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THE REACTION OF TROPONE WITH SULFONIUM YLIDS

A SYNTHESIS OF 2,3-HOMOTROPONES AND 2,3-4,5-DIHOMOTROPONES

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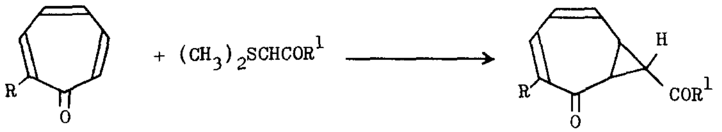
The first synthesis of a 2,3-homotropone was carried out by Pettit et al$^{1)}$ from cyclooctatetraene via several steps. In this communication we would like to report a convenient one step synthesis of 2,3-homotropone derivatives and new tricyclic compounds, 2,3-4,5-dihomotropone (tricyclo[6,1,0,0^{5,7}]nona-3-en-2-one) derivatives, by the reaction of tropone with sulfonium ylids.

The equimolar reaction of tropone (Ia) with ethoxycarbonylmethylenedimethylsulfurane (IIa) in tetrahydrofuran at 50-60°C for 4-6 hours gave IIIa in 75% yield. IIIa: mp 70-71°C; $C_{11}H_{12}O_3$ (based on mass spectrum and analytical data); IR $\bar{\nu}$(nujol) 1745, 1645, 1625 cm^{-1}; UV λmax (ethanol) 292 (ε=50,000), 350 (shoulder, ε=9,000)mμ; mass spectrum m/e 192(M^+), 147, 146, 119, 118, 112, 91. The NMR spectral data in $CDCl_3$ and in D_2SO_4 are shown in Table I. From these data, especially owing to NMDR, the structure of IIIa was confirmed as a 2,3-homotropone derivative, that is 8-ethoxycarbonylbicyclo[5,1,0]-octa-3,5-dien-2-one. In a comparison of the chemical shifts of IIIa in $CDCl_3$ with those in D_2SO_4, all proton signals except H_g shift downfield about 0.5-1.5 ppm, but only H_g shifts upfield about 0.5 ppm. This shows that in sulfuric acid, IIIa has a ring current in the seven membered ring, and that H_g is situated over this ring current. A similar ring current is observed in nonsubstituted homotropone$^{1)}$, which also supports the homotropone structure of IIIa.

Analogous reactions of 2-methyl tropone (Ib), 2-phenyltropone (Ic), and 2-chlorotropone (Id) with ylids (IIb, IIc) gave the corresponding homotropone derivatives (IIIb-g) shown in scheme I.

SCHEME I

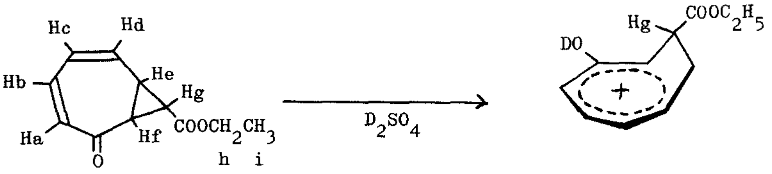


Ia: R=H
Ib: $R=CH_3$
Ic: R=Ph
Id: R=Cl

IIa: R^1=OEt
IIb: R^1=Ph
IIc: R^1=p-BrPh*

* p-BrPh: p-bromophenyl

IIIa: R=H, R^1=OEt(mp 70-71°, yield 75%)
IIIb: R=H, R^1=Ph (92°, 55%)
IIIc: R=H, R^1=p-BrPh (140°, 57.4%)
IIId: $R=CH_3$, R^1=Ph (122-123°, 80%)
IIIe: R=Ph, R^1=Ph (oil, 62%)
IIIf: R=Ph, R^1=p-BrPh (oil, 30%)
IIIg: R=Cl, R^1=Ph (153-154°, 55.7%)



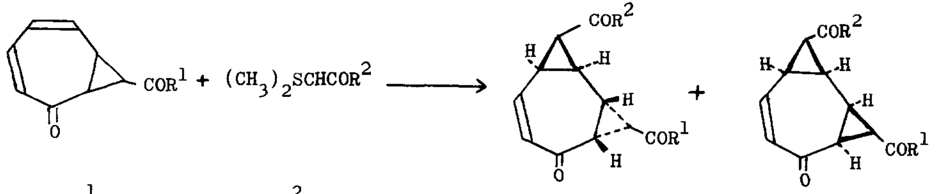
IIIa

TABLE I

The NMR spectral data of IIIa (100MHz)

Proton assignment	Chemical shift (δ ppm) in $CDCl_3$	in D_2SO_4	Multiplicity (in $CDCl_3$)	Coupling constant (Hz, in $CDCl_3$)
Hi	1.28	1.60	t	J_{ab}= 12.6, J_{af}= 1.8
He	2.35	4.02	dddd	J_{bc}= 7.3, J_{bd}≐ 1
Hg	2.60	2.15	dd	J_{cd}= 11.5, $J_{ce} > 0$
Hf	2.92	4.02	ddd	J_{de}= 7.0
Hh	4.20	4.75	q	J_{ef}= 9.0, J_{eg}= 5.6
Hc	5.85	7.1	ddd	J_{fg}= 5.5
Ha	6.05	7.3	dd	J_{hi}= 7.0
Hb	6.30	7.8	ddd	
Hd	6.52	8.03	ddd	

SCHEME II



IV

V

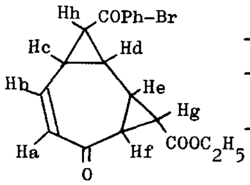
IIIa: R^1=OEt
IIIb: R^1=Ph
IIIc: R^1=p-BrPh

IIa: R^2=OEt
IIb: R^2=Ph
IIc: R^2=p-BrPh

IVa, Va: R^1=OEt, R^2=p-BrPh
IVb, Vb: R^1=R^2=Ph
IVc: R^1=R^2=p-BrPh
IVd: R^1=p-BrPh, R^2=OEt

TABLE II

Homotropone	Ylid	Solvent	Product, mp, yield	
IIIa	IIc	Benzene	IVa 151°, 54.6% ;	Va 123°, 2.2%
IIIb	IIb	THF	IVb 218-221°, 90%	
IIIb	IIb	Benzene	IVb 218-221°, 11.6% ;	Vb 246-248°, 51.6%
IIIc	IIc	THF	IVc 257-258°, 63%	
IIIc	IIa	Benzene	IVd 181°, 33.5%	



IVa, Va

TABLE III

The NMR spectral data of IVa and Va (100 MHz, in $CDCl_3$)

	IVa		Va	
Protone assignment	Chemical shift(δ,ppm)	Coupling constant(Hz)	Chemical shift	Coupling constant
Ha	5.73	J_{ab}= 12.7	5.80	J_{ab}= 12.8
Hb	6.55	J_{bc}= 7.3	6.11	J_{bc}=6.5
Hc	2.24	J_{ch}= 5.0	2.2 ~2.7	J_{ch} } 9.3, 8.3
Hd	2.5-2.7	J_{dh}= 5.0		J_{dh}
He		J_{cd}= ~ 9		J_{fa}= 1.7
Hf	2.53	J_{fa}= 1.5	2.71	J_{fg}= 6.3
Hg	2.5-2.7		2.2-2.7	
Hh	2.87		3.16	
CH_2	4.16		4.14	
CH_3	1.27		1.23	
Ph-H(4H)	7.62, 7.81		7.55, 7.76	

The further reactions of IIIa with p-bromophenacylidenedimethylsulfurane (IIc) in benzene at 80°C for 7 hours gave IVa (54.6%) and its stereoisomer Va (2.2%). These compounds were isolated and purified with silica gel column chromatography, followed by recrystallization from benzene. IVa: mp 151°C; $C_{19}H_{17}O_4Br$ (based on mass spectrum and analytical data); IR ν(nujol) 1720, 1665, 1650 cm^{-1}; UV λmax (ethanol) 264 (ε=26,000) mμ; mass spectrum m/e 390 (M^+, d, Br^{81}), 362 (d), 344 (d), 333 (d), 317 (d), 307 (d), 299 (d), 263 (d), 250 (d), 237 (d), 224 (d), 208, 205, 185 (d), 157 (d), 149, 131, 115, 112, 105, 91. The NMR spectral data are shown in Table III. From these data, the structure of IVa was confirmed as a 2,3-4,5-dihomotropone derivative, that is 6-p-bromobenzoyl-9-ethoxycarbonyltricyclo[6,1,0,$0^{5,7}$]nona-3-en-2-one. Va: mp 123°C; $C_{19}H_{17}O_4Br$ (based on mass spectrum and analytical data); IR (nujol) 1710, 1665, 1645, 1635 cm^{-1}; UV spectrum and fragmentation pattern of the mass spectrum are completely identical to those of IVa. The NMR spectral data are shown in Table III. These data shows Va is a stereo isomer of IVa. X-ray analysis[2)] showed that the two cyclopropane rings in IVa are trans in configuration, and consequently in Va they were presumed to be situated cis. Dihomotropones (IVb-d, Vb) were obtained by analogous reactions shown in scheme II and their melting points and yields are listed in Table II. When the reactions of tropone with two molar equivalent ylids (IIb, IIc) were carried out in tetrahydrofuran, IVb, IVc were obtained as main products.

REFERENCES

1. J.D. Holmes and R. Pettit; J. Amer. Chem. Soc. 85 2531 (1963).

2. The result of X-ray analysis will be reported next time.