, diglyme) or photolysis (29°, pentane or THF) of the sodium salt of tropone tosylhydrazone (**3**)¹ in the presence of excess phenyl-



acetylene resulted in a C₁₅H₁₂ hydrocarbon in 21–25% yield in addition to a trace of heptafulvalene. From its spectral and chemical properties, this material was assigned the structure of 8-phenylbicyclo[5.2.0]nona-1,3,5,8-tetraene (**4**). The nmr spectrum of **4** (CDCl₃) shows a multiplet between 7.6 and 7.2 (5 H, aromatic), a doublet at 6.46 (1.4 Hz, 1 H, H₈), a multiplet between 6.35 and 5.65 (5 H, H₂–H₆), and a narrow multiplet at 4.76 ppm (1 H, H₇). The extent of the conjugation is indicated by the uv spectrum which has maxima (in *n*-pentane) at 370 nm (ϵ 9000) and 269 (31,000).⁶ The ir and mass spectra are in agreement with the proposed structure.⁹ When **4** was heated at 140° in diglyme, it was smoothly converted to 2-phenylindene,¹⁰ a conversion that is strong supporting evidence for the assigned structure. Additional evidence for this structure was obtained by generating **1** in the presence of β -deuteriophenylacetylene. The nmr spectrum of the product (**4**-d₁) showed no resonance at 6.46 ppm. In addition, the line width of the signal at 4.76 ppm was reduced. When **4**-d₁ was heated at 145°, 2-phenylindene-d₁ was produced. From the nmr spec-

trum, it was concluded that the deuterium had equilibrated (presumably as a secondary reaction) between the 1 and 3 positions of the indene.

By comparison with the addition of cycloheptatrienyldiene to styrene,^{2,3} the primary product of the addition of **1** to phenylacetylene is probably the spirononon-tetraene, **5**.¹² Unstable, even at room temperature,



5 undergoes what is probably a stepwise rearrangement¹³ to the tetraene, **4**. The instability of **5** relative to **6** is not surprising, since cyclopropenes undergo thermal ring opening much more readily than cyclopropanes.¹⁴ The thermal conversion of **4** to 2-phenylindene is analogous to the rearrangement of **7** to 2-phenylindane.²

(12) To date, there has appeared no verified two-step addition of cycloheptatrienyldiene (or an isomeric cycloheptatetraene) to a multiple bond.

(13) A concerted, thermal [1,7]-sigmatropic shift is unlikely based on orbital symmetry considerations: R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, GmbH, Weinheim Bergstr., 1970.

(14) In view of (1) the large difference in the activation energy for ring openings of cyclopropenes and cyclopropanes (~30 kcal/mol¹⁵), (2) the probability that the rearrangement of **5** to **4** is stepwise and (3) the facile rearrangement of **6** to **7**, it is highly unlikely that **5** will be isolable under ordinary conditions. The question remains open whether replacement of the phenyl group by hydrogen (**2**, R = H) will increase the energy of activation for the rearrangement sufficiently to permit isolation of the parent spirononon-tetraene.

(15) (a) R. Srinivasan, *J. Amer. Chem. Soc.*, **91**, 6250 (1969); (b) E. W. Schlag and B. S. Rabinovitch, *ibid.*, **82**, 5996 (1960).

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The Reaction of Alkyl- and Aryldichloroboranes with Ethyl Diazoacetate at Low Temperature¹

Summary: Ethyl diazoacetate reacts readily at low temperatures with aryl- and alkylidichloroboranes to give after protonolysis the corresponding ethyl arylacetates and alkylacetates in yields ranging from quantitative for the aryl to approximately 60% for the alkyl derivatives.

Sir: Trialkylboranes react with a variety of functionally substituted alkyldiazo compounds.² How-

(1) Joint publication was decided on after we learned of our related research in this area. The Purdue group investigated the alkyl-, the Alberta group the arylidichloroborane series.

(2) (a) J. Hooz and S. Linke, *J. Amer. Chem. Soc.*, **90**, 5936 (1968); (b) J. Hooz and D. M. Gunn, *Chem. Commun.*, 139 (1969); (c) J. Hooz and S. Linke, *J. Amer. Chem. Soc.*, **90**, 6891 (1968); (d) J. Hooz and G. F. Morrison, *Can. J. Chem.*, **48**, 868 (1970); (e) J. Hooz and D. M. Gunn, *J. Amer. Chem. Soc.*, **91**, 6195 (1969).

(1) W. M. Jones and C. L. Ennis, *J. Amer. Chem. Soc.*, **91**, 6391 (1969).

(2) E. E. Waali and W. M. Jones, *ibid.*, in press.

(3) (a) K. G. Untch, private communication; (b) L. W. Christensen, E. E. Waali, and W. M. Jones, *J. Amer. Chem. Soc.*, **94**, 2118 (1972).

(4) E. E. Waali and W. M. Jones, *Syn. Commun.*, **3**, 49 (1973).

(5) H. E. Simmons and T. Fukunaga, *J. Amer. Chem. Soc.*, **89**, 5208 (1967); R. Hoffmann, A. Imamura, and G. D. Zeiss, *ibid.*, **89**, 5219 (1967); M. J. Goldstein and R. Hoffmann, *ibid.*, **93**, 6193 (1971).

(6) Walborsky and Pendleton⁷ reported the uv spectrum of 1-phenyl 1,3,5,7-octatetraene [λ_{\max} 365 nm (ϵ 72,300), 337 (85,000), and 236 (11,000)]. The difference in the maxima and extinction coefficients between **4** and this model compound are expected since **4** has several cis and s-cis bonds and the model compound is all trans.⁸

(7) H. M. Walborsky and J. F. Pendleton, *J. Amer. Chem. Soc.*, **82**, 1405 (1960).

(8) R. M. Silverstein and R. M. Bassler, "Spectrometric Identification of Organic Compounds," Wiley, New York, N. Y., 1967, p 157.

(9) Ir (neat film) ν 3070 (w), 3010 (m), 2850 (w), 1662 (m), 1482 (m), 1446 (m), 759 (s), 703 (s), 692 (s); mass spectrum *m/e* (rel intensity) 192 (100), 106 (45), 105 (41), 86 (50), 84 (73). The tetraene, **4**, is sensitive to oxygen. It was reduced over Pt/C with the uptake of 4 equiv of hydrogen. The resulting hydrocarbon was shown to have the formula C₁₅H₂₀ by mass spectrometry and satisfactory elemental analysis.

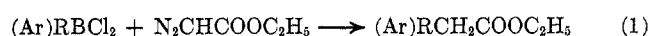
(10) Mp 166–167° (lit.¹¹ mp 167.5); nmr (CDCl₃) 7.7 to 7.1 (m, 10 H, aromatic and olefinic) and 3.79 ppm (narrow m, 2 H, benzylic).

(11) F. Mayer, A. Sieglitz, and W. Ludwig, *Chem. Ber.*, **54**, 1397 (1921).

ever, reaction is sluggish (and yields poorer) for organoboranes containing bulky alkyl groups. Also, the reaction permits the transfer of only one of three possible alkyl groups. To maximize the synthetic utility of this process, it is clearly desirable to achieve selective alkyl/aryl group migration from a suitable series of readily available "mixed" organoborane derivatives.^{3,4}

This problem has partially been overcome by the discovery that dialkylchloroboranes react readily at -78° with ethyl diazoacetate to give the corresponding esters in high yields.⁵ Unfortunately, even in these reactions only one of the two available alkyl groups is used.

The accessibility of both alkylchloroboranes⁶ and arylchloroboranes⁷ led to the exploration of their reactions with a typical α -diazocarbonyl derivative, ethyl diazoacetate (eq 1).



When ethyl diazoacetate (1 M in THF) was added to a solution of phenyldichloroborane (1 M in THF, -25°), nitrogen was quantitatively evolved. Protonolysis provided ethyl phenylacetate (92%). Repetition of the reaction in THF with *n*-butyldichloroborane (100% N_2 evolution) gave relatively poor results, 43% ethyl hexanoate and 30% ethyl chloroacetate.⁸ Various solvents, including THF, ether, toluene, pentane, and dichloromethane, were investigated at temperatures ranging from -25 to -78° . The best results for the alkyl series, yields of 57–71% of the alkyl ester, were obtained in ether (-62°). When applied to a series of alkyl- and arylchloroboranes under optimum conditions, all reactions evolved nitrogen (>95%) within 90 min. Table I summarizes the results.

The following procedure for the preparation of ethyl *p*-chlorophenylacetate is representative. A dry 50-ml flask equipped with a magnetic stirring bar and septum inlet is flushed with nitrogen. The flask is cooled to -25° (Dry Ice-carbon tetrachloride-acetone slush bath) and charged with 1.89 g (10 mmol) of *p*-chlorophenyldichloroborane in 10 ml of THF. To this solution is added, dropwise, 1.25 g (11 mmol) of ethyl diazoacetate in 10 ml of THF at such a rate (1 ml/3–5 min) that nitrogen is smoothly evolved (~ 1.5 hr). At this temperature, 5 ml of water and 5 ml of methanol are added. Finally, the cooling

(3) Boronic esters $[\text{RB}(\text{OR}')_2]$ prove to be unsatisfactory owing to the decreased electrophilicity of boron in these derivatives. Only 5–20% N_2 evolution occurs when either diethoxy-*n*-butylborane or dimethoxycyclopentylborane is treated with ethyl diazoacetate. Resonance contributions ($>\text{B}-\text{OR} \leftrightarrow >\text{B}^+=\text{OR}$) apparently outweigh the inductive effect of alkoxy, and initial coordination (eq 2, OR in place of Cl) is unfavorable. Unpublished results of G. F. Morrison (University of Alberta).

(4) Alkylchloroboranes react rapidly and in high yield with organic azides to produce the corresponding secondary amines: H. C. Brown, M. M. Midland, and A. B. Levy, *J. Amer. Chem. Soc.*, **95**, 2394 (1973).

(5) H. C. Brown, M. M. Midland, and A. B. Levy, *J. Amer. Chem. Soc.*, **94**, 3662 (1972).

(6) H. C. Brown and N. Ravindran, *J. Amer. Chem. Soc.*, **95**, 2396 (1973).

(7) J. Hooz and J. G. Calzada, *Org. Prep. Proc. Int.*, **4**, 219 (1972).

(8) The ethyl chloroacetate could conceivably arise from the reaction of hydrochloric acid (formed in the hydrolysis of the chloroborane intermediates) with residual diazo ester. However, the fact that nitrogen evolution is essentially complete indicates that residual diazo ester cannot be significant, so that this path can be ruled out as a major source of the chloroacetate. Consequently, we conclude that in this system transfer of chlorine from boron to carbon must occur competitively with the transfer of the alkyl groups.

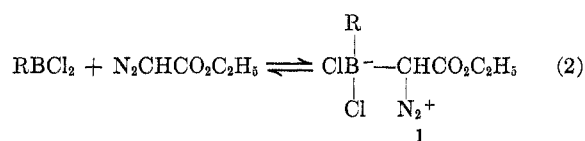
TABLE I
REACTION OF ALKYL AND ARYLDICHLOROBORANES WITH
ETHYL DIAZOACETATE TO GIVE THE CORRESPONDING ETHYL
ALKYL- OR ARYLACETATES

Alkyl- or arylchloroborane	Procedure ^a	Product	Yield, ^b %	% ethyl chloroacetate ^c
<i>n</i> -Butyl	A	Ethyl hexanoate	57	32
2-Methyl-1-pentyl	A	Ethyl 3-methylheptanoate	61	29
3-Hexyl	A	Ethyl 3-ethylhexanoate	60	26
Cyclopentyl	A	Ethyl cyclopentylacetate	71	22
Cyclohexyl	A	Ethyl cyclohexylacetate	57	26
<i>exo</i> -Norbornyl	A	Ethyl <i>exo</i> -norbornylacetate	60	26
Phenyl ^d	A	Ethyl phenylacetate	87	9
Phenyl ^d	B	Ethyl phenylacetate	92	5
Phenyl ^{d,e}	B	Ethyl phenylacetate	100 (98)	
<i>p</i> -Chlorophenyl ^e	B	Ethyl <i>p</i> -chlorophenylacetate	100 (91)	
<i>p</i> -Tolyl ^e	B	Ethyl <i>p</i> -tolylacetate	100 (95)	
<i>p</i> -Biphenyl ^e	B	Ethyl <i>p</i> -biphenylacetate	100 (91)	

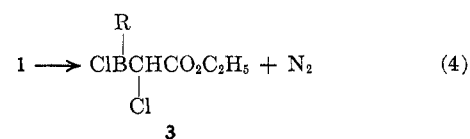
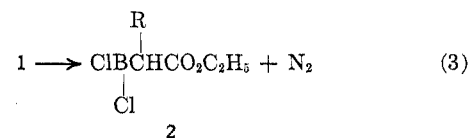
^a In procedure A each experiment used 5 mmol of ethyl diazoacetate in 5 ml of ether which was added to 5 mmol of alkylchloroborane in 5 ml of ether at -62° . Procedure B consisted of using THF as solvent at -25° on a 10-mmol scale. Otherwise the procedures were identical. ^b Analysis by glpc. Isolated yields are in parentheses. ^c These yields represent upper limits of chlorine transfer. See ref 8. ^d Commercially available from Aldrich. ^e A 10% excess of ethyl diazoacetate was used.

bath is removed. The mixture is poured into saturated aqueous Na_2CO_3 solution (75 ml) and extracted with three 50-ml portions of ether. Distillation of the dried (MgSO_4), concentrated residue affords 1.80 g (91%) of ethyl *p*-chlorophenylacetate, bp 106–107 (3.5 mm), mp 31–32° (lit.⁹ mp 32°).

These results suggest a mechanism involving initial Lewis acid-base coordination to produce the quaternary boron intermediate 1 (eq 2), followed by loss of nitro-

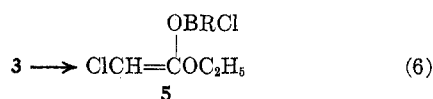
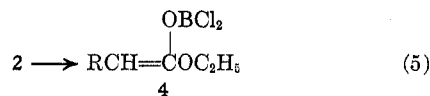


gen, with either subsequent or concurrent migration of an alkyl (aryl) group (eq 3) or chlorine (eq 4).



(9) R. v. Walther and A. Wetzlich, *J. Prakt. Chem.*, **61**, 169 (1900).

Pasto and Wojtkowski¹⁰ have recently isolated several enol borinates and suggest that intermediates such as **2** or **3** exist in the isomeric enol borinate forms **4** or **5**. Thus, if this reaction involves an α borate ester, the boron must migrate to oxygen (eq 5 and 6). Such intermediates are rapidly hydrolyzed by water.



Since α -haloboranes rearrange upon addition of a nucleophile,¹¹ methanolysis of **2** or **3** should give alkyl homologated esters unless protonolysis competes with the rearrangement. In an attempt to increase the yield of alkyl homologation, nucleophiles such as pyridine and triethylamine were added. After transfer, protonolysis should then give the alkyl ester. However, the yields of alkyl ester did not improve, suggesting that the rearrangement to the enol borinates **4** and **5** may be fast and irreversible even at -62° . Alternatively, the α transfer must be slow at these temperatures even when catalyzed by good nucleophiles. Attempts to identify definitively the intermediates by nmr were unsuccessful owing to the complicated spectrum of the mixture.

If the reasonable assumption is made that the conversion to the enol borinate is faster than rearrangement, the yields of chloro, alkyl, and aryl esters indicate their relative migratory aptitude. The data in Table I thus suggests the migratory aptitude to be in the order $\text{Ar} > \text{R} > \text{Cl}$. Such an order for aryl *vs.* alkyl has previously been observed in the rearrangements of α -haloboranes.¹²

In spite of some limitations, this reaction provides a highly useful and operationally simple method for converting alkenes/arenes to their corresponding two-carbon chain-lengthened ethyl esters. Simple procedures have recently become available for the synthesis of the required alkyldichloroboranes⁶ and aryl-dichloroboranes.⁷

We are continuing to explore the use of alkyl and aryl-dichloroboranes in organic synthesis.

Acknowledgment.—One of us (J. H.) wishes to thank the National Research Council of Canada for financial support. Mr. G. T. Morrison and Dr. R. B. Layton (University of Alberta) conducted the initial exploratory experiments with phenyldichloroborane.

(10) D. J. Pasto and P. W. Wojtkowski, *Tetrahedron Lett.*, 215 (1970).

(11) H. C. Brown and Y. Yamamoto, *J. Amer. Chem. Soc.*, **93**, 2796 (1971).

(12) D. S. Matteson and R. W. H. Mah, *J. Amer. Chem. Soc.*, **85**, 2599 (1963).

(13) University of Alberta, Postdoctoral Research Fellow, 1970–1972.

(14) National Science Foundation Predoctoral Fellow, 1970–1972.

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α -Halocarbonyl Compounds. II. A Position-Specific Preparation of α -Bromo Ketones by Bromination of Lithium Enolates. A Position-Specific Introduction of α,β -Unsaturation into Unsymmetrical Ketones

Summary: Low-temperature bromination of specifically generated ketone enolates under aprotic conditions produces position-specific α -bromo ketones which can be converted to α,β -unsaturated ketones; no Favorskii rearrangement or other base-catalyzed side reactions and no positional equilibration of bromine are observed.

Sir: Because α -halocarbonyl compounds are useful synthetic intermediates in a number of widely different organic transformations,¹ we have been interested for some time in devising some new efficient methods for their preparation.² Common methods for preparing α -halo ketones, in general, provide little position selectivity if both α and α' positions are available for direct halogenation.^{1a,3a} The available, generally applicable methods³ for specific preparation of either α - or α' -halogenated unsymmetrical ketones usually require extensive reaction sequences or produce the desired product in only moderate yield, often still contaminated with significant amounts of isomeric halo ketone. Even the well-known bromination of isomerically specific, neutral enol derivatives^{3c,d} of unsymmetrical ketones, *e.g.*, enol acetates, suffers the disadvantage that acidic by-products may catalyze equilibration of starting material or of product halo ketone. Consequently, both α - and α' -bromo ketones, as well as polybrominated materials, may be observed.

Perhaps the most obvious method for position-specific halogenation of unsymmetrical ketones, the quenching of position-specific enolate anions⁴ by halogen, has not received appropriate attention because of the attendant possibility of subsequent reactions (Favorskii rearrangements and/or alkylations and condensations) of the often quite reactive α -halo ketones under strongly basic reaction conditions. However, we wish to report that bromination of lithium enolates at low temperature is as effective a method for preparing specifically α - or α' -

(1) See a–d for examples. (a) H. O. House, "Modern Synthetic Reactions," 2nd ed, W. A. Benjamin, Menlo Park, Calif., pp 459–478. (b) H. C. Brown, *et al.*, *J. Amer. Chem. Soc.*, **90**, 6218 (1968); **91**, 2147 (1969); **91**, 6852 (1969). (c) T. A. Spencer, R. W. Britton, and D. S. Watt, *ibid.*, **89**, 5727 (1967). (d) R. Joly, J. Warnant, G. Nominé, and D. Bertin, *Bull. Soc. Chim. Fr.*, 366 (1958).

(2) (a) P. L. Stotter and K. A. Hill, "γ-Halotiglates: Ubiquitous Reagents for Natural Products Synthesis," paper delivered before the Second International Symposium on Synthesis in Organic Chemistry, Cambridge, England, July 1971. (b) P. L. Stotter and K. A. Hill, *Tetrahedron Lett.*, 4067 (1972).

(3) (a) Other halogenation methods (direct and indirect) which may, in certain cases, provide positional selectivity are also reviewed in ref 1a. (b) E. J. Corey, T. H. Topie, and W. A. Wozniak, *J. Amer. Chem. Soc.*, **77**, 5415 (1955). (c) H. Piotrowska, W. Wojnarowski, B. Waegell, and G. Ourisson, *Bull. Soc. Chim. Fr.*, 3511 (1965). (d) We have observed that direct bromination of the less substituted enol silyl ether derived from 2-methylcyclohexanone gives a complex product mixture at -20° ; more promising results were obtained at -70° , but some difficulties were nonetheless encountered in our attempts to separate product bromo ketone from trimethylsilanol and hexamethyldisiloxane on work-up.

(4) (a) H. O. House and B. M. Trost, *J. Org. Chem.*, **30**, 2502 (1965), and references cited therein. (b) G. Stork and P. F. Hudrlik, *J. Amer. Chem. Soc.*, **90**, 4462, 4464 (1968); H. O. House, L. J. Czuba, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, **34**, 2324 (1969). (c) H. O. House, M. Gall, and H. D. Olmstead, *ibid.*, **36**, 2361 (1971).