of fractional distillation to isolate the product. The yield of recrystallized product was 38%.

Thujaketonic Acid.—A solution of thujalactone (500 mg., 3 mmoles), chromium trioxide (220 mg., 2.2 mmoles), two drops of concentrated sulfuric acid and three drops of water in 6.5 ml. of glacial acetic acid was allowed to stand at 27° for 5 hours. Sodium carbonate was added to neutralize the sulfuric acid and the solvent was removed *in vacuo* to yield a viscous liquid which was dissolved in ether and extracted with 10% sodium carbonate solution. The ether layer was washed with water and dried over anhydrous magnesium sulfate. Removal of the solvent afforded 0.30 g. of starting material. The basic aqueous layer was acidified with hydrochloric acid and extracted with ether, which was dried over anhydrous magnesium sulfate. Removal of the ether left 0.18 g. of liquid. When seeded with a crystal of thujaketonic acid (prepared from thujone by permanganate oxidation[60]) the product crystallized. Recrystallization from benzene–petroleum ether afforded thujaketonic acid, m.p. 74.5–75.3°; infrared spectrum (CCl_4): 944, 1022(wk), 1092, 1172, 1220, 1380, 1684, 2880 $cm.^{-1}$.

The product formed a 2,4-dinitrophenylhydrazone which was recrystallized from ethanol, m.p. 161–162°; ultraviolet spectrum: *368 mμ (ε 22000).*

Several other methods for the preparation of thujaketonic acid were attempted but the yields were low. These methods consisted of: (1) base hydrolysis of thujalactone followed by chromium trioxide–pyridine oxidation, (2) base hydrolysis of thujalactone followed by sodium hypobromite oxidation and (3) chromium trioxide oxidation of thujalactone at 15–20° in acetic acid.[61]

Conversion of Normaalione (XI) to γ-Maaliene (IX).—A 0.9 *M* solution of *n*-butyllithium (3.15 ml.) in anhydrous ether was added under vigorous stirring to a suspension of methyl-triphenylphosphonium bromide (1.02 g.) in 12 ml. of ether. After 2 hours at room temperature normaalione (0.5 g.) in 15 ml. of ether was added and the solution stirred overnight. Tetrahydrofuran (50 ml.)[62] was added and the ether removed by distillation. After 6 hours at reflux the solution was poured in water, extracted with petroleum ether and the organic layer washed with water and then dried with sodium sulfate. The solvent was removed by evaporation and the residue chromatographed over 15 g. of alumina (Woelm, neutral, act. I). Hexane eluted 400 mg. (80%) of an oil which after distillation had an infrared spectrum identical with that of highly purified γ-maaliene (IX) prepared by pyrolysis of maaliacetate (VIII).

Deuterium Exchange of Carone (XVI).—Sodium (0.149 g.) was dissolved in EtOD (3 ml.). After the addition of carone (0.9 g.) the solution was allowed to reflux for 20 minutes and the deuterioethanol removed by evaporation. Three additional exchanges were carried out using 2 ml. of EtOD each time. After the last exchange the residue was taken up in petroleum ether, the organic phase washed with D_2O and dried. The deuterated carone was purified by distillation, b.p. 95–105° (3.8 mm.) (bath temperature measured). Its mass spectrum indicated the presence of 80% dideuteriocarone and 20% monodeuteriocarone. The above exchange was repeated using deuteriocarone and ethanol. The product obtained had an infrared spectrum identical with that of carone.[63]

Deuterium Exchange of LIX.[64]—Dihydroeudesmol[65] (230 mg., m.p. 85–86°) was dehydrated by means of $POCl_3$ in pyridine.[37,54] Ozonolysis of the mixture of olefins (−60° in methanol–carbon tetrachloride solution) and work-up in the usual way[57] afforded an oil, the active hydrogens of which were exchanged with deuterium (*cf.* procedure used on normaalione (XI)). Distillation of the deuterated material in a micro-distillation apparatus afforded 138 mg. of colorless oil which, upon mass-spectral analysis, showed mass peaks at 212 (tetradeuterated nor-ketone LIX), 194 (tetradeuterated LIV minus $-CD_3$), 184 (tetradeuterated trisnorketone derived from XXXIX) and 46 (CD_3CO- group).

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[60] F. Tiemann and F. W. Semmler, *Ber.*, **30**, 429 (1897).

[61] Method of E. J. Corey and J. J. Ursprung, THIS JOURNAL, **78**, 5041 (1956).

[62] Modification of F. Sondheimer and R. Mechoulam, *ibid.*, **79**, 5029 (1957).

[63] We are indebted to Dr. T. Matsuura for these experiments.

[64] We wish to thank Dr. I. M. Goldman for this experiment.

[65] We are indebted to Dr. D. Arigoni, ETH, for providing this material.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE, CAIRO UNIVERSITY]

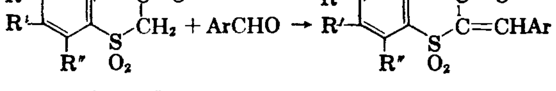
Experiments with 2-Arylidene-3(2H)-thianaphthenone-1,1-dioxides. II. Reactions of *p*-Thiocresol and of Grignard Reagents with 2-Arylidene-3(2H)-thianaphthenone-1,1-dioxides

BY AHMED MUSTAFA AND MOHAMED MOHAMED SALLAM

RECEIVED SEPTEMBER 22, 1958

The condensation reaction of substituted 3(2H)-thianaphthenone-1,1-dioxides (I) with aromatic aldehydes now has been further investigated. Oxidation of 2-arylidene-3(2H)-thianaphthenone and its substituted derivatives (IIIa-e) with hydrogen peroxide proved to be a general method for the preparation of 2-arylidene-3(2H)-thianaphthenone-1,1-dioxide and its substituted derivatives (*cf.* IIa,b,g,i,k). 2-Arylidene-3(2H)-thianaphthenone-1,1-dioxides (II) undergo an addition reaction with *p*-thiocresol, yielding the thiol adducts believed to have structure V. Conjugate addition, without any indication of cleavage, now has been observed when substances of type II are allowed to react with arylmagnesium halides, yielding colorless reaction products, believed to have structures VII.

Recently[1,2] the condensation of 3(2H)-thianaphthenone-1,1-dioxides (1) with aromatic aldehydes has been reported; *e.g.*, 3(2H)-thianaphthenone-1,1-dioxide (Ia) condenses with benzaldehyde to give 2-benzylidene-3(2H)-thianaphthenone-1,1-dioxide (IIa). We now have extended the study of this condensation reaction and have obtained a number of new arylidene derivatives (IIc-f,h,j,l). Oxidation of 2-arylidene-3(2H)-thianaphthenone and its substituted derivatives (IIIa-e, respectively) with hydrogen peroxide also leads to the formation of the corresponding 2-arylidene-3(2H) thianaphthenone-1,1-dioxides (IIa,b,j,i,k) in good yield.



Ia, R = R′ = R″ = H
b, R′ = R″ = H; R = CH_3
c, R = R″ = H; R′ = CH_3
d, R = R′ = H; R″ = CH_3

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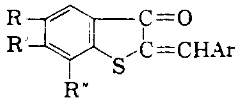
[1] A. Mustafa and S. M. A. D. Zayed, THIS JOURNAL, **79**, 3500 (1957).

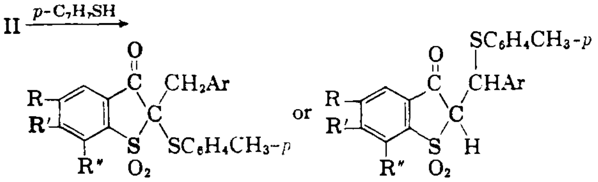
[2] W. Asker, A. F. A. Shalaby and S. M. A. D. Zayed, *J. Org. Chem.*, **23**, 1781 (1958).

IIa, R = R′ = R″ = H; Ar = C_6H_5
b, R = R′ = R″ = H; Ar = $C_6H_4OCH_3$-*p*
c, R = R′ = R″ = H; Ar = $C_6H_4CH_3$-*p*
d, R = R′ = R″ = H; Ar = $C_6H_4CH_3$-*m*
e, R = R′ = R″ = H; Ar = $C_6H_3:O_2CH_2(3:4)$
f, R = R′ = R″ = H; Ar = $C_6H_4CH{=}CH{-}CH{=}$
g, R′ = R″ = H; R = CH_3; Ar = C_6H_5
h, R′ = R″ = H; R = CH_3; Ar = $C_6H_4OCH_3$-*p*
i, R = R″ = H; R′ = CH_3; Ar = C_6H_5
j, R = R″ = H; R′ = CH_3; Ar = $C_6H_4OCH_3$-*p*
k, R = R′ = H; R″ = CH_3; Ar = C_6H_5
l, R = R′ = H; R″ = CH_3; Ar = $C_6H_4OCH_3$-*p*



IIIa, R = R′ = R″ = H; Ar = C_6H_5
b, R = R′ = R″ = H; Ar = $C_6H_4OCH_3$-*p*
c, R′ = R″ = H; R = CH_3; Ar = C_6H_5
d, R = R″ = H; R′ = CH_3; Ar = C_6H_5
e, R = R′ = H; R″ = CH_3; Ar = C_6H_5

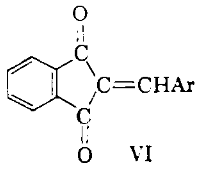
In conjunction with a study of the pharmacological action of sulfur-containing compounds against Bilhariazis snails,[3] we have also extended our study of the addition, *e.g.*, of *p*-thiocresol, to the double bond at position 2, which is conjugated with the unsaturated group in 2-arylidene-3(2H)-thianaphthenone-1,1-dioxides(IIb,e,h,j,l). The latter like the 2-arylideneindan-1,3-diones[4] undergo addition reaction with *p*-thiocresol in absence of a catalyst to give colorless adducts which can be represented by IV or V.



IV V

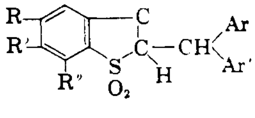
In view of the well-established mechanism for the addition of thiols to α,β-unsaturated compounds,[5] structure V is preferable. The fact that the adduct V(R = R′ = R″ = H; Ar = $C_6H_4OCH_3$-*p*) dissolves in cold aqueous sodium hydroxide solution with a yellow color and is liberated upon neutralization with ice-cold dilute hydrochloric acid is also in accord with structure V. When this thiol adduct was heated above its melting point for a few minutes and then cooled, the arylidene derivative IIb was regenerated. The ease of removal of the addend indicates that the substance is the result of simple addition and that no unexpected reaction has occurred.

The action of Grignard reagents on 2-arylidene-3(2H)-thianaphthenone-1,1-dioxides(IIa-b; g-l), which are examples of arylidene derivatives of cyclic β-ketosulfones, has also been studied in an extension of earlier work.[6] The reaction of Grignard reagents with arylidene derivatives of cyclic β-diketones (VI) is known.[7]



VI

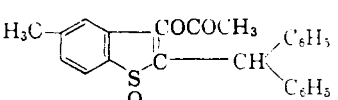
The arylidene derivatives of cyclic β-ketosulfones II are similar in that the ethylenic bond is in conjugation with the carbonyl group and also behaves as if conjugated with the sulfone group.[8] In the case of unsaturated β-ketosulfones, *e.g.*, α-phenylsulfonyl-β-benzoylethylene, cleavage of the addition product occurs during the reaction with phenylmagnesium bromide and the cleavage products immediately react further.[9]



VIIa, R = R′ = R″ = H; Ar = Ar′ = C_6H_5
b, R = R′ = R″ = H; Ar = C_6H_5; Ar′ = $C_6H_4OCH_3$-*p*
c, R′ = R″ = H; R = CH_3; Ar = Ar′ = C_6H_5
d, R′ = R″ = H; R = CH_3; Ar = C_6H_5; Ar′ = C_6H_4-OCH_3-*p*
e, R′ = R″ = H; R = CH_3; Ar = Ar′ = $C_6H_4OCH_3$-*p*
f, R = R″ = H; R′ = CH_3; Ar = Ar′ = C_6H_5
g, R = R″ = H; R′ = CH_3; Ar = C_6H_5; Ar′ = C_6H_4-OCH_3-*p*
h, R = R″ = H; R′ = CH_3; Ar = Ar′ = $C_6H_4OCH_3$-*p*
i, R = R′ = H; R″ = CH_3; Ar = Ar′ = C_6H_5
j, R = R′ = H; R″ = CH_3; Ar = C_6H_5; Ar′ = C_6H_4-OCH_3-*p*
k, R = R′ = H; R″ = CH_3; Ar = Ar′ = $C_6H_4OCH_3$-*p*

Conjugate addition,[10] without any indication of cleavage reaction, now has been observed when IIa-b,g-l are treated with arylmagnesium halides, yielding reaction products believed to have structures VII.

The structure of VIIa, which is taken as an example of compounds VIIa-k, is inferred from the fact that it is colorless. Whereas, IIa reacts with phenylhydrazine to give the corresponding hydrazone derivative of Ia,[1] VIIa is recovered unchanged when treated with the same reagent under similar experimental conditions; a fact which may be taken in support of a saturated cyclic β-ketosulfone structure for VIIa. Treatment of VIIc with acetic anhydride gives a product whose analysis is that of a monoacetyl derivative, believed to have structure VIII.



VIII

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(3) A. Mustafa, A. H. E. Harhash and M. Kamel, THIS JOURNAL, **77**, 3860 (1955); N. O. Nolan, H. W. Bond and E. R. Mann, *Am. J. Med. & Hyg.*, **2** (4), 716 (1953).

(4) A. Mustafa, *J. Chem. Soc.*, 1370 (1951).

(5) T. Posner, *Ber.*, **35**, 809 (1902); B. H. Nicolet, THIS JOURNAL, **53**, 3066 (1931); P. S. Bailey and J. C. Smith, *J. Org. Chem.*, **21**, 709, (1956); R. M. Ross and F. W. Raths, THIS JOURNAL, **73**, 129 (1951); R. M. Ross, H. L. Bushy and R. L. Rolih, *ibid.*, **73**, 540 (1951); R. M. Ross, *ibid.*, **71**, 3458 (1958); *cf.* also references 1 and 2.

(6) *Cf.* A. Mustafa and co-workers, *ibid.*, **77**, 5630 (1955); *J. Org. Chem.*, **22**, 157 (1957); **23**, 1992 (1958).

(7) E. P. Kohler, *Am. Chem. J.*, **37**, 369 (1907).

(8) The behavior of α,β-unsaturated sulfones toward organomagnesium compounds is similar to the behavior of comparable ketones in that the ethylenic bond behaves as if conjugated, yet the sulfone cannot participate in 1,4-addition without more than eight electrons in the valence shell of the sulfur atom. Addition of phenylmagnesium bromide to styryl *p*-tolyl sulfone was reported to be analogous to the addition to benzalacetophenone (E. P. Kohler and H. Potter, THIS JOURNAL, **57**, 1316 (1935)).

(9) E. P. Kohler and R. G. Larsen, *ibid.*, **57**, 1448 (1935).

(10) H. Potter, *ibid.*, **76**, 5472 (1954).

TABLE I

2-ARYLIDENE-3(2H)-THIANAPHTHENONE-1,1-DIOXIDES (II)

Arylidene deriv.[a]	Reaction temp., °C.	M.p.,[b] °C.	Yield, %	Solvent for crystn.[c]	Color with concd. H_2SO_4	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found
IIc	160	182	70	A, colorless	Yellow	$C_{16}H_{12}O_3S$	67.60	67.19	4.23	4.46	11.23	10.73
IId	160	186	68	A, colorless	Orange	$C_{16}H_{12}O_3S$	67.60	67.52	4.23	4.56	11.23	10.86
IIe	185	251	65	B, yellow	Violet	$C_{16}H_{10}O_5S$	61.10	61.26	3.10	3.23	10.10	10.08
IIf	170	192	72	A, dark yellow	Red	$C_{17}H_{12}O_3S$	68.92	68.92	4.05	4.12	10.18	10.09
IIh	180	207	60	B, yellow	Red	$C_{17}H_{14}O_4S$	64.79	64.56	4.49	4.48	10.10	9.96
IIj	185	256	60	B, yellow	Red	$C_{17}H_{14}O_4S$	64.79	64.72	4.49	4.41	10.10	9.72
IIl	185	224	58	A, yellow	Red	$C_{17}H_{14}O_4S$	64.79	64.86	4.49	4.63	10.10	9.88

[a] Prepared after method A. [b] All melting points are uncorrected. [c] A = alcohol;. B = benzene.

TABLE II

THIOL ADDUCTS (V) FROM 2-ARYLIDENE-3(2H)-THIANAPHTHENONE-1,1-DIOXIDES (II) AND *p*-THIOCRESOL

Arylidene deriv.	Reaction temp., °C.	M.p.,[a] °C,	Yield, %	Color with concd. H_2SO_4	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found
IIb	110	126	82	Red	$C_{23}H_{20}O_4S_2$	65.09	65.47	4.71	4.68	15.11	15.01
IIe	125	144	86	Violet	$C_{23}H_{18}O_5S_2$	63.01	62.95	4.10	4.34	14.60	14.34
IIh	125	140	77	Red	$C_{24}H_{22}O_4S_2$	65.75	65.44	5.02	5.20	14.61	14.80
IIj	140	157	79	Red	$C_{24}H_{22}O_4S_2$	65.75	65.88	5.02	4.93	14.61	13.89
IIl	120	138	80	Red	$C_{24}H_{22}O_4S_2$	65.75	65.94	5.02	5.16	14.61	14.32

[a] Melting points are uncorrected.

TABLE III

GRIGNARD PRODUCTS (VII) FROM 2-ARYLIDENE-3(2H)-THIANAPHTHENONE-1,1-DIOXIDES (II)

Arylidene deriv.	Grignard[a] reagent	Product	M.p.,[b] °C.	Yield, %	Color with concd. H_2SO_4	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found
IIa	A	VIIa[c]	173	70	Yellow	$C_{21}H_{16}O_3S$	72.41	72.19	4.60	4.32	9.19	8.78
IIa	B	VIIb	161	58	Yellow	$C_{22}H_{18}O_4S$	69.81	69.63	4.76	4.94	8.46	8.03
IIb	A	VIIb[c]	161	63	Yellow	$C_{22}H_{,8}O_4S$	69.81	69.65	4.76	5.01	8.46	8.23
IIg	A	VIIc	199	62	Yellow	$C_{22}H_{18}O_3S$	72.92	72.84	4.97	4.83	8.84	9.11
IIg	B	VIId	171	54	Yellow	$C_{23}H_{20}O_4S$	70.41	70.50	5.10	5.04	8.16	8.06
IIh	A	VIId	171	58	Yellow	$C_{23}H_{20}O_4S$	70.41	70.55	5.10	5.21	8.16	7.93
IIh	B	VIIe	185	70	Red	$C_{24}H_{22}O_5S$	68.24	67.99	5.21	5.17	7.58	7.68
IIi	A	VIIf	168	68	Yellow	$C_{22}H_{18}O_3S$	72.92	72.63	4.97	4.96	8.84	7.99
IIi	B	VIIg[d]	170	51	Yellow	$C_{23}H_{20}O_4S$	...	...	..	..	..	..
IIj	A	VIIg	170	53	Yellow	$C_{23}H_{20}O_4S$	70.41	70.14	5.10	5.33	8.16	7.90
IIj	B	VIIh	158	67	Red	$C_{24}H_{22}O_5S$	68.24	68.71	5.21	5.27	7.58	7.33
IIk	A	VIIi	160	63	Yellow	$C_{22}H_{18}O_3S$	72.92	72.72	4.97	4.90	8.84	9.01
IIk	B	VIIj[d]	154	51	Yellow	$C_{24}H_{20}O_4S$	...	...	..	..	..	..
IIl	A	VIIj	154	54	Yellow	$C_{23}H_{20}O_4S$	70.41	70.72	5.10	5.29	8.16	7.95
IIl	B	VIIk	169	66	Red	$C_{24}H_{22}O_5S$	68.24	68.62	5.21	5.63	7.58	7.25

[a] A = phenylmagnesium bromide; B = *p*-methoxyphenylmagnesium bromide. [b] Melting points are not corrected. [c] This experiment was carried out with S.M.A.D. Zayed. [d] Identified by m.p. and mixed m.p.

The finding that VIIb is obtained by the action of *p*-methoxyphenylmagnesium bromide on IIa and by the action of phenylmagnesium bromide on IIb may be taken in favor of the assigned structure for the Grignard products.

3-(2H)-Thianaphthenone-1,1-dioxide(Ia) having less tendency for enolization,[11] proved to be stable toward the action of phenylmagnesium bromide under similar conditions, illustrating the stability of the hetero-ring toward the action of Grignard reagents. The activity of the vinyl group in II may be compared with the activity of the same group in V.

The infrared spectra of compound VII, *e.g.*, VIIa, was found to be consistent with the proposed structure. It has no band in the –OH region, and has a strong band at 5.90 μ attributed to a carbonyl group conjugated to the benzene ring supported by ultraviolet absorption data[12] ($\lambda_{\max}^{\text{alc}}$ 251 mμ (ϵ 10,022)).

Experimental

Preparation of 2-Arylidene-3(2H)-thianaphthenone-1,1-dioxide Derivatives (II). Method (A). By the Condensation of 3(2H)-thianaphthenone-1,1-dioxides(I) with Aromatic Aldehydes. General Procedure.[1]—A mixture of 1.0 g. of the appropriate 3(2H)-thianaphthenone-1,1-dioxide(I) and 2 ml. of the aromatic aldehyde was heated for three hours over an oil-bath at the given temperature (*cf.* Table I). The reaction mixture was then cooled to room temperature and triturated with 5 ml. of cold ethyl alcohol. The resulting solid was crystallized from benzene.

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(11) A. Kohen and S. Smiles, *J. Chem. Soc.*, 408 (1930); A. A. Lier and S. Smiles, *ibid.* 523 (1931); A. W. Weston and C. M. Suter, THIS JOURNAL, **61**, 389 (1938); F. Arndt, A. Kirsch and P. Nachwey, *Ber.*, **59**, 1074 (1926); H. D. Hartough and S. L. Meisel, "Compounds with Condensed Thiophene Rings," Interscience Publishers, Inc., New York, N. Y., 1954, p. 157.

(12) A. L. Wilds, *et al.*, THIS JOURNAL, **69**, 1985 (1947); Ramart-Lucas and M. J. Hoch, *Bull. soc. chim. France*, [5] **2**, 327 (1935).

The new arylidene derivatives (IIc–f, h, j, l) listed in Table I, are difficultly soluble in cold ethyl alcohol, ether and acetic acid, but soluble in acetone and boiling benzene.

Method (B). By the Oxidation of 2-Arylidene-3(2H)-thianaphthenone Derivatives(III).—A solution of 1.0 g. of each of IIIa,[13] IIIb,[14] IIIc,[15] IIId[16] and IIIe[17] in 20 ml. of glacial acetic acid was treated with 3 ml. of hydrogen peroxide (30%) and the reaction mixture was heated on a boiling water-bath for half an hour. The cooled reaction mixture was then poured into ice-cold water. The solid that separated was filtered off, washed with cold water and crystallized from benzene in almost colorless crystals.

Oxidation products IIa, b, g, i, and k are obtained in 82, 90, 87, 81 and 85% yield, respectively (identified by m.p. and mixed m.p.).

Action of *p*-Thiocresol on 2-Arylidene-3(2H)-thianaphthenone-1,1-dioxides. General Procedure.—A mixture of 0.5 g. of the appropriate arylidene derivative (II) and 0.5 g. of *p*-thiocresol was heated on an oil-bath at the given temperature (*cf.* Table [illegible]) for 3 hours. The cooled reaction mixture was washed with light petroleum (b.p. 40–60°) and the resulting solid was crystallized from benzene–petr. ether (b.p. 60–80°).

The thiol-adducts V listed in Table II are colorless crystalline compounds which dissolve readily in benzene and chloroform, but are difficultly soluble in cold ethyl alcohol, ether and acetic acid. They dissolve in aqueous sodium hydroxide (10%) with a yellow color.

Action of Grignard Reagents on 2-Arylidene-3(2H)-thianaphthenone-1,1-dioxides (IIa–b, g–l).—The following illustrates the general procedure: To a Grignard solution (prepared from 0.9 g. of magnesium and 9.0 g. of bromobenzene in 50 ml. of dry ether) was added a solution of 1.0 g. of each of (IIa–b, g–l) in dry benzene (50 ml.). After evaporation of the ether, the mixture was heated for three hours on a steam-bath. After standing overnight at 25°, it was poured slowly into 100 ml. of saturated aqueous ammonium chloride solution to which 3 ml. of concentrated hydrochloric acid was added, and then extracted with ether. The ethereal layer was dried over anhydrous sodium sulfate, filtered and evaporated. The residue left behind was washed several times with light petroleum and a little ethyl alcohol until it solidified. It was crystallized from benzene.

The Grignard products VII, listed in Table III, are difficultly soluble in ethyl alcohol and ether, give no color with ferric chloride solution and are insoluble in aqueous sodium hydroxide (10%).

Action of Phenylmagnesium Bromide on 3(2H)-Thianaphthenone-1,1-dioxide (Ia).—To a Grignard solution (prepared from 0.9 g. of magnesium and 9.0 g. of bromobenzene in 50 ml. of dry ether) was added a solution of 1.0 g. of Ia in dry benzene (50 ml.). The reaction was processed as mentioned previously. The product obtained was identified as 3(2H)-thianaphthenone-1,1-dioxide (m.p. and mixed m.p.).

Action of Acetic Anhydride on VIIc.—A suspension of 0.5 g. of VIIe in acetic anhydride (10 ml.) was refluxed for one hour. The resulting solution was poured into ice-cold water. The solid product that separated was filtered off and crystallized from acetic acid as colorless crystals, m.p. 164°.

Anal. Calcd. for $C_{24}H_{20}O_4S$: C, 71.29; H, 4.95; S, 7.92. Found: C, 71.13; H, 5.13; S, 8.20.

The monoacetyl derivative VIII was soluble in aqueous sodium hydroxide and gave a yellow color with concentrated sulfuric acid.

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[CONTRIBUTION FROM THE DOW CORNING CORPORATION]

The Effect of Substituent Fluoroalkyl Groups on the Alkali-catalyzed Hydrolysis of Silanes[1]

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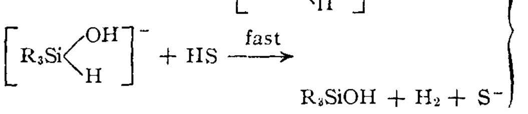
The second-order rate constants for the alkali-catalyzed hydrolysis of the silicon-hydrogen bond in four fluoroalkylsilanes have been determined. It was found that a trifluoromethyl group, even though separated from the silicon atom, *i.e.*, the reaction center, by two or three methylene groups, increases the rate of hydrolysis by an appreciable amount. The ease of polarization of the silicon atom has been suggested for this quite large increase in rate.

Introduction

During the course of work in this Laboratory, it became apparent that information was needed on the effect of various fluoroalkyl groups on the reactivity of the silicon atom in fluoroalkylsilicon compounds. Therefore, a program was initiated to study the influences of various fluoroalkyl groups on the rate of alkali-catalyzed hydrolysis of the silicon–hydrogen bond. This reaction was selected since the kinetics were quite well defined by several previous studies.[2–9]

Price[2] made the first kinetic study of the alkali-catalyzed hydrolysis and found the reaction was first order in silane, first order in hydroxide ion and probably first order in solvent. Using an alcohol-water medium, pseudo first-order kinetics were observed, since the base is regenerated from the water present in the reaction solvent.

Two mechanisms consistent with the observed data have been formulated[6]



$$\left.\begin{array}{l} R_3SiH + OH^- \xrightarrow{\text{slow}} \left[R_3Si\begin{smallmatrix}OH\\H\end{smallmatrix}\right]^- \\ \left[R_3Si\begin{smallmatrix}OH\\H\end{smallmatrix}\right]^- + HS \xrightarrow{\text{fast}} R_3SiOH + H_2 + S^- \end{array}\right\} \quad (1)$$

$$R_3SiH + OH^- + HS \longrightarrow R_3SiOH + H_2 + S^- \quad (2)$$

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