CHEMISTRY LETTERS, pp. 1241-1242, 1981.

KETENE-ANTHRACENE ADDUCT,
A PRECURSOR OF SUBSTITUTED ACETYLENES

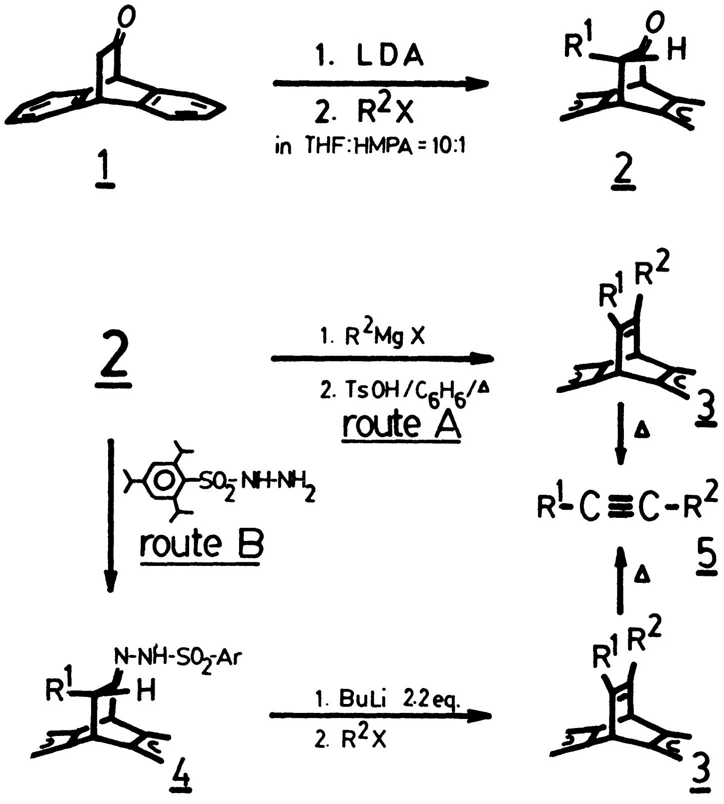
Bongkoch TARNCHOMPOO, Yodhathai THEBTARANONTH,* and Suchada UTAMAPANYA
Department of Chemistry, Faculty of Science, Mahidol University,
Rama 6 Road, Bangkok 4, Thailand

Prapani KASEMSRI
Department of Chemistry, Faculty of Science, Chulalongkorn University,
Bangkok 5, Thailand

The ketene-anthracene adduct 1 serves as a good precursor in the synthesis of substituted acetylenes, in which the key step is the retro Diels-Alder reaction.

We wish to demonstrate in this communication that the ketene-anthracene adduct 1,1) a well known candidate for the substituted ketene precursor,2) can serve as a convenient starting block in the preparation of substituted acetylenes. This method provides an alternative approach to the acetylenic bond, whose construction elimination reactions are usually employed for.3) The synthetic sequence is illustrated in the Scheme.

The ketene adduct 1 was directly alkylated via its lithium enolate (1.2 eq. of LDA in THF: HMPA = 10:1) to give 2. Conversion of the alkylated adduct 2 to the acetylene precursor 3 could be accomplished via routes A or B. In route A, however, dehydration of the intermediate alcohol (TsOH, boiling benzene) proceeded cleanly only when R^2 = Ar (see Scheme), the reaction being otherwise slow and yielding several minor products which required tedious chromatographic separation. Hence when $R^2 \neq$ Ar, route B, which employed the Shapiro reaction,4) was preferred, even though product yields were lower. Thus, 2 was converted nearly quantitatively to 4 by treatment with triisopropylbenzenesulphonyl hydrazide.5) Conversion of 4 to the acetylene precursor 3 was effected by a slow introduction of *n*-BuLi (2.2 eq.) to a solution of 4 in DME (20 ml of DME for 1 mmole of reagent) at -78°, then raising the temperature and keeping it at 0° for 3 hr, followed by addition of the corresponding alkyl halide to the intermediate vinyl anion. As predicted, the retro Diels-Alder reaction of 3 offered no difficulty (flash vacuum pyrolysis at 500-550°/0.05mm, using 30"x0.5" glass column packed with glass chips and wrapped with heating coil) and the crude pyrolysates were shown to be pure acetylenes (GC., NMR.).6)



R^1	R^2	Mp° of 3	% of 5 from 2
H	Ph	129-130	~100
Me	Ph	170-2	"
Et	Ph	160-1	"
$PhCH_2$	Ph	106-8	"
Me	Et	102-3	82
Et	Et	97-8	80
$PhCH_2$	Me	96	60
$PhCH_2$	Et	88-9	72

It can be seen by this method that the adduct 1 is quite versatile and can be employed as either $-C \equiv C^+$ (route A) or $-C \equiv C^-$ (route B) equivalents in the synthesis of acetylenes.

References

1) P.F.Hudrlik, A.M.Hudrlik, and C.N.Wan, *J.Org.Chem.*, *40*, 1116 (1975).

2) H.Hart, D.L.Dean, and D.N.Buchanan, *J.Am.Chem.Soc.*, *95*, 6294 (1973); J.L.Ripoll, *Tetrahedron Report Number 45*, *Tetrahedron*, *34*, 19 (1978).

3) For review see "The Chemistry of the Carbon-Carbon Triple Bond", Vol 1 and 2, Saul Patai Ed., John Wiley & Sons, Inc., New York, 1978; for recent report see H.J.Reich and W.W.Willis, Jr., *J.Am.Chem.Soc.*, *102*, 5967 (1980).

4) R.H.Shapiro, *Organic Reactions*, *23*, 405 (1976); for recent application see R.M.Adlington and A.G.M.Barrett, *J.Chem.Soc.,Chem.Comm.*, 65 (1981).

5) A.R.Chamberlin, J.E.Stemke, and F.T.Bond, *J.Org.Chem.*, *43*, 147 (1978).

6) We thank Mrs.P.Poochaiwattananon, Mrs.J.Udcharchon, and Miss A.Srisuthtiprut for spectroscopic, MS, and analytical services.

(Received June 1, 1981)