thawed under vacuum, and finally sealed under vacuum. After the tube had been heated for the indicated time and temperature (Table I) it was cooled and opened and 30 ml of H_2O was added. The solution was acidified to litmus with 3 *N* HCl and extracted with three 30-ml portions of ether, and the combined ether extracts were dried (K_2CO_3), concentrated on a rotary evaporator, and analyzed by tlc and vpc. The products were separated by preparative chromatography and identified by comparison of their ir spectra with those of authentic samples or as indicated below. Yields were calculated from the vpc trace taking into account the response factors of the individual products. Variations from these reaction conditions are noted in Table I.

Product Identification.—2-Piperidinothianaphthene (**2**), mp 100–100.5° (lit.[8] mp 98–100°), and 3-piperidinothianaphthene (**3**), mp 65–66° (lit.[21] mp 64–65°), were prepared for comparison purposes by the cited methods. 2-Piperidino-3-bromothianaphthene (**7**) was compared with the independently synthesized sample described below and 2,3-dipiperidinothianaphthene (**8**), mp 101–102.5°, was identified from its nmr spectrum [δ 7.0–7.7 (m, 4, ArH), 3.2 (m, 4, CH_2N), 2.9 (m, 4, CH_2N), 1.6 (m, 12, CH_2)] and analysis.

Anal. Calcd for $C_{18}H_{24}N_2S$ (**8**): C, 71.94; H, 8.06; N, 9.33. Found: C, 72.02; H, 7.93; N, 9.17.

2-Piperidino-3-bromothianaphthene (7).—To a solution of 5.4 g of **2** in 25 ml of dry, distilled dioxane was added with stirring 4.0 g of Br_2 in 25 ml of dioxane over a period of 20 min. The yellow precipitate which formed was filtered and washed with dioxane and $CHCl_3$ to give 9.4 g (100%) of the highly insoluble iminium salt **9**: nmr (DMSO) δ 7.1–7.6 (m, 4, ArH), 3.8 (s, 1, CHBr), 1.5–1.8 (m, 6, CH_2); the CH_2N peaks (*ca.* 3.1) are partially blocked out by the DMSO absorption; ir 1622 cm^{-1}.

Anal. Calcd for $C_{13}H_{15}Br_2NS$ (**9**): C, 41.38; H, 4.01; N, 3.72. Found: C, 41.15; H, 4.27; N, 3.63.

To a mixture of 5.7 g of **9** and 50 ml of anhydrous ether was added 1.5 g of pyridine. After about 5 min the yellow salt **9** was replaced by white pyridinium bromide. Filtration, evaporation of the filtrate to dryness, and recrystallization of the residue from low-boiling petroleum ether gave 3.3 g (74%) of **7**: mp 76–77°; nmr δ 7.0–7.7 (m, 4, ArH), 3.0 (m, 4, CH_2N), 1.5 (m, 6, CH_2); sodium fusion indicated the presence of N, S, and Br.

Anal. Calcd for $C_{13}H_{14}BrNS$ (**7**): C, 52.68; H, 4.77; N, 4.73. Found: C, 52.90; H, 4.82; N, 4.63.

7 is unstable at room temperature and sensitive to air and moisture. It was stored under N_2 at 0°.

Registry No.—**1**, 7342-82-7; **2**, 33880-37-4; **5**, 5394-13-8; **6**, 6287-82-7; **7**, 38359-65-8; **8**, 38359-66-9; **9**, 38359-67-0.

Acknowledgment.—This research was supported by grants from the Robert A. Welch Foundation and the TCU Research Foundation.

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[21] G. van Zyl, D. C. DeJongh, V. L. Heasley, and J. W. van Dyke, *J. Org. Chem.*, **26**, 4946 (1961).

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tert-Butylacetylene Revisited. An Improved Synthesis. Methyl Migration during Bromination

WAYNE L. COLLIER AND R. S. MACOMBER*

Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221

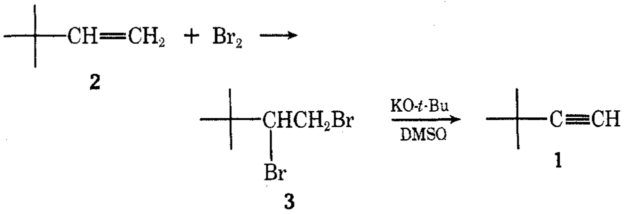
Received September 12, 1972

A synthesis of *tert*-butylacetylene, superior in all respects to the conventional procedure, is described involving bromination of *tert*-butylethylene (**2**), and double dehydrobromination of the *vic*-dibromide (**3**) with potassium *tert*-butoxide–dimethyl sulfoxide in overall yields of 81%. The bromination of **2** was found to give 70–90% yields of **3**, accompanied by 1-bromo-3,3-dimethylbutane and a crystalline product formulated as tetra(bromomethyl)ethylene (**4**), a new compound. The mechanism of formation of **4** and its ineffectiveness as a dienophile are described.

tert-Butylacetylene (**1**) is a highly useful synthetic reagent, serving for example as the source of the *tert*-butylethynyl group in a great many propargyl alcohols and related compounds. The usual preparation[1] of **1** involves the reaction of pinacolone with phosphorus pentachloride to form a relatively sensitive *gem*-dichloride, which is then treated with a sodium hydroxide melt to promote a double dehydrochlorination. Both steps in the sequence are only moderately efficient, owing to the lability of the intermediate dichloride and the harsh conditions required for the elimination.

We attempted to improve the overall yield by substituting potassium *tert*-butoxide in dimethyl sulfoxide (DMSO) for the sodium hydroxide, and found that this substantially increases the yield in the second step to >90%. Still, the difficulties encountered in the first step precluded significant improvement.

Recently we devised an obvious alternative preparation of **1** which is superior in all respects (simplicity, time requirements, yields, and economy) to the original method. This procedure involves the bromination of *tert*-butylethylene (**2**) and subsequent double dehydrobromination of the *vic*-dibromide with KO-*t*-Bu–DMSO. The reaction of **2** with either bromine[2] or *N*-bromosuccinimide[3] has been reported to give the desired dibromide **3**. In our hands, the addition of bromine to **2** at −78° afforded **3** in 90% yield, and this was treated with 2 equiv of KO-*t*-Bu in DMSO, from which **1** could be isolated in 91% yield. The overall yield from olefin to acetylene was 81%.



The bromination of **2** is interesting in another regard. When the addition of bromine to **2** was carried out at room temperature, gaseous HBr was liberated in significant amounts. Moreover, two side products could then be readily isolated. The first of these, formed in 10% (isolated) yield, was found to be 1-bromo-3,3-dimethylbutane,[4] which is known to arise from the anti-Mar

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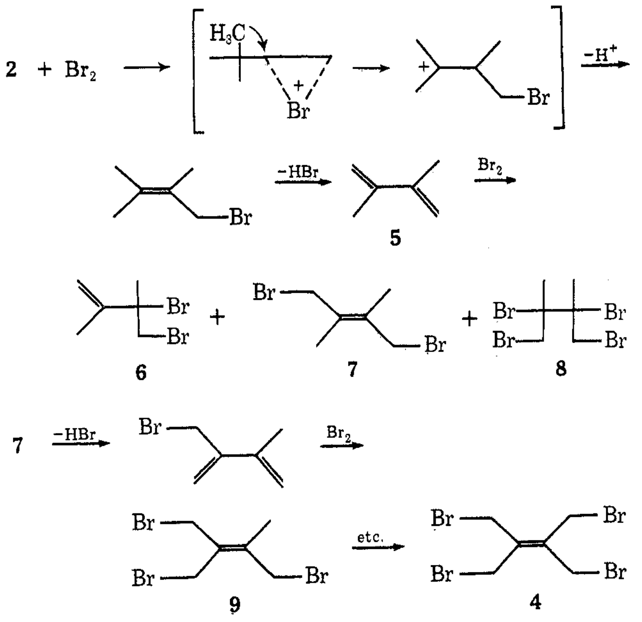
[1] (a) P. Ivitzky, *Bull. Soc. Chim. Fr.*, **35**, 357 (1924); (b) P. D. Bartlett and L. J. Rosen, *J. Amer. Chem. Soc.*, **64**, 543 (1942).

[2] M. F. Claessens, *Bull. Soc. Chim. Fr.*, **5**, 113 (1909).

[3] A. Guillemonat, G. Peiffer, J.-C. Traynard, and A. Leger, *ibid.*, 1192 (1964).

[4] Interestingly, the earlier report[2] included a vague description of a lower boiling monobromide then believed to be $C_6H_{11}Br$ on the basis of bromine content (calcd 49.08; found 46.48). We feel that compound was the same monobromide we have identified (calcd for $C_6H_{13}Br$: Br, 48.41). An allusion was also made to a liquid tribromide of unknown structure (**9**?) and an undescribed crystalline solid.

kovnikov addition of HBr to **2**.[5] The second side product, a straw-colored, crystalline solid (sparingly soluble in most organic solvents), exhibited a mass spectrum with parent ions at *m/e* 404, 402, 400, 398, and 396 in the ratio 1:4:6:4:1—four bromine atoms! The molecular formula $C_6H_8Br_4$ was confirmed by elemental analysis. Surprisingly the compound showed no outstanding functionality in its infrared spectrum, and its pmr spectrum consisted of a lone singlet at δ 4.19. We believe this to be the previously unknown symmetrical tetrabromide **4** [tetra(bromomethyl)ethylene].[6] Some evidence can be advanced regarding the mechanism by which **4** arises under these conditions, realizing that a methyl migration must be involved at some stage.[7] A possible pathway to **4** is shown below.



It has in fact been reported[8] that the bromination of 2,3-dimethyl-1,3-butadiene (**5**) at −15° gives two bromides, solid **7** (80%, stereochemistry unspecified, but probably trans considering steric effects) and a minor amount of a liquid dibromide (presumably **6**), which could be interconverted at 100°. We found that bromination of **5** at −10° yields two compounds with similar glc characteristics. They were initially present in comparable amounts, but upon standing the later eluting one (**6**) isomerized to the other, which was identical with **7**. (The more highly substituted double bond in **7** should render it more stable than **6**.) However, bromination of **5** with excess bromine, or bromination of **7**, led to several new products, including tetrabromide **4** (5%), a second tetrabromide (**8**, 20%) and a compound believed to be tribromide **9** (60%). Interestingly, **8** was easily isolated from the bromination product mixture of **5**, while **4** was not. Yet, although reexamination of the bromination products from **2** by glc revealed the presence of **8** (**8**/**4** = 4), it was **4** that could be isolated, not **8**! This must reflect the fact that **8** is less soluble than **4** in **9**, while **4** is less soluble than **8** in dibromide **3**. The yields of **4** from **2** and **5** were functions of the reaction conditions; excess bromine, higher temperatures, and extended reaction times favored its formation. Thus, bromination of **2** at −78° gave only **3** and negligible amounts of side products, while reaction at room temperature afforded **4** in yields as high as 2%. It is thus highly likely that **5** is formed during the bromination of **2** at room temperature, and that **4** arises from reactions of the type shown above. Further work on the details of these transformations is in progress.

There remained the possibility that **4** could exhibit some degree of dienophilicity if the electron-withdrawing inductive effect of the four bromine atoms compensated for their unfavorable steric bulk. Attempts were made to thermally cycloadd **4** to anthracene, but, after 18 hr at reflux in toluene, no reaction could be detected by glc.[9] Thus, **4** exhibits no tendency to undergo Diels–Alder addition to a moderately reactive diene.

Experimental Section[10]

General.—Instruments used were as follows: pmr, Varian A-60 and T-60 (referred to internal TMS); ir, Perkin-Elmer Model 700 and 337, and Beckman IR-12 (carbon tetrachloride solution unless otherwise noted); mass spectra, Hitachi RMU-7; analytical glc, Hewlett-Packard Model 700 (TC detection) fitted with dual 8 ft × 0.125 in. aluminum columns packed with 12% silicon oil 550 on 80–100 Chromosorb W-AW, DMSC (helium flow rate 30 cc/min, injection port 215°, initial column temperature 85° for 2 min, then programmed to 215° at 30°/min). These conditions gave the following relevant retention times (min): 1-bromo-3,3-dimethylbutane (2.1), **3** (5.9), **7** (7.0), **6** (7.2), **9** (9.8), **8** (12.0), and **4** (12.4). Melting points were measured with an oil bath and are uncorrected. Microanalyses were performed by Chemalytics, Tempe, Ariz.

Bromination of 2.—*tert*-Butylethylene (**2**) (42 g, 0.50 mol) was magnetically stirred at room temperature in a three-neck flask fitted with an addition funnel and a reflux condenser, while bromine (80 g, 0.50 mol) was added dropwise over 2 hr. During the addition and subsequent stirring, HBr (identified by trapping in water) was evolved in significant amount. After stirring for an additional 21 hr, water (50 ml) was added. The organic phase was separated and the aqueous phase was extracted with 3 × 35 ml of ether. The combined organic phases were dried (anhydrous magnesium sulfate) and then rotary evaporated under vacuum, leaving 109.6 g of a clear yellow liquid. Glc showed 8.6% 1-bromo-3,3-dimethylbutane[11] and 84% **3**. Distillation through a 9-in. Vigreux column at 12 mm afforded 8.5 g of the monobromide, bp 40–41° (pot 80–100°), and 87.2 g (72%) of **3**, bp 81–83° [lit.[3] bp 84–85° (12 mm)] (pot 100–145°). Compound **3** exhibited the following spectral data: mass spectrum (70 eV) *m/e* 242, 244, 246 (1:2:1); ir 2955 (vs), 1470 (s), 1375 (s), 1257 (s), and 1223 cm^{-1} (s); pmr[12] δ 1.14 (s, 9 H), 3.35–4.20 (overlapping multiplets, 3 H). The monobromide showed the following spectral characteristics: mass spectrum (70 eV) *m/e* 164, 166 (1:1); ir 2930 (s), 2840 (m), 1450 (m), 1350 (m), 1237 (m), and 640 cm^{-1} (m); pmr[12] δ 0.97 (s, 9 H), 1.84 (t, J = 8.5 Hz, 2 H), 3.37 (t, J = 8.5 Hz, 2 H).[13] The boiling point of this compound

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[5] Patent application abstracted in *Chem. Abstr.*, **63**, P2897*b* (1965).

[6] The double bond in **4** (invisible in its ir spectrum owing to the dipole moment selection rule) is resistant to further bromination, but the compound does give a positive test with potassium permanganate.

[7] Previous attempts to detect rearrangement during the bromination of **2** in methanol were unsuccessful: W. H. Puterbaugh and M. S. Newman, *J. Amer. Chem. Soc.*, **79**, 3469 (1957).

[8] E. H. Farmer, C. D. Lawrence, and W. D. Scott, *J. Chem. Soc.*, 510 (1930).

[9] For comparison, maleic anhydride reacts with anthracene to yield >50% of the adduct after 2–3 hr at 80°: G. R. Robinson and T. L. Jacobs, "Laboratory Practice of Organic Chemistry," Macmillan, New York, N. Y., 1962.

[10] Caution: a number of the polybrominated compounds prepared here are potent lachrymators. Due caution should be exercised in all stages of the work.

[11] Glc percentages are not corrected for differences in response factors, which may be significant for compounds with differing numbers of heavy atoms.

[12] Carbon tetrachloride solution.

[13] The two triplets were somewhat complex, but bore an exact mirror image relationship to each other.

at 1 atm was 137–139° (lit.[14] bp 137–138°), and its reaction with KO-*t*-Bu–DMSO gave **2**.

If the addition of bromine was carried out at −78° over 3 hr (with 2 hr additional stirring) using chloroform as solvent, glc showed less than 2% of product other than **3**, which could be isolated as above in 90% yield.

Isolation of 4.—If the undistilled product mixture from the room-temperature bromination of **2** was allowed to sit at −20° for 4 days, 4.1 g of straw-colored crystals could be isolated by filtration. The melting point was found to be 159–161° after recrystallization (chloroform) and sublimation (80–100°, 1 mm). The partial mass spectrum (70 eV) was as follows: *m/e* 404, 402, 400, 398, 396 (1:4:6:4:1), 323, 321, 319, 317 (1:3:3:1, M − Br), 242, 240, 238 (1:2:1, M − 2Br), 161, 159 (1:1, M − 3Br). Additional spectral data follow: ir (KBr) 3045 (w), 2993 (w), 1465 (s), 1441 (s), 1237 (s), 1205 (s), 1121 (w), 1098 (m), 877 (s), 866 (s), 740 (s), 665 (vs), 568 (m), and 499 cm^{-1} (m); pmr[15] δ 4.19 (s); uv (pentane) λ_{max} 218 nm (log ϵ 4.09) and 251 (4.03).

Anal. Calcd for $C_6H_8Br_4$: C, 18.03; H, 2.02; Br, 79.96. Found: C, 18.12; H, 1.93; Br, 80.14.

***tert*-Butylacetylene (1).**—To 115 g (0.710 mol) of KO-*t*-Bu[16] was added 150 ml of fresh (dry) DMSO, and the suspension was stirred for 30 min. Dibromide **3** (87.2 g, 0.357 mol) was added dropwise over 1 hr, and then the mixture was warmed slowly and distilled through a 9-in. Vigreux column to give 26.7 g (0.326 mol, 91.3%) of the acetylene, bp 36–38° (lit.[1] bp 36.4–37.8°). The product was >99% pure by glc. Spectral data for **1** follow: ir 3310 (vs), 2985 (vs), 2145 (m), 1480 (s), 1460 (s), 1370 (s), 1260 (vs), 1215 cm^{-1} (s); pmr[12] δ 1.21 (s, 9 H), 1.91 (s, 1 H).

Bromination of 5.—Reaction of **5** with 1 equiv of bromine at −10° as previously described[8] led to a mixture of two products as described in the text. Dibromide **7** could be isolated therefrom, showing (after recrystallization from chloroform) mp 43–44° (lit.[8] mp 47°); ir (chloroform) 3000 (m), 2940 (m), 1450 (m), 1385 (m), 1200 (s), 1070 (m), 930 (m), 870 cm^{-1} (m); pmr[15] δ 1.88 (s, 6 H), 4.00 (s, 4 H).

Bromination of 5 with Excess Bromine.—To 1.82 g (22.2 mmol) of the diene in a flask fitted with a reflux condenser atop an addition funnel was added 7.10 g (44.4 mmol) of bromine over 30 min. The addition is highly exothermic, with the reaction mixture staying at 60°. During the last half of the addition HBr was liberated copiously, and crystalline material began to form. Chloroform (5 ml) was added, and the solution was filtered to give 550 mg of **8**: mp (after recrystallization from chloroform) 138–140°; pmr[15] δ 2.12 (s, 6 H), 4.09 (d, J = 11.5 Hz, 2 H), 4.36 (d, J = 11.5 Hz, 2 H);[17] ir (chloroform) 2850 (m), 1440 (w), 1380, (w), 1257 (w), 1010 (w), 855 cm^{-1} (w); mass spectrum, no parent ion from 20 to 70 eV, very intense isotope clusters in the region *m/e* 322 (q, M − Br) and 242 (t, M − 2Br).

Anal. Calcd for $C_6H_{10}Br_4$: C, 17.94; H, 2.51; Br, 79.56. Found: C, 17.74; H, 2,06; Br, 79.56.

The filtrate from above was further diluted with 40 ml of chloroform, washed with dilute sodium thiosulfate, and dried over magnesium sulfate. Removal of solvent and two short-path distillations afforded **9**, bp 76–78° (0.15 mm). The yield of **9** was 1–2 g, depending on the pot temperature, as decomposition took place. Spectral data follow: pmr[15] δ 1.97 (s, 3 H), 4.05 (s, 2 H), 4.15 (s, 2 H), 4.20 (s, 2 H); ir (neat) 2960 (m), 1640 (m), 1450 (s), 1380 (s), 1300 (m), 1200 (vs), 948 (m), 880 (s), 860 (s), 700 cm^{-1} (s); mass spectrum (45 eV) *m/e* 318, 320, 322, 324 (1:3:3:1).

Anal. Calcd for $C_6H_9Br_3$: C, 22.46; H, 2.83; Br, 74.71. Found: C, 22.57; H, 2.28; Br, 75.14.

Registry No.—**1**, 917-92-0; **2**, 558-37-2; **3**, 640-21-1; **4**, 30432-16-7; **5**, 513-81-5; **7**, 34619-20-0; **8**, 24173-07-7; **9**, 38400-50-9; 1-bromo-3,3-dimethylbutane, 1647-23-0.

Acknowledgment.—The authors gratefully acknowledge the financial assistance provided by Research Corporation in the form of a Frederick Gardner Cottrell Grant.

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[14] L. Schmerling and J. P. West, *J. Amer. Chem. Soc.*, **74**, 3592 (1952).

[15] Deuteriochloroform solution.

[16] This was prepared in the conventional way (L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967) from metallic potassium and *tert*-butyl alcohol. After evacuation for 2 hr at 145° (1 mm), the product was 73% (w/w) butoxide and 27% alcohol.

[17] The absorptions at δ 4.09 and 4.36 actually constitute an (AB) pattern, the nonequivalence caused by the neighboring asymmetric center

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Reactions of Lone Pair Electron Donors with Unsaturated Electrophiles. I. The Addition of Tetrahydrofuran and Oxetane to Dimethyl Acetylenedicarboxylate[1]

Goran Ahlgren[2]

Department of Organic Chemistry, Royal Institute of Technology, S-10044 Stockholm 70, Sweden

Received October 10, 1972

Tetrahydrofuran and oxetane give cis-trans isomeric 1:1 adducts with dimethyl acetylenedicarboxylate. The reaction can be initiated thermally, photochemically, or by free-radical sources. All three processes are shown to be free-radical chain reactions, presumably involving a vinyl radical intermediate, formed by addition of an ether radical to the dimethyl acetylenedicarboxylate. Possible mechanisms for the chain initiations in the thermal and photochemical reactions are discussed. Secondary isomerizations take place in the photochemical reactions, yielding vinyl ethers through a shift of the double bond.

The addition of cyclic ethers to unsaturated substrates has attracted some attention in recent years. Tetrahydrofuran (THF) adds to maleic anhydride,[3] diethyl maleate,[3] and azodicarboxylate[4] to give α-substituted tetrahydrofuranes by formal addition of the α-C–H ether bond across the unsaturated linkage. These reactions take place by initiation with dibenzoyl peroxide or azoisobutyronitrile and by direct irradiation; they are believed to be radical chain reactions involving THF radicals. Similarly, THF has been added to 7,7,8,8-tetracyanoquinodimethane and tetracyanoethylene by direct irradiation.[5] Tetrahydropyran and *p*-dioxane will not produce 1:1 adducts with unsaturates under these conditions.[3] They can, however, be added to diethyl maleate and various simple olefins under ketone-sensitized uv irradiation[6]; in this case, a radical chain reaction was believed to be initiated by hydrogen abstraction by the excited ketone.[6]

Recently, Singh reported on the photochemical addition of THF, tetrahydropyran, and *p*-dioxane to dimethyl acetylenedicarboxylate (DMAD).[7] He found that THF adds to DMAD by direct irradiation to give

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[1] Presented in part at the XXIII International Congress of Pure and Applied Chemistry, Boston, Mass., 1971.

[2] Department of Chemistry, University of California, Berkeley, Calif. 94720, where this work was completed.

[3] R. L. Jacobs and G. C. Ecke, *J. Org. Chem.*, **28**, 3036 (1963).

[4] R. Askani, *Chem. Ber.*, **98**, 2551 (1965).

[5] J. Diekmann and C. J. Pedersen, *J. Org. Chem.*, **28**, 2879 (1963).

[6] I. Rosenthal and D. Elad, *Tetrahedron*, **23**, 3193 (1967).

[7] P. Singh, *J. Org. Chem.*, **37**, 836 (1972).