(1951); (d) R. E. Parker and N. S. Isaacs, *ibid.*, **59**, 737 (1959); (e) S. Winstein and R. B. Henderson in "Heterocyclic Compounds," Vol. 1, R. C. Elderfield, Ed., Wiley, New York, N. Y., 1950, Chapter 1.
(9) P. D. Bartlett and S. D. Ross, *J. Amer. Chem. Soc.*, **70**, 926 (1948).
(10) S. J. Cristol, J. R. Douglass, and J. S. Meek, *J. Amer. Chem. Soc.*, **73**, 816 (1951).
(11) N. G. Gaylord and E. I. Becker, *J. Org. Chem.*, **15**, 305 (1950).
(12) M. S. Kharasch and H. G. Clapp, *J. Org. Chem.*, **3**, 355 (1938).
(13) (a) D. F. Evans and G. V. Fazakerley, *J. Chem. Soc.*, 184 (1971); (b) G. E. Paris and E. C. Ashby, *J. Amer. Chem. Soc.*, **93**, 1206 (1971); (c) J. A. Magnuson and J. D. Roberts, *J. Org. Chem.*, **37**, 133 (1972).
(14) (a) M. S. Kharasch and O. Reinmuth in "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Englewood Cliffs, N. J., 1954, Chapter XIV; (b) H. O. House, *J. Amer. Chem. Soc.*, **77**, 3070, 5083 (1955).
(15) (a) We had difficulty repeating precise product ratios for this method of combination, whereas for regular addition results were highly reproducible. (b) At this time, we have no conclusive evidence to explain why dilution and increased addition time maximize the rearrangement pathway. However, it seems reasonable that inverse addition, as well as the slow addition time for this mode, allows greater contact time between the Grignard's Lewis acid component and the epoxide. Thus, when the Grignard reagent is added to the epoxide it reacts, but the Lewis acid component persists in the presence of the oxirane to perpetuate isomerization. In this manner, the concentration of the rearrangement intermediate builds up prior to the addition of more nucleophile. For the regular combination mode, however, the epoxide is consumed immediately upon addition, and no accumulation of rearrangement intermediate is possible. This explanation would also account for the sensitivity of product distribution to slight changes in reaction conditions with the inverse mode.
(16) A. J. Birch and M. Smith, *Proc. Chem. Soc.*, 356 (1962).
(17) J. A. Marshall, W. I. Fanta, and H. Roebke, *J. Org. Chem.*, **31**, 1016 (1966).
(18) J. A. Marshall and H. Roebke, *J. Org. Chem.*, **33**, 840 (1968).
(19) Biphenyl (10–15%) accompanied the reaction products, presumably a result of cupric ion promoted coupling. See R. C. Fuson in "Reactions of Organic Compounds," Wiley, New York, N. Y., 1962, p 446.
(20) House[13b] gives evidence that in the presence of $MgBr_2$ epoxides are converted to bromohydrins prior to rearrangement. See H. O. House in "Modern Synthetic Reactions," W. A. Benjamin, New York, N. Y., 1965, p 123. Often this possibility is not implicated[8,13a] in the rearrangement, but it does afford an explanation of our data.
(21) The vinyl Grignard had to be prepared in THF. In studies where ether was involved, the THF was removed by rotating evaporator under nitrogen bleed. Some THF undoubtedly remained coordinated to the vinylmagnesium halide.
(22) D. Klimenko, *J. Russ. Phys.-Chem. Soc.*, **43**, 212 (1911).
(23) J. Colonge and G. Poilane, *Bull. Soc. Chim. Fr.*, 953 (1955).
(24) G. Dupont, R. Dulou, and G. Lefebvre, *Bull. Soc. Chim. Fr.*, 816 (1954).
(25) J. Colonge and G. Descotes, *Bull. Soc. Chim. Fr.*, 815 (1959).
(26) K. N. Campbell and L. T. Eby, *J. Amer. Chem. Soc.*, **63**, 216 (1941).
(27) K. N. Campbell and L. T. Eby, *J. Amer. Chem. Soc.*, **63**, 2683 (1941).
(28) R. J. Tedeschi and G. Clark, Jr., *J. Org. Chem.*, **27**, 4323 (1962).
(29) This value could be in error owing to the fact that they were probably distilling two products which were formed in their work (see Discussion).
(30) R. Delaby, *C. R. Acad. Sci.*, **194**, 1248 (1932). A discrepancy exists in Delaby's work; see E. C. Coyner and G. A. Ropp, *J. Amer. Chem. Soc.*, **69**, 2231 (1947).
(31) L. A. Walter, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 757.
(32) D. Seyferth, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 258.

Vinyl Triflates in Synthesis. I. *tert*-Butylacetylene

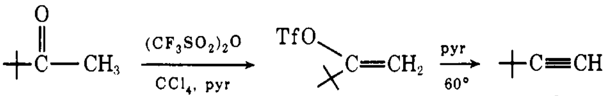
Robert J. Hargrove[1] and Peter J. Stang*

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

Received October 9, 1973

The recent paper by Collier and Macomber[2] on an improved synthesis of *tert*-butylacetylene (**1**) and the relative importance of this substance[3] prompts us to report a new synthesis in two steps of this material, in moderate yield under mild conditions, starting from the readily available pinacolone (**2**).

In this preparation pinacolone (**2**) is readily converted by methods previously developed[4] into 3,3-dimethyl-1-buten-2-yl triflate (**3**), which in turn easily eliminates CF_3SO_3H in the presence of pyridine to give **1** of >99% purity.



2 **3** **1**

Although a variety of conditions[4] were tried for the conversion of **2** into **3** and gc was used to follow the extent of reaction, on the scale employed (20.0 mmol), **3** could only be isolated in yields of 35–45%. It was evident from the results of gc monitoring that the best results on larger scale preparation would be obtained by not permitting the reactions to go to completion but rather allowing the reaction to proceed to only $\sim$60% conversion and reisolation and recycling of the unreacted pinacolone. In this manner, overall conversions of 60–70% could be readily achieved.

A number of different bases such as Et_3N and *t*-BuOK and solvents such as THF, dioxane, and CCl_4 were tried for the elimination of CF_3SO_3H from **3** and formation of **1**. However, the best results and yields (90%) were obtained when pyridine was used as both solvent and base. Interestingly, *in situ* elimination, *i.e.*, preparation and elimination of **3** in the same reaction, resulted in lower or only comparable yields of **1** (based on **2**) than the two-step process.

Triflate **3** is presumably formed through base-catalyzed enolization of the ketone and subsequent acylation of the enol with triflic anhydride. There is little doubt[5] that the elimination of HOTf to form acetylene is an E-2 process under the reaction conditions employed.

This procedure then represents an alternative and simple preparation of *tert*-butylacetylene (**1**) in very high purity, albeit in only moderate yield, from a readily available precursor, pinacolone. Furthermore, preliminary results indicate[6] that this may represent a general procedure for the conversion of certain ketones, such as ring-substituted acetophenones, and simple dialkyl ketones and aldehydes, as exemplified by valeraldehyde, into acetylenes in moderate yields.

Experimental Section

Boiling points are uncorrected. The nmr spectra were recorded on a Varian A-60 spectrometer using TMS as an internal standard; infrared spectra were obtained on a Beckman IR-5 spectrophotometer. Gas-liquid chromatography was performed on a Varian Aerograph Model 90-P unit using a 15 ft × 0.25 in. column with 15% SF-96 on Chromosorb W.

3,3-Dimethyl-1-buten-2-yl Triflate (3). A solution of 2.0 g (0.020 mol) of pinacolone (**2**) and 1.74 g (0.022 mol) of pyridine in 25 ml of anhydrous CCl_4 was cooled to −22° by means of a Dry Ice-CCl_4 slush bath. Over a period of 10 min 6.20 g (0.022 mol) of triflic anhydride was added with continuous swirling to the above cold solution, whereupon a white solid precipitate formed. The mixture was allowed to slowly warm to about 15° and maintained at that temperature for 60 hr, during which time the solution turned dark black. Gc monitoring showed that at this point the mixture consisted of $\sim$60% product and $\sim$40% unreacted ketone.

Prior to work-up an additional 20 ml of anhydrous CCl_4 was added to the mixture, which was then quickly washed with two 10-ml portions of ice-water. The water layer in turn was back extracted with three 10-ml portions of CCl_4. The combined organic layer was dried over anhydrous $MgSO_4$ and the solvent was distilled under reduced pressure. Distillation of the residue yielded 1.85 g (40% yield, 66% conversion) of colorless product: bp 42–45° (17 mm) [lit.[7] bp 45–50° (15 mm)]; ir 1650 (C=C), 1410 (S=O), 1210 cm^{-1} (CF); nmr (CCl_4) δ 1.18 (s, 9 H), 4.97 (d, 1 H, J = 4.1 Hz), 5.04 (d, 1 H, J = 4.1 Hz). The unreacted ketone may be recovered by elution with pentane on silica gel prior to distillation or through careful distillation.

tert-**Butylacetylene (1).** Triflate **3** (2.32 g, 0.010 mol) was added to 1.58 g (0.020 mol) of dry pyridine in a 10-ml round-bottom flask and connected to a short-path bulb-to-bulb distillation apparatus. The mixture was heated to 60° and the product was collected over a 15-hr period in a Dry Ice-acetone-cooled receiver, yielding 0.74 g (90%) of **1**, >99% pure by glc: nmr (neat) δ 1.22 (s, 9 H), 2.02 (s, 1 H); ir (CCl_4) 3320 ($C{\equiv}CH$), 2130 cm^{-1} ($C{\equiv}C$).

Acknowledgments. Financial support by the Research Corporation and the University of Utah Research Committee is gratefully acknowledged.

Registry No.—**1**, 917-92-0; **2**, 75-97-8; **3**, 27701-32-2; triflic anhydride, 358-23-6.

References and Notes

(1) University of Utah Graduate Research Fellow, 1972–1973.
(2) W. L. Collier and R. S. Macomber, *J. Org. Chem.*, **38**, 1367 (1973).
(3) L. Brandsma, "Preparative Acetylenic Chemistry," Elsevier, Amsterdam, 1971.
(4) T. E. Dueber, *et al.*, *Angew. Chem., Int. Ed. Engl.*, **9**, 521 (1970); P. J. Stang and T. E. Dueber, *Org. Syn.*, **54**, 000 (1974).
(5) P. J. Stang, *Progr. Phys. Org. Chem.*, **10**, 205 (1973); P. J. Stang and R. Summerville, *J. Amer. Chem. Soc.*, **91**, 4600 (1969).
(6) R. J. Hargrove, D. P. Fox, and P. J. Stang, unpublished observations.
(7) A. G. Martinez, M. Hanack, R. H. Summerville, P. v. R. Schleyer, and P. J. Stang, *Angew. Chem., Int. Ed. Engl.*, **9**, 302 (1970).

Reaction of Bromotrichloromethane with α-Alkyltoluenes and α,α-Dialkyltoluenes[1]

Kombiz O. Eghdami, Gerald Jay Gleicher,* and
William D. Totherow

*Department of Chemistry, Oregon State University,
Corvallis, Oregon 97331*

Received June 25, 1973

The relationship between free-radical formation and hydrocarbon structure have usually been based upon consideration of electronic factors. Tertiary radicals are known to be more stable than secondary or primary species. For example, the relative order of reactivity, cumene > ethylbenzene > toluene, for hydrogen abstraction by the trichloromethyl radical has been known for some time.[2] Steric effects, however, may also be of importance. Examples where the relatively small chlorine[3] or bromine[4] atoms show reluctance to attack electronically favored, albeit sterically hindered, positions have been reported. Larger radicals should exhibit even greater steric demands. Minisci and coworkers, utilizing various dialkylammonium radical cations as hydrogen abstracting agents, have observed that the penultimate position of several straight-chain compounds is preferentially attacked.[5] This selectivity is increased as the size of the alkyl groups attached to the nitrogen atom of the abstracting agent becomes larger. It has also been claimed that the selectivity associated with benzylic hydrogen abstractions depends in part on similar steric factors.[6,7] Cases involving benzylic hydrogen abstraction by large radicals from hindered positions seem to show enhanced substituent effects.

Andrews, Keefer, Friedrich, and their coworkers have examined hydrogen abstraction from the benzyl position of α-substituted toluenes.[8,9] In their most recent work they obtained a good correlation of relative rates of hydrogen abstraction by bromine atom with the $\sigma_p{}^+$ parameters of the substituents.[9] The large negative ρ value was taken as evidence for both appreciable charge development in transition state and for the possibility of direct resonance interaction between the substituent and the nascent radical. Although it was stated that steric factors were unimportant in this system, subsequent work indicated that these factors might be involved.[7] Use of the Taft four-parameter equation[10] was required to treat α-substituted toluenes with large substituents.

$$\log \frac{k_x}{k} = \sigma^+\rho + sE_s$$

To examine the importance of steric effects, it was decided to study hydrogen abstraction from α-alkyltoluenes and α,α-dialkyltoluenes by bromotrichloromethane.[11] As relatively small variations in electronic factors should exist among these compounds of a similar structural type, the steric factors operative might become more obvious. In Table I are found the results of the present experiments. All runs were initiated photolytically at 70° and carried out in replicate.

Table I
Relative Rates of Hydrogen Abstraction from α-Alkyltoluenes and α,α-Dialkyltoluenes by Bromotrichloromethane at 70° [a]

Compd	Registry no.	k_X/k_{cumene} Exptl	k_X/k_{cumene} Calcd
Cumene	98-82-8	1.000	0.701
sec-Butylbenzene	135-98-8	0.48 ± 0.04	0.491
3-Phenylpentane	1196-58-3	0.17 ± 0.02	0.348
Ethylbenzene	100-41-4	0.15 ± 0.01	0.127
n-Propylbenzene	103-65-1	0.12 ± 0.01	0.089
Isobutylbenzene	538-93-2	0.042 ± 0.002	0.034
Toluene	108-88-3	0.017 ± 0.001[b]	0.023
Neopentylbenzene	1007-26-7	0.003 ± 0.0005[c]	0.003

[a] All kinetic results expressed per benzylic hydrogen. [b] Obtained relative to neopentylbenzene. [c] Obtained relative to isobutylbenzene.

The above data could be treated in several ways. Qualitatively the standard electronic dependence is noted with all tertiary and most secondary systems being more reactive than toluene. Several linear free energy treatments were utilized in attempts to correlate the data. The best least-squares correlation was obtained using the relationship

$$\log \frac{k}{k_{\text{cumene}}} = -5.78(\Sigma\sigma^+) + 0.85(\Sigma E_s) - 3.75$$

The calculated values of the relative rates are also shown in Table I. The average deviation between these calculated values and their experimental counterparts is less than 25%. It is felt that this is creditable considering the range of nearly three powers of ten between the extreme relative rates shown by members of this series. Figure 1 illustrates the correlation between experimental and calculated logarithms of relative rates. The correlation shows a slope nearly equal to unity and a correlation coefficient of 0.980.

Experimental Section

Materials. Bromotrichloromethane, chlorobenzene, toluene, ethylbenzene, propylbenzene, cumene, isobutylbenzene, *sec*-butylbenzene, and neopentylbenzene were obtained from commercial sources. The remaining compound, 3-phenylpentane, was prepared from the reaction of 3-pentanone with phenylmagnesium bromide to yield 3-phenyl-3-pentanol followed by dehydration and catalytic hydrogenation. All materials were distilled before use. Physical properties corresponded with values in the literature. Purities greater than 99% were determined by glc.

Product Studies. Prior work has shown that exclusive benzylic bromination occurs for toluene, ethylbenzene, cumene,[6] propylbenzene,[13] and neopentylbenzene.[7] It was assumed that the remaining compounds studied would proceed in identical manner.