with argon as the diluent; a significant amount of CHD_2X was produced. Indeed, to account fully for all the observations we are forced to the conclusion that, after the first atom switch, sufficient vibrational excitation is retained in the singly exchanged product so that a second atom switch occasionally occurs prior to de-excitation by collision.

$$C\overset{*}{H}_3X + D_2 \longrightarrow C\overset{*}{H}_2DX + DH$$

$$C\overset{*}{H}_2DX + D_2 \longrightarrow CHD_2X + DH$$
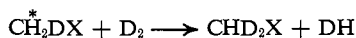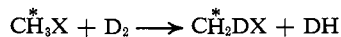
Typical data are given in Table I. At the present time we are in the process of designing and executing quantitative experiments to measure: (1) the relative efficiencies for de-excitation and for exchange by various diluent gases; (2) the temperature dependence of the ratio of de-excitation to exchange rates, in order to obtain some measure of the role of translational energy; (3) the local temperature distributions in the mixing zone; (4) the absolute rates of the reaction by using rapid flow systems; (5) kinetic isotope effects in reactions between $CH_2\overset{*}{D}X$ and HD, and $CD_2\overset{*}{H}X$ and HD; and (6) to look for infrared emission from the reaction zone as the total pressure and fraction of diluent are reduced.

Table I. Typical Product Distribution

Reactants (temp., °C.)[a]	Diluent	Product analysis[b]
CH_2N_2, HBr (25.1)	CD_4	CH_3Br (80), CH_2DBr (12), CHD_2Br (8)
CH_2N_2, HBr (44.5)	D_2	CH_3Br (78), CH_2DBr (19), CHD_2Br (3)
CH_2N_2, DBr [HBr] (45.3)	CH_4	CH_3Br (47), CH_2DBr (40), CHD_2Br (13)
CH_2N_2, DBr [HBr] (19.6)	He	CH_3Br (41), CH_2DBr (44), CHD_2Br (11), CD_3Br (4)
CH_2N_2, DBr [HBr] (−27.5)	CH_4	CH_3Br (52), CH_2DBr (43), CHD_2Br (5)
CH_2N_2, DCl [HCl] (25.0)	Ar	CH_3Cl (15), CH_2DCl (59.4), CHD_2Cl (18), CD_3Cl (7.3)

[a] The brackets indicate impurity present. [b] Per cent yield in parentheses.

Diazold (N-methyl-N-nitroso-p-toluenesulfonamide) was used as the precursor of CH_2N_2, which was generated *in vacuo* by the technique of Dessaux and Durand.[6] It was dried by passing through potassium hydroxide pellets and stored at the required pressure in a 5-cc. bulb. An equal pressure of diluent gas was added at a total pressure of ≈100 mm. The reaction vessel was a 250-cc. bulb with a 1-mm. bore capillary inlet tube leading to its center. The reactor and capillary were surrounded by a dewar to maintain the system at the desired temperature. The bulb was filled to a total pressure of 20 mm. with a 1:10 mixture of hydrogen bromide (or DBr or HCl) and the diluent gas (Ar, CD_4, D_2). Using a constricted inlet, on opening the stopcock, gas flowed into the reaction vessel over a period of about 1 sec. The gases were allowed to mix for 24 hr. before removing a sample for analysis by mass spectrometry. The mass spectral patterns for methyl bromide, methane, and the deuteriomethanes were obtained using authentic samples (and correcting

(6) O. Dessaux and M. Durand, *Bull. soc. chim. France*, 41 (1963).

for impurities). The cracking patterns for the deuteriomethyl bromides were not available; these were computed from the pattern for methyl bromide and the C^{12}/C^{13} isotope ratio. The reaction

$$C\overset{*}{H}_3Br + CD_4 \overset{\nearrow CH_2DBr + CHD_3}{\searrow CD_3Br + CH_3D}$$
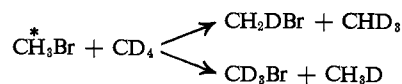
was studied at 25.1°. Product distribution showed that no more than 1% exchange of the bromine atom occurred to give methyl-d_3 bromide but there was about 12% H–D exchange to produce methyl-d_1 bromide.

Diazomethane reacts with deuterium bromide to give methyl-d_1 bromide. However, if the lifetime of the activated molecule is long, further reaction may occur. Using a 1:10 mixture of deuterium bromide in argon at room temperature, mass spectral analysis showed that the products included methyl-d_3 and methyl-d_2 bromide as well as methyl-d_1 bromide. These can only be accounted for by the assumption that there is subsequent reaction of the activated methyl-d_1 bromide with deuterium bromide.

$$CH_2\overset{*}{D}Br + DBr \longrightarrow CHD_2Br + HBr$$

$$CH_2\overset{*}{D}Br + CHD_2Br \longrightarrow CH_3Br + CD_3Br$$
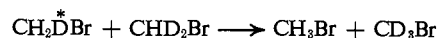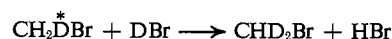
The experiment was repeated using a 24.5:1 mixture of helium and deuterium bromide at room temperature. Since helium is a more efficient deactivator than argon, the percentages of methyl-d_3 and methyl-d_2 bromides were reduced by factors of five and two, respectively, as expected.

S. H. Bauer, David Marshall, Tomas Baer
*Department of Chemistry, Cornell University
Ithaca, New York*

Preparation of the Ketone Tautomer of a Phenol by a Cope Rearrangement[1]

Sir:

It has recently been suggested that steric repulsions between o-t-butyl groups should tend to convert 3,4-di-t-butylphenol to its nonplanar ketonic tautomer.[2] Although the reactions of the phenol and of 3,4-di-t-butylaniline suggested that the tautomeric forms were readily formed, no direct evidence for the presence of the tautomers could be obtained.[2] We now wish to report that the presence of a t-butyl group at C-3 can allow preparation of the ketonic form of a phenol by thermal processes.

Irradiation of 4-allyl-2,6-di-t-butyl-4-methylcyclohexa-2,5-dienone (1)[3] in the manner previously described[4] gave a product whose infrared spectrum (λ_{max} 6.05 and 6.35 μ) and ultraviolet spectrum in methanol [λ_{max} 309 mμ (ϵ 3045)] suggested that it consisted mainly of the

(1) Reactions of Cyclohexadienones. XIV. Part XIII: B. Miller, *J. Am. Chem. Soc.*, 87, 5115 (1965).
(2) A. W. Burgstahler, P. L. Chien, and M. O. Abdel-Rahman, *ibid.*, 86, 5281 (1964).
(3) B. Miller, *J. Org. Chem.*, 30, 1964 (1965).
(4) B. Miller and H. Margulies, *Chem. Commun.*, 314 (1965).
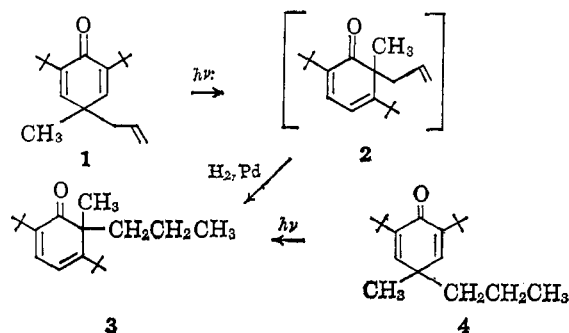
expected conjugated cyclohexadienone 2.[4] The structure assigned to 2 was confirmed by isolation of dienone 3 [b.p. 115–116° (1.0 mm.), λ_{max} 310 mμ (ϵ 3900)] in an over-all 69% yield from 1 by hydrogenation of 2 in benzene using a Pd on CaCO$_3$ catalyst. Irradiation of the cross-conjugated dienone 4 provided an independent synthesis of 3.

Although the identity of 2 as the principal photo-rearrangement product of 1 was established, 2 could not be isolated in a pure state. On attempted chromatography on alumina, silica gel, or Florisil, as well as on a variety of g.l.p.c. columns, 2 underwent a Cope rearrangement to phenol 5. Reaction of 2 with a 1% solution of sulfuric acid in acetic acid also converted it, essentially instantaneously, to 5, while reaction of 2 with acetic anhydride gave a 59% yield (based on 1) of the acetate 6 [b.p. 137–138° (0.1 mm.)], which could also be obtained by acetylation of 5.
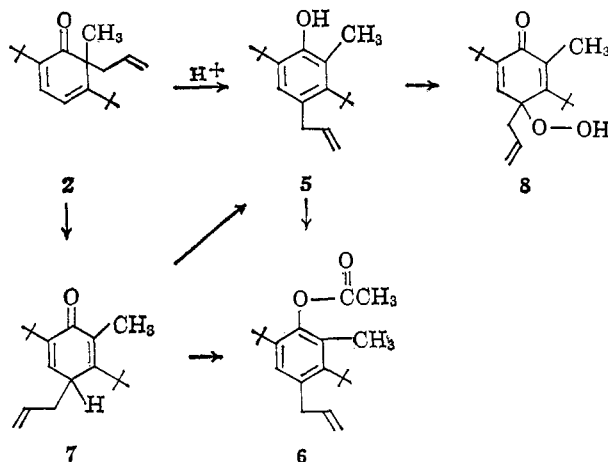
Although its acetate was stable and easily isolated, phenol 5 could be isolated and stored only when extreme care was taken to avoid contact with oxygen. On exposure of 5 to air for even a few minutes, crystals of the keto hydroperoxide 8 [m.p. 123–124.5°, λ_{max} (MeOH) 242 mμ, λ_{max} 3.00 and 6.18 μ] began to form.

When 2 is heated to 110° for 5 min. or to 70° for 1 hr., its characteristic absorption maxima at 310 mμ and 6.35 μ disappear. The product, however, retains an intense conjugated carbonyl peak at 6.17 μ and an ultraviolet band (in methanol) at 244 mμ (ϵ 9400) typical of cross-conjugated cyclohexadienones. No hydroxyl peak appears in its infrared spectrum.

No changes occur in the spectra of the ketonic product when it is kept at room temperature for 5 months. After heating to 220°, however, or on attempted chromatography on alumina, silica gel, or Florisil, only phenol 5 can be isolated from the product. Com-

Right column:

pound 5 is also obtained instantly by dissolving the product in 1% sulfuric acid in acetic acid or *in 1 N sodium methoxide in methanol*.[5] Reaction of the crude ketone with sulfuric acid in acetic anhydride gave 6 in 62% yield.

The properties of the product of thermal rearrangement of 2 require its formulation as the cross-conjugated cyclohexadienone 7.[6]

The thermal stability of 7,[7] as well as the remarkably rapid autoxidation of 5, may be attributed to steric interference between the adjacent allyl and *t*-butyl groups in 5. Since this interference is decreased when 5 is converted to cyclohexadienones, the rate of aromatization of 7 to 5 under neutral conditions is much lower than usual, and the rate of oxidation of 5 much higher. As the work of Burgstahler, *et al.*,[2] indicated, however, once the phenolic form is obtained no detectable amounts of dienone remain in equilibrium with it.

The elemental analyses and n.m.r. spectra of all new compounds agree with the assigned structures.

(5) In contrast, 2 is stable in basic solutions.

(6) Formations of ketonic tautomers of phenols by thermal rearrangements have long been postulated as intermediate steps in the *ortho* and *para* Claisen rearrangements. It has been assumed, however, that aromatization of the dienones would be much faster than allylic rearrangements. See S. J. Rhoads in "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., pp. 660–677.

(7) Thermal rearrangements of other 6-allylcyclohexa-2,4-dienones under similar conditions give only phenols, with no indications of the presence of the ketonic tautomers; *e.g.*, D. Y. Curtin and R. J. Crawford, *J. Am. Chem. Soc.*, 79, 3156 (1957).

Bernard Miller

Chemical Research and Development Laboratories
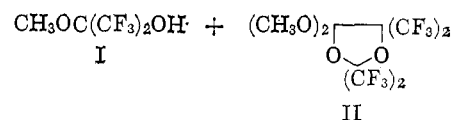Agricultural Division, American Cyanamid Company
Princeton, New Jersey
Received October 5, 1965

Cyclic Ethers from Hexafluoroacetone

Sir:

We wish to report several new reactions of hexafluoroacetone which may involve dialkoxycarbene[1] and "silene"[2] intermediates.

Hexafluoroacetone reacts with trimethyl orthoformate at 150°, in a 3:1 mole ratio, to give the hemiketal I[3] and 2,2,4,4-tetrakis(trifluoromethyl)-5,5-dimethoxy-1,3-dioxolane (II) [79.4%, b.p. 161° (760 mm.), b.p. $(CH_3O)_3CH + 3(CF_3)_2C=O \longrightarrow$

$$CH_3OC(CF_3)_2OH + (CH_3O)_2 \underset{O \diagdown O}{\overset{}{\boxed{}}}(CF_3)_2$$
$$\underset{I}{} \qquad \underset{(CF_3)_2}{}$$
$$II$$

−1 to 0°, $n^{25}D$ 1.3225].[4] The reaction proceeds readily

(1) Dialkoxycarbenes have been proposed as intermediates in several reactions recently: (a) E. J. Corey and R. A. E. Winter, *J. Am. Chem. Soc.*, 85, 2677 (1963); (b) D. M. Lemal, *Tetrahedron Letters*, 11, 579 (1964); (c) J. Hine, "Divalent Carbon," The Ronald Press, New York, N. Y., 1964, p. 70.

(2) (a) P. S. Skell and E. J. Goldstein, *J. Am. Chem. Soc.*, 86, 1442 (1964); (b) O. M. Nefedov and M. N. Manakov, *Angew. Chem.*, 76, 270 (1964).

(3) C. Woolf, Abstracts of Papers Presented at the 132nd National Meeting of the American Chemical Society, New York, N. Y., Sept.1957, p. 23M.

(4) Satisfactory elemental analyses and infrared and proton n.m.r. spectra for all of the new compounds were obtained. The fluorine n.m.r. and mass spectra of compounds II and X are in agreement with the proposed structures.