125° (5 mm), which solidified on standing: nmr (CCl_4) δ 2.41 and 2.42 (2 singlets, 3 each, $-SCH_3$ and $COCH_3$), 7.08 (d, 1, 3-H), 7.40 (d, 1, $J_{3,5}$ = 0.9 Hz, 5-H).

Anal. Calcd for $C_7H_8O_2S$: C, 53.82; H, 5.16; S, 20.53. Found: C, 53.66; H, 5.26; S, 20.37.

1-(4-Methylthio-2-furyl)ethanol.—To a stirred solution of 4-methylthio-2-acetylfuran (7.81 g, 0.05 mol) in 75 ml of anhydrous methanol, placed in an ice water bath, was added sodium borohydride (1.41 g, 0.0374 mol) at a rate such that the temperature was kept below 20°. The mixture was stirred for 5 hr and worked up in the usual fashion to give 7.7 g (97%) of 1-(4-methylthio-2-furyl)ethanol as a pale yellow liquid: nmr (CCl_4) δ 1.40 (d, 3, CH_3), 2.27 (s, 3, SCH_3), δ 3.60 (s, 1, OH), 4.64 (q, 1, $J_{CH_3,H}$ = 6.5 Hz, CHOH), 6.11 (d, 1, 3-H), 7.13 (d, 1, $J_{3,5}$ = 0.9 Hz, 5-H).

1-(4-Methylthio-2-furyl)ethyl *p*-nitrobenzoate (1) was prepared from 1-(4-methylthio-2-furyl)ethanol (7.60 g, 0.048 mol) in 50 ml of pyridine, cooled in an ice water bath, and *p*-nitrobenzoyl chloride (8.907 g, 0.048 mol). After work-up in the usual fashion, 1-(4-methylthio-2-furyl)ethyl *p*-nitrobenzoate (8.0 g, 54%) was obtained as yellow crystals from hexane: mp 46°; nmr ($CDCl_3$) δ 1.80 (d, 3, $J_{CH_3,H}$ = 6.5 Hz, CH_3), 2.42 (s, 3, SCH_3), 6.26 (q, 1, CHOPNB), 6.53 (d, 1, $J_{3,5}$ = 0.85 Hz, 3-H), 7.38 (d, 1, 5-H).

Anal. Calcd for $C_{14}H_{13}NO_5S$: C, 54.71; H, 4.26; N, 4.56; S, 10.43. Found: C, 54.46; H, 4.08; N, 4.32; S, 10.28.

Kinetic Procedures.—Kinetic procedures have been described previously.[3-5]

Registry No.—4-Methylthio-2-acetylfuran, 934-64-5; 1-(4-methylthio-2-furyl)ethanol, 34858-77-0.

The Reaction of Some Acyclic α,β-Unsaturated Ketone Systems with *N*-Bromosuccinimide

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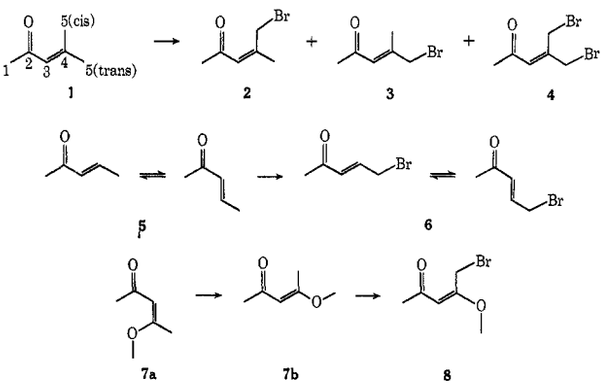
A preliminary communication by Buu-Hoi[1] in 1946 reported that mesityl oxide and 3-penten-2-one underwent bromination by *N*-bromosuccinimide (NBS) to give α-bromo ketones rather than allyl bromides; the unstable products of reaction were characterized purely on the basis of gross chemical reactivity such as ease of reaction with primary aromatic amines. These results were regarded with reservation by Djerassi,[2] who noted the possibility of allylic rearrangement of the primary products of reaction: *initial* formation of α-bromo ketones from acyclic α,β-unsaturated ketones would have belied experience to date, which indicated that substitution allylic to the olefinic bond was the general rule for cyclic systems. Later, the work of DePuy and coworkers[3] established unequivocally that 4-bromo-2-cyclopentenone was the exclusive product of reaction of 2-cyclopentenone with NBS under radical-promoting conditions.

Recent investigations of possible synthetic routes to models of the tetracycline A and B rings[4] have demonstrated that selective substitution allylic to the olefinic bond is achieved by similar bromination of cyclohex-2-enones and 3-methoxycyclohex-2-enones. It was noted also that the liquid 4-bromo-2-cyclohexenone slowly isomerized to roughly a 1:1 mixture of 6-bromo and 4-bromo ketones. In order to determine the effect of the greater conformational freedom of acyclic α,β-unsaturated ketones upon the pattern of bromine substitution and on the tendency of bromination products toward allylic rearrangement, mesityl oxide (**1**), 3-penten-2-one (**5**), and the methyl enol ethers (**7**) of acetylacetone[5] were brominated using NBS (Scheme I),

SCHEME I



and the products were subjected to detailed nmr spectroscopic analysis.

No product of bromine substitution α to carbonyl could be detected from the reaction of any of these four substrates, bromination allylic to the olefinic bond being the exclusive mode of substitution. *No evidence of allylic rearrangement could be perceived in the case of these acyclic allylic bromides.* All products of bromination are obviously predominantly in the s-cis conformation.

Assignment of both configuration and conformation was possible from a consideration of either benzene-induced solvent shifts (Table I) or $Eu(thd)_3$[6]-induced chemical shift data applying the carbonyl-plane rule in the former case[5] and assuming complexation at carbonyl oxygen in the latter.[7]

Mesityl oxide (**1**) reacted with 1 molar equiv of NBS to yield a mixture of approximately equal proportions of the isomeric allylic monobromides **2** and **3** (36 and 44%,[8] respectively), contaminated with an appreciable amount of the allylic dibromide **4** (20%[8]); **1** was readily and quantitatively converted to **4** by reaction with 2 molar equiv of NBS. Table II gives Δ_{Eu} values for **2**–**8**.

It is evident that the relative percentage of **2** and **3** represent an equilibrium ratio. The product mixture could be separated by thin layer chromatography (tlc) into three distinct bands corresponding to **2**, **3**, and **4**. However, isomerization of **2** and **3** was so rapid that the fractions obtained by elution of the chromatograms were invariably mixtures of the two compounds, although significantly enriched in the respective isomers (approximately 75 and 40%[8] of **3**). The equilibrium

(1) N. P. Buu-Hoi, *Experientia*, **2**, 310 (1946).
(2) C. Djerassi, *Chem. Rev.*, **43**, 271 (1948).
(3) C. H. DePuy, M. Isaks, K. L. Eilers, and G. F. Morris, *J. Org. Chem.*, **29**, 3503 (1964); C. H. DePuy, C. E. Lyons, and L. B. Rodewald, *J. Chem. Eng. Data*, **11**, 102 (1966).
(4) D. V. C. Awang, A. Vincent, W. L. Wilson, and H. W. Avdovich, *Can. J. Chem.*, **50**, 104 (1972).
(5) D. V. C. Awang, *ibid.*, **49**, 2672 (1971).
(6) Tris(2,2,6,6-tetramethyl-3,5-heptanedionato)europium(III), also referred to as tris(dipivalomethanato)europium(III), $Eu(DPM)_3$.
(7) H. Hart and G. M. Love, *Tetrahedron Lett.*, 625 (1971)
(8) Determined by integration of the areas of nmr signal peaks.

TABLE I

NMR CHEMICAL SHIFT[a,b] AND BENZENE SHIFT DATA FOR SUBSTRATES AND PRODUCTS OF BROMINATION

Compd		C_1H	C_3H	C_4H	cis[b] C_5H	trans[b] C_5H	OCH
1	CCl_4	2.07 (3 H)	6.02 (m, 1 H)		2.08 (d, 3 H) ($J_{3,5}$ = 1.5 Hz)	1.87 (d, 3 H) ($J_{3,5}$ = 1.5 Hz)	
	$\Delta_{C_6H_6}^{CCl_4}$	+0.22	+0.23		−0.02	+0.35	
2	CCl_4	2.13 (3 H)	6.06 (m, 1 H)		4.47 (2 H)	2.00 (d, 3 H) ($J_{3,5}$ = 1.8 Hz)	
	$\Delta_{C_6H_6}^{CCl_4}$	+0.23	+0.48		+0.13	+0.37	
3	CCl_4	2.13 (3 H)	6.25 (m, 1 H)		2.18 (d, 3 H) ($J_{3,5}$ = 1.8 Hz)	3.87 (2 H)	
	$\Delta_{C_6H_6}^{CCl_4}$	+0.23	+0.50		+0.13	+0.50	
4	CCl_4	2.22 (3 H)	6.30 (m, 1 H)		4.63 (2 H)	4.12 (2 H)	
	$\Delta_{C_6H_6}^{CCl_4}$	+0.32	+0.52		+0.11	+0.45	
5	CCl_4	2.12 (3 H)	6.00 (pq, 1 H) ($J_{3,4}$ = 16, $J_{3,6}$ = 1.5 Hz)	6.75 (pq, 1 H) ($J_{4,5}$ = 6.5 Hz)		1.90 (pd, 3 H)	
	$\Delta_{C_6H_6}^{CCl_4}$	+0.23	+0.12	+0.32		+0.47	
6	CCl_4	2.20 (3 H)	6.15 (d, 1 H) ($J_{3,4}$ = 16 Hz)	6.78 (pt, 1 H) ($J_{4,5}$ = 7 Hz)		6.00 (d, 2 H)	
	$\Delta_{C_6H_6}^{CCl_4}$	+0.48	+0.43	+0.47		+0.72	
7a	CCl_4	2.13 (3 H)	4.96 (1 H)			2.00 (3 H)	3.80 (3 H)
	$\Delta_{C_6H_6}^{CCl_4}$	−0.10	−0.15			+0.43	+0.52
7b	CCl_4	2.03 (3 H)	5.40 (1 H)		2.18 (3 H)		3.61 (3 H)
	$\Delta_{C_6H_6}^{CCl_4}$	+0.07	+0.17		−0.12		+0.43
8	CCl_4	2.14 (3 H)	5.48 (1 H)		4.43 (2 H)		3.70 (3 H)
	$\Delta_{C_6H_6}^{CCl_4}$	+0.28	+0.27		−0.03		+0.68

[a] Chemical shifts are in parts per million downfield relative to internal tetramethylsilane. [b] See illustration of 1 in Scheme I for clarification of notation: d, doublet; m, multiplet; pd, pair of doublets; pq, pair of quartets; pt, pair of triplets.

ratio was attained within hours of storage at room temperature of the nmr sample solutions.

Both methyl enol ethers of acetylacetone, **7a** and **7b**, were converted to allylic bromide **8** in quantitative yield upon treatment with 1 molar equiv of NBS. **7b** is probably an intermediate in the conversion of **7a** to **8**, since unreacted ether consists of only **7b** when reaction of **7a** was conducted with a deficiency of NBS or if the reaction was aborted before complete consumption of 1 molar equiv of the reagent; the mechanism of isomerization likely involves rapid and reversible addition of a bromine atom, by analogy with the generally accepted mechanism of olefin isomerization.[9]

3-Penten-2-one (**5**) underwent bromination to produce the allylic bromide **6**, which, like **5**,[11] apparently exists as a dynamic mixture of s-cis and s-trans conformers, since the shift data are not compatible with their representation as predominantly either one of the two species.

TABLE II

Δ_{Eu}[a] VALUES[b] FOR PROTONS OF SUBSTRATES AND PRODUCTS OF BROMINATION

Compd	C_1	C_3	C_4	cis C_5H	trans C_5H	OCH
2	2.9	1.5		2.1	0.9	
3	3.6	2.7		2.2	1.3	
4	3.3	2.5		3.0	1.3	
5	6.6	5.3	4.8		1.7	
6	4.2	3.8	3.3		0.8	
7a	5.0	6.3			1.8	2.0
7b	10.0	6.8		8.8		2.7
8	6.5	4.5		6.3		2.1

[a] Δ_{Eu} represents the slope of the straight line obtained from a plot of δ *vs.* Eu(thd)$_3$/substrate molar ratio [P. V. DeMarco, T. K. Elzey, R. B. Lewis, and E. Wenkert, *J. Amer. Chem. Soc.*, **92**, 5734, 5737 (1970)]; the larger the Δ_{Eu} value the greater the particular proton or set of protons is shifted downfield by the shift reagent. [b] Because of limited solubility, reliable Δ_{Eu} values for 1 could not be obtained. However, the maximum displacements of chemical shift for the protons of this compound are consistent with the assignments made on the basis of all other criteria, being −1.57, 1.33, 1.17, and 0.55 ppm for C_1, cis C_5, C_3, and trans C_5 protons, respectively.

Experimental Section

Nmr spectra were recorded on a Varian A-60A spectrometer operated at an ambient probe temperature of 40 ± 2°.

Materials.—Mesityl oxide, 3-penten-2-one, and acetylacetone were obtained commercially and vacuum distilled before using. The methyl enol ethers of acetylacetone were prepared as previously described.[5]

General Bromination Procedure.—NBS brominations were conducted in the standard manner[12] employing a 100-W, Photoflood No. 2 lamp to maintain reflux of carbon tetrachloride while providing a catalytic radiative source. Irradiation was halted as soon as it was estimated, visually, that the NBS had been consumed. The reaction product was quickly cooled, succinimide was filtered off, and the filtrate was concentrated.

Nmr analysis of the filtrates indicated that better than 95% conversion to product was achieved in all cases.

Bromination products were isolated by preparative thin layer chromatography (tlc) on silica gel GF_{254} using benzene–ether (9:1).

Registry No.—NBS, 128-08-5; **1**, 141-79-7; **2**, 34764-74-4; **3**, 34764-75-5; **4**, 34764-76-6; **5**, 3102-33-8; **6**, 34764-77-7; **7a**, 10556-93-1; **7b**, 10556-94-2; **8**, 34764-80-2.

Acknowledgment.—The authors are grateful to Mr. H. W. Avdovich for recording of the nmr spectra and to

(9) P. S. Fredericks and J. M. Tedder, *J. Chem. Soc.*, **144** (1960); B. P. McGrath and J. M. Tedder, *Proc. Chem. Soc.*, 80 (1961). The possibility of hydrogen abstraction and isomerization of the mesomeric radical produced, followed by rehydrogenation, appears unattractive in the light of the observation by Wolfe and Campbell[10] that unreacted olefin in the NBS bromination of cyclohexane-*3,3,6,6-d*$_4$ is unisomerized.

(10) S. Wolfe and P. G. C. Campbell, *Can. J. Chem.*, **43**, 1184 (1965).

(11) J. Ronayne, M. V. Sargent, and D. H. Williams, *J. Amer. Chem. Soc.*, **88**, 5288 (1966).

(12) L. Horner and E. H. Winkelmann in "Newer Methods of Preparative Organic Chemistry," Vol. 3, W. Foerst, Ed., Academic Press, London, 1964, p 151.

Dr. W. L. Wilson for helpful discussions. We are indebted also to Mr. H. Séguin of the National Research Council of Canada for performing the elemental microanalyses.

Friedel–Crafts Isomerization of Tetramethylacetophenones

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In 1952 Baddeley and Pendleton[1] reported that, in the presence of excess aluminum chloride at 100°, acetyldurene (2,3,5,6-tetramethylacetophenone) (**1**) was converted to acetylprehnitine (2,3,4,5-tetramethylacetophenone) (**7**, 80%), aromatic hydrocarbon (10%), and diacetyldurene (**6**, 10%). The formation of the latter two products was ascribed to fission of the acetyldurene into durene and acetyl cation, followed by electrophilic attack on a second molecule of acetyldurene to produce diacetyldurene. Transfer of the acyl group from one aromatic nucleus to another would be analogous to the well-known Friedel–Crafts transalkylation reaction.[2] More recently nmr studies have been conducted on ketones in the presence of Friedel–Crafts catalysts. Treatment of aliphatic,[3] alicyclic,[4] and aromatic ketones[5] with such strong acids as fluorosulfuric acid, fluorosulfuric acid–antimony pentafluoride, and related systems led in all instances to the observation of O-protonation producing stable cation systems.

We felt that these data were inconsistent and set about trying to resolve the question. The inconsistency is centered about the facts that the nmr data[3-5] require that, in the presence of acid, acetyldurene and related systems are O-protonated, whereas the transacylation data require a second protonation (Scheme I).

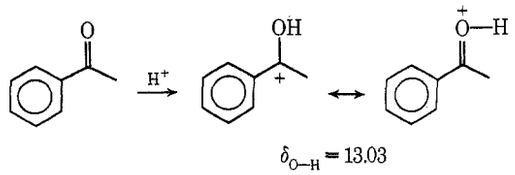
Although no benzenium ions such as **3** were observed by low-temperature nmr (protons in species such as **3** or **5** are observed at δ 4.5–5.5),[6] a small steady-state concentration would be stable under the reaction conditions. To effect transacylation **3a**, if present at all, must undergo the unlikely sequence outlined above: loss of $(CH_3CO)^+$ and H^+ followed by attack by the weak electrophile $(CH_3CO)^+$ on the *protonated* 2,3,5,6-tetramethylacetophenone to give **5** and finally **6**. On the other hand ions **3b–3d**, if present, are able to undergo intra- and intermolecular methyl shifts.

We have repeated the isomerization of acetyldurene with aluminum chloride with the results shown below.

We observed no hydrocarbon or diacetyltetramethylbenzene product as was reported in the earlier study,

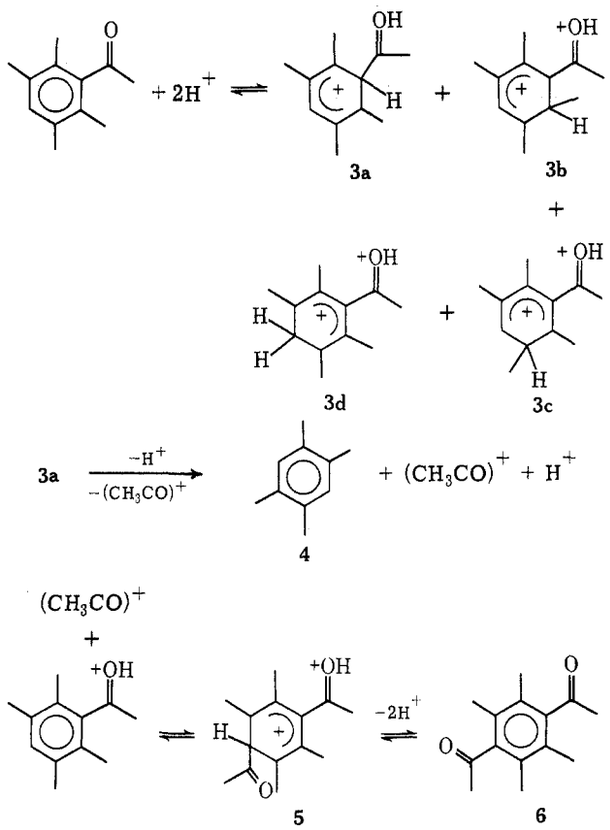
SCHEME I

A. Nmr[5]

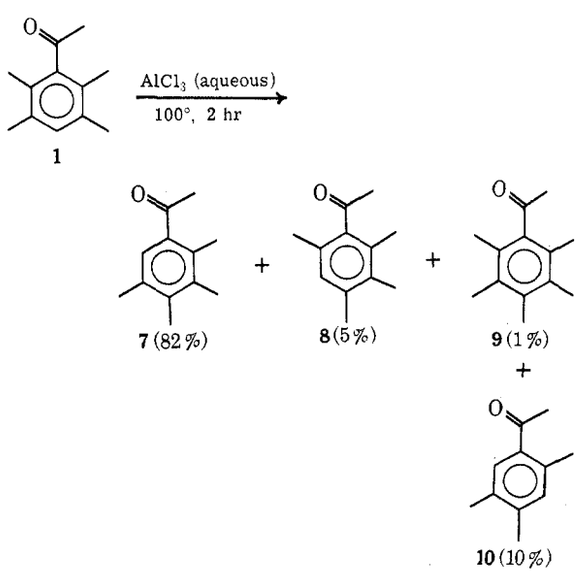


$\delta_{O-H} = 13.03$

B. Transacylation[1]



and believe our results are consistent with the nmr data presented above. A combination of Friedel–Crafts transalkylation and isomerization reactions can account for all products formed. Scheme II, which presents one possible pathway, indicates that indeed when enough



(1) G. Baddeley and A. G. Pendleton, *J. Chem. Soc.*, 807 (1952).
(2) G. A. Olah, "Friedel-Crafts and Related Reactions," Vol. I, G. A. Olah, Ed., Wiley, New York, N. Y., 1963.
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(4) G. A. Olah and M. Calin, *ibid.*, **90**, 938 (1968).
(5) G. C. Levy and S. Winstein, *ibid.*, **90**, 3574 (1968); M. Brookhart, G. C. Levy, and S. Winstein, *ibid.*, **89**, 1735 (1967); T. Birchall and R. J. Gillespie, *Can. J. Chem.*, **43**, 1045 (1965).
(6) G. A. Olah, *J. Amer. Chem. Soc.*, **87**, 1103 (1965).