Preparation and Some Reactions of 3-*endo*-Substituted Tricyclo-[3.2.0.0^{2,7}]heptan-6-ones

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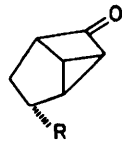
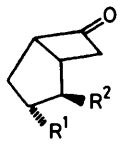
3-*endo*-Substituted tricyclo[3.2.0.0^{2,7}]heptan-6-ones have been prepared by treatment of 3-*endo*-substituted 2-*exo*-halogenobicyclo[3.2.0]heptan-6-ones or 5-*endo*-substituted 7-*anti*-halogenobicyclo[2.2.1]heptan-2-ones with potassium t-butoxide. The tricyclic ketones have been treated with various nucleophiles, including cyanide ion, halide ion, water, and methanol to give the corresponding 5-*endo*,7-*anti*-disubstituted bicyclo[2.2.1]heptan-2-one exclusively.

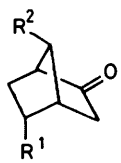
THE first indication that tricyclo[3.2.0.0^{2,7}]heptan-6-ones might prove to be useful intermediates in synthesis can



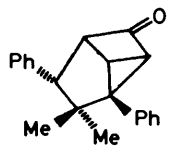
(1) R = Br
(4) R = H
(16) R = OMe
(17) R = OCH_2Ph
(18) R = OTHP
(22) R = OCOMe



(2) $R^1 = R^2$ = Br
(9) R^1 = OMe, R^2 = Br
(10) R^1 = OCH_2Ph, R^2 = Br
(11) R^1 = OTHP, R^2 = Br
(19) R^1 = OCOMe, R^2 = Cl
(20) R^1 = OCOMe, R^2 = Br
(21) R^1 = OCOMe, R^2 = I



(3) R^1 = Br, R^2 = OEt
(5) R^1 = H, R^2 = Cl
(6) R^1 = H, R^2 = OMe
(12) R^1 = Br, R^2 = CN
(13) R^1 = OMe, R^2 = CN
(14) R^1 = OCH_2Ph, R^2 = CN
(15) R^1 = OTHP, R^2 = CN
(23) R^1 = OMe, R^2 = OH
(24) $R^1 = R^2$ = OMe
(25) R^1 = OCOMe, R^2 = Cl
(26) R^1 = OCOMe, R^2 = Br
(27) R^1 = OMe, R^2 = C_4H_9



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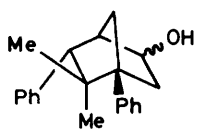


(8)

be credited to Dreiding *et al.* who noted that the tricycloheptanone (1), formed *in situ* from the dibromobicyclo-[3.2.0]heptanone (2), reacted with ethoxide ion to give 5-*endo*-bromo-7-*anti*-ethoxybicyclo[2.2.1]heptan-2-one (3) as the sole product in high yield.[1] Later, Whitham and Lumb suggested that tricyclo[3.2.0.0^{2,7}]heptan-6-one (4) was intermediate in the conversion of 7-*anti*-chlorobicyclo[2.2.1]heptan-2-one (5) into 7-*anti*-methoxybicyclo[2.2.1]heptan-2-one (6) using methoxide ion.[2] Recently Paquette has shown that the polysubstituted tricycloalkanone (7) gave the bicycloheptanol (8) on treatment with sodium borohydride.[3]

In the above cases, the nucleophile attacks the tricyclic compound regiospecifically at C-1. We have now shown that such homoconjugate addition reactions to tricyclo[3.2.0.0^{2,7}]heptan-6-ones are ready and can be performed with many nucleophiles. The tricyclic ketone may be prepared *in situ*, or may be isolated and treated with the requisite nucleophile in a separate reaction.

The dibromoketone (2) and the alkoxybromoketones (9)—(11)[4] gave the corresponding 7-cyanobicyclo-[2.2.1]heptan-2-ones (12)—(15) on treatment with a small quantity of methoxide ion in methanol containing excess of potassium cyanide.[5] The corresponding tricyclic ketones (1) and (16)—(18) were considered to be probable intermediates in these reactions: evidence in favour of this postulate accrued through isolation of the reactive intermediates. Thus, treatment of the 2-bromobicycloheptanones (2) and (9)—(11) with potassium t-butoxide in benzene gave the tricyclic ketones (1) and (16)—(18). The optimum work-up procedure entailed dilution of the reaction mixture with ether, filtration, and evaporation of the filtrate at ambient temperature. 2-*exo*-Chloro- (19), 2-*exo*-bromo- (20), and 2-*exo*-iodo-3-*endo*-acetoxybicyclo[3.2.0]heptan-6-one (21) could each be cyclised in a similar manner to give the crystalline acetoxytricycloheptanone (22). In all cases, practically quantitative yields of the tricyclic ketones were obtained.

As expected, treatment of the tricycloalkanone (16) with cyanide ion in methanol gave only the norbornanone (13) in very high yield. Independently, Gilbert *et al.* prepared the bromoalkanone (1) by a method similar to that described above, determined the molecular structure of (1) by *X*-ray crystallography, and noted the outcome of the reaction of (1) with cyanide ion.[6]

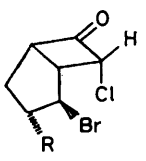
The tricyclic compounds could be isolated and handled without the need for special precautions, but attempted distillation or exposure of the compounds to the atmosphere for long periods of time led to extensive decomposition.

[1] E. Mitch and A. S. Dreiding, *Chimia* (*Switz.*), 1960, **14**, 424.
[2] J. T. Lumb and G. H. Whitham, *Chem. Comm.*, 1966, 400.
[3] L. A. Paquette, K. H. Fuhr, S. Porter, and J. Clardy, *J. Org. Chem.*, 1974, **39**, 467.
[4] Z. Grudzinski and S. M. Roberts, *J.C.S. Perkin I*, 1975, 1767.
[5] S. M. Roberts, *J.C.S. Chem. Comm.*, 1974, 948.
[6] J. C. Gilbert, T. Luo, and R. E. Davies, *Tetrahedron Letters*, 1975, 2545.

We have found that the tricycloheptanones were extremely susceptible to attack by nucleophiles. For example, shaking the methoxy compound (16) with aqueous tetrahydrofuran gave the 7-*anti*-hydroxynorbornanone (23) only, while dissolution of (16) in methanol gave a very high yield of the dimethoxybicycloheptanone (24) after 48 h. Treatment of the tricyclic ketone (22) with an aqueous solution of chloride or bromide ion gave the 7-*anti*-chloro- (25) or the 7-*anti*-bromo-bicycloheptanone (26) respectively. Note that the tricycloheptanone (22) could be reformed from the 7-halogenobicyclo[2.2.1]heptanones (25) and (26) by treatment with potassium butoxide.

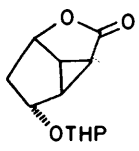
The methoxytricycloalkanone (16) reacted with lithium n-butyl(pentynyl)cuprate under very mild conditions to give the 7-*anti*-butylnorbornanone (27). Vinylcuprate reagents react in a similar way.[7]

7-Substituted 2-bromobicyclo[3.2.0]heptan-6-ones can be rearranged to 3-substituted norbornanones. For example, 7-chlorobicycloheptanone (28) gave 3-*exo*-chloro-7-*anti*-cyano-5-*endo*-methoxybicyclo[2.2.1]-heptan-2-one (29) on treatment with potassium cyanide



(28) R = OMe
(30) R = OCOMe

(29) R^1 = OMe, R^2 = CN
(31) R^1 = OCOMe, R^2 = SPh



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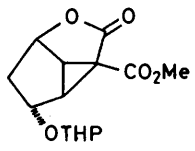

(33)

and sodium methoxide in methanol. Similarly, the chloro-ketone (30) gave the 7-*anti*-phenylthio-ketone (31) on reaction with sodium benzenethiolate in tetrahydrofuran. Note that the final step in the latter reactions is epimerization at C-3 in the bicyclo[2.2.1]heptanone system under the basic reaction conditions to give the thermodynamically more stable compound having the chlorine atom in the *exo*-configuration.

The pronounced reactivity of the tricyclo[3.2.0.$0^{2,7}$]-heptan-6-ones is due to the inherent strain imposed on the three-membered ring. It is now generally accepted that nucleophilic opening of cyclopropane rings takes place readily when two geminal activating groups are present [8] (ester, ketone, cyano, and phosphonium groups have been employed as activating groups; presumably a nitro [9] or a sulphoxide group [10] could serve a similar purpose). Only when very reactive nucleophiles are employed (*e.g.* thiolate ions [11]) or when the three-membered ring is under considerable strain [12] will just one activating group suffice.

Thus the strain factor is critical for the reactivity of the tricyclo[3.2.0.$0^{2,7}$]heptan-6-one system. This is underlined by the fact that the analogous, presumably unstrained,[13] cyclopropyl-lactone (32) is inert towards most nucleophiles [14] while the diactivated system (33) is known to undergo cyclopropyl ring opening with organocuprate reagents.[15]

The regioselectivity of the attack by the nucleophilic species on the tricyclo[3.2.0.$0^{2,7}$]heptanone has been attributed to the weakness of the C(1)–C(7) bond.[6] However, we feel that another valid explanation might be that the approach of the nucleophile to C(1) from a direction collinear with the C(1)–C(7) bond is very much less congested than the approach to C(2) along the line of the C(2)–C(7) bond.

The stereochemistry of the bicyclo[2.2.1]heptan-2-ones formed in the reactions described above was determined by n.m.r. spectroscopy using double irradiation techniques where necessary. The assignments were consistent with the previously described coupling data.[16] From the chemical shift data it is apparent that (a) the bridgehead proton *more distant* from the carbonyl group resonates at lower field than the bridgehead proton adjacent to the carbonyl group,[17] and (b) due to the neighbouring substituent at C(5), the proton in the *endo*-configuration at C(3) resonates at lower field than the corresponding proton in the *exo*-configuration.[18]

EXPERIMENTAL

N.m.r. spectra were obtained with Varian A 60 or HA 100 or Perkin-Elmer EM 360 spectrometers for solutions in carbon tetrachloride unless otherwise stated. I.r. spectra were run with a Perkin-Elmer 257 spectrophotometer. Silica gel (B.D.H.) was used for preparative chromatography and silica gel G (Merck) for analytical chromatography. Anhydrous magnesium sulphate was used as the

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[14] T. V. Lee, S. M. Roberts, and R. F. Newton, unpublished results.
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drying agent for solutions in organic solvents. Distillations were accomplished by using the Büchi Kugelröhr (bulb-to-bulb) system and the temperatures reported are oven temperatures at distillation.

3-endo-*Acetoxy*-2-exo-*chlorobicyclo*[3.2.0]*heptan*-2-*one* (19). —Bicyclo[3.2.0]hept-2-en-6-one [19] (1.0 g) was shaken with freshly prepared chlorine water (20 ml) for 1 h before standing at room temperature for 18 h. The aqueous solution was extracted with chloroform (2 × 20 ml) and the organic extracts were washed with saturated sodium hydrogencarbonate solution (2 × 10 ml). The dried organic fraction was evaporated and the residue was dissolved in pyridine (6.0 ml). Acetic anhydride (1.0 g) was added. After 48 h at room temperature, chloroform (20 ml) was added and the solution was extracted with 4N-sulphuric acid (2 × 20 ml) and with saturated aqueous sodium hydrogencarbonate (2 × 20 ml). The aqueous washes were back-extracted with chloroform (2 × 15 ml). The combined organic extracts were dried, evaporated, and the residue was distilled to give the *ketone* (19) (0.40 g), b.p. 95° at 0.01 mmHg, $\nu_{max.}$ 1 780, 1 740, and 1 230 cm^{-1}, δ 5.23 (1 H, m, H-3), 4.28 (1 H, s, H-2), 3.90—3.00 (4 H, m, H-1, -5, and 2 × H-7), 2.80—1.90 (2 H, m, 2 × H-4), and 1.91 (3 H, s, OCOMe) (Found: M^+, 202.039 3. $C_9H_{11}BrClO_3$ requires M, 202.039 5).

3-endo-*Acetoxy*-2-exo-*iodobicyclo*[3.2.0]*heptan*-6-*one* (21). —A solution of bicyclo[3.2.0]hept-2-en-6-one (1.0 g) in glacial acetic acid (20 ml) was treated with iodine (1.35 g) and potassium iodate (0.57 g).[20] After stirring for 24 h at room temperature, ether (50 ml) and saturated aqueous sodium chloride (25 ml) were added. The separated ethereal phase was washed with saturated aqueous sodium hydrogencarbonate (2 × 20 ml), aqueous sodium thiosulphate (30 ml), and saturated aqueous sodium chloride (2 × 20 ml). The aqueous extracts were back-extracted with ether and the combined ether fractions were dried and evaporated. Chromatography over silica using ethyl acetate in light petroleum (b.p. 60—80°) as eluant gave the *ketone* (21) (1.8 g), $\nu_{max.}$ 1 780, 1 740, and 1 230 cm^{-1}; δ 5.45 (1 H, d, H-3), 4.40 (1 H, s, H-2), 3.85 (1 H, tm, H-5), 3.55 (1 H, dd, H-1), 3.40—2.90 (2 H, m, 2 × H-7), 2.72 (1 H, ddd, H-4-*exo*), 2.31 (1 H, d, H-4-*endo*), and 1.97 (3 H, s, OCOMe) (Found: M^+, 293.975 5. $C_9H_{11}IO_3$ requires M, 293.975 5).

3-endo-*Substituted Tricyclo*[3.2.0.$0^{2,7}$]*heptan*-6-*ones*.—To potassium t-butoxide (1.0 g) suspended in dry benzene (30 ml) at 0° was added the ketone (1.0 g) in benzene (2 ml). The mixture was allowed to warm to room temperature over 2 h; after a further 4 h, the mixture was poured into dry ether, filtered, and the filtrate was evaporated.

(a) 3-endo-*Methoxytricyclo*[3.2.0.$0^{2,7}$]*heptan*-6-*one* (16). 2-*exo*-Bromo-3-*endo*-methoxybicyclo[3.2.0]heptan-6-one (9) gave the *methoxytricycloheptanone* (16) (95%), $\nu_{max.}$ 1 750 cm^{-1}; δ 4.37 (1 H, dm, *J* 7.5 Hz, H-3), 3.33 (3 H, s, OMe), 3.40—3.00 (2 H, m, H-5 and -7), 2.90—2.70 (2 H, m, H-1 and -2), 2.20 (1 H, ddd, H-4-*exo*), and 1.75 (1 H, d, H-4-*endo*).

(b) 3-endo-*Acetoxytricyclo*[3.2.0.$0^{2,7}$]*heptan*-6-*one* (22). 3-*endo*-Acetoxy-2-*exo*-halogenobicyclo[3.2.0]heptan-6-one (19)—(21) or 5-*endo*-acetoxy-7-*anti*-halogenobicyclo[2.2.1]-heptan-2-one (25), (26) each gave the *acetoxytricycloheptanone* (22) (90—97%), m.p. 48—50°, $\nu_{max.}$ 1 748 and 1 730 cm^{-1}; δ 5.28 (1 H, dd, *J* 7.5 and 3.5 Hz, H-3), 3.2—2.95 (2 H, m, H-5 and -7), 2.82 (1 H, m, H-1), 2.68 (1 H, dt, *J* 7.5 and 3.5 Hz, H-2), 2.28 (1 H, ddd, *J* 14.5, 7.5, and 4.5 Hz, H-4-*exo*), 1.96 (3 H, s, OCOMe), and 1.76 (1 H, d, *J* 14.5 Hz, H-4-*endo*) (Found: C, 65.0; H, 5.6. $C_9H_{14}O_3$ requires C, 65.1; H, 6.0%).

(c) 3-endo-*Tetrahydropyranyloxytricyclo*[3.2.0.$0^{2,7}$]*heptan*-6-*one* (18). 2-*exo*-Bromo-3-*endo*-tetrahydropyranyloxybicyclo[3.2.0]heptan-6-one (11) gave the *ketone* (18) (95%).

(d) 3-endo-*Benzyloxytricyclo*[3.2.0.$0^{2,7}$]*heptan*-6-*one* (17). 3-*endo*-Benzyloxy-2-*exo*-bromobicyclo[3.2.0]heptan-6-one (10) gave the *tricycloalkanone* (17) (94%), m.p. 60.5°, $\nu_{max.}$ 1 750 cm^{-1}; δ 7.15 (5 H, s, C_6H_5), 4.40—4.10 (3 H, m, H-3 and OCH_2), 2.90—2.25 (4 H, m, H-1, -2, -5, and -7), and 2.20—1.35 (2 H, m, 2 × H-4).

5-endo-*Substituted* 7-*Cyanobicyclo*[2.2.1]*heptan*-2-*ones*.—*Method A*. To a solution of potassium cyanide (1.0 g) in methanol (30 ml) containing sodium methoxide (0.05 g) at 0° was added dropwise a solution of the 3-*endo*-substituted 2-*exo*-bromobicyclo[3.2.0]heptan-6-one (1.5 g) in methanol (10 ml). After 2 h at 0°, chloroform (50 ml) and water (50 ml) were added. The chloroform layer was removed and washed with water (2 × 20 ml) and the aqueous fractions were back-extracted with chloroform (2 × 20 ml). The combined organic extracts were dried and evaporated.

Method B. A solution of the 3-*endo*-substituted tricyclo[3.2.0.$0^{2,7}$]heptan-6-one (0.5 g) in cold methanol (5 ml) was added dropwise to a solution of potassium cyanide (0.5 g) in methanol (10 ml) at 0°. After 2 h at 0° the mixture was treated as in method A.

(a) 7-anti-*Cyano*-5-endo-*methoxybicyclo*[2.2.1]*heptan*-2-*one* (13) was obtained from the bicyclic ketone (9) using method A (87%) and from the tricyclic ketone (16) using method B (85%) as a solid, m.p. 53—54°, $\nu_{max.}$ 2 250 and 1 755 cm^{-1}, δ 4.14 (1 H, ddd, H-5), 3.18 (3 H, s, OMe), 3.00 (1 H, dd, H-4), 2.92 (1 H, dt, H-7), 2.69 (1 H, d, H-1), 2.45 (1 H, ddd, H-6-*exo*), 2.42 (1 H, d, H-3-*endo*), 1.95 (1 H, dd, H-3-*exo*), and 1.39 (1 H, ddd, H-6-*endo*) (Found: M^+, 165.079 6. $C_9H_{11}NO_2$ requires M, 165.079 0).

(b) 5-endo-*Bromo*-7-anti-*cyanobicyclo*[2.2.1]*heptan*-2-*one* (12) was prepared from the ketone (2) using method A as a solid (50%), m.p. 96—98°, $\nu_{max.}$ 2 255 and 1 760 cm^{-1} (Found: C, 44.8; H, 3.5; N, 6.3. C_8H_8BrNO requires C, 44.9; H, 3.7; N, 6.5%).

(c) 5-endo-*Benzyloxy*-7-anti-*cyanobicyclo*[2.2.1]*heptan*-2-*one* (14) from the bicycloheptanone (10) using method A was a solid (87%), m.p. 83—84.5°; $\nu_{max.}$ 2 260 and 1 760 cm^{-1}; δ 7.29 (5 H, s, C_6H_5), 4.46 (1 H, m, H-5), 4.43 (2 H, s, OCH_2), 3.05—2.50 (3 H, m, H-1, -4, and -7), 2.53 (1 H, d, H-3-*endo*), 2.43 (1 H, ddd, H-6-*exo*), 1.81 (1 H, dd, H-3-*exo*), and 1.40 (1 H, dt, H-6-*endo*) (Found: M^+, 241.109 7. $C_{15}H_{15}NO_2$ requires M, 241.110 2).

(d) 7-anti-*Cyano*-5-endo-*tetrahydropyranyloxybicyclo*-[2.2.1]*heptan*-2-*one* (15) obtained from the ketone (11) was a solid (82%), m.p. 92—95°; $\nu_{max.}$ 2 255, 1 755, and 1 040 cm^{-1} (Found: M^+, 235.121 4. $C_{13}H_{17}NO_3$ requires M, 235.120 8).

(e) 3-exo-*Chloro*-7-anti-*cyano*-5-endo-*methoxybicyclo*-[2.2.1]*heptan*-2-*one* (29) obtained from the dihalogeno-ketone (28) using method A was a solid (55%), m.p. 79—81°; $\nu_{max.}$ 2 255, 1 765, and 1 090 cm^{-1}; δ($CDCl_3$) 4.48 (1 H, s, H-3-*endo*), 4.42 (1 H, m, H-5), 3.43 (3 H, s, OMe), 3.35—2.95 (3 H, m, H-1, -4, and -7), 2.70 (1 H, ddd, H-6-*exo*), and 1.61 (1 H, dt, H-6-*endo*) (Found: C, 53.6; H, 5.2; N, 6.6. $C_9H_{10}ClNO_2$ requires C, 54.1; H, 5.0; N, 7.0%).

7-anti-*Hydroxy*-5-endo-*methoxybicyclo*[2.2.1]*heptan*-2-*one*

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(23).—3-*endo*-Methoxytricyclo[3.2.0.0^{2,7}]heptan-6-one (16) (0.8 g) was dissolved in 50% aqueous tetrahydrofuran (10 ml). After 18 h at room temperature chloroform (10 ml) was added. The organic phase was separated and the aqueous phase was washed with chloroform (2 × 10 ml). The combined organic extracts were dried and evaporated and the residue was chromatographed over silica using ethyl acetate–light petroleum (b.p. 60—80°) as eluant, to give the *hydroxy-ketone* (23) (52%), b.p. 95° at 0.01 mmHg; $\nu_{max.}$ 3 410, 1 740, and 1 100 cm^{-1}; δ($CDCl_3$) 4.50—4.15 (2 H, m, H-5 and -7), 3.33 (3 H, s, OMe), 2.95—2.45 (4 H, m, H-1, -4, -6-*exo*, and OH), 2.62 (1 H, d, H-3-*endo*), 1.93 (1 H, dd, H-3-*exo*), and 1.45 (1 H, dm, H-6-*endo*) (Found: C, 61.5; H, 8.0. $C_8H_{12}O_3$ requires C, 61.5; H, 7.7%).

5-endo,7-anti-*Dimethoxybicyclo*[2.2.1]*heptan*-2-*one* (24).—The tricyclic ketone (16) (0.5 g) was dissolved in methanol (5 ml). After 48 h the solvent was removed *in vacuo* and the residue was distilled to give the *dimethoxybicycloheptanone* (24) (0.45 g), b.p. 80° at 0.005 mmHg; $\nu_{max.}$ 1 758 cm^{-1}; δ 4.16 (1 H, m, H-5), 3.85 (1 H, m, H-7), 3.35 (6 H, s, 2 × OMe), 2.90—2.50 (2 H, m, H-1 and -4), 2.57 (1 H, d, H-3-*endo*), 2.40 (1 H, ddd, H-6-*exo*), 1.83 (1 H, dd, H-3-*exo*), and 1.40 (1 H, dm, H-6-*endo*) (Found: C, 63.9 H, 7.8. $C_9H_{14}O_3$ requires C, 63.5; H, 8.2%).

5-endo-*Acetoxy*-7-anti-*chlorobicyclo*[2.2.1]*heptan*-2-*one* (25).—The tricyclic ketone (22) (1.2 g) was dissolved in benzene (50 ml) and vigorously stirred with saturated aqueous ammonium chloride (50 ml) for 2 h. After separation of the organic layer, the aqueous phase was washed with chloroform. The combined organic fractions were dried and evaporated and the residue was chromatographed over silica using ethyl acetate in light petroleum as eluant to give the *halogeno-ketone* (25) as a crystalline solid (35%), m.p. 53°; $\nu_{max.}$ 1 755 and 1 730 cm^{-1} (Found: C, 53.7; H, 5.5. $C_9H_{11}ClO_3$ requires C, 53.35; H, 5.5%).

5-endo-*Acetoxy*-7-anti-*bromobicyclo*[2.2.1]*heptan*-2-*one* (26).—The tricycloheptanone (22) (1.0 g) was added to saturated aqueous potassium bromide (20 ml) containing cetyltriethylammonium chloride (1 ml). After 18 h, chloroform (100 ml) was added. The organic phase was separated, dried, and the solvent evaporated to give a residue which was chromatographed over silica using ethyl acetate in light petroleum as eluant. The *ketone* (26) was obtained as a pale yellow oil (10%) (Found: M^+, 247.096 1. $C_9H_{11}BrO_3$ requires M, 247.096 3).

7-anti-*Butyl*-5-endo-*methoxybicyclo*[2.2.1]*heptan*-2-*one* (27).—To n-butyl-lithium (1.92 g in hexane) in dry diethyl ether (80 ml) was added a freshly prepared solution of pent-1-ynylcopper (3.88 g) in dry diethyl ether (50 ml) and hexamethylphosphorus triamide (9.7 g) under argon at −78°. After 15 min, 3-*endo*-methoxytricycloheptanone (16) (4.1 g) was added with stirring. After 2 h, saturated aqueous ammonium chloride (100 ml) was added. The organic layer was separated, washed with 2N-sulphuric acid (50 ml), and filtered. The filtrate was washed with aqueous sodium hydrogencarbonate and water. The dried solution was evaporated and the residue was chromatographed over silica using ethyl acetate in light petroleum as eluant to give the ketone (27) as a yellow oil (60%); $\nu_{max.}$ 1 750 cm^{-1} (Found: C, 73.1; H, 10.3. $C_{12}H_{20}O_2$ requires C, 73.5; H, 10.2%).

5-endo-*Acetoxy*-3-exo-*chloro*-7-anti-*phenylthiobicyclo*[2.2.1]*heptan*-2-*one* (31).—To the chloro-ketone (30) (12.0 g) in dry tetrahydrofuran (30 ml) was added with stirring sodium benzenethiolate (14.0 g). The milky suspension was stirred for 24 h. Diethyl ether was added and the organic solution was washed with aqueous sodium hydrogencarbonate (2 × 100 ml). The dried solution was evaporated and the residue was chromatographed over silica using chloroform as eluant to give the *ketone* (31) as an oil (64%); $\nu_{max.}$ 1 765 and 1 740 cm^{-1} (Found: M^+, 310.042 7. $C_{15}H_{15}ClO_3S$ requires M, 310.043 0).

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