869. *Some Derivatives of Tricyclo*$[6,2,1,0^{2,7}]$*Undecane; the Thermolysis of* exo,exo-3-*Diazotricyclo*$[6,2,1,0^{2,7}]$*undecane.*

By C. Swithenbank and M. C. Whiting.

Stepwise reduction of the Diels–Alder adduct from benzoquinone and cyclopentadiene, *via* the perhydro-derivative and its monoethylene ketal, ultimately to the parent hydrocarbon is described. In the course of acid-catalysed ketalisation under vigorous conditions the *exo,exo*-keto-ketal is obtained, and the *exo,exo*-configuration is retained throughout the transformation series. Milder conditions give another keto-ketal, probably the *endo,endo*-compound, whose further transformations are less certain stereochemically.

The need for tricyclo$[6,2,1,0^{2,7}]$undecan-3-one, *e.g.*, (I), led us to examine, first, the possible Diels–Alder reaction between cyclopentadiene and cyclohex-2-enone, and, when this failed under all the conditions investigated, the removal of one ketone group from the known [1] *endo,endo*-tricyclo$[6,2,1,0^{2,7}]$undecane-3,6-dione (II). In this work we encountered an " isomer," m. p. 246°, of the original dione, which had been reported by Bergel and Widman.[2] Its high melting point and low volatility, and the fact that its formation was apparently diminished when light was excluded during the hydrogenation of the Diels–Alder adduct (III), led us to the view that it was a photo-dimer. Having failed to obtain a monosemicarbazone, we attempted to convert the diketone (II) (m. p. 56—57°) into a monoethylene ketal. Unexpectedly, significant quantities of a bisketal were not formed, but two different keto-ketals were obtained, the isomer, m. p. 56—57° [probably (IV)], formed under mild conditions being readily hydrolysed back to diketone (II), while that, m. p. 108—108·5°, formed under more drastic conditions gave, on hydrolysis, an isomeric diketone (VI), m. p. 66—67°. This in turn was reconverted into the higher-melting keto-ketal (V) under mild conditions; clearly the diketones (II) and (VI) are stereoisomers, equilibrated under the conditions of vigorous ketalisation. Indeed, direct acid-catalysed isomerisation of (II) to (VI) was effected, although the difficulty of separating the isomers resulted in a low yield. The diketone (VI) was independently prepared by Cookson and Hill [3] by alkali-catalysed epimerisation of its isomer (II). These authors reached and proved a similar conclusion regarding Bergel and Widman's " isomer," m. p. 246°, and showed by nuclear magnetic resonance that the diketone, m. p. 66—67°, was indeed the *exo,exo*-isomer (VI) rather than the *exo,endo*-form (XV). This, in view of

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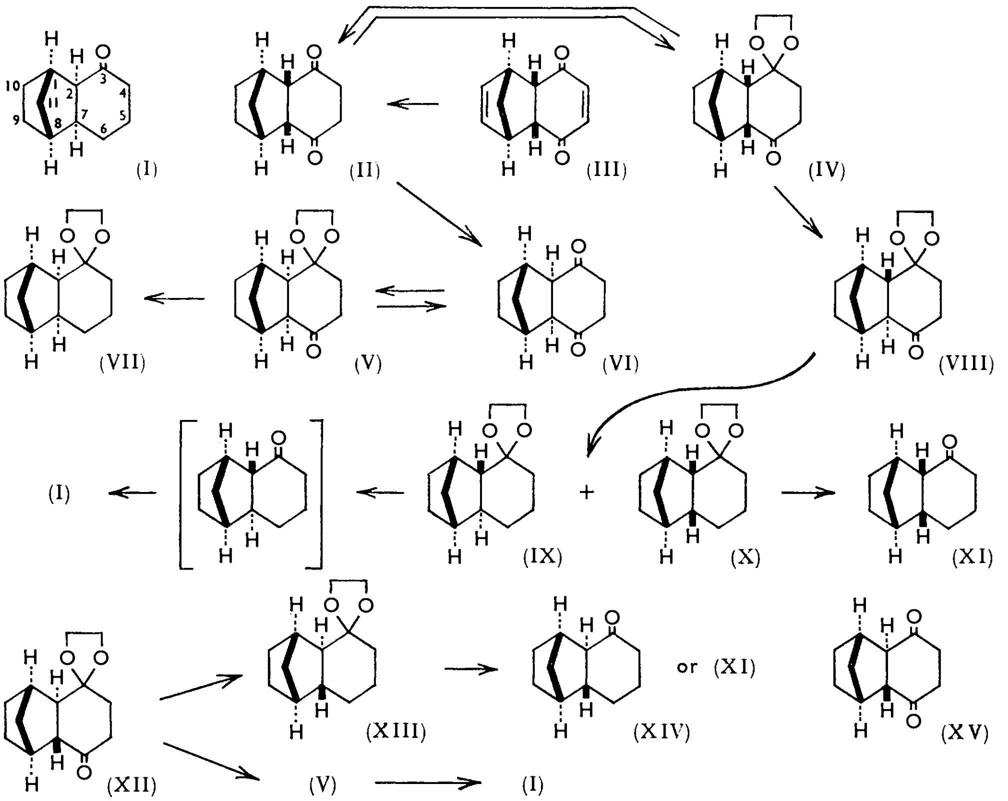
[1] Albrecht, *Annalen*, 1906, **348**, 34; Diels, Blom, and Koll, *ibid.*, 1925, **443**, 274; Diels and K. Alder, *ibid.*, 1928, **460**, 98.

[2] Bergel and Widman, *Annalen*, 1928, **467**, 89.

[3] Cookson and Hill, *J.*, 1963, 2023.

the enthalpy advantage of *trans*-perhydroindane over *cis*-hydroindane,[4] and of the generally great stability of *endo,exo*-isomers of 2,3-disubstituted bicyclo[2,2,1]heptanes, we were unwilling to accept as proved merely from a contemplation of molecular models, even though these did suggest that *trans*-fused tricyclo[6,2,1,$0^{2,7}$]undecanes are unstable through ring-strain. It follows that the keto-ketal, m. p. 108—108·5°, is also the *exo,exo*-isomer (V); the keto-ketal, m. p. 56—57°, is taken to be the *endo,endo*-isomer (IV), although we do not altogether rule out the possibility that steric hindrance to ketalisation of *endo*-groups and epimerisation might lead to the formation of the *endo,exo*-isomer (XII) and its hydrolysis *via* the unstable form (XV) back to the *endo,endo*-diketone (II). The main objection to the latter view is that one would expect the second epimerisation to take place even more readily during ketalisation than the first, so that the stable isomer (V) would be the only product. However, conformational analysis of these systems is not straightforward, and the ketal groups profoundly affect reactivity (once one is present, ketalisation of the other ketonic group becomes virtually impossible in either configuration, so epimerisation might also be retarded).



The compounds isolated were all racemates.

Huang-Minlon reduction of the *exo,exo*-keto-ketal (V) gave an apparently homogeneous monoketal (VII), hydrolysed to a ketone which showed one peak on gas–liquid chromatography and gave good yields of a crystalline 2,4-dinitrophenylhydrazone and a methanesulphonylhydrazone. This is thus presumably the *exo,exo*-ketone (I) which we wished to prepare. Similar reduction of the low-melting keto-ketal (IV or possibly XII) gave, however, a ketal, hydrolysed to a ketone, each of which, though analytically pure, had an

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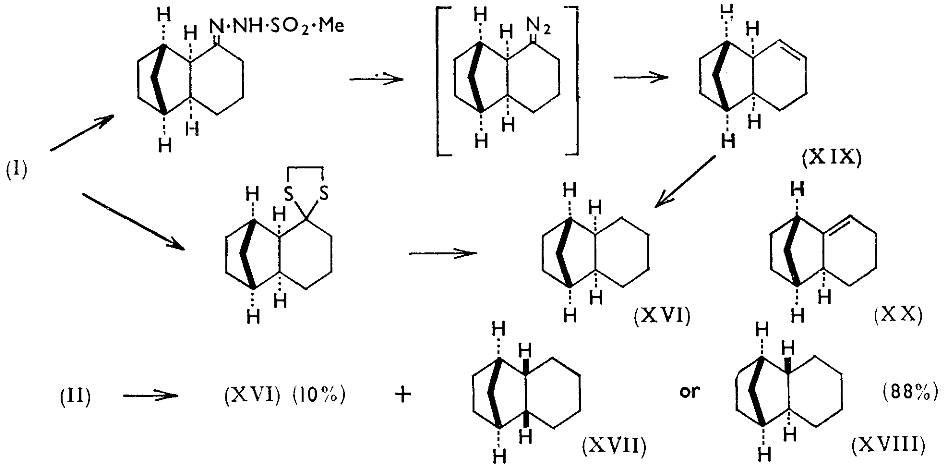
[4] Allinger and Coke, *J. Amer. Chem. Soc.*, 1960, **82**, 2554.

appreciable range of refractive index. The ketone showed two peaks of comparable area on gas–liquid chromatography, one with a retention time identical with that of the *exo,exo*-ketone (I). The infrared spectrum of the ketone mixture derived from the lower-melting keto-ketal showed all the peaks present in that of the ketone (I), and although no crystalline derivative was obtained there is little doubt that this was one component of the mixture. Assuming that the keto-ketal had configuration (IV), we conclude that the relatively unstable isomer (VIII), present in equilibrium with (IV), is reduced much faster than the latter. Comparable amounts of ketals (IX) and (X) are formed and these are hydrolysed to ketones (I) and (XI). [If the keto-ketal is form (XII), it would be reduced directly to ketal (XIII) and *via* its epimer (V) to (VII); the monoketone mixture would be (I) and either the *exo,endo*-form (XIV) or the *endo,endo*-isomer (XI). We prefer the earlier interpretation.]

A bisdithioketal was readily prepared from the *endo,endo*-diketone (II) at 0°. On reduction with Raney nickel it gave an unidentified hydrocarbon, $C_{11}H_{16}$ (rather than $C_{11}H_{18}$). The *exo,exo*-monoketone (I) gave a crystalline dithioketal which was reduced (Raney nickel, followed by hydrogenation) to a chromatographically homogeneous hydrocarbon, $C_{11}H_{18}$, presumably *exo,exo*-tricyclo[6,2,1,$0^{2,7}$]undecane (XVI). Direct Huang-Minlon reduction of the *endo,endo*-diketone (II) gave a hydrocarbon which showed three peaks, in ratio approximating to 88 : 10 : 2, on gas–liquid chromatography. The middle peak was identical in retention time with the *exo,exo*-tricycloundecane (XVI); the component responsible for the larger peak was isolated and differed spectroscopically from that hydrocarbon, and had formula $C_{11}H_{18}$, being probably the *endo,endo*-form (XVII) or the *exo,endo*-isomer (XVIII) of tricyclo[6,2,1,$0^{2,7}$]undecane.

Treatment of the methanesulphonylhydrazone of the *exo,exo*-ketone (I) with a solution of sodium in acetamide[5] gave an olefin which behaved as homogeneous on gas–chromatography on Apiezon L or tritolyl phosphate. Hydrogenation over palladium (uptake theoretical) converted it into a chromatographically homogeneous compound, inseparable from *exo,exo*-tricyclo[6,2,1,$0^{2,7}$]undecane and readily distinguished from the *endo,endo*- or *endo,exo*-isomer, prepared as above. We conclude that the 3-diazotricyclo[6,2,1,$0^{2,7}$]undecane, formed from the sulphonylhydrazone,[5,6] gives exclusively the tricycloundec-3-ene (XIX); the isomer (XX) would probably have been separable from (XIX) and, if hydrogenated at all under the mild conditions used, would almost certainly



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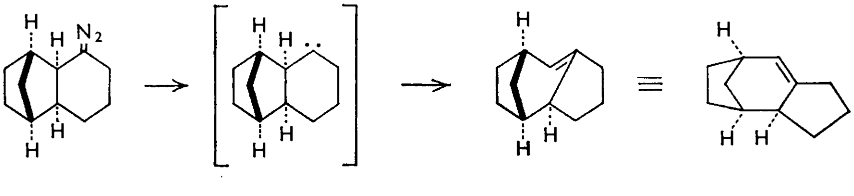
[5] Powell and Whiting, *Tetrahedron*, 1959, **7**, 305; 1961, **12**, 168.

[6] Friedman and Shechter, *J. Amer. Chem. Soc.*, 1959, **81**, 5512; De Puy and Froemsdorf, *ibid.*, 1960, **82**, 634.

have given the *endo,exo*-tricycloundecane (XVIII), probably separable from the *exo,exo*-tricycloundecane. This conclusion agrees with those of Powell and Whiting [5] on the stereospecificity and possibly concerted nature of the thermolysis of secondary diazo-compounds, and with the unambiguous behaviour of *endo,endo*-3-diazotricyclo[5,2,1,$0^{2,6}$]-decane; [7] we do not suggest that our proof is rigorous. The apparent failure of the system to rearrange skeletally when an electron-deficient (carbene) centre was established adjacent to a bicyclo[2,2,1]heptane system adds to recent evidence [5,6] on the general reluctance of the intermediates in thermolysis of diazo-compounds to do so, as the reaction avoided is in this case stereoelectronically and energetically favourable:



EXPERIMENTAL

endo,endo-*Tricyclo*[6,2,1,$0^{2,7}$]*undecane*-3,6-*dione* (II).—The cyclopentadiene-*p*-benzoquinone adduct (III) (100 g.) in chloroform (500 c.c.) was shaken in hydrogen in the presence of hydrated platinum dioxide (1 g.) (absorption theoretical, *ca.* 29 l.). The solution was filtered and the solvent was removed. Crystallisation of the residue from light petroleum (*ca.* 5 l.) gave the diketone (II) (77 g., 75%) as needles, m. p. 56—57° (Diels and Alder give [8] m. p. 56—57°) (Found: C, 74·4; H, 7·65. Calc. for $C_{11}H_{14}O_2$; C, 74·15; H, 7·9%). Extraction of the catalyst with ethanol gave a sparingly soluble compound, m. p. 246°, believed [3] to be a photo-dimer, the formation of which was minimised by carrying out hydrogenation in a dim light.

The diketone, m. p. 56—57°, gave a *dioxime*, which after crystallisation from aqueous ethanol had m. p. 219—220° (decomp.) (Found: C, 63·65; H, 7·7; N, 13·3. $C_{11}H_{16}N_2O_2$ requires C, 63·45; H, 7·75; N, 13·45%).

endo,endo-*Tricyclo*[6,2,1,$0^{2,7}$]*undecane*-3,6-*dione Monoethylene Ketal*.—The diketone (II) (80 g.), ethylene glycol (50 g.), toluene-*p*-sulphonic acid (450 mg.), and benzene (1·5 l.) were heated under reflux in a Dean and Stark apparatus (water produced, 11·5 c.c.). After cooling, washing with sodium hydrogen carbonate, and removal of benzene under reduced pressure, the product crystallised from light petroleum (b. p. 40—60°), giving the *monoketal* (76 g., 76%), m. p. 56—57°, strongly depressed on admixture with the *endo,endo*-diketone (Found: C, 70·15; H, 8·5. $C_{13}H_{18}O_3$ requires C, 70·25; H, 8·15%).

On transketalisation with a 1% solution of hydrochloric acid (*d* 1·16) in acetone at 20° for 18 hr. the *endo,endo*-diketone was obtained, having m. p. and mixed m. p. 56—57°.

exo,exo-*Tricyclo*[6,2,1,$0^{2,7}$]*undecane*-3,6-*dione Monoethylene Ketal* (V).—(*a*) The *endo,endo*-diketone (II) (10 g.), ethylene glycol (7 g.), toluene-*p*-sulphonic acid (1 g.), and benzene (160 c.c.) were heated under reflux for 36 hr. in a Dean and Stark apparatus. After cooling, removal of acidic material, and evaporation of the solvent the residue was crystallised from light petroleum (b. p. 60—80°), giving the *keto-ketal* (6·75 g., 55%), m. p. 108—108·5° (Found: C, 70·2; H, 8·15. $C_{13}H_{18}O_3$ requires C, 70·25; H, 8·15%).

(*b*) The *exo,exo*-diketone (VI) (107 mg.), ethylene glycol (170 mg.), toluene-*p*-sulphonic acid (5 mg.), and benzene (5 c.c.) were heated under reflux for 6 hr., the water produced being removed continuously. Isolation of the product gave the keto-ketal (V) (105 mg., 85%), m. p. and mixed m. p. 108—108·5°.

Transketalisation. The keto-ketal (1 g.) was dissolved in a 2% solution of hydrochloric acid (*d* 1·16) in acetone (25 c.c.). After 3 days at 20° the product was isolated; two recrystallisations from light petroleum gave the *exo,exo*-diketone (600 mg., 73%), m. p. 58—62°. Although it was not yet quite pure its infrared spectrum was almost identical with that of a specimen, m. p. 66—67°, and readily distinguished from that of the *endo,endo*-isomer.

exo,exo-*Tricyclo*[6,2,1,$0^{2,7}$]*undecan*-3-*one Ethylene Ketal* (VII).—The keto-ketal (V) (5·42 g.),

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[7] R. W. Alder and Whiting, *J.*, 1963, 4595.

[8] Diels and K. Alder, *Annalen*, 1928, **460**, 98.

hydrazine hydrate (20 c.c.), potassium hydroxide (20 g.), and diethylene glycol (400 c.c.) were heated under reflux in nitrogen for 3 hr. Water and an excess of hydrazine were then collected until the temperature reached 210°, then heating was continued under reflux for a further 8 hr. The mixture was cooled to 20°, diluted with water, and extracted with ether (5 × 40 c.c.); the distillate was also extracted with ether (3 × 15 c.c.), and the combined extracts were washed with water (2 × 80 c.c.), dried, and evaporated. Distillation of the residue (3·33 g., 66%) gave the *ketal* (VII), b. p. 66—68°/0·04 mm., n_D^{25} 1·5052—1·5054 (Found: C, 75·15; H, 9·5. $C_{13}H_{20}O_2$ requires C, 74·95; H, 9·7%).

exo,exo-*Tricyclo*[6,2,1,$0^{2,7}$]*undecan*-3-*one* (I).—The ketal (VII) (17 g.) was kept in a solution of sulphuric acid (1·2 g.) in methanol (60 c.c.) at 20° for 18 hr. Water (200 c.c.) was added and the product was isolated with ether; distillation gave the *ketone* (I) (almost theoretical yield), b. p. 60—63°/0·1 mm., n_D^{25} 1·5031—1·5051 (Found: C, 80·15; H, 9·85. $C_{11}H_{16}O$ requires C, 80·45; H, 9·85%). Gas–liquid chromatography on dinonyl phthalate gave one symmetrical peak, and the compound is probably therefore essentially pure. Its 2,4-*dinitrophenylhydrazone* had m. p. 179—181° (Found: C, 59·15; H, 5·9; N, 16·4. $C_{17}H_{20}N_4O_4$ requires C, 59·3; H, 5·85; N, 16·25%).

Reduction of endo,endo-*Keto-ketal* (IV).—The lower-melting keto-ketal (76 g.), hydrazine hydrate (200 c.c.), potassium hydroxide (150 g.), and diethylene glycol (1500 c.c.) were similarly heated for 5 hr. at 145—150° and, after distillation of water and hydrazine, for 6 hr. at 210—215°. Isolation of the product gave a ketal mixture (57 g., 80%), b. p. 85—90°/0·04 mm., n_D^{25} 1·5040—1·5060 (Calc. for $C_{13}H_{20}O_2$: C, 74·95; H, 9·65. Found: C, 75·05; H, 9·75%). Hydrolysis with 3% hydrochloric acid in acetone (150 c.c.) for 4 hr. under reflux and isolation gave a ketone mixture, probably (I) and (XI) (32 g., 70%), b. p. 54—57°/0·05 mm., n_D^{25} 1·5070—1·5090 (Calc. for $C_{11}H_{16}O$: C, 80·45; H, 9·85. Found: C, 80·45; H, 9·8%). Gas chromatography on dinonyl phthalate revealed two peaks of similar area, one of which coincided with that of ketone (I); its infrared spectrum was more complex than that of ketone (I) and included all the latter's main peaks.

endo,endo(?)-*Tricyclo*[6,2,1,$0^{2,7}$]*undecane*-3,6-*dione Bis*(*ethylene Dithioketal*).—The *endo,endo*-diketone (6·5 g.), ethane-1,2-dithiol (6·5 g., 2 mol.), and benzene (20 c.c.) were cooled to 0° and dry hydrogen chloride was passed through the mixture for 3·5 hr.; after 3 days at 0° the mixture was evaporated *in vacuo*; the residue solidified. Recrystallisation from ethyl acetate gave the *bis*(*dithioketal*) (7·7 g., 64%), m. p. 153—154° (Found: C, 55·1, 55·2; H, 7·05, 7·25; S, 38·35. $C_{15}H_{22}S_4$ requires C, 54·55; H, 6·7; S, 38·75%). Desulphurisation of this compound (6·5 g.) was effected with Raney nickel (35 g.) in ethanol (150 c.c.) during 44 hours' boiling. After filtration, evaporation of the solvent through a fractionating column, steam-distillation, and isolation with pentane, the hydrocarbon formed (*ca.* 0·5 g.) had b. p. 90—91°/10 mm., n_D^{18} 1·5160—1·5162 (Found: C, 89·15; H, 10·6. $C_{11}H_{16}$ requires C, 89·1; H, 10·9. Calc. for $C_{11}H_{18}$: C, 87·9; H, 12·1%). The compound has the former composition, but its structure is unknown.

exo,exo-*Tricyclo*[6,2,1,$0^{2,7}$]*undecan*-3-*one* 3-(*Ethylene Dithioketal*).—The ketone (I) (2 g.) was treated with ethane-1,2-dithiol (1·5 g.) in dry benzene (25 c.c.), and dry hydrogen chloride was passed through the solution for 2 hr. at 0°. After being kept at 0° overnight the solution was evaporated at 20°/10 mm. and the residue was dissolved in ethyl acetate and cooled to −70°; the *dithioketal* (2·3 g., 72%), m. p. 38—39°, separated (Found: C, 64·9; H, 8·2; S, 27·0. $C_{13}H_{20}S_2$ requires C, 65·0; H, 8·4; S, 26·6%).

exo,exo-*Tricyclo*[6,2,1,$0^{2,7}$]*undecane* (XVI).—The preceding dithioketal (2·15 g.), Raney nickel (24 g.), and ethanol (50 c.c.) were heated under reflux for 3 days. Filtration, evaporation, and isolation of the hydrocarbon fraction gave a product which showed a wide ange of refractive index and it was therefore shaken in hydrogen in the presence of palladium–barium carbonate (250 mg.) in light petroleum for 5 hr. Filtration, removal of solvent, and distillation afforded the *hydrocarbon*, b. p. 200°, n_D^{25} 1·4933, which gave one symmetrical peak on gas–liquid chromatography on Apiezon L (Found: C, 87·9; H, 12·25. $C_{11}H_{18}$ requires C, 87·9; H, 12·1%).

Reduction of the endo,endo-*Diketone* (II).—The *endo,endo*-diketone (10 g.), hydrazine hydrate (55 c.c.), diethylene glycol (200 c.c.), and potassium hydroxide (50 g.) were heated under reflux for 2·5 hr., then after distillation of water and hydrazine for 6 hr. at 210°. The distillate was extracted with pentane, and the glycol solution with ether; the ether was distilled and the residue steam-distilled, the steam-distillate being again extracted with pentane. The pentane extracts were combined and evaporated, and the residue was distilled from potassium, giving a product (3 g.), b. p. 89—90°/9 mm., 215°/760 mm., n_D^{18} 1·5014—1·5030 (Found: C, 88·15;

H, 11·95. Calc. for $C_{11}H_{18}$: C, 87·9; H, 12·1%). Gas chromatography on Apiezon L revealed three peaks with retention times 43, 54, and 62 min., relative areas 2 : 10 : 88, respectively; these were unchanged after attempted hydrogenation. The central peak was augmented when *exo,exo*-tricycloundecane was added. The compound giving the main peak was isolated by preparative gas–liquid chromatography for the determination of its infrared spectrum.

exo,exo-*Tricyclo*[6,2,1,$0^{2,7}$]*undecan*-3-*one Methanesulphonylhydrazone*.—The ketone (I) (8·77 g.) was added dropwise to a solution of methylsulphonhydrazide[5] (6·26 g.) in ethanol (52 c.c.) at 20°. The product slowly separated; after a few days water was added to complete precipitation and the product was collected. Recrystallisation from ethyl acetate gave the *sulphonylhydrazone* (11·6 g., 78%), m. p. 169—171° (Found: C, 55·7; H, 7·6; N, 11·25. $C_{12}H_{20}N_2O_2S$ requires C, 56·25; H, 7·85; N, 10·95%).

exo,exo-*Tricyclo*[6,2,1,$0^{2,7}$]*undec*-3-*ene* (XIX).—Sodium (620 mg.) was dissolved in molten acetamide (21 g.) at 10 mm. and the solution was cooled. The above sulphonylhydrazone (2 g.) was added and the mixture was heated to 156° in a bromobenzene-vapour bath and maintained there until nitrogen evolution had virtually ceased. After cooling to 65°, water (100 c.c.) was added and the solution was extracted with pentane (6 × 15 c.c.); the solution was washed with water (2 × 10 c.c.), and the solvent was removed. Distillation of the residue (920 mg.) gave an *olefin*, b. p. 76—77°/8 mm., n_D^{25} 1·5092—1·5099 (Found: C, 89·2; H, 10·9. $C_{11}H_{16}$ requires C, 89·1; H, 10 9%).

This hydrocarbon (248 mg.) was shaken in ethanol in hydrogen in the presence of 10% palladium–calcium carbonate (100 mg.) (uptake theoretical); after filtration, evaporation to 1 c.c., and addition of water (5 c.c.), extraction with light petroleum (5 c.c.) gave a solution which was used directly for gas–liquid chromatography (Apiezon L). It gave a single symmetrical peak, inseparable from that of the hydrocarbon obtained by Raney nickel desulphurisation of the dithioketal described above.

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