affording 4.2 g (47% yield) of a white solid (mp 70–75°) with a molecular weight of 2.6×10^3. The polymer was completely soluble in cold benzene. Characteristic infrared absorptions were ν (NCH) 2810, ($SiCH_3$) 1245, and (SiNSi) 880 cm^{-1}.

Anal. Calcd for $(C_9H_{21}NSi_2)_n$: C, 54.2; H, 10.6; N, 7.02; Si, 28.2. Found: C, 55.2; H, 11.1; N, 7.12; Si, 27.2.

Copolymers with Styrene.—Compound IV (10 g, 0.050 mole) and *n*-butyllithium (0.48×10^{-2} mole) were dissolved in toluene (40 ml) and styrene (6.34 g, 0.0610 mole) was added. The solution turned orange and grew warm. Additional styrene was added for a total of 20 g (0.20 mole). Within 30 min the solution became an orange gelatinous mass. This was extracted with toluene and methyl alcohol and devolatilized at 1 mm for 20 hr to yield a white brittle polymer (16 g, 53% yield) which did not melt to 300° and was insoluble in toluene. Characteristic infrared absorptions were ν (NCH) 2810, ($C_{ar}C_{ar}$) 1600, ($SiCH{=}CH_2$) 1595, ($SiCH_3$) 1250, and (SiNSi) 900 and 880 cm^{-1}. There was no indication of $SiOCH_3$.

Anal. Calcd for $[(C_9H_{21}NSi_2)(C_8H_8)_{1.2}]_n$: C, 69.0; H, 9.5; N, 4.3; Si, 17.3. Found: C, 68.9; H, 9.5; N, 4.4; Si, 16.8.

In a similar preparation, IV (10.9 g, 0.0544 mole) and styrene (5.2 g, 0.050 mole) in benzene (60 ml) were treated with *n*-butyllithium (0.64×10^{-2} mole), resulting in an orange solution and noticeable exotherm. After 0.5 hr the viscous solution was poured into methyl alcohol. The polymer which precipitated was devolatilized at 1 mm for 24 hr to give a brittle white solid (9.5 g, 57% yield) which became quite soft at 90°. This polymer was soluble in benzene and had a molecular weight of 1.4×10^3. The infrared spectrum showed more $SiCH{=}CH_2$ than was present in the earlier preparation.

Anal. Calcd for $[(C_9H_{21}NSi_2)(C_8H_8)_{1.5}]_n$: C, 63.6; H, 9.9; N, 5.3; Si, 21.3. Found: C, 62.2; H, 9.9; N, 5.3; Si, 20.8.

Stability of Dimethylaminosilanes in the Presence of *n*-Butyllithium.—Trimethyldimethylaminosilane (1.17 g, 0.010 mole), dimethylbisdimethylaminosilane (1.46 g, 0.010 mole), and methyltrisdimethylaminosilane (1.75 g, 0.010 mole) were placed under helium in separate vials fitted with septums. *n*-Butyllithium (0.010 mole) in hexane was added to each vial. Samples were periodically withdrawn and analyzed by vpc for the aminosilane. After 68 and 116 hr at ambient temperature, 93 and 83%, respectively, of the trimethyldimethylaminosilane remained, 99 and 89% of the dimethylbisdimethylaminosilane remained, and 100 and 96% of the methyltrisdimethylaminosilane was unreacted. In all cases, a small amount of precipitate, presumably lithium dimethylamide, became evident. The product from trimethyldimethylaminosilane and *n*-butyllithium was identified as *n*-butyltrimethylsilane by comparison of its retention time with that of an authentic sample.

Stability of Dialkylaminosilane in the Presence of Lithium Dialkylamides.—Diethylamine (0.073 g, 0.0010 mole) and *t*-butyllithium (1.5 *M* in pentane; 0.67 ml, 0.0010 mole) were combined under helium in a vial fitted with a septum. The addition of trimethyldimethylaminosilane (0.117 g, 0.0010 mole) and triethylamine (2.00 ml) dissolved the lithium diethylamide. By the same method, a solution of lithium dimethylamide (0.0010 mole) and trimethyldiethylaminosilane (0.0010 mole) in triethylamine (2.00 ml) was prepared. The solutions were analyzed by vpc. No exchange of amino groups could be detected in either system during 84 hr at ambient temperature.

Registry No.—I, 13391-72-5; II, 13368-45-1; III, 13391-74-7; IV, 7688-44-0; vinyldimethylmethylaminosilane, 7688-43-9.

Organic Photochemistry. III. Photochemical Reaction of 5-Chlorotropolone and Its Methyl Ether[1,2]

TOSHIO MUKAI AND TADAO SHISHIDO[3]

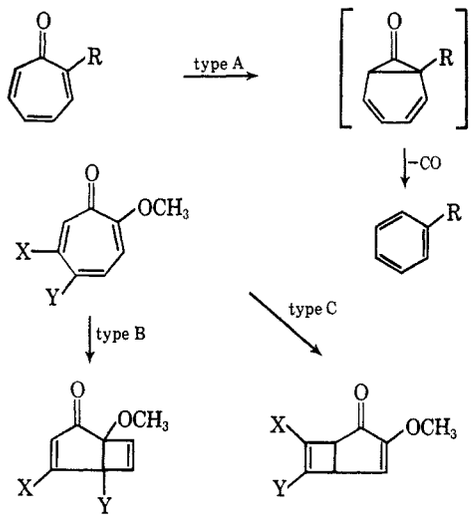
Department of Chemistry, Faculty of Science, Tohoku University, Sendai, Japan

Received December 20, 1966

Irradiation of 5-chlorotropolone methyl ether (I) in methanol using a high-pressure mercury lamp produced three photoproducts: 6-chloro-7-methoxy- and 6-chloro-3-methoxy-$\Delta^{3,6}$-bicyclo[3.2.0]heptadien-2-one (II) and (III) and methyl 4-keto-2-cyclopentenylideneacetate (IV). The irradiation of 5-chlorotropolone (XIV) in the same manner afforded four photoproducts, a methanol adduct XV and a dimer XVI, besides III and IV. The structure of XV and XVI including stereochemistry was elucidated and the mechanistic pathway for products was also discussed.

There are three different modes of cyclization, type A, B, and C in Scheme I, in the photo-induced valence isomerization of a troponoid system.[4] Previous studies have established that the nature of the substituents in the troponoid system play a major role in the control of the reaction path.[4] In general, tropolones and their methyl ethers[5,6] and alkyl-substituted derivatives[7] follow type B cyclization, whereas aromatic substituted systems such as colchicine,[8] isocolchicine,[9] and 5-phenyltropolone methyl ether[1] undergo type C isomerization. Type A cyclization has only been observed on irradiation of tropone[4] and 2-phenyltropone.[10]

SCHEME I



(1) Preceding paper in this series: T. Mukai and T. Miyashi, *Tetrahedron*, **23**, 1613 (1967).

(2) Support of this work by Sankyo Co. Tokyo is gratefully acknowledged.

(3) From the M.S. Thesis of T. Shishido, Fuji Film Industry Co., Minamiashigara, Kanagawa Prefecture.

(4) O. L. Chapman, *Advan. Photochem.* **1**, 323 (1963).

(5) (a) W. G. Dauben, K. Koch, and W. E. Thiessen, *J. Am. Chem. Soc.*, **81**, 6087 (1959); (b) E. J. Forbes and R. A. Ripley, *Chem. Ind.* (London), 589 (1960).

(6) (a) O. L. Chapman and D. J. Pasto, *J. Am. Chem. Soc.*, **80**, 6685 (1958); (b) *ibid.*, **82**, 3642 (1960).

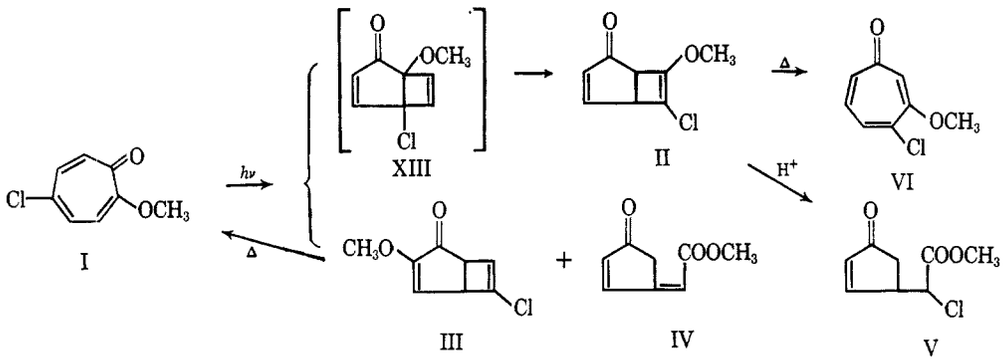
(7) (a) W. G. Dauben, K. Koch, O. L. Chapman, and S. L. Smith, *ibid.*, **83**, 1768 (1961); (b) *ibid.*, **85**, 2616 (1963).

(8) (a) E. J. Forbes, *J. Chem. Soc.*, 3864 (1955); (b) O. L. Chapman, H. G. Smith, and R. W. King, *J. Am. Chem. Soc.*, **85**, 803 (1963).

(9) (a) W. G. Dauben and D. A. Cox, *ibid.*, **85**, 2130 (1963); (b) O. L. Chapman, H. G. Smith, and P. A. Barks, *ibid.*, **85**, 3171 (1963).

(10) Irradiation of 2-phenyltropone in methanol afforded biphenyl (1.5% yield) and 1-phenyl- and 7-phenyl-$\Delta^{3,6}$-bicyclo[3.2.0]heptadien-2-ones (16%). Details will be reported by the authors.

SCHEME II



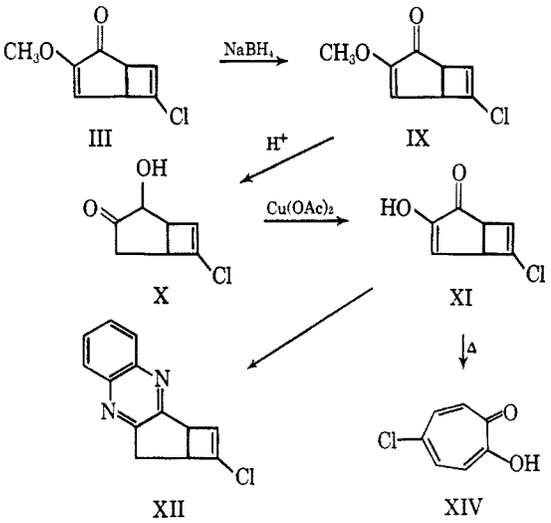
In order to investigate the effect of the chlorine substituent on the photo-induced valence isomerization, the photochemistry of 5-chlorotropolone and its methyl ether was studied. Irradiation of I produced three photoproducts, II, III, and IV, in 10, 30, and 10% yields, whose structures were determined as follows. Compound II, on refluxing with dilute acid, afforded methyl 4-keto-cyclopentenylchloroacetate (V).[7] Pyrolysis of II at 430° yielded 4-chloro-3-methoxytropone (VI), whose structure was supported by the infrared spectrum exhibiting strong bands (1626, 1595 cm^{-1}) characteristic of the tropone nucleus and by the peculiar ultraviolet spectrum similar to that of 3-methoxytropone derivatives.[11] On the other hand, attempted hydrolysis of compound III with dilute acid resulted in the recovery of III, but pyrolysis of III at 430° afforded 5-chlorotropolone methyl ether (I) (Scheme II).

On catalytic reduction using palladium–carbon as catalyst, compound IV consumed 2 equiv of hydrogen to give the known methyl 4-keto-cyclopentanylacetate (VII).[5] When the hydrogenation was interrupted after 1 equiv of hydrogen had been consumed, another known compound, methyl 4-keto-2-pentenylacetate[5] (VIII), was obtained.

A series of experiments which strongly support the validity of the structural assignment of III was carried out. Reduction of III with sodium borohydride yielded a vinyl ether IX, which, without isolation, was treated with a dilute acid to afford a ketol X. Oxidation of X with cupric acetate gave a dione XI which was completely enolic, as evidenced from its nmr and infrared spectra. Nevertheless it formed a quinoxaline derivative XII when heated with *o*-phenylenediamine in ethanol. Pyrolysis of XI at 400° afforded 5-chlorotropolone (XIV) (Scheme III). Of these photoproducts obtained from 5-chlorotropolone methyl ether (I), the compounds II and IV belong to the category of type B cyclization product, II being derived from a primary product XIII by rearrangement[7] and IV from II *via* the product V. On the other hand, the main product III is type C cyclization product. Thus, a ratio of type B to C isomerization induced by irradiation of 5-chlorotropolone methyl ether can be estimated as 20–30.

To study the differences between the photochemical behavior of 5-chlorotropolone (XIV) and its methyl ether (I), the irradiation of XIV was carried out. As shown in Scheme IV, a methanol adduct XV and a dimer XVI were obtained in 15 and 7% yields in addition to the products III and IV in 9 and 4% yields, respectively. The structures of new products XV and XVI were elucidated from the following evidence. The infrared spectrum of XV shows a carbonyl band (1761 cm^{-1}) ascribed to an α-substituted cyclopentanone but not to 2-cyclopentenone. The nmr spectrum of XV indicates the presence of two methoxyl groups and one olefinic proton at the C_7 position. Heating XV in a dilute acid afforded the known compound XI. Thus, structures XVa or XVb are proposed for XV, the former being preferable to the latter on the basis of the infrared spectral evidence for a CH_2CO group (1406 cm^{-1}).

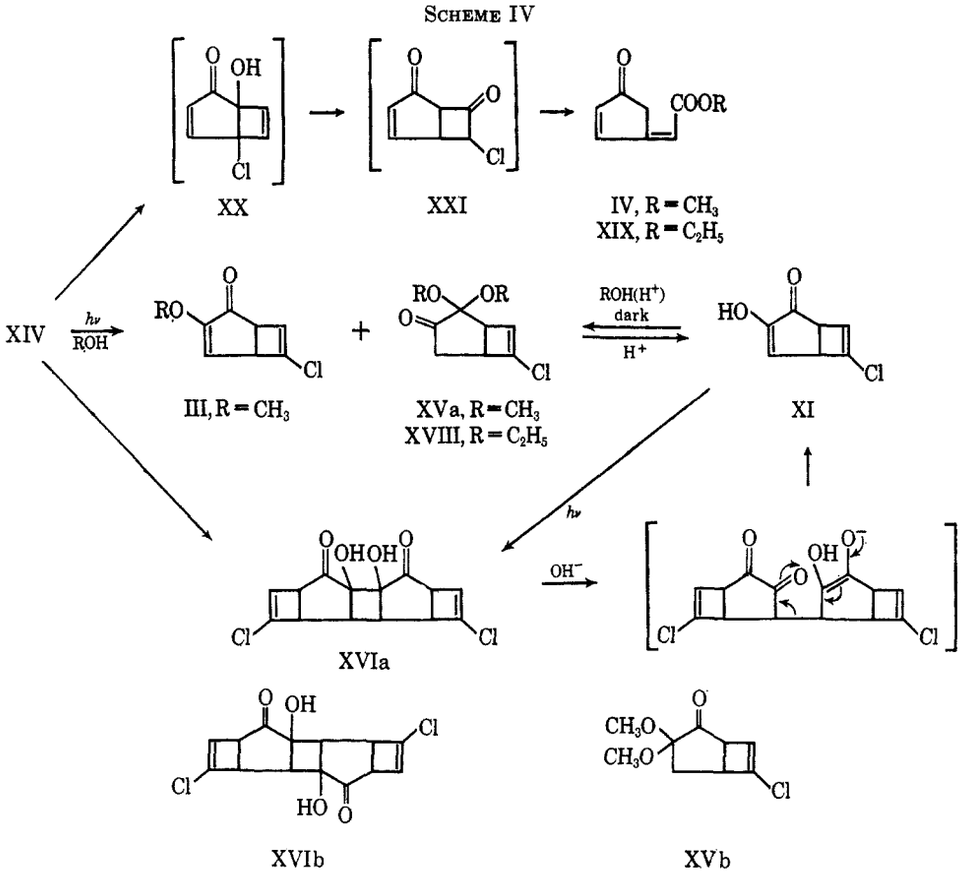
SCHEME III



The product XVI was found to be a dimer by the molecular weight determination and its spectral data indicate that the dimer is not a conjugated ketone, but a saturated five-membered ring ketone. The pyrolysis of the dimer failed to yield any single product and refluxing in 3 *N* hydrochloric acid resulted in the recovery of XVI. However, when the dimer was treated with 5% of sodium hydroxide solution at room temperature, XI could be obtained in 70% yield. On the other hand, irradiation of XI in ethanol afforded the dimer XVI in 80% yield. These facts certify that the dimer XVI is composed of two molecules of XI, for which either a head-to-head (XVIa) or head-to-tail structure (XVIb) are possible without consideration of its stereochemistry. The above alkaline decomposition of XVI to XI suggests that a 1,3-ketol structure such as XVIa is preferable to the other XVIb, because the decomposition pathway could only be illustrated reasonably as shown in Scheme IV. Furthermore the formation of the carbonate XVII established the stereochemistry of

(11) (a) R. B. Johns, A. W. Johnoson, and M. Tisler, *J. Chem. Soc.*, 4605 (1954); (b) S. Seto, *Sci. Rept. Tohoku Univ., First Ser.*, **37**, 377 (1953).

SCHEME IV



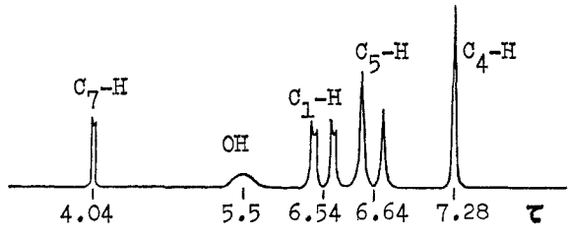
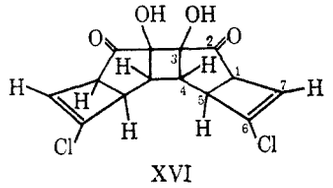
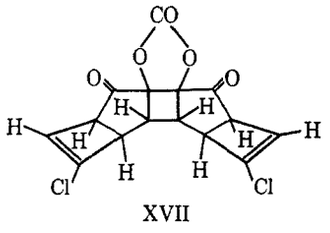


Figure 1.—Nmr spectrum of XVI (60 Mc in pyridine).

the dimer XVI as the head-to-head *cis* form. Additional evidence for the stereochemistry could be obtained from the nmr spectrum shown in Figure 1, in which signals are rather simple, suggesting a symmetrical structure. The signals appear as an AB pattern perturbed by one vinyl proton (C_1 and C_5 protons are designated as A and B, $J_{1,5} = 3.5$ cps, $J_{1,7} = 0.9$ cps), a split singlet owing to C_7-vinyl proton, a singlet ascribed to C_4 proton, and a broad peak owing to hydroxyl group. The spectrum indicates that the coupling constant between C_4 and C_5 protons is nearly zero, which posture could only be explained by the fact that two hydrogen atoms are situated in the *trans* rather than *cis* configuration.[12]



XVI



XVII

Since it became clear that the irradiation of 5-chlorotropolone (XIV) in methanol resulted in the formation of the interesting products such as XV and XVI, the photochemistry of XIV was carried out in ethanol to establish the generality of the reaction. In this case, the four photoproducts XI, XVI, XVIII, and XIX were also obtained in 3, 10, 15, and 5% yields, respectively. From the striking similarity of the spectral data and chemical behavior of XVIII and XIX to those of XV and IV, their structures were assigned as shown in Scheme IV. Thus, the irradiation of XIV in ethanol gave almost the same result as in methanol, except for isolation of XI instead of III.

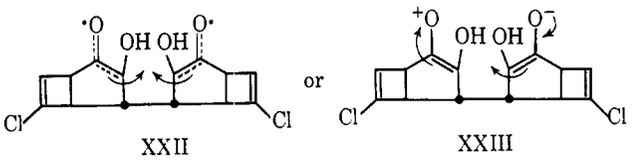
Except for XI, all photoproducts of XIV come from secondary reaction. For example, IV or XIX are derived from a type B cyclization product XX through rearrangement to XXI followed by ring-opening reaction.[7] The compound XVI is the dimer of the primary product XI, a similar relationship having been observed in the photochemistry of colchicine.[13] That is, α-lumicolchicine, a photodimer, was obtained by the irradiation of β-lumicolchicine, which is a primary photoproduct of colchicine. However, it should be noted that the stereochemistry of XVI is different from

(12) In XVI, the strain resulting from two four-membered rings twists the five-membered ring and makes the dihedral angle of C_4 and C_5 protons nearly 90°.

(13) (a) O. L. Chapman, H. G. Smith, and R. W. King, *J. Am. Chem. Soc.*, **85**, 3914 (1961); (b) *ibid.*, **85**, 806 (1963); (c) G. O. Schenck, H. J. Kuhn, and O. A. Neumuller, *Tetrahedron Lettrs*, 16 (1961).

that of α-lumicolchicine, which has head-to-head *trans* form. Recently, the mechanism for the photocycloaddition of cycloalkenone derivatives has been discussed; in some cases a concerted one-step cyclization[14] was preferred and sometimes a two-step one.[13,15] The dimer XVI is the first example of the head-to-head *cis* dimer in the photochemistry of cyclopentenones. Its formation could be tentatively illustrated by a following two-step mechanism. In the dimerization step of XI, the stabilization of a diradical XXII or a charged intermediate XXIII led to the formation of the head-to-head dimer preferentially to the head-to-tail one.[13b] The nonbonding interaction between an excited molecule and a ground-state one is not so extensive as in the dimerization of β-lumicolchicine, thus resulting in *cis* dimerization. Furthermore, an attractive force ascribed to hydrogen bonding between two hydroxyl groups may play an important role in giving the *cis* form. Thus, *cis* arrangement of the hydrogen at C_4 position requires the second step to give the *cis*-diol, since a *trans* five–four-membered ring is excluded on steric ground. However, a concerted process can not completely be discarded for the photodimerization of XI giving XVI.

XI ⟶



XXII XXIII

The formation of III requires simultaneous occurrence of the cyclization and methylation. The formation of XV or XVIII requires further the addition of the alcohol. Examples of such addition reactions of solvents were observed in the photochemistry of isocolchicine,[9a] α,β-unsaturated ketone,[16] and some steroidal 3,5-dienes.[17] In the present study, however, there is the possibility that the hydrogen chloride liberated in the formation of IV or XIX catalyzes the etherification or alcohol addition to the primary photoproduct XI. To clarify these possibilities, XI was allowed to stand *in the dark* in methanol containing a trace of hydrogen chloride at room temperature and, indeed, the methylated product III and methanol addition product XV could be isolated in 33 and 35% yields, respectively. On the other hand, as mentioned before, irradiation of XI in ethanol resulted in only the formation of the dimer XVI, without the formation of etherified product or solvent addition product. These facts made quite clear that irradiation of XIV afforded the type C cyclization product XI as the primary reaction, which proceeded by photochemical change to the dimer XVI and nonphotochemically to III and XV or XVIII. Thus, the ratio of type B to C isomerization induced during irradiation of 5-chlorotropolone (XIV) is estimated as 4:31 in methanol and 5:28 in ethanol.

Chapman already pointed out that in the photolysis of simple tropolones or their methyl ethers, type B cyclization is preferred to type C cyclization because of the effect of hydroxyl or methoxyl groups in the tropone ring.[4] Indeed, so far this has been the case in most instances,[6,7] except for the case of 5-phenyltropolone methyl ether.[1] The present study demonstrates that the introduction of a chlorine substituent at the C_5 position, not only in tropolone but in the methyl ether, leads to a change in the cyclization mode from type B to a mixture of B and C.

Experimental Section

Nmr spectra were measured in carbon tetrachloride or deuteriochloroform on a Varian A-60 spectrometer using tetramethylsilane as internal standard (multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = complex multiplet). Coupling constants of the photoproducts are almost in agreement with those of literature.[18]

Irradiation of 5-Chlorotropolone Methyl Ether (I).—A solution of 2 g (11.7 mmoles) of I dissolved in 300 ml of methanol was placed in a Pyrex cylindrical vessel equipped with a glass tube for cooling water and for nitrogen gas stream and flushed with pure nitrogen for 30 min prior to irradiation. The irradiation was carried out externally by Toshiba H-400P (400-w high-pressure mercury lamp). During the irradiation, the solution was agitated with magnetic stirring and a slow stream of nitrogen. The temperature of the reaction solution was maintained below 35° by cooling with running water. The reaction was followed by ultraviolet spectral determination of solutions withdrawn periodically. After 25 hr of irradiation, the absorption maxima of I at 330–380 mμ had almost disappeared. The solution was concentrated under reduced pressure to give 1.9 g of a brown oil as residue. The oil was dissolved in benzene and cyclohexane (1:1) and after removal of insoluble polymers, the solution was passed through on alumina column (activity III, 70 g). Evaporation of the eluted benzene–cyclohexane (1:1) fraction afforded 200 mg (10%) of 6-chloro-7-methoxy-$\Delta^{3,6}$-bicyclo[3.2.0]heptadien-2-one (II) as a pale yellow oil which distilled at 2 mm by heating in an oil bath at 50–60°: λ_{max}^{MeOH} 262 mμ (log ε 3.14); ν_{max}^{oil} 1715 (cyclopentenone), 1590, 1042, and 875 cm^{-1}; nmr, τ 6.36 (C_1H, d, 1 H), 3.95 (C_3H, d, 1 H), 2.33 (C_4H, q, 1 H), 6.52 (C_5H, m, 1 H), and 6.12 (C_7OCH_3, s, 3 H) with $J_{1,5}$ = 2.8, $J_{3,4}$ = 5.4, $J_{3,5}$ = 1.8, and $J_{4,5}$ = 2.8 cps.

Anal. Calcd for $C_8H_7O_2Cl$: C, 56.33; H, 4.11. Found: C, 55.57; H, 4.21.

Evaporation of the eluted benzene fraction gave 600 mg (30 %) of 6-chloro-3-methoxy-$\Delta^{3,6}$-bicyclo[3.2.0]heptadien-2-one (III) as colorless needles: mp 65° (after recrystallization from cyclohexane); λ_{max}^{MeOH} 232 and 265 mμ (log ε 3.99 and 3.92); ν_{max}^{KBr} 1706 (C=O), 1613, 714 cm^{-1}; nmr, τ 6.18 (C_1H, t, 1 H), 6.20 (C_3OCH_3, s, 3 H), 3.90 (C_4H, d, 1 H), 6.67 (C_5H, q, 1 H), and 3.72 (C_7H, d, 1 H) with $J_{1,5} = J_{1,7}$ = 3.6 and $J_{4,5}$ = 2.0 cps.

Anal. Calcd for $C_8H_7O_2Cl$: C, 56.33; H, 4.11. Found: C, 56.63; H, 4.46.

Elution with benzene–ether (1:1) gave 200 mg (10%) of methyl 4-keto-2-cyclopentenylideneacetate (IV) as colorless needles: mp 75° (after recrystallization from cyclohexane); λ_{max}^{MeOH} 275 mμ (log ε 4.46); ν_{max}^{KBr} 1721 (ester), 1709 (cyclopentenone), 1642, 814, and 735 cm^{-1}; nmr, τ 2.29 (C_2H, d, 1 H), 3.15 (C_3H, d, 1 H), 6.72 (C_5H, d, 2 H), 4.80 (side-chain H, t, 1 H), and 6.28 ($COOCH_3$, s, 3 H) with $J_{2,3}$ = 4.8 and $J_{5,6}$ = 2.0 cps.

Anal. Calcd for $C_8H_8O_3$: C, 63.15; H, 5.30. Found: C, 63.15; H, 5.20.

By elution with ether, 300 mg (15%) of 5-chlorotropolone methyl ether (I), mp 123°, was recovered.

Pyrolysis of 6-Chloro-7-methoxy-$\Delta^{3,6}$-bicyclo[3.2.0]heptadien-2-one (II).—A solution of 170 mg (1 mmole) of II in 3 ml of benzene was dropped (1 drop/2 sec) into a Pyrex helix packed, vertical column (0.8 cm × 13 cm) preheated at 430°. During the pyrolysis, a stream of nitrogen was passed through the column (1 bubble/4 sec) to sweep products out. The pyrolysate was collected in a long-neck flask immersed in an ice–salt bath. The column was washed with benzene and the combined solution of the pyrolysate and the washing was concentrated giving 150 mg of a brown oil. The oil was dissolved in benzene and the solution was passed through an alumina column (activity III, 8 g). Evaporation of the eluted ether solution afforded 60 mg

(14) P. E. Eaton, *J. Am. Chem. Soc.*, **84**, 2344, 2454 (1962).
(15) E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *ibid.*, **86**, 5570 (1964).
(16) T. Matsuura and K. Ogura, *ibid.*, **88**, 2602 (1966).
(17) G. Just and C. C. Leznoff, *Can. J. Chem.*, **42**, 79 (1964).
(18) O. L. Chapman, *J. Am. Chem. Soc.*, **85**, 2014 (1963).

(53%) of brown crystals, mp 90–95°, which, on recrystallization from benzene–cyclohexane (1:9), afforded 30 mg of 4-chloro-3-methoxytropone (VI) as yellowish plates: mp 99°; λ_{max}^{MeOH} mμ (log ε) 226 (4.48), 245 (4.57), 254 (4.56), 263 (4.33), 315 (4.02), 327 (4.03), 360 (3.78), and 377 (3.56);[11] ν_{max}^{KBr} 1626, 1595, 1562, 844, and 702 cm^{-1}; nmr, τ 6.10 (C_3OCH_3, s, 3 H), 2.57–3.55 (C_2, C_{5-7}H, m, 4 H).

Anal. Calcd for $C_8H_7O_2Cl$: C, 56.33; H, 4.11. Found: C, 56.63; H, 4.25.

Pyrolysis of 6-Chloro-3-methoxy-Δ^{3,6}-bicyclo[3.2.0]heptadien-2-one (III).—A solution of 180 mg (1.1 mmole) of III dissolved in 3 ml of benzene was pyrolyzed in the same manner as mentioned for II. The pyrolysate was evaporated to give 160 mg of dark brown crystals, mp 102–110°, which, on recrystallization from cyclohexane, afforded 135 mg (75%) of colorless needles, mp 123°. These were confirmed to be identical with 5-chlorotropolone methyl ether (I) by the mixture melting point determination and the comparison of the infrared spectrum.

Hydrolysis of 6-Chloro-7-methoxy-Δ^{3,6}-bicyclo[3.2.0]heptadien-2-one (II) with Acid.—A solution of 100 mg (0.6 mmole) of II dissolved in 3 ml of methanol and 2 ml of 1 *N* hydrochloric acid was refluxed in a water bath for 2 hr. After methanol had been evaporated, a residue was added to 10 ml of water, neutralized with sodium carbonate, and extracted with chloroform. The chloroform extract was washed with water, dried over sodium sulfate, and evaporated to give 85 mg (75%) of a brownish yellow oil. This oil was dissolved in benzene and petroleum ether (1:1) which was passed through an alumina column (activity III, 3 g). Evaporation of the eluted benzene solution afforded 65 mg (59%) of methyl 4-keto-2-cyclopentenylchloroacetate (V) as a pale yellow oil which distilled under 3 mm by heating in an oil bath at 110–115°: λ_{max}^{MeOH} 270 and 214 mμ; ν_{max}^{oil} 1739 (ester), 1718 cm^{-1} (cyclopentenone); nmr, τ 6.1–6.5 (C_1H, m, 1 H), 2.51 (C_2H, q, 1 H), 3.68 (C_3H, q, 1 H), 7.2–7.6 (C_5H, m, 2 H), 5.53 (side-chain H, d, 1 H), and 6.20 ($COOCH_3$, s, 3 H) with $J_{1,2} = J_{1,3} = 2.4$, $J_{1,6} = J_{2,3} = 6.6$ cps.

Anal. Calcd for $C_8H_9O_3Cl$: C, 49.73; H, 5.02. Found: C, 50.09; H, 4.81.

Treatment of 6-Chloro-3-methoxy-Δ^{3,6}-bicyclo[3.2.0]heptadien-2-one (III) with Dilute Acid.—A solution of 100 mg (0.6 mmole) of III in 3 ml of methanol and 2 ml of 1 *N* hydrochloric acid was refluxed for 2 hr and then treated in the same manner as in the hydrolysis of II with acid. Thus, 85 mg (85%) of the starting material III was recovered as colorless needles, mp 65°.

Hyrogenation of Methyl 4-Keto-2-cyclopentenylidenacetate (IV). A.—A solution of 30 mg (0.2 mmole) of IV in 5 ml of methanol was hydrogenated over 20 mg of 10% Pd–C when 9 ml (0.4 mmole) of hydrogen was consumed. After Pd–C had been removed by filtration, the filtrate was evaporated to give 18 mg (60%) of a pale yellow oil VII, ν_{max}^{oil} 1737 cm^{-1}. To a solution of the oil dissolved in 1 ml of methanol, a methanolic solution of 2,4-dinitrophenylhydrazine containing sulfuric acid was added and the resulting solution was allowed to stand at room temperature. Thus, 15 mg of 2,4-dinitrophenylhydrazone of VII were obtained as yellow-orange crystals, mp 130–133°, λ_{max}^{MeOH} 362 mμ, which were proved to be identical with authentic sample, mp 133°,[5] by mixture melting point determination.

B.—Hydrogenation of a solution of 60 mg (0.4 mmole) of IV in 5 ml of methanol was carried out in the presence of 40 mg of 10% Pd–C. In this case, it was interrupted after 9 ml (0.4 mmole) of hydrogen had been consumed. After removal of the catalyst, evaporation of methanol from the filtrate afforded 50 mg of a brownish oil which by the usual manner gave 2,4-dinitrophenylhydrazone as red crystals: mp 135°, λ_{max}^{MeOH} 375 mμ. The crystals were found to be identical with 2,4-dinitrophenylhydrazone of VIII, mp 135°,[5] by mixture melting point determination and comparison of the infrared spectra.

Preparation of 6-Chloro-2-hydroxy-Δ^{6}-bicyclo[3.2.0]hepten-3-one (X).—To a solution of 100 mg (0.6 mmole) of III in 10 ml of methanol, 14 mg (0.6 mmole) of sodium borohydride was added and the reaction mixture was stirred for 24 hr at room temperature. After the solution had been acidified with 1 *N* hydrochloric acid, it was added to 30 ml of water and extracted with chloroform. The extract was washed with water, dried over sodium sulfate, and evaporated to give of 85 mg (65%) of colorless crystals, mp 55–57°. Recrystallization from cyclohexane afforded 55 mg of X as colorless needles: mp 60–61°, ν_{max}^{KBr} 3472 (OH), 1737 cm^{-1} (cyclopentanone).

Anal. Calcd for $C_7H_7O_2Cl$; C, 53.02; H, 4.45. Found: C, 53.28; H, 4.63.

Preparation of 6-Chloro-3-hydroxy-Δ^{3,6}-bicyclo[3.2.0]heptadien-2-one (XI).—A solution of 240 mg (1.2 mmole) of cupric acetate monohydrate dissolved in 4 ml of water was added to a solution of 100 mg (0.6 mmole) of X in 5 ml of methanol. After it had been refluxed on a boiling-water bath for 30 min, the solution was evaporated to give an oil containing a darkly colored precipitate. After removal of the precipitate by filtration, the filtrate was dissolved in chloroform and the solution was washed with water, dried over sodium sulfate, and evaporated to give 86 mg of a brown oil as residue. When the oil distilled under 2 mm by heating in an oil bath at 70–80°, it afforded crystals, which, on recrystallization from benzene–cyclohexane (1:9), gave 45 mg (45%) of XI as colorless crystals: mp 103°; λ_{max}^{MeOH} 271 and 230 mμ (log ε 3.71 and 3.70); ν_{max}^{KBr} 3145 (OH), 1675 cm^{-1} (cyclopentenone); nmr, τ 6.08 (C_1H, t, 1 H), 3.78 (C_3OH, broad s, 1 H), 3.89 (C_4H, d, 1 H), 6.52 (C_5H, q, 1 H), and 3.38 (C_7H, d, 1 H), with $J_{1,5} = J_{1,7} = 3.6$ and $J_{4,5} = 2.0$ cps.

Anal. Calcd for $C_7H_5O_2Cl$: C, 53.70; H, 3.23. Found: C, 54.01; H, 3.28.

Reaction of 6-Chloro-3-hydroxy-Δ^{3,6}-bicyclo[3.2.0]heptadien-2-one (XI) with *o*-Phenylenediamine.—A solution of 20 mg (0.13 mmole) of XI and 30 mg (0.28 mmole) of *o*-phenylenediamine in 3 ml of ethanol was refluxed on a boiling-water bath for 3 hr. Evaporation of ethanol afforded 25 mg (50%) of quinoxaline derivative XII as colorless needles: mp 115°; λ_{max}^{MeOH} 324 and 241 mμ (log ε 4.12 and 4.40); ν_{max}^{KBr} no NH, 1603 and 1323 cm^{-1}.

Anal. Calcd for $C_{13}H_9N_2Cl$: C, 68.27; H, 3.97; N, 12.25. Found: C, 68.39; H, 4.17; N, 12.05.

Pyrolysis of 6-Chloro-3-hydroxy-Δ^{3,6}-bicyclo[3.2.0]heptadien-2-one (XI).—A solution of 30 mg (0.2 mmole) of XI dissolved in 1 ml of benzene was pyrolyzed at 400° by the same manner as that of II. Evaporation of benzene from the combined solution of the pyrolysate and the benzene washing afforded 9 mg (30%) of 5-chlorotropolone, mp 184°, which was identical with an authentic sample XIV.

Irradiation of 5-Chlorotropolone (XIV). A. In Methanol.—As had been described in the irradiation of methyl ether I, a solution of 2 g (12.8 mmoles) of XIV in 300 ml of methanol was irradiated using Toshiba H-400P lamp. After 30 hr of the irradiation, the absorption maxima around 330–380 mμ almost disappeared. The solution was concentrated under reduced pressure affording an oil as residue, which crystallized partly on being digested with 150 ml of ether. The filtration gave 140 mg (7%) of a dimer XVI as colorless needles: mp 235°, (after recrystallization from choloroform); λ_{max}^{MeOH} end absorption at 210 mμ; ν_{max}^{KBr} 3510, 3257 (OH), 1757 cm^{-1} (cyclopentanone).

Anal. Calcd for $C_{14}H_{10}O_4Cl_2$: C, 53.70; H, 3.23; mol wt, 313. Found: C, 53.61; H, 3.03; mol wt, 301 (osmotic method).

The ethereal filtrate was washed with 80 ml of an aqueous solution saturated with sodium hydrogen carbonate. The alkaline washing was acidified by addition of dilute hydrochloric acid and extracted with chloroform. The chloroform extract was washed with water, dried over sodium sulfate, and evaporated to afford 240 mg (12%) of the starting material XIV as pale yellow needles, mp 185° (after recrystallization from chloroform). The ether layer containing neutral materials was washed with water, dried over sodium sulfate, and evaporated to give 1.2 g of a brown oil. This oil was dissolved in 15 ml of benzene and petroleum ether (bp 30°) (1:1) and the solution was passed through an alumina column (activity III, 35 g). Evaporation of the eluted benzene–petroleum ether (1:1) fraction gave 300 mg (15%) of ketal XV as a brownish oil: bp 80–83° (2 mm); λ_{max}^{MeOH} end absorption at 210 mμ; nmr, τ 7.5 (C_1H, m, 1 H), 6.63 and 6.81 (C_2OCH_3, s, each 3 H), 7.55 (C_4H, m, 2 H), 6.7 (C_5H, m, 1 H), and 4.19 (C_7H, d, 1 H) with $J_{1,7} < 1.0$ cps.[19]

Anal. Calcd for $C_9H_{11}O_3Cl$: C, 53.34; H, 5.47. Found: C, 53.22; H, 5.18.

From benzene elution 175 mg (9%) of III as colorless needles, mp 65°, was obtained. Evaporation of eluted benzene–ether (1:1) fraction gave 80 mg (4%) of IV as colorless crystals, mp 75° (after recrystallization from cyclohexane). Evaporation of of eluted methanol solution afforded 250 mg of a brown viscous oil, the composition of which has not been determined.

B. In Ethanol.—The irradiation of XIV in ethanol was carried out in the same manner as the irradiation of I. The work-up procedure was also exactly the same as A. Thus, 2

(19) (a) L. A. Paquette, J. H. Barrett, R. P. Spitz, and R. Pitcher, *J. Am. Chem. Soc.*, **87**, 3417 (1965); (b) L. A. Paquette and J. H. Barrett, *ibid.*, **88**, 1718 (1966).

g (12.8 mmoles) of XIV afforded 200 mg (10%) of the dimer XVI and 300 mg (15%) of the starting material XIV in the step before the chromatography. In the chromatography, the evaporation of eluted benzene–petroleum ether (1:1) fraction gave 300 mg (15%) of a ketal XVIII as colorless needles: mp 72° (after recrystallization from petroleum ether); λ_{max}^{MeOH} end absorption at 210 mμ; ν_{max}^{KBr} 2994, 1754 cm^{-1}; nmr, τ 6.1–8.0 (C_1, C_4, C_5H and CH_2 of ethyl, m, 8 H), 4.18 (C_7H, d, 1 H), 8.70 and 8.81 (CH_3 of ethyl, t, 6 H) with $J_{1,7} < 1.0$[19] and $J_{CH_3CH_2} = 6.6$ cps.

Anal. Calcd for $C_{11}H_{15}O_3Cl$: C, 57.37; H, 6.55. Found: C, 57.71; H, 6.51.

Elution with benzene–ether (9:1) afforded 95 mg (5%) of XIX as colorless needles: mp 42° (after recrystallization from petroleum ether); λ_{max}^{MeOH} 273 mμ (log ε 4.15); ν_{max}^{KBr} 1724 (ester), 1706 (cyclopentenone), 1642 cm^{-1}; nmr, τ 2.20 (C_2H, d, 1 H), 3.43 (C_3H, d, 1 H), 6.59 (C_5H, d, 2 H), 3.98 (side-chain H, t, 1 H), 5.72 and 8.69 (OC_2H_5, q and t, 5 H) with $J_{2,3} = 4.8$, $J_{5,6} = 2.0$, and $J_{CH_3CH_2} = 6.6$ cps.

Anal. Calcd for $C_9H_{10}O_3$: C, 65.05; H, 6.07. Found: C, 64.91; H, 6.39.

From the eluted ether solution, 60 mg (3%) of XI as colorless needles, mp 103°, was obtained (after recrystallization from benzene–cyclohexane, 1:9).

Hydrolysis of 2,2-Dimethoxy- (XV) and 2,2-Diethoxy-6-chloro-Δ^6-bicyclo[3.2.0]hepten-3-one (XVIII). A.—To a mixture of 2 ml of dioxane and 3 ml of 0.5 *N* hydrochloric acid, 150 mg (0.7 mmole) of XV was added and the resulting solution was heated on a boiling-water bath for 1 hr. The solution was poured into 20 ml of water and extracted with ether. The ether extract was washed with water, dried over sodium sulfate, and evaporated to give 125 mg of an orange oil as residue. When 2 ml of benzene was added to the oil, crystals separated and 45 mg of colorless needles, mp 99–102°, was obtained by filtration. Evaporation of the filtrate afforded 80 mg of an orange oil, which, on distillation under 2 mm in an oil bath heated at 70–80°, gave 30 mg of colorless needles, mp 100–102°. The combined crystals, mp 103° (65 mg, 57%, after recrystallization from benzene–cyclohexane), were proved to be identical with XI by the mixture melting point determination and by comparison of the infrared spectra.

B.—Compound XVIII (200 mg, 0.9 mmole) was dissolved in a mixture of 4 ml of 0.5 *N* hydrochloric acid, 2 ml of ethanol, and 0.5 ml of dioxane. The solution was treated in the same manner as described in A, giving 140 mg of pale yellow crystals which, on sublimation at 70–80° under 2 mm, afforded 75 mg (54%) of XI as colorless needles, mp 103° (after recrystallization from benzene–cyclohexane).

Decomposition of the Dimer XVI to the Monomer XI.—To a mixture of each 2 ml of dioxane and water and 1 ml of 5% aqueous sodium hydroxide solution, 50 mg (0.16 mmole) of XVI was dissolved. The resulting solution was allowed to stand overnight at room temperature, during which time it became red. The solution was acidified by addition of dilute hydrochloric acid and extracted with chloroform. The chloroform extract was washed with water, dried over sodium sulfate, and evaporated to give 35 mg (70%) of XI as colorless needles, mp 103° (after recrystallization from benzene–cyclohexane). A solution of 50 mg (0.16 mmole) of XVI dissolved in each 2 ml of dioxane and 6 *N* hydrochloric acid was heated on a boiling-water bath for 2 hr when, however, XVI was recovered in a quantitative yield.

Irradiation of 6-Chloro-3-hydroxy-Δ^{3,6}-bicyclo[3.2.0]heptadien-2-one (XI).—A solution of 30 mg (0.2 mmole) of XI in 6 ml of ethanol was placed in Pyrex tube and flushed with pure nitrogen for 5 min. After the tube had been sealed, the solution was irradiated externally with the Toshiba H-400P lamp placed 20 cm from the tube. After 15 hr of irradiation, the absorption maxima around 271 mμ of XI disappeared. Evaporation of the solution afforded 25 mg (80%) of colorless needles, mp 235° (after recrystallization from chloroform), which were identical with the dimer XVI.

Reaction of the Dimer XVI with Phosgene.—To a solution of 80 mg (0.25 mmole) of XVI in 3 ml of chloroform and 3 ml of pyridine, 8 ml of a toluene solution containing 40% phosgene was added. After the resulting solution had been allowed to stand at room temperature for 2 days, it was added to 30 ml of water to decompose the excess phosgene. The organic layer separated, was washed with water, dried over sodium sulfate, and evaporated under reduced pressure to give 72 mg (85%) of colorless crystals, mp 255°. Recrystallization from benzene–ether (1:5) afforded carbonate XVII as colorless needles: mp 255°; ν_{max}^{KBr} 1869, 1852, and 1789 cm^{-1}; mass spectrum (*m/e*) 340 and 338 (molecular ion).

Anal. Calcd for $C_{15}H_8O_5Cl_2$: C, 53.12; H, 2.38. Found: C, 53.42; H, 2.70.

Methylation of 6-Chloro-3-hydroxy-Δ^{3,6}-bicyclo[3.2.0]heptadien-2-one (XI).—A few bubbles of hydrogen chloride gas were flushed through a solution of 25 mg (0.16 mmole) of XI dissolved in 3 ml of methanol. The resulting solution was allowed to stand in the dark at room temperature for 2 hr. The evaporation of the solution afforded 30 mg of a dark red oil which was dissolved in benzene–cyclohexane (1:2) and the solution was chromatographed on alumina (activity III, 1 g). Evaporation of eluted benzene solution gave 15 mg (35%) of a colorless oil, which was proved to be identical with ketal XV by comparison of the infrared spectrum. Elution with benzene–ether followed by evaporation afforded 10 mg (33%) of colorless crystals, mp 63° (after recrystallization from cyclohexane), which were found to be identical with III by the mixture melting point determination.

Registry No.—I, 13187-38-7; II, 13168-79-1; III, 13168-80-4; IV, 13187-39-8; V, 13168-81-5; VI, 13168-82-6; 2,4-dinitrophenylhydrazone of VII, 13168-83-7; 2,4-dinitrophenylhydrazone of VIII, 13168-84-8; X, 13168-85-9; XI, 13168-86-0; XIV, 3084-17-1; XVa, 13168-87-1; XVIa, 13168-88-2; XVII, 13168-89-3; XVIII, 13168-90-6; XIX, 13296-18-9.

Synthesis of Terminal Perfluoromethylene Olefins

MARTIN H. KAUFMAN, JOHN D. BRAUN, AND JOSÉ G. SHDO

Naval Weapons Center, China Lake, California

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A novel class of potential monomers, 1,1-difluoro-2-di- and -trihalomethylalk-1-enes, has been synthesized. The reaction of lithium aluminum hydride with the highly halogenated olefins $RHC{=}C(CF_2X)_2$, where R is hydrocarbon or hydrogen and X is Cl or F, results in the formation of terminal perfluoromethylene olefins of the general type $CF_2{=}C(CF_2X)R'$, where R′ is hydrocarbon and X is F, Cl, or H. An S_N2' reaction is believed to be involved in the synthesis. Concentration of reagents, mode of addition, and reaction temperature all affect the product yield, which varies from 43 to 84%. For example, a 65% yield of $CF_2{=}C(CF_2H)CH_3$ results from the reaction of 1 mole of $CH_2{=}C(CF_2Cl)_2$ with 2 moles of lithium aluminum hydride in ether at 0°.

Terminal perfluoromethylene olefins of the general type $CF_2{=}C(CF_2X)R'$, where R′ is a hydrocarbon group and X is F, Cl, or H, may offer unique properties when polymerized. With a view toward ultimately studying such polymers, a program of synthesis of the monomeric precursors was undertaken.

Although a number of synthetic routes for the preparation of 1,1-difluoro-2-trifluoromethylprop-1-ene (I)