propenal prepared from acetylene, 1-butanethiol and carbon monoxide.

3-(Benzylthio)-2-propenal.—Using the procedure described above, there was charged into the bomb 124 g. of benzylthiol, 2.5 g. of 1,1′-azodicyclohexanecarbonitrile and 26 g. of acetylene. The reaction was carried out at 98–100° for a period of 16.7 hours while maintaining a pressure of 960–1000 atm. by carbon monoxide injection. From a composite of three such runs, there was obtained the desired propenal distilling at 107–112° (1.3 mm.), $n^{25}\text{D}$ 1.6167 (1.6 g., 0.5% yield). There was also isolated by distillation 228.4 g. of the disulfide, b.p. 175–180° (3 mm.) (79.4% yield), and 110 g. of benzylthiol was recovered.

The infrared spectrum of the propenal fraction was similar to that of 3-(*n*-butylthio)-2-propenal and in addition showed aromatic vibrations. *Anal.* Calcd. for $C_{10}H_{10}OS$: C, 67.4; H, 5.6; S, 18.0. Found: C, 69.3; H, 6.6; S, 19.6. A brown dinitrophenylhydrazone melted at 158–160° after recrystallization from acetone. *Anal.* Calcd. for $C_{16}H_{14}N_4O_4S$: C, 53.6; H, 3.9; N, 15.6; S, 8.9. Found: C, 52.8; H, 3.9; N, 15.2; S, 9.0.

Synthesis of 3-(Phenylthio)-2-propenal.—Using the procedure described above, 55 g. of benzenethiol, 1 g. of 1,1′-azodicyclohexanecarbonitrile and 26 g. of acetylene were heated at 100° for 16 hours under a pressure of 920–960 atmospheres maintained by carbon monoxide injection. From a composite of three such runs, there was obtained 7 g. of crude 3-(phenylthio)-2-propenal distilling at 65–144° (18–18.5 mm.) with a small flat at 157–158° (18 mm.) (1.5 g.) and 46 g. of the disulfide distilling at 155° (2 mm.) (63% yield). The recovered benzenethiol amounted to 80.1 g.

The elemental analysis of the propenal cut indicated disulfide impurity. *Anal.* Calcd. for C_9H_8OS: C, 66.0; H, 4.9; S, 19.6. Found: C, 66.7; H, 5.5; S, 22.4. A chocolate-brown 2,4-dinitrophenylhydrazone melted at 193–194° after recrystallization from toluene. *Anal.* Calcd. for $C_{15}H_{12}O_4N_4S$: C, 52.4; H, 3.5; N, 16.2. Found: C, 52.3; H, 3.9; N, 15.9.

Synthesis of 1,2-Bis-(*n*-butylthio)-ethane.—Using the procedure described above, acetylene was injected at 11–16 atm. into 1-butanethiol (100 g.) containing 3 ml. of di-*t*-butyl peroxide during 6.5 hours at 125–135°. After stripping 47.5 g. of unreacted 1-butanethiol from the reaction mixture, the residual liquid was distilled at 68–114° (1 mm.), largely at 111–114° (1 mm.) (42 g.). Redistillation of this fraction gave 38 g. (63% yield) of the disulfide distilling at 121–124° (5 mm.), $n^{25}\text{D}$ 1.4947. The disulfide (2.0 g.) was refluxed with 20 ml. of 30% hydrogen peroxide for one hour. The resulting disulfone was recrystallized from methanol and melted at 177–178°.[6]

In a "control" run (no catalyst), 1-butanethiol (68 g.) was treated with acetylene as described above at 130° for 4.5 hours at a gage pressure of 18 atm. There was recovered 58.5 g. of 1-butanethiol, and there was no evidence for the formation of disulfide.

Synthesis of 1,2-Bis-(benzylthio)-ethane.—A mixture of 100 g. of benzylthiol and 1.5 g. of 1,1′-azodicyclohexanecarbonitrile was treated with acetylene as described above for 5.2 hours at 100–112° at a gage pressure of 13–15 atm. From the reaction mixture there was recovered by distillation 53 g. of benzylthiol. The disulfide distilled at 175–183° (2 mm.) and melted at 38°[7] (48.8 g., 94% yield). The disulfone, prepared by oxidation with 30% hydrogen peroxide and purified by recrystallization from acetic acid, appeared to darken and sublime at temperatures slightly higher than 300°.

Synthesis of 1,2-Bis-(ethylthio)-ethane.—When a mixture of ethanethiol (42 g.), acetylene (26 g.) and di-*t*-butyl peroxide (2.5 ml.) was heated in the presence of carbon monoxide at a bomb gage pressure of 80–90 atm. and 100–130°, only the disulfide distilling at 112–114° (35 mm.), $n^{25}\text{D}$ 1.5094 (32.0 g., 50% yield), was isolated. *Anal.* Calcd. for $C_6H_{14}S_2$: C, 48.0; H, 9.3; S, 42.6. Found: C, 48.43; H, 9.4; S, 41.3. The disulfone, made by adding the disulfide to 30% hydrogen peroxide, melted at 131–132°.[8] *Anal.* Calcd. for $C_6H_{14}O_4S_2$: S, 29.9. Found: S, 29.9. Thus carbon monoxide at comparatively low pressure does not participate in the acetylene–thiol reaction.

Acknowledgment.—The author is pleased to express his gratitude for the valuable suggestions of Dr. T. L. Cairns.

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(6) T. C. Whitner, Jr., and E. E. Reid, THIS JOURNAL, **43**, 638 (1921), gave the boiling point of the disulfide as 129–130° (5 mm.), $n^{20}\text{D}$ 1.4962, and the melting point of the disulfone as 182°.

(7) E. Fromm, H. Benzinger and F. Schafer, *Ann.*, **394**, 327 (1912), report the melting point of the disulfide as 38°; these authors report that the disulfone begins to sublime at 304°.

(8) R. Otto, *J. prakt. Chem.*, [2] **36**, 437 (1887), gives the melting point of 1,2-bis-(ethylthio)-ethane as 136.5°.

WILMINGTON 98, DEL.

COMMUNICATIONS TO THE EDITOR

DIRECT MONOALKYLATION OF STEROIDS AT C_4

Sir:

It has been reported[1,2] that direct alkylation is unsuitable as a means of preparing 4-alkyl-3-keto-Δ^4-steroids; however, conditions used in this laboratory have given good yields of monoalkylated products.

Testosterone (1.77 g.) in boiling *t*-butyl alcohol (35 ml.) was added to a boiling solution of potassium (0.36 g.) in the same solvent (20 ml.). A solution of methyl iodide (0.87 g.) in *t*-butyl alcohol (100 ml.) was added dropwise over a 2.5-hour period to the stirring and refluxing basic solution. After a further 0.5 hour at reflux the product was isolated. Chromatography on silica gave 3 well separated crystalline peaks. The first eluted with ethyl acetate-benzene (1:19) was identified as 17β-hydroxy-4,4-dimethylandrost-5-en-3-one (Ia) (conversion 9%[3]; m.p. 184-185.5°; $[\alpha]\text{D}$ $-5°$ (c 1.04)[4]; infrared 3.03μ, 5.82μ, 6.03μ; calcd. for $C_{21}H_{32}O_2$: C, 79.69; H, 10.19. Found: C, 79.30, 79.41; H, 10.21, 10.21). The second, 4-methyltestosterone[2] (IIa, conversion 44%) was eluted with ethyl acetate–benzene (1:9) (m.p. 168.5-170.5°; $[\alpha]\text{D}$ $+137°$ (c 1.02); $\lambda_{\text{max.}}$ 250 mμ (ϵ14,200), infrared 2.88μ, 6.04μ, 6.22μ). This material was identical, as shown by a mixture m.p. and comparison of the infrared spectra, with a sample of IIa

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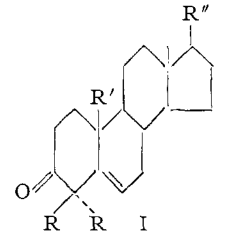
(1) G. D. Meakins and O. R. Rodig, *J. Chem. Soc.*, 4679 (1956).

(2) F. Sondheimer and Y. Mazur, THIS JOURNAL, **79**, 2906 (1957).

(3) Conversions, yields and recoveries are based on weights of crystalline chromatography fractions which contained no more than 10% impurity as shown by physical constants or further purification.

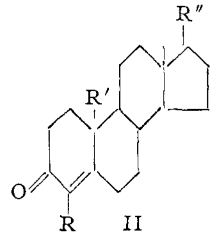
(4) Optical rotations, spectra and analytical data determined by the Analytical Department in charge of Dr. R. T. Dillon. Optical rotations are in chloroform, ultraviolet spectra in methanol and infrared spectra in potassium bromide.

prepared through the enol lactone by the general method of Fujimoto[5] (m.p. 167–168.5°; calcd. for $C_{20}H_{30}O_2$: C, 79.42; H, 10.00. Found: C, 79.21; H, 10.29). The third peak comprised recovered testosterone (recovery 33%) and was eluted with ethyl acetate–benzene (1:9 and 1:4). Yields of Ia and IIa were thus 14% and 66%, respectively. No evidence of O-alkylation at the 17-hydroxyl was obtained.



I

a, R = CH_3; R′ = CH_3; R″ = OH
b, R = allyl; R′ = CH_3; R″ = OH
c, R = CH_3; R′ = H; R″ = OH



II

a, R = CH_3; R′ = CH_3; R″ = OH
b, R = allyl; R′ = CH_3; R″ = OH
c, R = *n*-butyl; R′ = CH_3; R″ = OH
d, R = CH_3; R′ = H; R″ = OH
e, R = CH_3; R′ = H; R″ = $OCOCH_3$

Testosterone on similar alkylation with allyl bromide followed by chromatography of the crude product on silica gave 17β-hydroxy-4,4-diallyl-androst-5-en-3-one (Ib) (conversion 11%; yield 14%; m.p. 108–109.5°; $[\alpha]_D$ −12° (*c* 0.66); infrared 2.92μ, 5.84μ, 5.93μ, 6.04μ, 6.11μ; Calcd. for $C_{25}H_{36}O_2$: C, 81.47; H, 9.85. Found: C, 81.13; H, 9.84.) on elution with ethyl acetate–benzene (1:19) and 4-allyltestosterone (IIb) (conversion 46%; yield 55%; m.p. 124.5-125° with presoftening; $[\alpha]_D$ +125° (*c* 1.11); $\lambda_{max.}$ 250mμ (ϵ 15,000); infrared 2.87μ, 2.94μ, 6.04μ, 6.25μ; calcd. for $C_{22}H_{32}O_2$: C, 80.44; H, 9.82. Found: C, 80.64; H, 9.99) with ethyl acetate–benzene (1.9). Testosterone (recovery 16%) was eluted with ethyl acetate–benzene (1:4). When *n*-butyl iodide was used in the alkylation 4-*n*-butyltestosterone (IIc) (62%; m.p. 127.5–128.5°; $[\alpha]_D$ +113° (*c* 1.02); $\lambda_{max.}$ 251mμ (ϵ 15,000); infrared 3.11μ, 6.00μ, 6.23μ; calcd. for $C_{23}H_{36}O_2$: C, 80.18; H, 10.53. Found: C, 80.24; H, 10.73) was obtained. A material (10%) was eluted from the column before IIc which showed no ultraviolet absorption in the region of 250 mμ and was assumed, without further characterization, to be the dialkylated product.

19-Nortestosterone (with 1.25 moles methyl iodide) gave 17β-hydroxy-4,4-dimethyl-19-norandrost-5-en-3-one (Ic) (16%; m.p. 149.5-150°; $[\alpha]_D$ +33° (*c* 0.36); infrared 3.01μ, 5.85μ, 6.06μ.; calcd. for $C_{20}H_{30}O_2$: C, 79.42; H, 10.00. Found: C, 79.02; H, 9.96) and 4-methyl-19-nortestosterone (IId) (50%; m.p. 158–159°; $[\alpha]_D$ +52° (*c* 0.74); $\lambda_{max.}$ 250 mμ (ϵ 15,400); infrared 2.82μ, 6.04μ, 6.22μ). This material was shown to be identical on the basis of its infrared spectrum and a mixture m.p. with a sample of the compound prepared through the enol lactone (m.p. 154–158.5°; calcd. for $C_{19}H_{28}O_2$: C, 79.12; H, 9.78. Found: C, 78.99; H, 9.63); *acetate*[6] (IIe; m.p. 128–129°; $[\alpha]_D$ +42° (*c* 0.85); $\lambda_{max.}$ 249.5 mμ (ϵ 17,100); calcd. for $C_{21}H_{30}O_3$: C, 76.32; H, 9.15. Found: C, 76.03; H, 9.06).

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[5] G. I. Fujimoto, THIS JOURNAL, **73**, 1856 (1951).

[6] J. A. Hartman, A. J. Tomasewski and A. S. Dreiding, *ibid.*, **78**, 5662 (1956).

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THE ADDITION OF TETRACYANOETHYLENE TO DIPHENYLDIMETHYLENECYCLOBUTENE

Sir:

Possible synthetic routes to the still unknown genuine cyclobutadienes, which might be effected under mild conditions, are Diels–Alder additions with dimethylenecyclobutenes. The principal objective of the reported synthesis of diphenyldimethylenecyclobutene (I)[1] was, in fact, to investigate this approach. We now wish to report the first results of this study.

It was found that the triene I was unreactive toward maleic anhydride, N-phenylmaleimide and acetylene dicarboxylic ester at moderate temperatures (25–75°), in sharp contrast to the high Diels–Alder activity of the closely related model compound 1,2-dimethylenecyclobutane.[2] At elevated temperatures polymerization occurred in all instances with no isolable crystalline products being realized. Thus, from the reaction of I with acetylenedicarboxylic ester at 150°, there was obtained, after careful chromatography, an amorphous product in low yield which decomposed at 160–170°, depending upon the rate of heating. *Anal.* Calcd. for $(C_{24}H_{20}O_4)_n$: C, 77.40; H, 15.41. Found: C, 77.60; H, 15.53. The infrared spectrum of this polymeric product indicated that it comprised combined I and dienophile.

The foregoing suggested that a dienophile of unusual activity would be required to coax the triene I into undergoing a Diels–Alder addition. The recently described tetracyanoethylene[3] appeared uniquely attractive for this purpose. From this and I, in benzene at room temperature, there was obtained a colorless crystalline stable adduct (*ca.* 40% yield), m.p. 175–176° (dec.) after recrystallization from ether. Calcd. for $C_{24}H_{14}N_4$: C, 80.43; H, 3.94; N, 15.63. Found: C, 80.73; H, 4.08; N, 15.39. The mild conditions employed for the addition suggested that the adduct had either the cyclobutadiene structure II or the spiran structure III, resulting from 1,4- or 1,2-addition

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[1] A. T. Blomquist and Y. C. Meinwald, THIS JOURNAL, **79**, 5317 (1957).

[2] A. T. Blomquist and J. A. Verdol, *ibid.*, **77**, 1806 (1955).

[3] T. L. Cairns, R. A. Carboni, D. D. Coffman, V. A. Engelhardt, R. E. Heckert, E. L. Little, E. G. McGeer, B. C. McKusick and W. J. Middleton, *ibid.*, **79**, 2340 (1957).