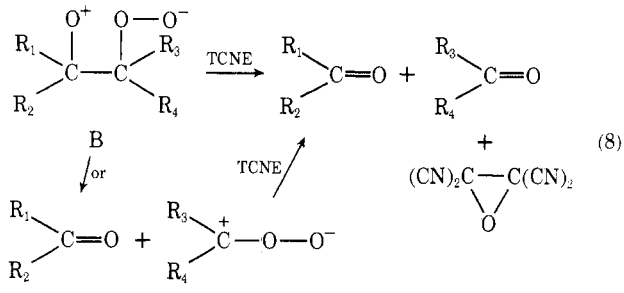
unusual stability or have been well characterized.[21-23] The major product isolated from 2 was fluorenone and that from 3 was the corresponding epoxide. The results indicate that dioxetanes were not formed in appreciable amounts in these two reactions. The formation of epoxide from hindered olefins has been noted before,[24] and 3 is apparently another such case. 3,3-Pentamethylene-4-methyl-1,2-dioxetane, the dioxetane derived from 4, is known to be quite stable at −20° but will decompose with chemiluminescence at higher temperatures.[24] After 4 was ozonated in the presence of TCNE at −78°, the reaction mixture was quickly fractionated at −20°. Acetaldehyde and cyclohexanone, the expected decomposition products of the dioxetane, were isolated in separate fractions of the distillate, indicating that the dioxetane was not the intermediate in the formation of products. Therefore, carbonyl compounds formed in the ozonation of olefins in the presence of TCNE may be derived from the reduction of zwitterion intermediate B during the ozonation (reaction 8).



(8)

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References and Notes

(1) R. Criegee, *Rec. Chem. Progr.*, **18**, 111 (1957).
(2) P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958).
(3) R. W. Murray, *Accounts Chem. Res.*, **1**, 313 (1968).
(4) T. J. Jacobs, *J. Amer. Chem. Soc.*, **58**, 2272 (1936).
(5) R. Criegee and M. Lederer, *Justus Liebigs Ann. Chem.*, **583**, 29 (1953).
(6) E. Dalliwigk, H. Paillard, and E. Briner, *Helv. Chim. Acta*, **35**, 1377 (1952).
(7) H. Paillard and C. Wieland, *Helv. Chim. Acta*, **21**, 1356 (1938).
(8) P. S. Bailey, Y. Chang, and W. W. L. Kwie, *J. Org. Chem.*, **27**, 1198 (1962).
(9) W. B. DeMore and C. Lin, *J. Org. Chem.*, **38**, 984 (1973).
(10) R. Criegee and P. Güunther, *Chem. Ber.*, **96**, 1564 (1963).
(11) P. Story, E. A. Whited, and J. A. Alford, *J. Amer. Chem. Soc.*, **94**, 2143 (1972); see, however, footnotes 22 and 23.
(12) R. C. Fuson and H. D. Porter, *J. Amer. Chem. Soc.*, **70**, 895 (1948).
(13) H. W. Geluk, *Synthesis*, 652 (1970).
(14) L. I. Smith, F. L. Greenwood, and O. Hudrlick, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 673.
(15) H Wynberg, E. Boelema, J. H. Wieringa, and J. Strating, *Tetrahedron Lett.*, 3613 (1970).
(16) E. Grovenstein, Jr., W. Postman, and J. W. Taylor, *J. Org. Chem.*, **25**, 68 (1960).
(17) G. Ponzio and M. Torres, *Gazz. Chim. Ital.*, **59**, 478 (1929).
(18) H. Bloch, H. Lehr, H. Erlenmeyer, and K. Nolger, *Helv. Chim. Acta*, **28**, 1412 (1945).
(19) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, San Francisco, Calif., 1962, p 45.
(20) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "Systematic Identification of Organic Compounds," 4th ed, Wiley, New York, N. Y., 1956, pp 285–286.
(21) J. H. Wieringa, J. Strating, H. Wynberg, and W. Adam, *Tetrahedron Lett.*, 169 (1972).
(22) N. C. Yang and R. V. Carr, *Tetrahedron Lett.*, 5143 (1972). Since the publication of this paper, we were unable to reproduce the result reported consistently. A correction has been sent to the Editor of *Tetrahedron Letters*. Similar experiences were also noted in the laboratories of Professors R. Criegee and E. H. White. The authors appreciate their private communications about their findings.
(23) K. R. Kopecky, P. A. Lockwood, J. E. Filbey, and R. W. Reid, *Can. J. Chem.*, **51**, 468 (1973).
(24) (a) P. D. Bartlett and M. Stiles, *J. Amer. Chem. Soc.*, **77**, 2806 (1955); (b) R. Criegee, *Advan. Chem. Ser.*, **1**, 133 (1959); (c) R. W. Murray, R. D. Youssefyeh, and P. R. Story, *J. Amer. Chem. Soc.*, **89**, 2429 (1967); (d) P. S. Bailey and A. G. Lane, *ibid.*, **89**, 4473 (1967).

Bromination of 2-Phenyl-2-methallylindan-1,3-dione

Alexander L. Johnson* and Fred Davidson

Contribution No. 2095 from the Central Research Department, E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware 19898

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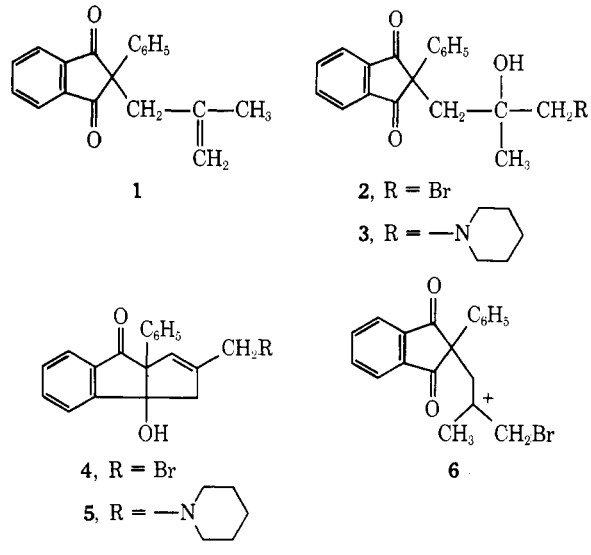
Aren, Zitsmanis, and Valter[1] have claimed that the bromination of 2-phenyl-2-methallylindan-1,3-dione (1) in glacial acetic acid produces the tricyclic primary bromide 4 and that displacement of the bromine in 4 by piperidine gives the tricyclic amine 5. Their structure proof was based upon incomplete elemental analyses, integrated carbonyl absorption in the infrared, and ultraviolet spectra.

We have repeated their experiments and find that the correct structures of the bromination product of 1 and its piperidine displacement product are 2 and 3, respectively.



Our results differ from those reported[1] in the following respects. (1) The correct molecular formulas of 2 and 3 were established by mass spectrum and complete elemental analysis; the difference of a molecule of water from the earlier structures 4 and 5 would not be evident from the incomplete analyses previously reported. (2) The nmr spectra of the products are inconsistent with structures 4 and 5 because the aliphatic regions show only methylene and methyl protons and no vinyl or allylic protons. The exocyclic NCH_2 group in 3 appears as an AB quartet in the nmr, indicating nonequivalence of the two protons.[2] Models indicate that hydrogen bonding between the piperidine nitrogen and the tertiary hydroxyl group would be possible. (3) The presence of the CH_2Br group in 2 is established by its nmr position,[3] by the loss of CH_2Br in the mass spectrum, and by a strong band at 1250 cm^{-1} in the infrared.[4] The formation of product 2 can be accounted for through the intermediacy of carbonium ion 6 during bromination, and the displacement with piperidine to form 3 probably involves the assistance of the hydroxyl group in 2.

Experimental Section[5]

2-Phenyl-2-methallylindan-1,3-dione (1) was prepared according to the literature[1,6] in 82% yield after recrystallization from EtOH: mp 97–98°; ν_{max} ($CHCl_3$) 1740, 1705, and 1240 cm^{-1}; λ_{max} 342 nm (ϵ 166), 302 (630), and 225 (46,500); ^1H nmr δ 8.08–7.68 (m, C_6H_4), 7.55–7.12 (m, C_6H_5), 4.67 (s, vinyl CH_2), 3.03 (s, allylic CH_2), and 1.52 ppm (s, CH_3); mass spectrum *m/e* 276 (M^+), 261 [$(M - CH_3)^+$], 233 [$(M - C_3H_7)^+$ and $(M - CH_3 -$

CO)$^+$], 221 [(M − C_4H_7)$^+$], and 165 [(221 − 2CO)$^+$]. *Anal.* Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.64; H, 5.71.

2-Phenyl-2-(2-hydroxy-2-methyl-3-bromopropyl)indan-1,3-dione (2). The addition of 5.80 g (36.2 mmol) of Br_2 in 10 ml of HOAc to a suspension of 1 (10.0 g, 36.2 mmol) in 50 ml of HOAc was accompanied by decoloration, dissolution of the solid, a mild exotherm, and the evolution of HBr. After 1.5 hr at 25°, the mixture was poured into 250 ml of H_2O, and the crude solid thus obtained was recrystallized from 50 ml of EtOH, yield 10.34 g (29.0 mmol, 80%) of **2** as colorless crystals:[7] mp 143–145° dec; ν_{max} (KBr) 3400, 1705, 1265, 1240 cm^{-1}; λ_{max} 332 nm (ϵ 329), 287 (1510), and 248 (11,900); ^{1}H nmr δ 8.00–7.50 (m, C_6H_4), 7.33–7.17 (m, C_6H_5), 3.73 (s, CH_2Br), 2.87 (s, CH_2), and 1.27 ppm (s, CH_3); mass spectrum *m/e* 444 and 446 after silylation [(M + TMS)$^+$], 372 and 374 (M$^+$), 293 [(M − Br)$^+$], 279 [(M − CH_2Br)$^+$], and 275 [(293 − H_2O)$^+$]. *Anal.* Calcd for $C_{19}H_{17}BrO_3$: C, 61.14; H, 4.59; Br, 21.41; *m/e* 372.0361. Found: C, 61.47; H, 4.26; Br, 21.33; *m/e* 372.0363.

2-Phenyl-2-[2-hydroxy-2-methyl-3-(1-piperidinyl)propyl]-indan-1,3-dione (3). A mixture of bromo compound **2** (3.57 g, 10 mmol), DMF (5 ml), and piperidine (2.1 g, 25 mmol) was left at 25° for 4 days.[1] The crude product, isolated by dilution of the mixture with H_2O, was recrystallized from 15 ml of EtOH, yield 3.08 g (8.2 mmol, 82%) of colorless needles[8] of **3**: mp 130–131°; ν_{max} ($CHCl_3$) 1720 cm^{-1}; λ_{max} 331 nm (ϵ 405), 293 (1610), and 247 (11,600); ^{1}H nmr δ 8.58 (broad, OH), 8.03–7.40 (m, C_6H_4), 7.20 (s, C_6H_5), 3.13–2.52 (AB, exocyclic NCH_2), 2.65 (m, ring NCH_2), 2.40 (s, acyclic CH_2), 1.40 (m, ring CH_2), and 1.15 ppm (s, CH_3); mass spectrum *m/e* 377 (M$^+$) and 98 [($C_6H_{12}N$)$^+$, base peak]. *Anal.* Calcd for $C_{24}H_{27}NO_3$: C, 76.36; H, 7.21; N, 3.71; *m/e* 377.1989. Found: C, 76.30; H, 6.98; N, 3.60; *m/e* 377.2013.

Registry No.—**1**, 26151-51-9; **2**, 51270-74-7; **3**, 51270-75-8; piperidine, 110-89-4.

References and Notes

(1) A. K. Aren, A. Kh. Zitsmanis, and S. P. Valter, *J. Org. Chem. USSR, Engl. Transl.*, **5**, 2090 (1969).
(2) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Oxford, 1969, pp 372–374, discuss the CH_AH_BUCXYZ system in some detail.
(3) *Cf.* Sadtler Spectrum No. 9168M ($BrCH_2CH_2OH$), Sadtler Research Laboratories, Inc., Philadelphia, Pa.
(4) R. M. Silverstein and G. C. Basler, "Spectrometric Identification of Organic Compounds," 2nd ed, Wiley, New York, N. Y., 1967, p 102.
(5) Melting points were uncorrected; ir spectra were determined on a Perkin-Elmer 621 instrument, uv spectra in EtOH on a Carey 14 instrument, nmr spectra in $CDCl_3$ (*vs.* TMS) on a Varian Associates A-60 instrument, and mass spectra on a CEC 110B high-resolution instrument by direct injection.
(6) Literature values for **1** are mp 100–101°; ν_{max} (Nujol) 1744 and 1710 cm^{-1}; λ_{max} (EtOH) 336 nm (ϵ 2000) and 226 (3600).
(7) Literature values for **4** are mp 141–142°; ν_{max} (Nujol) 3430 and 1712 cm^{-1}; λ_{max} (EtOH) 291 nm (ϵ 900) and 249 (11,500); formula $C_{19}H_{15}BrO_2$.
(8) Liteeature values for **5** are mp 138–139°; ν_{max} (Nujol) 1708 cm^{-1}; λ_{max} (EtOH) 294^s nm (ϵ 1700) and 248 (11,800); formula $C_{24}H_{25}NO_2$.

Halogenation of Carbonyl Compounds *via* Silyl Enol Ethers[1]

Robert H. Reuss[1b] and Alfred Hassner*

Department of Chemistry, University of Colorado, Boulder, Colorado 80302

Received October 15, 1973

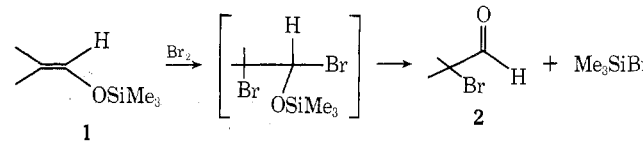
In connection with other studies we needed several α-bromo aldehydes and, since such compounds are prepared by bromination of aldehydes only with difficulty,[2] we sought an alternative method. Several recent syntheses have been described,[3] but they represent homologation reactions. Vinyl acetates and enamines of the corresponding aldehyde have also been used to prepare the desired compounds.[4] In line with our interest in electrophilic additions to olefins,[5] it occurred to us that bromination of silyl enol ethers (**1**) followed by spontaneous β cleavage of volatile trimethylbromosilane[6] should afford the desired product (**2**). Since the silyl enol ethers are readily generated in high yield,[7] this method would provide a simple route to synthetically useful[8] α-bromo aldehydes.

Table I
Synthesis of α-Haloaldehydes from the Corresponding Aldehyde *via* Silyl Enol Ethers

$$R_1R_2CHCHO \xrightarrow[Et_3N]{Me_3SiCl} R_1R_2C{=}CHOTMS \xrightarrow{X_2} \underset{R_1R_2CCHO\ (X = Br, Cl)}{\overset{X}{|}}$$

Entry	X_2	R_1	R_2	% yield of **2**
1	Br_2	$PhCH_2$	H	77
2	Br_2	Ph	Me	75
3	Br_2	C_6H_{17}	H	94
4	Br_2	$-CH_2CH_2CH{=}CHCH_2-$		57[a]
5	Br_2	$-CH_2CH_2CH_2\underset{CO_2C_2H_5}{\overset{}{|}}CHCH_2-$		62
6	Br_2	Me	Me	51[b]
7	Cl_2	$PhCH_2$	H	95
8	Br_2	$(CH_2)_4CN$	H	42[c]

[a] Some bromination of the double bond observed in the crude product. [b] Low yield of distilled product due to high volatility; reaction performed in Et_2O. [c] Ca. 10% yield of an unknown aldehyde was also obtained.



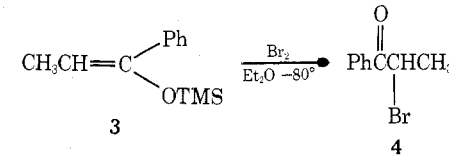
1 2

Our expectations were confirmed as shown in Table I. The silyl enol ethers were prepared according to the method of House[7] and were found to react instantaneously with 1 equiv of bromine in carbon tetrachloride at room temperature. The product was isolated by evaporating the solvent and trimethylbromosilane (bp 85°) and distilling the aldehyde. The technique is applicable to a wide range of aldehydes as well as to ketones. Particularly noteworthy is the bromination at the α position of the aldehyde in the presence of a double bond (see Table I) and an ester function (entry 5). α-Chloro aldehydes are obtained by using chlorine[9] in place of bromine (entry 7), although neither iodine nor iodine monochloride was reactive.

A limitation of the method is indicated by the fact that the silyl enol ethers of crotonaldehyde, 6-ketoheptanal (aldehyde silyl enol ether), and citronellal afforded polymeric products even when bromination was carried out at −80°.

While bromination of ketones generally presents no major problem,[2] various synthetic procedures have been devised for specific bromination where more than one regioisomer is possible.[2,10] Bromination of silyl enol ethers enables regiospecific halogen introduction since methods are available[7] for the synthesis or isolation of silyl enol ether regioisomers. A recent communication describes the bromination of lithium enolates, derived from silyl enol ethers, to afford α-bromo ketones.[11] However, we have found that preparation of the enolate is unnecessary.

The use of silyl enol ethers for the bromination of ketones is demonstrated by the quantitative conversion of silyl enol ether **3** to α-bromopropiophenone (**4**)[12] and the



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